

# Biochemical Thermodynamics

The branch of physical chemistry known as **thermodynamics** is concerned with the study of the transformations of energy. That concern might seem remote from chemistry, let alone biology; indeed, thermodynamics was originally formulated by physicists and engineers interested in the efficiency of steam engines. However, thermodynamics has proved to be of immense importance in both chemistry and biology. Not only does it deal with the energy output of chemical reactions but it also helps to answer questions that lie right at the heart of biochemistry, such as how energy flows in biological cells and how large molecules assemble into complex structures like the cell.

# The First Law

**C**lassical thermodynamics, the thermodynamics developed during the nineteenth century, stands aloof from any models of the internal constitution of matter: we could develop and use thermodynamics without ever mentioning atoms and molecules. However, the subject is greatly enriched by acknowledging that atoms and molecules do exist and interpreting thermodynamic properties and relations in terms of them. Wherever it is appropriate, we shall cross back and forth between thermodynamics, which provides useful relations between observable properties of bulk matter, and the properties of atoms and molecules, which are ultimately responsible for these bulk properties. The theory of the connection between atomic and bulk thermodynamic properties is called **statistical thermodynamics** and is treated in Chapter 12.

Throughout the text, we shall pay special attention to **bioenergetics**, the deployment of energy in living organisms. As we master the concepts of thermodynamics in this and subsequent chapters, we shall gradually unravel the intricate patterns of energy trapping and utilization in biological cells.

## The conservation of energy

Almost every argument and explanation in chemistry boils down to a consideration of some aspect of a single property: the *energy*. Energy determines what molecules can form, what reactions can occur, how fast they can occur, and (with a refinement in our conception of energy) in which direction a reaction has a tendency to occur.

As we saw in the *Fundamentals*:

**Energy** is the capacity to do work.

**Work** is motion against an opposing force.

These definitions imply that a raised weight of a given mass has more energy than one of the same mass resting on the ground because the former has a greater capacity to do work: it can do work as it falls to the level of the lower weight. The definition also implies that a gas at a high temperature has more energy than the same gas at a low temperature: the hot gas has a higher pressure and can do more work in driving out a piston. In biology, we encounter many examples of the relationship between energy and work. As a muscle contracts and relaxes, energy stored in its protein fibers is released as the work of walking, lifting a weight, and so on. In biological cells, nutrients, ions, and electrons are constantly moving across membranes and from one cellular compartment to another. The synthesis of biological molecules and cell division are also manifestations of work at the molecular level. The energy that produces all this work in our bodies comes from food.

### The conservation of energy

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### Exercises

People struggled for centuries to create energy from nothing, for they believed that if they could create energy, then they could produce work (and wealth) endlessly. However, without exception, despite strenuous efforts, many of which degenerated into deceit, they failed. As a result of their failed efforts, we have come to recognize that energy can be neither created nor destroyed but merely converted from one form into another or moved from place to place. This “law of the conservation of energy” is of great importance in chemistry. Most chemical reactions—including the majority of those taking place in biological cells—release energy or absorb it as they occur; so according to the law of the conservation of energy, we can be confident that all such changes—including the vast collection of physical and chemical changes we call life—must result only in the *conversion* of energy from one form to another or its transfer from place to place, not its creation or annihilation.

## 1.1 Systems and surroundings

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*We need to understand the unique and precise vocabulary of thermodynamics before applying it to the study of bioenergetics.*

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In thermodynamics, a **system** is the part of the world in which we have a special interest. The **surroundings** are where we make our observations (Fig. 1.1). The surroundings, which can be modeled as a large water bath, remain at constant temperature regardless of how much energy flows into or out of them. They are so huge that they also have either constant volume or constant pressure regardless of any changes that take place to the system. Thus, even though the system might expand, the surroundings remain effectively the same size.

We need to distinguish three types of system (Fig. 1.2):

An **open system** can exchange both energy and matter with its surroundings and hence can undergo changes of composition.

A **closed system** is a system that can exchange energy but not matter with its surroundings.

An **isolated system** is a system that can exchange neither matter nor energy with its surroundings.

An example of an open system is a flask that is not stoppered and to which various substances can be added. A biological cell is an open system because nutrients and waste can pass through the cell wall. You and I are open systems: we ingest, respire, perspire, and excrete. An example of a closed system is a stoppered flask: energy can be exchanged with the contents of the flask because the walls may be able to conduct heat. An example of an isolated system is a sealed flask that is thermally, mechanically, and electrically insulated from its surroundings.

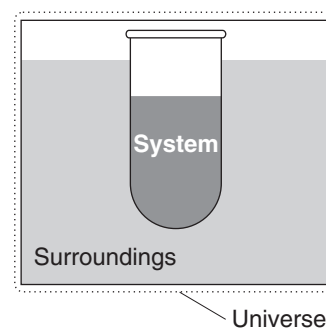
## 1.2 Work and heat

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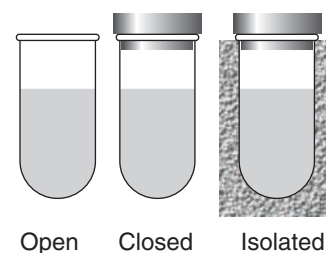
*Organisms can be regarded as vessels that exchange energy with their surroundings, and we need to understand the modes of such transfer.*

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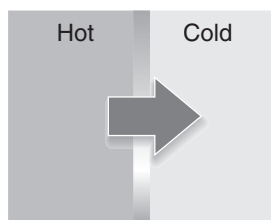
Energy can be exchanged between a closed system and its surroundings by doing work or by the process called “heating.” A system does work when it causes



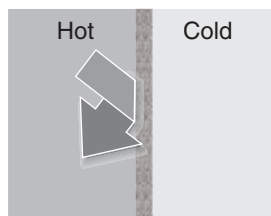
**Fig. 1.1** The sample is the system of interest; the rest of the world is its surroundings. The surroundings are where observations are made on the system. They can often be modeled, as here, by a large water bath. The universe consists of the system and surroundings.



**Fig. 1.2** A system is *open* if it can exchange energy and matter with its surroundings, *closed* if it can exchange energy but not matter, and *isolated* if it can exchange neither energy nor matter.



(a) Diathermic



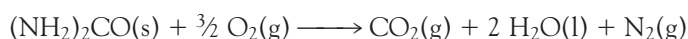
(b) Adiabatic

**Fig. 1.3** (a) A diathermic wall permits the passage of energy as heat; (b) an adiabatic wall does not, even if there is a temperature difference across the wall.

motion against an opposing force. We can identify when a system does work by noting whether the process can be used to change the height of a weight somewhere in the surroundings. **Heating** is the process of transferring energy as a result of a temperature difference between the systems and its surroundings. To avoid a lot of awkward circumlocution, it is common to say that “energy is transferred as work” when the system does work and “energy is transferred as heat” when the system heats its surroundings (or vice versa). However, we should always remember that “work” and “heat” are *modes of transfer* of energy, not *forms* of energy.

Walls that permit heating as a mode of transfer of energy are called **diathermic** (Fig. 1.3). A metal container is diathermic and so is our skin or any biological membrane. Walls that do not permit heating even though there is a difference in temperature are called **adiabatic**.<sup>1</sup> The double walls of a vacuum flask are adiabatic to a good approximation.

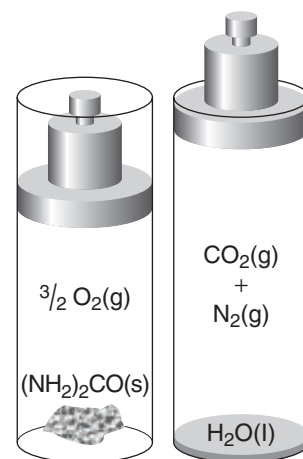
As an example of these different ways of transferring energy, consider a chemical reaction that is a net producer of gas, such as the reaction between urea,  $(\text{NH}_2)_2\text{CO}$ , and oxygen to yield carbon dioxide, water, and nitrogen:



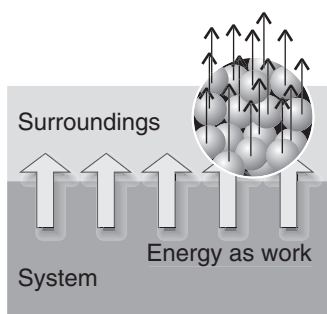
Suppose first that the reaction takes place inside a cylinder fitted with a piston, then the gas produced drives out the piston and raises a weight in the surroundings (Fig. 1.4). In this case, energy has migrated to the surroundings as a result of the system doing work, because a weight has been raised in the surroundings: that weight can now do more work, so it possesses more energy. Some energy also migrates into the surroundings as heat. We can detect that transfer of energy by immersing the reaction vessel in an ice bath and noting how much ice melts. Alternatively, we could let the same reaction take place in a vessel with a piston locked in position. No work is done, because no weight is raised. However, because it is found that more ice melts than in the first experiment, we can conclude that more energy has migrated to the surroundings as heat.

A process in a system that heats the surroundings (we commonly say “releases heat into the surroundings”) is called **exothermic**. A process in a system that is

<sup>1</sup>The word is derived from the Greek words for “not passing through.”

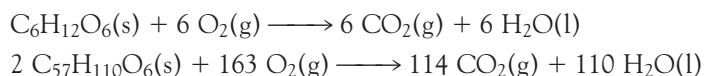


**Fig. 1.4** When urea reacts with oxygen, the gases produced (carbon dioxide and nitrogen) must push back the surrounding atmosphere (represented by the weight resting on the piston) and hence must do work on its surroundings. This is an example of energy leaving a system as work.



**Fig. 1.5** Work is transfer of energy that causes or utilizes uniform motion of atoms in the surroundings. For example, when a weight is raised, all the atoms of the weight (shown magnified) move in unison in the same direction.

heated by the surroundings (we commonly say “absorbs heat from the surroundings”) is called **endothermic**. Examples of exothermic reactions are all **combustions**, in which organic compounds are completely oxidized by  $O_2$  gas to  $CO_2$  gas and liquid  $H_2O$  if the compounds contain C, H, and O, and also to  $N_2$  gas if N is present. The oxidative breakdown of nutrients in organisms are combustions. So we expect the reactions of the carbohydrate glucose ( $C_6H_{12}O_6$ , **1**) and of the fat tristearin ( $C_{57}H_{110}O_6$ , **2**) with  $O_2$  gas to be exothermic, with much of the released heat being converted to work in the organism (Section 1.3):

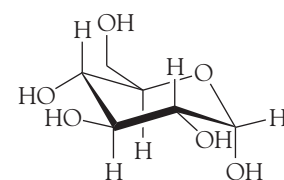


Endothermic reactions are much less common. The endothermic dissolution of ammonium nitrate in water is the basis of the instant cold packs that are included in some first-aid kits. They consist of a plastic envelope containing water dyed blue (for psychological reasons) and a small tube of ammonium nitrate, which is broken when the pack is to be used.

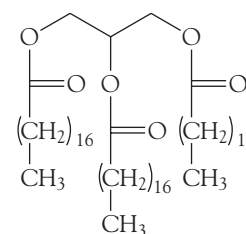
The clue to the molecular nature of work comes from thinking about the motion of a weight in terms of its component atoms. When a weight is raised, all its atoms move in the same direction. This observation suggests that *work is the transfer of energy that achieves or utilizes uniform motion in the surroundings* (Fig. 1.5). Whenever we think of work, we can always think of it in terms of uniform motion of some kind. Electrical work, for instance, corresponds to electrons being pushed in the same direction through a circuit. Mechanical work corresponds to atoms being pushed in the same direction against an opposing force.

Now consider the molecular nature of heating. When energy is transferred as heat to the surroundings, the atoms and molecules oscillate more rapidly around their positions or move from place to place more vigorously. The key point is that the motion stimulated by the arrival of energy from the system as heat is random, not uniform as in the case of doing work. This observation suggests that *heat is the mode of transfer of energy that achieves or utilizes random motion in the surroundings* (Fig. 1.6). A fuel burning, for example, generates random molecular motion in its vicinity.

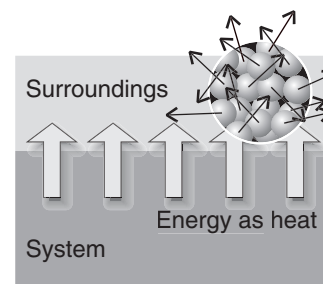
An interesting historical point is that the molecular difference between work and heat correlates with the chronological order of their application. The release of energy when a fire burns is a relatively unsophisticated procedure because the energy emerges in a disordered fashion from the burning fuel. It was developed—stumbled upon—early in the history of civilization. The generation of work by a burning fuel, in contrast, relies on a carefully controlled transfer of energy so that



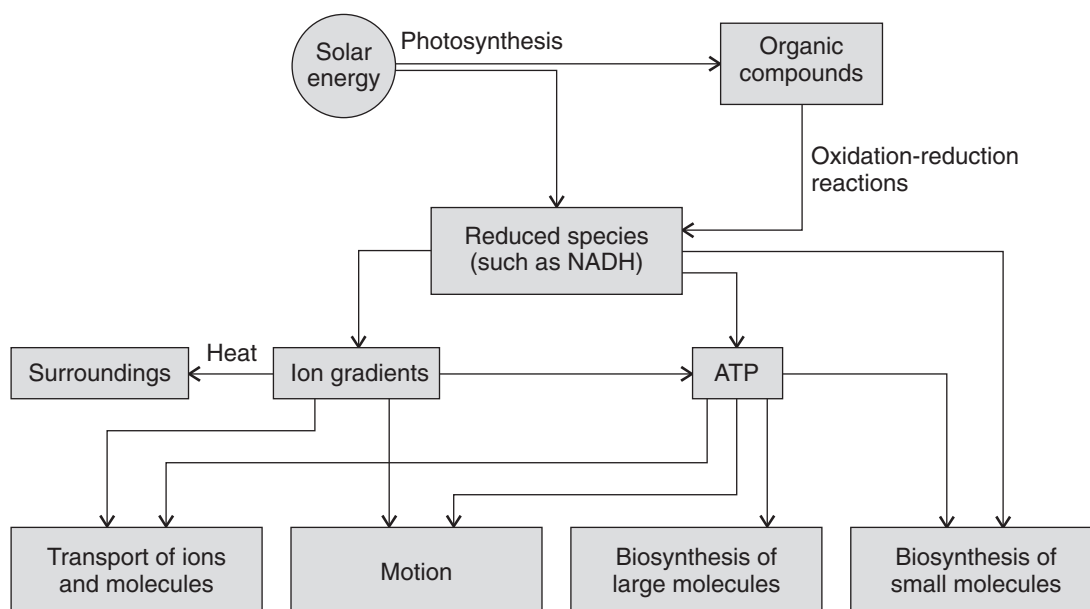
**1**  $\alpha$ -D-glucose



**2** Tristearin



**Fig. 1.6** Heat is the transfer of energy that causes or utilizes random motion in the surroundings. When energy leaves the system (the shaded region), it generates random motion in the surroundings (shown magnified).



**Fig. 1.7** Diagram demonstrating the flow of energy in living organisms. Arrows point in the direction in which energy flows. We focus only on the most common processes and do not include less ubiquitous ones, such as bioluminescence. (Adapted from D.A. Harris, *Bioenergetics at a glance*, Blackwell Science, Oxford [1995].)

vast numbers of molecules move in unison. Apart from Nature's achievement of work through the evolution of muscles, the large-scale transfer of energy by doing work was achieved thousands of years later than the liberation of energy by heating, for it had to await the development of the steam engine.

### 1.3 Energy conversion in living organisms

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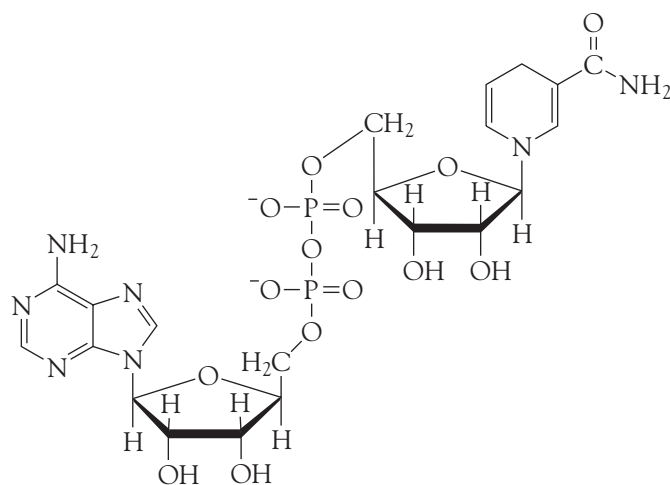
*To begin our study of bioenergetics, we need to trace the general patterns of energy flow in living organisms.*

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Figure 1.7 outlines the main processes of **metabolism**, the collection of chemical reactions that trap, store, and utilize energy in biological cells. Most chemical reactions taking place in biological cells are either endothermic or exothermic, and cellular processes can continue only as long as there is a steady supply of energy to the cell. Furthermore, as we shall see in Section 1.6, only the *conversion* of the supplied energy from one form to another or its transfer from place to place is possible.

The primary source of energy that sustains the bulk of plant and animal life on Earth is the Sun.<sup>2</sup> We saw in the *Prologue* that energy from solar radiation is ultimately stored during photosynthesis in the form of organic molecules, such as carbohydrates, fats, and proteins, that are subsequently oxidized to meet the energy demands of organisms. **Catabolism** is the collection of reactions associated with the oxidation of nutrients in the cell and may be regarded as highly controlled combustions, with the energy liberated as work rather than heat. Thus, even though the oxidative breakdown of a carbohydrate or fat to carbon dioxide and water is

<sup>2</sup>Some ecosystems near volcanic vents in the dark depths of the oceans do not use sunlight as their primary source of energy.



3 NADH

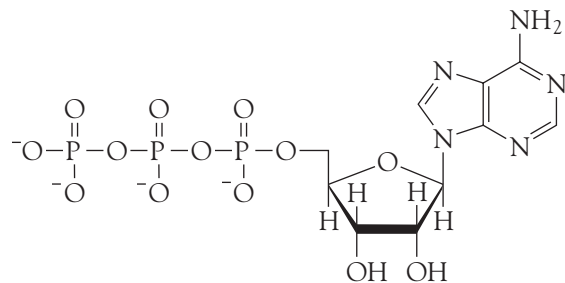
highly exothermic, we expect much of the energy to be expended by doing useful work, with only slight temperature increases resulting from the loss of energy as heat from the organism.

Because energy is extracted from organic compounds as a result of oxidation reactions, the initial energy carriers are reduced species, species that have gained electrons, such as reduced nicotinamide adenine dinucleotide, NADH (3). Light-induced electron transfer in photosynthesis also leads to the formation of reduced species, such as NADPH, the phosphorylated derivative of NADH. The details of the reactions leading to the production of NADH and NADPH are discussed in Chapter 5.

Oxidation-reduction reactions transfer energy out of NADH and other reduced species, storing it in the mobile carrier adenosine triphosphate, ATP (4), and in ion gradients across membranes. As we shall see in Chapter 4, the essence of ATP's action is the loss of its terminal phosphate group in an energy-releasing reaction. Ion gradients arise from the movement of charged species across a membrane and we shall see in Chapter 5 how they store energy that can be used to drive biochemical processes and the synthesis of ATP.

Figure 1.7 shows how organisms distribute the energy stored by ion gradients and ATP. The net outcome is incomplete conversion of energy from controlled combustion of nutrients to energy for doing work in the cell: transport of ions and

**COMMENT 1.1** See Appendix 4 for a review of oxidation-reduction reactions. ■



4 ATP

neutral molecules (such as nutrients) across cell membranes, motion of the organism (for example, through the contraction of muscles), and **anabolism**, the biosynthesis of small and large molecules. The biosynthesis of DNA may be regarded as an anabolic process in which energy is converted ultimately to useful information, the genome of the organism.

Living organisms are not perfectly efficient machines, for not all the energy available from the Sun and oxidation of organic compounds is used to perform work as some is lost as heat. The dissipation of energy as heat is advantageous because it can be used to control the organism's temperature. However, energy is eventually transferred as heat to the surroundings. In Chapter 2 we shall explore the origin of the incomplete conversion of energy supplied by heating into energy that can be used to do work, a feature that turns out to be common to all energy conversion processes.

Now we need to say a few words about how we shall develop the concepts of thermodynamics necessary for a full understanding of bioenergetics. Throughout the text we shall initiate discussions of thermodynamics with the perfect gas as a model system. Although a perfect gas may seem far removed from biology, its properties are crucial to the formulation of thermodynamics of systems in aqueous environments, such as biological cells. First, it is quite simple to formulate the thermodynamic properties of a perfect gas. Then—and this is the crucially important point—because a perfect gas is a good approximation to a vapor and a vapor may be in equilibrium with a liquid, the thermodynamic properties of a perfect gas are mirrored (in a manner we shall describe) in the thermodynamic properties of the liquid. In other words, we shall see that a description of the gases (or “vapors”) that hover above a solution opens a window onto the description of physical and chemical transformations occurring in the solution itself. Once we become equipped with the formalism to describe chemical reactions in solution, it will be easy to apply the concepts of thermodynamics to the complex environment of a biological cell. That is, we need to make a modest investment in the study of systems that may seem removed from our concerns so that, in the end, we can collect sizable dividends that will enrich our understanding of biological processes.

## 1.4 The measurement of work

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*In bioenergetics, the most useful outcome of the breakdown of nutrients during metabolism is work, so we need to know how work is measured.*

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We saw in Section F.3 that if the force is the gravitational attraction of the Earth on a mass  $m$ , the force opposing raising the mass vertically is  $mg$ , where  $g$  is the acceleration of free fall ( $9.81 \text{ m s}^{-2}$ ), and therefore that the work needed to raise the mass through a height  $h$  on the surface of the Earth is

$$\text{Work} = mgh \tag{1.1}$$

It follows that we have a simple way of measuring the work done by or on a system: we measure the height through which a weight is raised or lowered in the surroundings and then use eqn 1.1.

### **ILLUSTRATION 1.1** The work of moving nutrients through the trunk of a tree

Nutrients in the soil are absorbed by the root system of a tree and then rise to reach the leaves through a complex vascular system in its trunk and branches.



From eqn 1.1, the work required to raise 10 g of liquid water (corresponding to a volume of about 10 mL) through the trunk of a 20 m tree from its roots to its top-most leaves is

$$\text{Work} = (1.0 \times 10^{-2} \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (20 \text{ m}) = 2.0 \text{ kg m}^2 \text{ s}^{-2} = 2.0 \text{ J}$$

This quantity of work is equivalent to the work of raising a book like this one (of mass about 1.0 kg) by a vertical distance of 20 cm (0.20 m):

$$\text{Work} = (1.0 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (0.20 \text{ m}) = 2.0 \text{ kg m}^2 \text{ s}^{-2} = 2.0 \text{ J}$$

*A note on good practice:* Whenever possible, find a relevant derived unit that corresponds to the collection of base units in a result. We used  $1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ J}$ , hence verifying that the answer has units of energy. ■

When a system does work, such as by raising a weight in the surroundings or forcing the movement of an ion across a biological membrane, the energy transferred,  $w$ , is reported as a negative quantity. For instance, if a system raises a weight in the surroundings and in the process does 100 J of work (that is, 100 J of energy leaves the system by doing work), then we write  $w = -100 \text{ J}$ . When work is done on the system—for example, when we stretch a muscle from its relaxed position— $w$  is reported as a positive quantity. We write  $w = +100 \text{ J}$  to signify that 100 J of work has been done on the system (that is, 100 J of energy has been transferred to the system by doing work). The sign convention is easy to follow if we think of changes to the energy of the system: its energy decreases ( $w$  is negative) if energy leaves it and its energy increases ( $w$  is positive) if energy enters it (Fig. 1.8).

We use the same convention for energy transferred by heating,  $q$ . We write  $q = -100 \text{ J}$  if 100 J of energy leaves the system by heating its surroundings, so reducing the energy of the system, and  $q = +100 \text{ J}$  if 100 J of energy enters the system when it is heated by the surroundings.

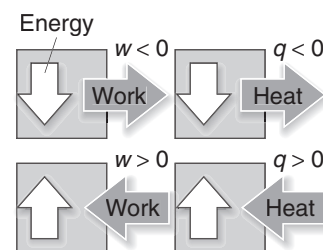
To see how energy flow as work can be determined experimentally, we deal first with **expansion work**, the work done when a system expands against an opposing pressure. In bioenergetics we are not generally concerned with expansion work, which can flow as a result of gas-producing or gas-consuming chemical reactions, but rather with work of making and moving molecules in the cell, muscle contraction, or cell division. However, it is far easier to begin our discussion with expansion work because we have at our disposal a simple equation of the state—the perfect gas equation of state (Section F.7)—that allows us to write simple expressions that provide important insights into the nature of work.

Consider the combustion of urea illustrated in Fig. 1.4 as an example of a reaction in which expansion work is done in the process of making room for the gaseous products, carbon dioxide and nitrogen in this case. We show in the following *Derivation* that when a system expands through a volume  $\Delta V$  against a constant external pressure  $p_{\text{ex}}$ , the work done is

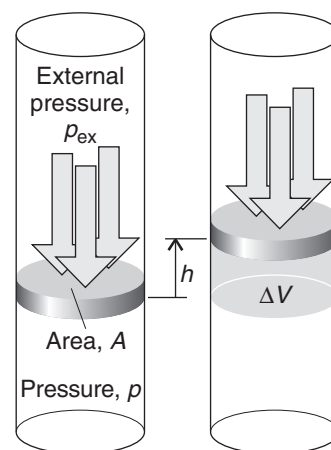
$$w = -p_{\text{ex}}\Delta V \quad (1.2)$$

#### DERIVATION 1.1 Expansion work

To calculate the work done when a system expands from an initial volume  $V_i$  to a final volume  $V_f$ , a change  $\Delta V = V_f - V_i$ , we consider a piston of area  $A$  moving out through a distance  $h$  (Fig. 1.9). There need not be an actual piston:



**Fig. 1.8** The sign convention in thermodynamics:  $w$  and  $q$  are positive if energy enters the system (as work and heat, respectively) but negative if energy leaves the system.



**Fig. 1.9** When a piston of area  $A$  moves out through a distance  $h$ , it sweeps out a volume  $\Delta V = Ah$ . The external pressure  $p_{\text{ex}}$  opposes the expansion with a force  $p_{\text{ex}}A$ .

we can think of the piston as representing the boundary between the expanding gas and the surrounding atmosphere. However, there may be an actual piston, such as when the expansion takes place inside an internal combustion engine.

The force opposing the expansion is the constant external pressure  $p_{\text{ex}}$  multiplied by the area of the piston (because force is pressure times area; Section F.5). The work done is therefore

$$\begin{aligned} \text{Work done by the system} &= \text{distance} \times \text{opposing force} \\ &= h \times (p_{\text{ex}}A) = p_{\text{ex}} \times (hA) = p_{\text{ex}} \times \Delta V \end{aligned}$$

The last equality follows from the fact that  $hA$  is the volume of the cylinder swept out by the piston as the gas expands, so we can write  $hA = \Delta V$ . That is, for expansion work,

$$\text{Work done by system} = p_{\text{ex}}\Delta V$$

Now consider the sign. A system does work and thereby loses energy (that is,  $w$  is negative) when it expands (when  $\Delta V$  is positive). Therefore, we need a negative sign in the equation to ensure that  $w$  is negative (when  $\Delta V$  is positive), so we obtain eqn 1.2.

According to eqn 1.2, the *external* pressure determines how much work a system does when it expands through a given volume: the greater the external pressure, the greater the opposing force and the greater the work that a system does. When the external pressure is zero,  $w = 0$ . In this case, the system does no work as it expands because it has nothing to push against. Expansion against zero external pressure is called **free expansion**.

### ILLUSTRATION 1.2 The work of exhaling air

Exhalation of air during breathing requires work because air must be pushed out from the lungs against atmospheric pressure. Consider the work of exhaling 0.50 L ( $5.0 \times 10^{-4} \text{ m}^3$ ) of air, a typical value for a healthy adult, through a tube into the bottom of the apparatus shown in Fig. 1.9 and against an atmospheric pressure of 1.00 atm (101 kPa). The exhaled air lifts the piston so the change in volume is  $\Delta V = 5.0 \times 10^{-4} \text{ m}^3$  and the external pressure is  $p_{\text{ex}} = 101 \text{ kPa}$ . From eqn 1.2 the work of exhaling is

$$w = -p_{\text{ex}}\Delta V = -(1.01 \times 10^5 \text{ Pa}) \times (5.0 \times 10^{-4} \text{ m}^3) = -51 \text{ Pa m}^3 = -51 \text{ J}$$

where we have used the relation  $1 \text{ Pa m}^3 = 1 \text{ J}$ . We now follow the approach in *Illustration 1.1* and compare this quantity of work with that required to raise an object against the force of gravity. We use eqn 1.1 to show that  $-51 \text{ J}$  is approximately the same as the work of lifting seven books like this one (a total of 7.0 kg) from the ground to the top of a standard desk (a vertical distance of 0.75 m):

$$w = -(7.0 \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (0.75 \text{ m}) = -52 \text{ kg m}^2 \text{ s}^{-2} = -52 \text{ J}$$

*A note on good practice:* Always keep track of signs by considering whether stored energy has left the system as work ( $w$  is then negative) or has entered it ( $w$  is then positive). ■

**SELF-TEST 1.1** Calculate the work done by a system in which a reaction results in the formation of 1.0 mol  $\text{CO}_2(\text{g})$  at  $25^\circ\text{C}$  and 100 kPa. (*Hint:* The increase in volume will be 25 L under these conditions if the gas is treated as perfect; use the relation  $1 \text{ Pa m}^3 = 1 \text{ J}$ .)

**Answer:** 2.5 kJ

Equation 1.2 shows us how to get the *least* expansion work from a system: we just reduce the external pressure—which provides the opposing force—to zero. But how can we achieve the *greatest* work for a given change in volume? According to eqn 1.2, the system does maximum work when the external pressure has its maximum value. The force opposing the expansion is then the greatest and the system must exert most effort to push the piston out. However, that external pressure cannot be greater than the pressure,  $p$ , of the gas inside the system, for otherwise the external pressure would compress the gas instead of allowing it to expand. Therefore, *maximum work is obtained when the external pressure is only infinitesimally less than the pressure of the gas in the system.* In effect, the two pressures must be adjusted to be the same at all stages of the expansion. In Section F.5 we called this balance of pressures a state of mechanical equilibrium. Therefore, we can conclude that *a system that remains in mechanical equilibrium with its surroundings at all stages of the expansion does maximum expansion work.*

There is another way of expressing this condition. Because the external pressure is infinitesimally less than the pressure of the gas at some stage of the expansion, the piston moves out. However, suppose we increase the external pressure so that it became infinitesimally greater than the pressure of the gas; now the piston moves in. That is, *when a system is in a state of mechanical equilibrium, an infinitesimal change in the pressure results in opposite directions of change.* A change that can be reversed by an *infinitesimal* change in a variable—in this case, the pressure—is said to be **reversible**. In everyday life “reversible” means a process that can be reversed; in thermodynamics it has a stronger meaning—it means that a process can be reversed by an *infinitesimal* modification in some variable (such as the pressure).

We can summarize this discussion by the following remarks:

1. A system does maximum expansion work when the external pressure is equal to that of the system at every stage of the expansion ( $p_{\text{ex}} = p$ ).
2. A system does maximum expansion work when it is in mechanical equilibrium with its surroundings at every stage of the expansion.
3. Maximum expansion work is achieved in a reversible change.

All three statements are equivalent, but they reflect different degrees of sophistication in the way the point is expressed. The last statement is particularly important in our discussion of bioenergetics, especially when we consider how the reactions of catabolism drive anabolic processes. The arguments we have developed lead to the conclusion that maximum work (whether it is expansion work or some other type of work) will be done if cellular processes are reversible. However, no process can be performed in a perfectly reversible manner, so the ultimate energetic limits of life can be estimated but never achieved.

We cannot write down the expression for maximum expansion work simply by replacing  $p_{\text{ex}}$  in eqn 1.2 by  $p$  (the pressure of the gas in the cylinder) because, as the piston moves out, the pressure inside the system falls. To make sure the entire process occurs reversibly, we have to adjust the external pressure to match the internal pressure at each stage, and to calculate the work, we must take into account the fact that the external pressure must change as the system expands. Suppose that we conduct the expansion isothermally (that is, at constant temperature) by immersing the system in a water bath held at a specified temperature. As we show in the following *Derivation*, the work of isothermal, reversible expansion of a perfect gas from an initial volume  $V_i$  to a final volume  $V_f$  at a temperature  $T$  is

$$w = -nRT \ln \frac{V_f}{V_i} \quad (1.3)$$

where  $n$  is the amount of gas in the system.

#### DERIVATION 1.2 Reversible, isothermal expansion work

Because (to ensure reversibility) the external pressure changes in the course of the expansion, we have to think of the process as taking place in series of small steps during each one of which the external pressure is constant. We calculate the work done in each step for the prevailing external pressure and then add all these values together. To ensure that the overall result is accurate, we have to make the steps as small as possible—infinitesimal, in fact—so that the pressure is truly constant during each one. In other words, we have to use the calculus, in which case the sum over an infinite number of infinitesimal steps becomes an integral.

When the system expands through an infinitesimal volume  $dV$ , the infinitesimal work,  $dw$ , done is

$$dw = -p_{\text{ex}}dV$$

This is eqn 1.2, rewritten for an infinitesimal expansion. However, at each stage, we ensure that the external pressure is the same as the current pressure,  $p$ , of the gas (Fig. 1.10), in which case

$$dw = -pdV$$

We can use the system's pressure to calculate the expansion work only for a reversible change, because then the external pressure is matched to the internal pressure for each infinitesimal change in volume.

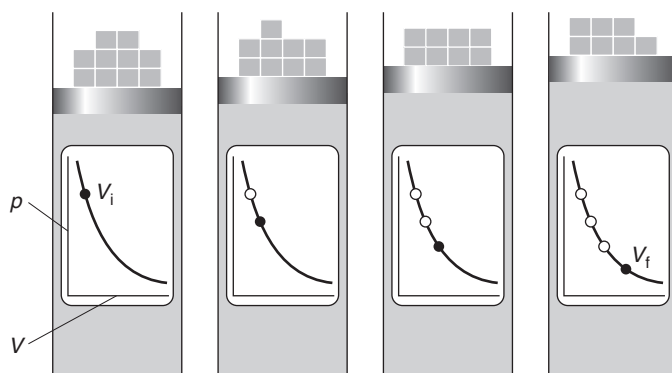
The total work when the system expands from  $V_i$  to  $V_f$  is the sum (integral) of all the infinitesimal changes between the limits  $V_i$  and  $V_f$ , which we write

$$w = -\int_{V_i}^{V_f} p dV$$

To evaluate the integral, we need to know how  $p$ , the pressure of the gas in the system, changes as it expands. For this step, we suppose that the gas is perfect, in which case we can use the perfect gas law to write

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

**COMMENT 1.2** For a review of calculus, see *Appendix 2*. As indicated there, the replacement of  $\Delta$  by  $d$  always indicates an infinitesimal change:  $dV$  is positive for an infinitesimal increase in volume and negative for an infinitesimal decrease. ■



**Fig. 1.10** For a gas to expand reversibly, the external pressure must be adjusted to match the internal pressure at each stage of the expansion. This matching is represented in this illustration by gradually unloading weights from the piston as the piston is raised and the internal pressure falls. The procedure results in the extraction of the maximum possible work of expansion.

At this stage we have

$$\text{For the reversible expansion of a perfect gas: } w = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

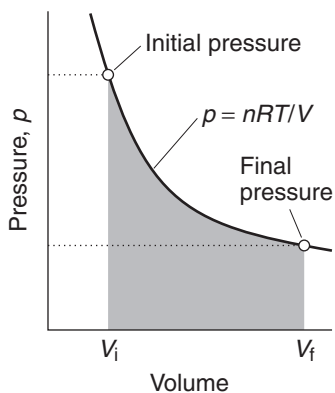
In general, the temperature might change as the gas expands, so in general  $T$  depends on  $V$ . For isothermal expansion, however, the temperature is held constant and we can take  $n$ ,  $R$ , and  $T$  outside the integral and write

$$\text{For the isothermal, reversible expansion of a perfect gas: } w = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

The integral is the area under the isotherm  $p = nRT/V$  between  $V_i$  and  $V_f$  (Fig. 1.11) and evaluates to

$$\int_{V_i}^{V_f} \frac{dV}{V} = \ln \frac{V_f}{V_i}$$

When we insert this result into the preceding one, we obtain eqn 1.3.



**Fig. 1.11** The work of reversible isothermal expansion of a gas is equal to the area beneath the corresponding isotherm evaluated between the initial and final volumes (the tinted area). The isotherm shown here is that of a perfect gas, but the same relation holds for any gas.

**COMMENT 1.3** A very useful integral in physical chemistry is

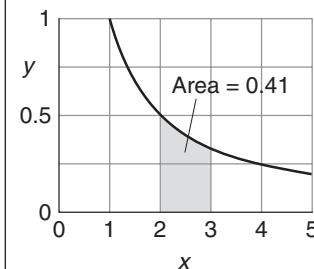
$$\int \frac{dx}{x} = \ln x + \text{constant}$$

where  $\ln x$  is the natural logarithm of  $x$ . To evaluate the integral between the limits  $x = a$  and  $x = b$ , we write

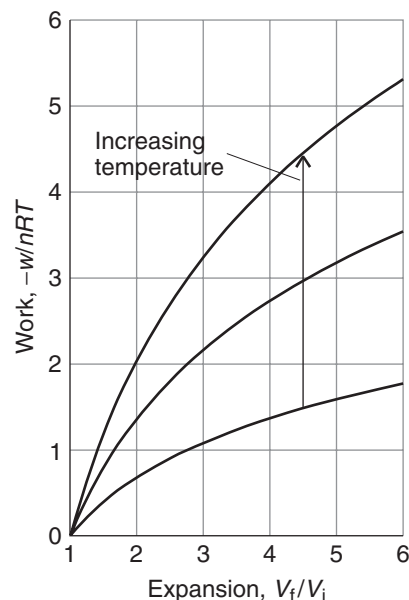
$$\begin{aligned} \int_a^b \frac{dx}{x} &= (\ln x + \text{constant}) \Big|_a^b \\ &= (\ln b + \text{constant}) - (\ln a + \text{constant}) \\ &= \ln b - \ln a = \ln \frac{b}{a} \end{aligned}$$

We encounter integrals of this form throughout this text.

It will be helpful to bear in mind that we can always interpret a “definite” integral (an integral with the two limits specified, in this case  $a$  and  $b$ ) as the area under a graph of the function being integrated (in this case the function  $1/x$ ) between the two limits. For instance, the area under the graph of  $1/x$  lying between  $a = 2$  and  $b = 3$  is  $\ln(3/2) = 0.41$ . ■



**Fig. 1.12** The work of reversible, isothermal expansion of a perfect gas. Note that for a given change of volume and fixed amount of gas, the work is greater the higher the temperature.



*A note on good practice:* Introduce (and keep note of) the restrictions only as they prove necessary, as you might be able to use a formula without needing to restrict it in some way.

Equation 1.3 will turn up in various disguises throughout this text. Once again, it is important to be able to interpret it rather than just remember it. First, we note that in an expansion  $V_f > V_i$ , so  $V_f/V_i > 1$  and the logarithm is positive ( $\ln x$  is positive if  $x > 1$ ). Therefore, in an expansion,  $w$  is negative. That is what we should expect: energy *leaves* the system as the system does expansion work. Second, for a given change in volume, we get more work the higher the temperature of the confined gas (Fig. 1.12). That is also what we should expect: at high temperatures, the pressure of the gas is high, so we have to use a high external pressure, and therefore a stronger opposing force, to match the internal pressure at each stage.

**SELF-TEST 1.2** Calculate the work done when 1.0 mol Ar(g) confined in a cylinder of volume 1.0 L at 25°C expands isothermally and reversibly to 2.0 L.

Answer:  $w = -1.7$  kJ

## 1.5 The measurement of heat

*A thermodynamic assessment of energy output during metabolic processes requires knowledge of ways to measure the energy transferred as heat.*

When a substance is heated, its temperature typically rises.<sup>3</sup> However, for a specified energy,  $q$ , transferred by heating, the size of the resulting temperature change,

<sup>3</sup>We say “typically” because the temperature does not always rise. The temperature of boiling water, for instance, remains unchanged as it is heated (see Chapter 3).

The conservation of energy

$\Delta T$ , depends on the “heat capacity” of the substance. The **heat capacity**,  $C$ , is defined as

$$C = \frac{q}{\Delta T} \quad (1.4a)$$

Energy supplied as heat  
Change in temperature

where the temperature change may be expressed in kelvins ( $\Delta T$ ) or degrees Celsius ( $\Delta\theta$ ); the same numerical value is obtained but with the units joules per kelvin ( $\text{J K}^{-1}$ ) and joules per degree Celsius ( $\text{J } ^\circ\text{C}^{-1}$ ), respectively. It follows that we have a simple way of measuring the energy absorbed or released by a system as heat: we measure a temperature change and then use the appropriate value of the heat capacity and eqn 1.4a rearranged into

$$q = C\Delta T \quad (1.4b)$$

For instance, if the heat capacity of a beaker of water is  $0.50 \text{ kJ K}^{-1}$  and we observe a temperature rise of  $4.0 \text{ K}$ , then we can infer that the heat transferred to the water is

$$q = (0.50 \text{ kJ K}^{-1}) \times (4.0 \text{ K}) = 2.0 \text{ kJ}$$

Heat capacities will occur extensively in the following sections and chapters, and we need to be aware of their properties and how their values are reported. First, we note that the heat capacity is an extensive property, a property that depends on the amount of substance in the sample:  $2 \text{ kg}$  of iron has twice the heat capacity of  $1 \text{ kg}$  of iron, so twice as much heat is required to change its temperature to the same extent. It is more convenient to report the heat capacity of a substance as an intensive property, a property that is independent of the amount of substance in the sample. We therefore use either the **specific heat capacity**,  $C_s$ , the heat capacity divided by the mass of the sample ( $C_s = C/m$ , in joules per kelvin per gram,  $\text{J K}^{-1} \text{ g}^{-1}$ ), or the **molar heat capacity**,  $C_m$ , the heat capacity divided by the amount of substance ( $C_m = C/n$ , in joules per kelvin per mole,  $\text{J K}^{-1} \text{ mol}^{-1}$ ). In common usage, the specific heat capacity is often called the *specific heat*.

For reasons that will be explained shortly, the heat capacity of a substance depends on whether the sample is maintained at constant volume (like a gas in a sealed vessel) as it is heated or whether the sample is maintained at constant pressure (like water in an open container) and free to change its volume. The latter is a more common arrangement, and the values given in Table 1.1 are for the **heat capacity at constant pressure**,  $C_p$ . The **heat capacity at constant volume** is denoted  $C_V$ .

### ILLUSTRATION 1.3 Using the heat capacity

The high heat capacity of water is ecologically advantageous because it stabilizes the temperatures of lakes and oceans: a large quantity of energy must be lost or gained before there is a significant change in temperature. The molar heat capacity of water at constant pressure,  $C_{p,m}$ , is  $75 \text{ J K}^{-1} \text{ mol}^{-1}$ . It follows that the

**COMMENT 1.4** Recall from introductory chemistry that an *extensive property* is a property that depends on the amount of substance in the sample. Mass, pressure, and volume are examples of extensive properties. An *intensive property* is a property that is independent of the amount of substance in the sample. The molar volume and temperature are examples of intensive properties. ■

**Table 1.1** Heat capacities of selected substances\*

Substance	Molar heat capacity, $C_{p,m}/(\text{J K}^{-1} \text{mol}^{-1})^*$
Air	29
Benzene, $\text{C}_6\text{H}_6(\text{l})$	136.1
Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$	111.46
Glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}(\text{s})$	99.2
Oxalic acid, $(\text{COOH})_2$	117
Urea, $\text{CO}(\text{NH}_2)_2(\text{s})$	93.14
Water, $\text{H}_2\text{O}(\text{s})$	37
$\text{H}_2\text{O}(\text{l})$	75.29
$\text{H}_2\text{O}(\text{g})$	33.58

\*For additional values, see the *Data section*.

increase in temperature of 100 g of water (5.55 mol  $\text{H}_2\text{O}$ ) when 1.0 kJ of energy is supplied by heating a sample free to expand is approximately

$$\Delta T = \frac{q}{C_p} = \frac{q}{nC_{p,m}} = \frac{1.0 \times 10^3 \text{ J}}{(5.55 \text{ mol}) \times (75 \text{ J K}^{-1} \text{ mol}^{-1})} = +2.4 \text{ K} \quad \blacksquare$$

In certain cases, we can relate the value of  $q$  to the change in volume of a system and so can calculate, for instance, the flow of energy as heat into the system when a gas expands. The simplest case is that of a perfect gas undergoing isothermal expansion. Because the expansion is isothermal, the temperature of the gas is the same at the end of the expansion as it was initially. Therefore, the mean speed of the molecules of the gas is the same before and after the expansion. That implies in turn that the total kinetic energy of the molecules is the same. But for a perfect gas, the *only* contribution to the energy is the kinetic energy of the molecules (recall Section F.7), so we have to conclude that the *total* energy of the gas is the same before and after the expansion. Energy has left the system as work; therefore, a compensating amount of energy must have entered the system as heat. We can therefore write

$$\text{For the isothermal expansion of a perfect gas: } q = -w \quad (1.5)$$

For instance, if we find that  $w = -100 \text{ J}$  for a particular expansion (meaning that 100 J has left the system as a result of the system doing work), then we can conclude that  $q = +100 \text{ J}$  (that is, 100 J must enter as heat). For free expansion,  $w = 0$ , so we conclude that  $q = 0$  too: there is no influx of energy as heat when a perfect gas expands against zero pressure.

If the isothermal expansion is also reversible, we can use eqn 1.3 for the work in eqn 1.5 and write

$$\text{For the isothermal, reversible expansion of a perfect gas: } q = nRT \ln \frac{V_f}{V_i} \quad (1.6)$$

When  $V_f > V_i$ , as in an expansion, the logarithm is positive and we conclude that  $q > 0$ , as expected: energy flows as heat into the system to make up for the energy lost as work. We also see that the greater the ratio of the final and initial volumes, the greater the influx of energy as heat.



## Internal energy and enthalpy

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Heat and work are *equivalent* ways of transferring energy into or out of a system in the sense that once the energy is inside, it is stored simply as “energy”: regardless of how the energy was supplied, as work or as heat, it can be released in either form. The experimental evidence for this **equivalence of heat and work** goes all the way back to the experiments done by James Joule, who showed that the same rise in temperature of a sample of water is brought about by transferring a given quantity of energy either as heat or as work.

### 1.6 The internal energy

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*To understand how biological processes can store and release energy, we need to describe a very important law that relates work and heat to changes in the energy of all the constituents of a system.*

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We need some way of keeping track of the energy changes in a system. This is the job of the property called the **internal energy**,  $U$ , of the system, the sum of all the kinetic and potential contributions to the energy of all the atoms, ions, and molecules in the system. The internal energy is the grand total energy of the system with a value that depends on the temperature and, in general, the pressure. It is an extensive property because 2 kg of iron at a given temperature and pressure, for instance, has twice the internal energy of 1 kg of iron under the same conditions. The **molar internal energy**,  $U_m = U/n$ , the internal energy per mole of material, is an intensive property.

In practice, we do not know and cannot measure the total energy of a sample, because it includes the kinetic and potential energies of all the electrons and all the components of the atomic nuclei. Nevertheless, there is no problem with dealing with the *changes* in internal energy,  $\Delta U$ , because we can determine those changes by monitoring the energy supplied or lost as heat or as work. All practical applications of thermodynamics deal with  $\Delta U$ , not with  $U$  itself. A change in internal energy is written

$$\Delta U = w + q \quad (1.7)$$

where  $w$  is the energy transferred to the system by doing work and  $q$  the energy transferred to it by heating. The internal energy is an accounting device, like a country’s gold reserves for monitoring transactions with the outside world (the surroundings) using either currency (heat or work).

We have seen that a feature of a perfect gas is that for any *isothermal* expansion, the total energy of the sample remains the same and that  $q = -w$ . That is, any energy lost as work is restored by an influx of energy as heat. We can express this property in terms of the internal energy, for it implies that the internal energy remains constant when a perfect gas expands isothermally: from eqn 1.7 we can write

$$\text{Isothermal expansion of a perfect gas: } \Delta U = 0 \quad (1.8)$$

In other words, *the internal energy of a sample of perfect gas at a given temperature is independent of the volume it occupies*. We can understand this independence by realizing that when a perfect gas expands isothermally, the only feature that changes is the average distance between the molecules; their average speed and therefore

total kinetic energy remains the same. However, as there are no intermolecular interactions, the total energy is independent of the average separation, so the internal energy is unchanged by expansion.

**EXAMPLE 1.1** Calculating the change in internal energy

Nutritionists are interested in the use of energy by the human body, and we can consider our own body as a thermodynamic “system.” Suppose in the course of an experiment you do 622 kJ of work on an exercise bicycle and lose 82 kJ of energy as heat. What is the change in your internal energy? Disregard any matter loss by perspiration.

**Strategy** This example is an exercise in keeping track of signs correctly. When energy is lost from the system,  $w$  or  $q$  is negative. When energy is gained by the system,  $w$  or  $q$  is positive.

**Solution** To take note of the signs, we write  $w = -622$  kJ (622 kJ is lost by doing work) and  $q = -82$  kJ (82 kJ is lost by heating the surroundings). Then eqn 1.7 gives us

$$\Delta U = w + q = (-622 \text{ kJ}) + (-82 \text{ kJ}) = -704 \text{ kJ}$$

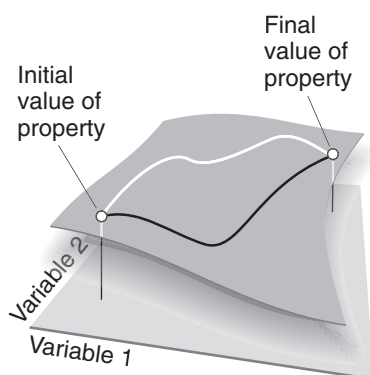
We see that your internal energy falls by 704 kJ. Later, that energy will be restored by eating.

*A note on good practice:* Always attach the correct signs: use a positive sign when there is a flow of energy into the system and a negative sign when there is a flow of energy out of the system. Also, the quantity  $\Delta U$  always carries a sign explicitly, even if it is positive: we never write  $\Delta U = 20$  kJ, for instance, but always  $+20$  kJ.

**SELF-TEST 1.3** An electric battery is charged by supplying 250 kJ of energy to it as electrical work (by driving an electric current through it), but in the process it loses 25 kJ of energy as heat to the surroundings. What is the change in internal energy of the battery?

**Answer:** +225 kJ ■

An important characteristic of the internal energy is that it is a **state function**, a physical property that depends only on the present state of the system and is independent of the path by which that state was reached. If we were to change the temperature of the system, then change the pressure, then adjust the temperature and pressure back to their original values, the internal energy would return to its original value too. A state function is very much like altitude: each point on the surface of the Earth can be specified by quoting its latitude and longitude, and (on land areas, at least) there is a unique property, the altitude, that has a fixed value at that point. In thermodynamics, the role of latitude and longitude is played by the pressure and temperature (and any other variables needed to specify the state of the system), and the internal energy plays the role of the altitude, with a single, fixed value for each state of the system.



**Fig. 1.13** The curved sheet shows how a property (for example, the altitude) changes as two variables (for example, latitude and longitude) are changed. The altitude is a state property, because it depends only on the current state of the system. The change in the value of a state property is independent of the path between the two states. For example, the difference in altitude between the initial and final states shown in the diagram is the same whatever path (as depicted by the dark and light lines) is used to travel between them.

The fact that  $U$  is a state function implies that a change,  $\Delta U$ , in the internal energy between two states of a system is independent of the path between them (Fig. 1.13). Once again, the altitude is a helpful analogy. If we climb a mountain between two fixed points, we make the same change in altitude regardless of the path we take between the two points. Likewise, if we compress a sample of gas until it reaches a certain pressure and then cool it to a certain temperature, the change in internal energy has a particular value. If, on the other hand, we changed the temperature and then the pressure but ensured that the two final values were the same as in the first experiment, then the overall change in internal energy would be exactly the same as before. This path independence of the value of  $\Delta U$  is of the greatest importance in chemistry, as we shall soon see.

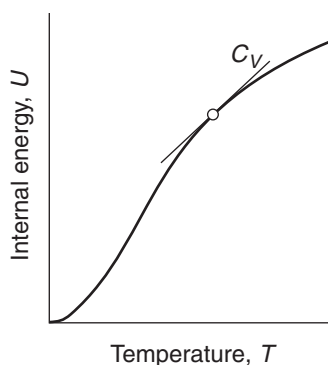
Suppose we now consider an isolated system. Because an isolated system can neither do work nor heat the surroundings, it follows that its internal energy cannot change. That is,

The internal energy of an isolated system is constant.

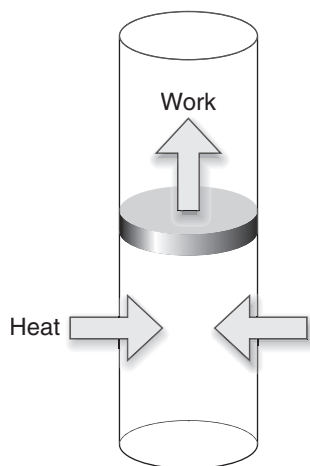
This statement is the **First Law of thermodynamics**. It is closely related to the law of conservation of energy but allows for transaction of energy by heating as well as by doing work. Unlike thermodynamics, mechanics does not deal with the concept of heat.

The experimental evidence for the First Law is the impossibility of making a “perpetual motion machine,” a device for producing work without consuming fuel. As we have already remarked, try as people might, they have never succeeded. No device has ever been made that creates internal energy to replace the energy drawn off as work. We cannot extract energy as work, leave the system isolated for some time, and hope that when we return, the internal energy will have become restored to its original value. The same is true of organisms: energy required for the sustenance of life must be supplied continually in the form of food as work is done by the organism.

The definition of  $\Delta U$  in terms of  $w$  and  $q$  points to a very simple method for measuring the change in internal energy of a system when a reaction takes place. We have seen already that the work done by a system when it pushes against a fixed external pressure is proportional to the change in volume. Therefore, if we carry out a reaction in a container of constant volume, the system can do no expansion work, and provided it can do no other kind of work (so-called non-



**Fig. 1.14** The constant-volume heat capacity is the slope of a curve showing how the internal energy varies with temperature. The slope, and therefore the heat capacity, may be different at different temperatures.



**Fig. 1.15** The change in internal energy of a system that is free to expand or contract is not equal to the energy supplied by heating because some energy may escape back into the surroundings as work. However, the change in enthalpy of the system under these conditions is equal to the energy supplied by heating.

expansion work, such as electrical work), we can set  $w = 0$ . Then eqn 1.7 simplifies to

$$\text{At constant volume, no non-expansion work: } \Delta U = q \quad (1.9a)$$

This relation is commonly written

$$\Delta U = q_V \quad (1.9b)$$

The subscript  $V$  signifies that the volume of the system is constant. An example of a chemical system that can be approximated as a constant-volume container is an individual biological cell.

We can use eqn 1.9 to obtain more insight into the heat capacity of a substance. The definition of heat capacity is given in eqn 1.4 ( $C = q/\Delta T$ ). At constant volume,  $q$  may be replaced by the change in internal energy of the substance, so

$$C_V = \frac{\Delta U}{\Delta T} \text{ at constant volume} \quad (1.10a)$$

The expression on the right is the slope of the graph of internal energy plotted against temperature, with the volume of the system held constant, so  $C_V$  tells us how the internal energy of a constant-volume system varies with temperature. If, as is generally the case, the graph of internal energy against temperature is not a straight line, we interpret  $C_V$  as the slope of the tangent to the curve at the temperature of interest (Fig. 1.14). That is, the constant-volume heat capacity is the derivative of the function  $U$  with respect to the variable  $T$  at a specified volume, or

$$C_V = \frac{dU}{dT} \text{ at constant volume} \quad (1.10b)$$

## 1.7 The enthalpy

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*Most biological processes take place in vessels that are open to the atmosphere and subjected to constant pressure and not maintained at constant volume, so we need to learn how to treat quantitatively the energy exchanges that take place by heating at constant pressure.*

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In general, when a change takes place in a system open to the atmosphere, the volume of the system changes. For example, the thermal decomposition of 1.0 mol  $\text{CaCO}_3(\text{s})$  at 1 bar results in an increase in volume of 89 L at  $800^\circ\text{C}$  on account of the carbon dioxide gas produced. To create this large volume for the carbon dioxide to occupy, the surrounding atmosphere must be pushed back. That is, the system must perform expansion work. Therefore, although a certain quantity of heat may be supplied to bring about the endothermic decomposition, the increase in internal energy of the system is not equal to the energy supplied as heat because some energy has been used to do work of expansion (Fig. 1.15). In other words, because the volume has increased, some of the heat supplied to the system has leaked back into the surroundings as work.

Another example is the oxidation of a fat, such as tristearin, to carbon dioxide in the body. The overall reaction is



In this exothermic reaction there is a net *decrease* in volume equivalent to the elimination of  $(163 - 114) \text{ mol} = 49 \text{ mol}$  of gas molecules for every 2 mol of tristearin molecules that reacts. The decrease in volume at 25°C is about 600 mL for the consumption of 1 g of fat. Because the volume of the system decreases, the atmosphere does work *on* the system as the reaction proceeds. That is, energy is transferred to the system as it contracts.<sup>4</sup> For this reaction, the decrease in the internal energy of the system is less than the energy released as heat because some energy has been restored by doing work.

We can avoid the complication of having to take into account the work of expansion by introducing a new property that will be at the center of our attention throughout the rest of the chapter and will recur throughout the book. The **enthalpy**,  $H$ , of a system is defined as

$$H = U + pV \quad (1.11)$$

That is, the enthalpy differs from the internal energy by the addition of the product of the pressure,  $p$ , and the volume,  $V$ , of the system. This expression applies to *any* system or individual substance: don't be misled by the  $pV$  term into thinking that eqn 1.11 applies only to a perfect gas. A change in enthalpy (the only quantity we can measure in practice) arises from a change in the internal energy and a change in the product  $pV$ :

$$\Delta H = \Delta U + \Delta(pV) \quad (1.12a)$$

where  $\Delta(pV) = p_f V_f - p_i V_i$ . If the change takes place at constant pressure  $p$ , the second term on the right simplifies to

$$\Delta(pV) = pV_f - pV_i = p(V_f - V_i) = p\Delta V$$

and we can write

$$\text{At constant pressure: } \Delta H = \Delta U + p\Delta V \quad (1.12b)$$

We shall often make use of this important relation for processes occurring at constant pressure, such as chemical reactions taking place in containers open to the atmosphere.

Enthalpy is an extensive property. The **molar enthalpy**,  $H_m = H/n$ , of a substance, an intensive property, differs from the molar internal energy by an amount proportional to the molar volume,  $V_m$ , of the substance:

$$H_m = U_m + pV_m \quad (1.13a)$$

<sup>4</sup>In effect, a weight has been lowered in the surroundings, so the surroundings can do less work after the reaction has occurred. Some of their energy has been transferred into the system.

This relation is valid for all substances. For a perfect gas we can go on to write  $pV_m = RT$  and obtain

$$\text{For a perfect gas: } H_m = U_m + RT \quad (1.13b)$$

At 25°C,  $RT = 2.5 \text{ kJ mol}^{-1}$ , so the molar enthalpy of a perfect gas differs from its molar internal energy by  $2.5 \text{ kJ mol}^{-1}$ . Because the molar volume of a solid or liquid is typically about 1000 times less than that of a gas, we can also conclude that the molar enthalpy of a solid or liquid is only about  $2.5 \text{ J mol}^{-1}$  (note: joules, not kilojoules) more than its molar internal energy, so the numerical difference is negligible.

Although the enthalpy and internal energy of a sample may have similar values, the introduction of the enthalpy has very important consequences in thermodynamics. First, notice that because  $H$  is defined in terms of state functions ( $U$ ,  $p$ , and  $V$ ), *the enthalpy is a state function*. The implication is that the change in enthalpy,  $\Delta H$ , when a system changes from one state to another is independent of the path between the two states. Second, we show in the following *Derivation* that the change in enthalpy of a system can be identified with the heat transferred to it at constant pressure:

$$\text{At constant pressure, no non-expansion work: } \Delta H = q \quad (1.14a)$$

This relation is commonly written

$$\Delta H = q_p \quad (1.14b)$$

the subscript  $p$  signifying that the pressure is held constant. Therefore, by imposing the constraint of constant pressure, we have identified an observable quantity (the energy transferred as heat) with a change in a state function, the enthalpy. Dealing with state functions greatly extends the power of thermodynamic arguments, because we don't have to worry about how we get from one state to another: all that matters is the initial and final states. For the particular case of the combustion of tristearin mentioned at the beginning of the section, in which 90 kJ of energy is released as heat at constant pressure, we would write  $\Delta H = -90 \text{ kJ}$  regardless of how much expansion work is done.

### DERIVATION 1.3 Heat transfers at constant pressure

Consider a system open to the atmosphere, so that its pressure  $p$  is constant and equal to the external pressure  $p_{\text{ex}}$ . From eqn 1.13a we can write

$$\Delta H = \Delta U + p\Delta V = \Delta U + p_{\text{ex}}\Delta V$$

However, we know that the change in internal energy is given by eqn 1.7 ( $\Delta U = w + q$ ) with  $w = -p_{\text{ex}}\Delta V$  (provided the system does no other kind of work). When we substitute that expression into this one we obtain

$$\Delta H = (-p_{\text{ex}}\Delta V + q) + p_{\text{ex}}\Delta V = q$$

which is eqn 1.14.

An endothermic reaction ( $q > 0$ ) taking place at constant pressure results in an increase in enthalpy ( $\Delta H > 0$ ) because energy enters the system as heat. On the other hand, an exothermic process ( $q < 0$ ) taking place at constant pressure corresponds to a decrease in enthalpy ( $\Delta H < 0$ ) because energy leaves the system as heat. All combustion reactions, including the controlled combustions that contribute to respiration, are exothermic and are accompanied by a decrease in enthalpy. These relations are consistent with the name *enthalpy*, which is derived from the Greek words meaning “heat inside”: the “heat inside” the system is increased if the process is endothermic and absorbs energy as heat from the surroundings; it is decreased if the process is exothermic and releases energy as heat into the surroundings.<sup>5</sup>

## 1.8 The temperature variation of the enthalpy

*To make full use of the enthalpy in biochemical calculations, we need to describe its properties, such as its dependence on temperature.*

We have seen that the internal energy of a system rises as the temperature is increased. The same is true of the enthalpy, which also rises when the temperature is increased (Fig. 1.16). For example, the enthalpy of 100 g of water is greater at 80°C than at 20°C. We can measure the change by monitoring the energy that we must supply as heat to raise the temperature through 60°C when the sample is open to the atmosphere (or subjected to some other constant pressure); it is found that  $\Delta H \approx +25$  kJ in this instance.

Just as we saw that the constant-volume heat capacity tells us about the temperature-dependence of the internal energy at constant volume, so the constant-pressure heat capacity tells us how the enthalpy of a system changes as its temperature is raised at constant pressure. To derive the relation, we combine the definition of heat capacity in eqn 1.4 ( $C = q/\Delta T$ ) with eqn 1.14 and obtain

$$C_p = \frac{\Delta H}{\Delta T} \quad \text{at constant pressure} \quad (1.15a)$$

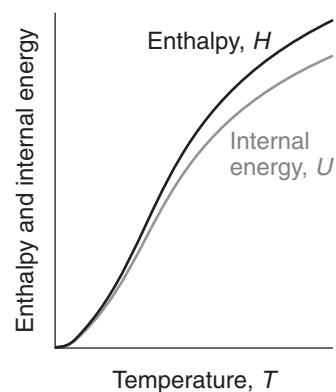
That is, the constant-pressure heat capacity is the slope of a plot of enthalpy against temperature of a system kept at constant pressure. Because the plot might not be a straight line, in general we interpret  $C_p$  as the slope of the tangent to the curve at the temperature of interest (Fig. 1.17), Table 1.1). That is, the constant-pressure heat capacity is the derivative of the function  $H$  with respect to the variable  $T$  at a specified pressure or

$$C_p = \frac{dH}{dT} \quad \text{at constant pressure} \quad (1.15b)$$

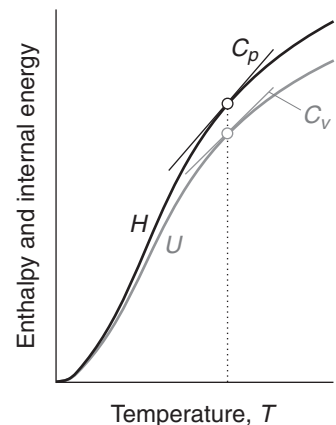
### ILLUSTRATION 1.4 Using the constant-pressure heat capacity

Provided the heat capacity is constant over the range of temperatures of interest, we can write eqn 1.15a as  $\Delta H = C_p \Delta T$ . This relation means that when the

<sup>5</sup>But heat does not actually “exist” inside: only energy exists in a system; heat is a means of recovering that energy or increasing it. Heat is energy in transit, not a form in which energy is stored.



**Fig. 1.16** The enthalpy of a system increases as its temperature is raised. Note that the enthalpy is always greater than the internal energy of the system and that the difference increases with temperature.



**Fig. 1.17** The heat capacity at constant pressure is the slope of the curve showing how the enthalpy varies with temperature; the heat capacity at constant volume is the corresponding slope of the internal energy curve. Note that the heat capacity varies with temperature (in general) and that  $C_p$  is greater than  $C_v$ .

temperature of 100 g of water (5.55 mol H<sub>2</sub>O) is raised from 20°C to 80°C (so  $\Delta T = +60$  K) at constant pressure, the enthalpy of the sample changes by

$$\begin{aligned}\Delta H &= C_p \Delta T = n C_{p,m} \Delta T = (5.55 \text{ mol}) \times (75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times (60 \text{ K}) \\ &= +25 \text{ kJ}\end{aligned}$$

The greater the temperature rise, the greater the change in enthalpy and therefore the more heating required to bring it about. Note that this calculation is only approximate, because the heat capacity depends on the temperature, and we have used an average value for the temperature range of interest. ■

The difference between  $C_{p,m}$  and  $C_{V,m}$  is significant for gases (for oxygen,  $C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_{p,m} = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ), which undergo large changes of volume when heated, but is negligible for most solids and liquids. For a perfect gas, you will show in Exercise 1.19 that

$$C_{p,m} - C_{V,m} = R \quad (1.16)$$

## Physical change

We shall focus on the use of the enthalpy as a useful bookkeeping property for tracing the flow of energy as heat during physical processes and chemical reactions at constant pressure. The discussion will lead naturally to a quantitative treatment of the factors that optimize the suitability of fuels, including “biological fuels,” the foods we ingest to meet the energy requirements of daily life.

First, we consider physical change, such as when one form of a substance changes into another form of the same substance, as when ice melts to water. We shall also include the breaking and formation of a bond in a molecule.

### 1.9 The enthalpy of phase transition

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*To begin to understand the complex structural changes that biological macromolecules undergo when heated or cooled, we need to understand how simpler physical changes occur.*

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To describe physical change quantitatively, we need to keep track of the numerical value of a thermodynamic property with varying conditions, such as the states of the substances involved, the pressure, and the temperature. To simplify the calculations, chemists have found it convenient to report their data for a set of standard conditions at the temperature of their choice:

The **standard state** of a substance is the pure substance at exactly 1 bar.<sup>6</sup>

We denote the standard state value by the superscript  $^\ominus$  on the symbol for the property, as in  $H_m^\ominus$  for the standard molar enthalpy of a substance and  $p^\ominus$  for the standard pressure of 1 bar. For example, the standard state of hydrogen gas is the pure gas at 1 bar and the standard state of solid calcium carbonate is the pure solid at 1 bar, with either the calcite or aragonite form specified. The physical state needs

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<sup>6</sup>Remember that 1 bar = 10<sup>5</sup> Pa exactly. Solutions are a special case and are dealt with in Chapter 3.



to be specified because we can speak of the standard states of the solid, liquid, and vapor forms of water, for instance, which are the pure solid, the pure liquid, and the pure vapor, respectively, at 1 bar in each case.

In older texts you might come across a standard state defined for 1 atm (101.325 kPa) in place of 1 bar. That is the old convention. In most cases, data for 1 atm differ only a little from data for 1 bar. You might also come across standard states defined as referring to 298.15 K. That is incorrect: temperature is not a part of the definition of standard state, and standard states may refer to any temperature (but it should be specified). Thus, it is possible to speak of the standard state of water vapor at 100 K, 273.15 K, or any other temperature. It is conventional, though, for data to be reported at the so-called **conventional temperature** of 298.15 K (25.00°C), and from now on, unless specified otherwise, all data will be for that temperature. For simplicity, we shall often refer to 298.15 K as “25°C.” Finally, a standard state need not be a stable state and need not be realizable in practice. Thus, the standard state of water vapor at 25°C is the vapor at 1 bar, but water vapor at that temperature and pressure would immediately condense to liquid water.

Before going on, we need to add a few more terms to our vocabulary. A **phase** is a specific state of matter that is uniform throughout in composition and physical state. The liquid and vapor states of water are two of its phases. The term “phase” is more specific than “state of matter” because a substance may exist in more than one solid form, each one of which is a solid phase. There are at least twelve forms of ice. No substance has more than one gaseous phase, so “gas phase” and “gaseous state” are effectively synonyms. The only substance that exists in more than one liquid phase is helium, although evidence is accumulating that water may also have two liquid phases.

The conversion of one phase of a substance to another phase is called a **phase transition**. Thus, vaporization (liquid  $\rightarrow$  gas) is a phase transition, as is a transition between solid phases (such as aragonite  $\rightarrow$  calcite in geological processes). With a few exceptions, most phase transitions are accompanied by a change of enthalpy, for the rearrangement of atoms or molecules usually requires or releases energy.

The vaporization of a liquid, such as the conversion of liquid water to water vapor when a pool of water evaporates at 20°C or a kettle boils at 100°C, is an endothermic process ( $\Delta H > 0$ ), because heating is required to bring about the change. At a molecular level, molecules are being driven apart from the grip they exert on one another, and this process requires energy. One of the body’s strategies for maintaining its temperature at about 37°C is to use the endothermic character of the vaporization of water, because the evaporation<sup>7</sup> of perspiration requires energy and withdraws it from the skin.

The energy that must be supplied as heat at constant pressure per mole of molecules that are vaporized under standard conditions (that is, pure liquid at 1 bar changing to pure vapor at 1 bar) is called the **standard enthalpy of vaporization** of the liquid and is denoted  $\Delta_{\text{vap}}H^\ominus$  (Table 1.2).<sup>8</sup> For example, 44 kJ of heat is required to vaporize 1 mol  $\text{H}_2\text{O}(l)$  at 1 bar and 25°C, so  $\Delta_{\text{vap}}H^\ominus = 44 \text{ kJ mol}^{-1}$ .

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<sup>7</sup>Evaporation is virtually synonymous with vaporization but commonly denotes vaporization to dryness.

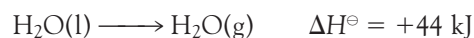
<sup>8</sup>The attachment of the subscript vap to the  $\Delta$  is the modern convention; however, the older convention in which the subscript is attached to the  $H$ , as in  $\Delta H_{\text{vap}}$ , is still widely used.

**Table 1.2** Standard enthalpies of transition at the transition temperature\*

Substance	Freezing point, $T_f$ /K	$\Delta_{\text{fus}}H^\ominus$ / (kJ mol <sup>-1</sup> )	Boiling point, $T_b$ /K	$\Delta_{\text{vap}}H^\ominus$ / (kJ mol <sup>-1</sup> )
Ammonia, NH <sub>3</sub>	195.3	5.65	239.7	23.4
Argon, Ar	83.8	1.2	87.3	6.5
Benzene, C <sub>6</sub> H <sub>6</sub>	278.7	9.87	353.3	30.8
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	158.7	4.60	351.5	43.5
Helium, He	3.5	0.02	4.22	0.08
Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub>	272.7	12.50	423.4	51.6
Mercury, Hg	234.3	2.292	629.7	59.30
Methane, CH <sub>4</sub>	90.7	0.94	111.7	8.2
Methanol, CH <sub>3</sub> OH	175.5	3.16	337.2	35.3
Propanone, CH <sub>3</sub> COCH <sub>3</sub>	177.8	5.72	329.4	29.1
Water, H <sub>2</sub> O	273.15	6.01	373.2	40.7

\*For values at 298.15 K, use the information in the *Data section*.

All enthalpies of vaporization are positive, so the sign is not normally given. Alternatively, we can report the same information by writing the **thermochemical equation**<sup>9</sup>



A thermochemical equation shows the standard enthalpy change (including the sign) that accompanies the conversion of an amount of reactant equal to its stoichiometric coefficient in the accompanying chemical equation (in this case, 1 mol H<sub>2</sub>O). If the stoichiometric coefficients in the chemical equation are multiplied through by 2, then the thermochemical equation would be written



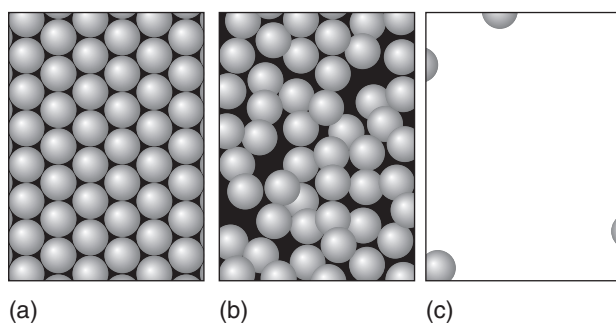
This equation signifies that 88 kJ of heat is required to vaporize 2 mol H<sub>2</sub>O(l) at 1 bar and (recalling our convention) at 298.15 K.

There are some striking differences in standard enthalpies of vaporization: although the value for water is 44 kJ mol<sup>-1</sup>, that for methane, CH<sub>4</sub>, at its boiling point is only 8 kJ mol<sup>-1</sup>. Even allowing for the fact that vaporization is taking place at different temperatures, the difference between the enthalpies of vaporization signifies that water molecules are held together in the bulk liquid much more tightly than methane molecules are in liquid methane. We shall see in Chapter 11 that the interaction responsible for the low volatility of water is the hydrogen bond, an attractive interaction between two species that arises from a link of the form A–H···B, where A and B are highly electronegative elements (such as oxygen) and B possesses one or more lone pairs of electrons (such as oxygen in H<sub>2</sub>O).

The high enthalpy of vaporization of water has profound ecological consequences, for it is partly responsible for the survival of the oceans and the generally

**COMMENT 1.5** The electronegativity of an element is the power of its atoms to draw electrons to itself when it is part of a compound. The concept should be familiar from introductory chemistry but is also discussed in Chapter 10. ■

<sup>9</sup>Unless otherwise stated, all data in this text are for 298.15 K.

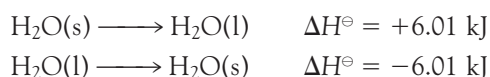


**Fig. 1.18** When a solid (a) melts to a liquid (b), the molecules separate from one another only slightly, the intermolecular interactions are reduced only slightly, and there is only a small change in enthalpy. When a liquid vaporizes (c), the molecules are separated by a considerable distance, the intermolecular forces are reduced almost to zero, and the change in enthalpy is much greater.

low humidity of the atmosphere. If only a small amount of heat had to be supplied to vaporize the oceans, the atmosphere would be much more heavily saturated with water vapor than is in fact the case.

Another common phase transition is **fusion**, or melting, as when ice melts to water. The change in molar enthalpy that accompanies fusion under standard conditions (pure solid at 1 bar changing to pure liquid at 1 bar) is called the **standard enthalpy of fusion**,  $\Delta_{\text{fus}}H^\ominus$ . Its value for water at  $0^\circ\text{C}$  is  $6.01 \text{ kJ mol}^{-1}$  (all enthalpies of fusion are positive, and the sign need not be given), which signifies that  $6.01 \text{ kJ}$  of energy is needed to melt  $1 \text{ mol H}_2\text{O(s)}$  at  $0^\circ\text{C}$  and 1 bar. Notice that the enthalpy of fusion of water is much less than its enthalpy of vaporization. In vaporization the molecules become completely separated from each other, whereas in melting the molecules are merely loosened without separating completely (Fig. 1.18).

The reverse of vaporization is **condensation** and the reverse of fusion (melting) is **freezing**. The molar enthalpy changes are, respectively, the negative of the enthalpies of vaporization and fusion, because the energy that is supplied (during heating) to vaporize or melt the substance is released when it condenses or freezes.<sup>10</sup> It is always the case that *the enthalpy change of a reverse transition is the negative of the enthalpy change of the forward transition* (under the same conditions of temperature and pressure):



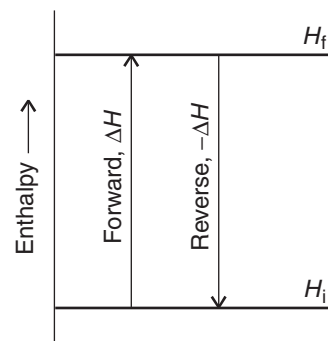
and in general

$$\Delta_{\text{forward}}H^\ominus = -\Delta_{\text{reverse}}H^\ominus \quad (1.17)$$

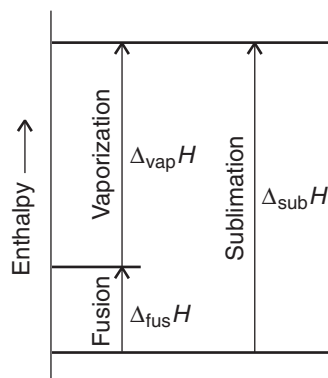
This relation follows from the fact that  $H$  is a state property, so it must return to the same value if a forward change is followed by the reverse of that change (Fig. 1.19). The high standard enthalpy of vaporization of water ( $+44 \text{ kJ mol}^{-1}$ ),

<sup>10</sup>This relation is the origin of the obsolescent terms “latent heat” of vaporization and fusion for what are now termed the enthalpy of vaporization and fusion.

**COMMENT 1.6** Links to computer animations illustrating changes in molecular motion during phase transitions will be found on the web site for this book. ■



**Fig. 1.19** An implication of the First Law is that the enthalpy change accompanying a reverse process is the negative of the enthalpy change for the forward process.



**Fig. 1.20** The enthalpy of sublimation at a given temperature is the sum of the enthalpies of fusion and vaporization at that temperature. Another implication of the First Law is that the enthalpy change of an overall process is the sum of the enthalpy changes for the possibly hypothetical steps into which it may be divided.

signifying a strongly endothermic process, implies that the condensation of water ( $-44 \text{ kJ mol}^{-1}$ ) is a strongly exothermic process. That exothermicity is the origin of the ability of steam to scald severely, because the energy is passed on to the skin.

The direct conversion of a solid to a vapor is called **sublimation**. The reverse process is called **vapor deposition**. Sublimation can be observed on a cold, frosty morning, when frost vanishes as vapor without first melting. The frost itself forms by vapor deposition from cold, damp air. The vaporization of solid carbon dioxide (“dry ice”) is another example of sublimation. The standard molar enthalpy change accompanying sublimation is called the **standard enthalpy of sublimation**,  $\Delta_{\text{sub}}H^\ominus$ . Because enthalpy is a state property, the same change in enthalpy must be obtained both in the *direct* conversion of solid to vapor and in the *indirect* conversion, in which the solid first melts to the liquid and then that liquid vaporizes (Fig. 1.20):

$$\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus \quad (1.18)$$

This result is an example of a more general statement that will prove useful time and again during our study of thermochemistry:

*The enthalpy change of an overall process is the sum of the enthalpy changes for the steps (observed or hypothetical) into which it may be divided.*

#### ILLUSTRATION 1.5 The enthalpy of sublimation of water

To use eqn 1.18 correctly, the two enthalpies that are added together must be for the same temperature, so to get the enthalpy of sublimation of water at  $0^\circ\text{C}$ , we must add together the enthalpies of fusion ( $6.01 \text{ kJ mol}^{-1}$ ) and vaporization ( $45.07 \text{ kJ mol}^{-1}$ ) for this temperature. Adding together enthalpies of transition for different temperatures gives a meaningless result. It follows that

$$\begin{aligned} \Delta_{\text{sub}}H^\ominus &= \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus = 6.01 \text{ kJ mol}^{-1} + 45.07 \text{ kJ mol}^{-1} \\ &= 51.08 \text{ kJ mol}^{-1} \end{aligned}$$

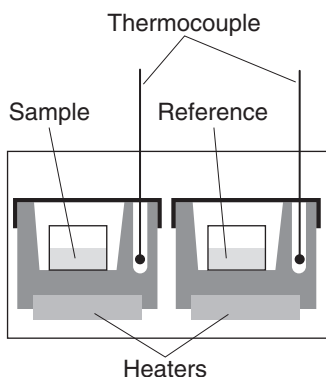
*A note on good practice:* Molar quantities are expressed as a quantity per mole (as in kilojoules per mole,  $\text{kJ mol}^{-1}$ ). Distinguish them from the magnitude of a property for 1 mol of substance, which is expressed as the quantity itself (as in kilojoules, kJ). All enthalpies of transition, denoted  $\Delta_{\text{trs}}H$ , are molar quantities. ■

### 1.10 Toolbox: Differential scanning calorimetry

*We need to describe experimental techniques that can be used to observe phase transitions in biological macromolecules.*

A **differential scanning calorimeter**<sup>11</sup> (DSC) is used to measure the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term “differential” refers to the fact that the behavior of the sample is compared to that of a reference material that does not undergo a physical or chemical change during the analysis. The term “scanning” refers to the fact that the temperatures of the sample and reference material are increased, or scanned, systematically during the analysis.

<sup>11</sup>The word *calorimeter* comes from “calor,” the Latin word for *heat*.



**Fig. 1.21** A differential scanning calorimeter. The sample and a reference material are heated in separate but identical compartments. The output is the difference in power needed to maintain the compartments at equal temperatures as the temperature rises.

A DSC consists of two small compartments that are heated electrically at a constant rate (Fig. 1.21). The temperature,  $T$ , at time  $t$  during a linear scan is

$$T = T_0 + \alpha t$$

where  $T_0$  is the initial temperature and  $\alpha$  is the temperature scan rate (in kelvin per second,  $\text{K s}^{-1}$ ). A computer controls the electrical power output in order to maintain the same temperature in the sample and reference compartments throughout the analysis.

The temperature of the sample changes significantly relative to that of the reference material if a chemical or physical process that involves heating occurs in the sample during the scan. To maintain the same temperature in both compartments, excess energy is transferred as heat to the sample during the process. For example, an endothermic process lowers the temperature of the sample relative to that of the reference and, as a result, the sample must be supplied with more energy (as heat) than the reference in order to maintain equal temperatures.

If no physical or chemical change occurs in the sample at temperature  $T$ , we can use eqn 1.4 to write  $q_p = C_p \Delta T$ , where  $\Delta T = T - T_0 = \alpha t$  and we have assumed that  $C_p$  is independent of temperature. If an endothermic process occurs in the sample, we have to supply additional “excess” energy by heating,  $q_{p,\text{ex}}$ , to achieve the same change in temperature of the sample and can express this excess energy in terms of an additional contribution to the heat capacity,  $C_{p,\text{ex}}$ , by writing  $q_{p,\text{ex}} = C_{p,\text{ex}} \Delta T$ . It follows that

$$C_{p,\text{ex}} = \frac{q_{p,\text{ex}}}{\Delta T} = \frac{q_{p,\text{ex}}}{\alpha t} = \frac{P_{\text{ex}}}{\alpha}$$

where  $P_{\text{ex}} = q_{p,\text{ex}}/t$  is the excess electrical power necessary to equalize the temperature of the sample and reference compartments.

A DSC trace, also called a *thermogram*, consists of a plot of  $P_{\text{ex}}$  or  $C_{p,\text{ex}}$  against  $T$  (Fig. 1.22). Broad peaks in the thermogram indicate processes requiring the transfer of energy by heating. We show in the following *Derivation* that the enthalpy change of the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}} dT \quad (1.19)$$

That is, the enthalpy change is the area under the curve of  $C_{p,\text{ex}}$  against  $T$  between the temperatures at which the process begins and ends.

**COMMENT 1.7** Electrical charge is measured in *coulombs*, C. The motion of charge gives rise to an electric current,  $I$ , measured in coulombs per second, or *amperes*, A, where

$$1 \text{ A} = 1 \text{ C s}^{-1}$$

If current flows through a potential difference  $\mathcal{V}$  (measured in volts, V), the total energy supplied in an interval  $t$  is

$$\text{Energy supplied} = I \mathcal{V} t$$

Because

$$1 \text{ A V s} = 1 (\text{C s}^{-1}) \text{ V s} \\ = 1 \text{ C V} = 1 \text{ J}$$

the energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds. For instance, if a current of 0.50 A from a 12 V source is passed for 360 s,

$$\text{Energy supplied} = (0.50 \text{ A}) \times (12 \text{ V}) \times (360 \text{ s}) = 2.2 \times 10^3 \text{ J}, \\ \text{or } 2.2 \text{ kJ}$$

The *rate of change of energy* is the power, expressed as joules per second, or *watts*, W:

$$1 \text{ W} = 1 \text{ J s}^{-1}$$

Because  $1 \text{ J} = 1 \text{ A V s}$ , in terms of electrical units  $1 \text{ W} = 1 \text{ A V}$ . We write the electrical power,  $P$ , as

$$P = (\text{energy supplied})/t \\ = I \mathcal{V} t/t = I \mathcal{V} \quad \blacksquare$$

**COMMENT 1.8**

Infinitesimally small quantities may be treated like any other quantity in algebraic manipulations. So, the expression  $dy/dx = a$  may be rewritten as  $dy = adx$ ,  $dx/dy = a^{-1}$ , and so on. ■

**DERIVATION 1.4** The enthalpy change of a process from DSC data

To calculate an enthalpy change from a thermogram, we begin by rewriting eqn 1.15b as

$$dH = C_p dT$$

We proceed by integrating both sides of this expression from an initial temperature  $T_1$  and initial enthalpy  $H_1$  to a final temperature  $T_2$  and enthalpy  $H_2$ .

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_{p,\text{ex}} dT$$

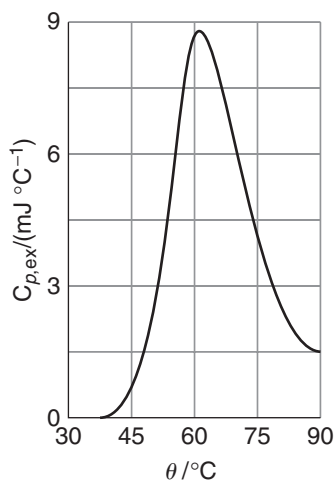
Now we use the integral  $\int dx = x + \text{constant}$  to write

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \Delta H$$

It follows that

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}} dT$$

which is eqn 1.19.



**Fig. 1.22** A thermogram for the protein ubiquitin. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* **74**, 236 [1997].)

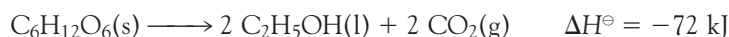
**CASE STUDY 1.1** Thermal Denaturation of a Protein

An important type of phase transition occurs in biological macromolecules, such as proteins and nucleic acids, and aggregates, such as biological membranes. Such large systems attain complex three-dimensional structures due to intra- and intermolecular interactions (Chapter 11). The disruption of these interactions is called **denaturation**. It can be achieved by adding chemical agents (such as urea, acids, or bases) or by changing the temperature, in which case the process is called **thermal denaturation**. Cooking is an example of thermal denaturation. For example, when eggs are cooked, the protein albumin is denatured irreversibly.

Differential scanning calorimetry is a useful technique for the study of denaturation of biological macromolecules. Every biopolymer has a characteristic temperature, the melting temperature  $T_m$ , at which the three-dimensional structure unravels with attendant loss of biological function. For example, the thermogram shown in Fig. 1.22 indicates that the widely distributed protein ubiquitin retains its native structure up to about 45°C and “melts” into a disordered state at higher temperatures. Differential scanning calorimetry is a convenient method for such studies because it requires small samples, with masses as low as 0.5 mg. ■

**Chemical change**

In the remainder of this chapter we concentrate on enthalpy changes accompanying chemical reactions, such as the fermentation of glucose into ethanol and  $\text{CO}_2$ , a reaction used by anaerobic organisms to harness energy stored in carbohydrates:

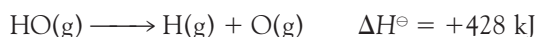


The value of  $\Delta H^\ominus$  given here signifies that the enthalpy of the system decreases by 72 kJ (and, if the reaction takes place at constant pressure, that 72 kJ of energy is released by heating the surroundings) when 1 mol  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$  decomposes into 2 mol  $\text{C}_2\text{H}_5\text{OH}(\text{l})$  to give 2 mol  $\text{CO}_2(\text{g})$  at 1 bar, all at  $25^\circ\text{C}$ .

## 1.11 The bond enthalpy

*To understand bioenergetics, we need to account for the flow of energy during chemical reactions as individual chemical bonds are broken and made.*

The thermochemical equation for the dissociation, or breaking, of a chemical bond can be written with the hydroxyl radical  $\text{OH}(\text{g})$  as an example:



The corresponding standard molar enthalpy change is called the **bond enthalpy**, so we would report the H–O bond enthalpy as  $428 \text{ kJ mol}^{-1}$ . All bond enthalpies are positive, so bond dissociation is an endothermic process.

Some bond enthalpies are given in Table 1.3. Note that the nitrogen-nitrogen bond in molecular nitrogen,  $\text{N}_2$ , is very strong, at  $945 \text{ kJ mol}^{-1}$ , which helps to account for the chemical inertness of nitrogen and its ability to dilute the oxygen in the atmosphere without reacting with it. In contrast, the fluorine-fluorine bond in molecular fluorine,  $\text{F}_2$ , is relatively weak, at  $155 \text{ kJ mol}^{-1}$ ; the weakness of this bond contributes to the high reactivity of elemental fluorine. However, bond enthalpies alone do not account for reactivity because, although the bond in molecular iodine is even weaker,  $\text{I}_2$  is less reactive than  $\text{F}_2$ , and the bond in CO is stronger than the bond in  $\text{N}_2$ , but CO forms many carbonyl compounds, such as  $\text{Ni}(\text{CO})_4$ . The types and strengths of the bonds that the elements can make to other elements are additional factors.

A complication when dealing with bond enthalpies is that their values depend on the molecule in which the two linked atoms occur. For instance, the total

**COMMENT 1.9** Recall that a radical is a very reactive species containing one or more unpaired electrons. To emphasize the presence of an unpaired electron in a radical, it is common to use a dot ( $\cdot$ ) when writing the chemical formula. For example, the chemical formula of the hydroxyl radical may be written as  $\cdot\text{OH}$ . Hydroxyl radicals and other reactive species containing oxygen can be produced in organisms as undesirable by-products of electron transfer reactions and have been implicated in the development of cardiovascular disease, cancer, stroke, inflammatory disease, and other conditions. ■

**Table 1.3** Selected bond enthalpies,  $\Delta H(\text{A—B})/(\text{kJ mol}^{-1})$

<i>Diatomic molecules</i>							
H—H	436	O=O	497	F—F	155	H—F	565
		N≡N	945	Cl—Cl	242	H—Cl	431
		O—H	428	Br—Br	193	H—Br	366
		C≡O	1074	I—I	151	H—I	299
<i>Polyatomic molecules</i>							
H—CH <sub>3</sub>	435	H—NH <sub>2</sub>	431	H—OH	492		
H—C <sub>6</sub> H <sub>5</sub>	469	O <sub>2</sub> N—NO <sub>2</sub>	57	HO—OH	213		
H <sub>3</sub> C—CH <sub>3</sub>	368	O=CO	531	HO—CH <sub>3</sub>	377		
H <sub>2</sub> C=CH <sub>2</sub>	699			Cl—CH <sub>3</sub>	452		
HC≡CH	962			Br—CH <sub>3</sub>	293		
				I—CH <sub>3</sub>	234		

standard enthalpy change for the atomization (the complete dissociation into atoms) of water:



is not twice the O–H bond enthalpy in  $\text{H}_2\text{O}$  even though two O–H bonds are dissociated. There are in fact two different dissociation steps. In the first step, an O–H bond is broken in an  $\text{H}_2\text{O}$  molecule:



In the second step, the O–H bond is broken in an OH radical:



The sum of the two steps is the atomization of the molecule. As can be seen from this example, the O–H bonds in  $\text{H}_2\text{O}$  and HO have similar but not identical bond enthalpies.

Although accurate calculations must use bond enthalpies for the molecule in question and its successive fragments, when such data are not available, there is no choice but to make estimates by using **mean bond enthalpies**,  $\Delta H_{\text{B}}$ , which are the averages of bond enthalpies over a related series of compounds (Table 1.4). For ex-

**Table 1.4** Mean bond enthalpies,  $\Delta H_{\text{B}}/(\text{kJ mol}^{-1})^*$

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348 (1) 612 (2) 838 (3) 518 (a) <sup>†</sup>									
N	388	305 (1) 613 (2) 890 (3)	163 (1) 409 (2) 945 (3)								
O	463	360 (1) 743 (2)	157	146 (1) 97 (2)							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259			496	250	212		264		
P	322									200	
Si	318		374	466							226

\*Values are for single bonds except where otherwise stated (in parentheses).

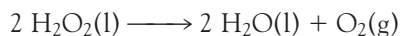
<sup>†</sup>(a) Denotes aromatic.



ample, the mean HO bond enthalpy,  $\Delta H_{\text{B}}(\text{H}-\text{O}) = 463 \text{ kJ mol}^{-1}$ , is the mean of the O–H bond enthalpies in  $\text{H}_2\text{O}$  and several other similar compounds, including methanol,  $\text{CH}_3\text{OH}$ .

### EXAMPLE 1.2 Using mean bond enthalpies

Use information from the *Data section* and bond enthalpy data from Tables 1.3 and 1.4 to estimate the standard enthalpy change for the reaction



in which liquid hydrogen peroxide decomposes into  $\text{O}_2$  and water at  $25^\circ\text{C}$ . In the aqueous environment of biological cells, hydrogen peroxide—a very reactive species—is formed as a result of some processes involving  $\text{O}_2$ . The enzyme catalase helps rid organisms of toxic hydrogen peroxide by accelerating its decomposition.

**Strategy** In calculations of this kind, the procedure is to break the overall process down into a sequence of steps such that their sum is the chemical equation required. Always ensure, when using bond enthalpies, that all the species are in the gas phase. That may mean including the appropriate enthalpies of vaporization or sublimation. One approach is to atomize all the reactants and then to build the products from the atoms so produced. When explicit bond enthalpies are available (that is, data are given in the tables available), use them; otherwise, use mean bond enthalpies to obtain estimates.

**Solution** The following steps are required:

	$\Delta H^\ominus/\text{kJ}$
Vaporization of 2 mol $\text{H}_2\text{O}_2(\text{l})$ , $2 \text{H}_2\text{O}_2(\text{l}) \longrightarrow 2 \text{H}_2\text{O}_2(\text{g})$	$2 \times (+51.6)$
Dissociation of 4 mol O–H bonds:	$4 \times (+463)$
Dissociation of 2 mol O–O bonds in HO–OH:	$2 \times (+213)$
Overall, so far: $2 \text{H}_2\text{O}_2(\text{l}) \longrightarrow 4 \text{H}(\text{g}) + 4 \text{O}(\text{g})$	+2381

We have used the mean bond enthalpy value from Table 1.4 for the O–H bond and the exact bond enthalpy value for the O–O bond in HO–OH from Table 1.3. In the second step, four O–H bonds and one O=O bond are formed. The standard enthalpy change for bond formation (the reverse of dissociation) is the negative of the bond enthalpy. We can use exact values for the enthalpy of the O–H bond in  $\text{H}_2\text{O}(\text{g})$  and for the O=O bond in  $\text{O}_2(\text{g})$ :

	$\Delta H^\ominus/\text{kJ}$
Formation of 4 mol O–H bonds:	$4 \times (-492)$
Formation of 1 mol $\text{O}_2$ :	–497
Overall, in this step: $4 \text{O}(\text{g}) + 4 \text{H}(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$	–2465

The final stage of the reaction is the condensation of 2 mol  $\text{H}_2\text{O}(\text{g})$ :



The sum of the enthalpy changes is

$$\Delta H^\ominus = (+2381 \text{ kJ}) + (-2465 \text{ kJ}) + (-88 \text{ kJ}) = -172 \text{ kJ}$$

The experimental value is  $-196 \text{ kJ}$ .

**SELF-TEST 1.4** Estimate the enthalpy change for the reaction between liquid ethanol, a fuel made by fermenting corn, and  $\text{O}_2(\text{g})$  to yield  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  under standard conditions by using the bond enthalpies, mean bond enthalpies, and the appropriate standard enthalpies of vaporization.

**Answer:**  $-1348 \text{ kJ}$ ; the experimental value is  $-1368 \text{ kJ}$  ■

## 1.12 Thermochemical properties of fuels

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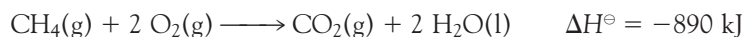
*We need to understand the molecular origins of the energy content of biological fuels, the carbohydrates, fats, and proteins.*

---

We saw in Section 1.3 that photosynthesis and the oxidation of organic molecules are the most important processes that supply energy to organisms. Here, we begin a quantitative study of biological energy conversion by assessing the thermochemical properties of fuels.

### (a) Enthalpies of combustion

The consumption of a fuel in a furnace or an engine is the result of a combustion. An example is the combustion of methane in a natural gas flame:



The **standard enthalpy of combustion**,  $\Delta_c H^\ominus$ , is the standard change in enthalpy per mole of combustible substance. In this example, we would write  $\Delta_c H^\ominus(\text{CH}_4, \text{g}) = -890 \text{ kJ mol}^{-1}$ . Some typical values are given in Table 1.5. Note that  $\Delta_c H^\ominus$  is a molar quantity and is obtained from the value of  $\Delta H^\ominus$  by dividing by the amount of organic reactant consumed (in this case, by 1 mol  $\text{CH}_4$ ).

According to the discussion in Section 1.6 and the relation  $\Delta U = q_V$ , the energy transferred as heat at constant volume is equal to the change in internal energy,  $\Delta U$ , not  $\Delta H$ . To convert from  $\Delta U$  to  $\Delta H$ , we need to note that the molar enthalpy of a substance is related to its molar internal energy by  $H_m = U_m + pV_m$  (eqn 1.13a). For condensed phases,  $pV_m$  is so small, it may be ignored. For example, the molar volume of liquid water is  $18 \text{ cm}^3 \text{ mol}^{-1}$ , and at 1.0 bar

$$\begin{aligned} pV_m &= (1.0 \times 10^5 \text{ Pa}) \times (18 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) = 1.8 \text{ Pa m}^3 \text{ mol}^{-1} \\ &= 1.8 \text{ J mol}^{-1} \end{aligned}$$

However, the molar volume of a gas, and therefore the value of  $pV_m$ , is about 1000 times greater and cannot be ignored. For gases treated as perfect,  $pV_m$  may be replaced by  $RT$ . Therefore, if in the chemical equation the difference (products – reactants) in the stoichiometric coefficients of *gas phase* species is  $\Delta \nu_{\text{gas}}$ , we can write

$$\Delta_c H = \Delta_c U + \Delta \nu_{\text{gas}} RT \quad (1.20)$$

Note that  $\Delta \nu_{\text{gas}}$  (where  $\nu$  is nu) is a dimensionless number.

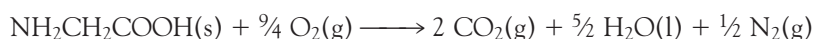
**Table 1.5** Standard enthalpies of combustion

Substance	$\Delta_c H^\ominus / (\text{kJ mol}^{-1})$
Carbon, C(s, graphite)	-394
Carbon monoxide, CO(g)	-394
Citric acid, C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> (s)	-1985
Ethanol, C <sub>2</sub> H <sub>5</sub> OH(l)	-1368
Glucose, C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-2808
Glycine, CH <sub>2</sub> (NH <sub>2</sub> )COOH(s)	-969
Hydrogen, H <sub>2</sub> (g)	-286
iso-Octane, * C <sub>8</sub> H <sub>18</sub> (l)	-5461
Methane, CH <sub>4</sub> (g)	-890
Methanol, CH <sub>3</sub> OH(l)	-726
Methylbenzene, C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (l)	-3910
Octane, C <sub>8</sub> H <sub>18</sub> (l)	-5471
Propane, C <sub>3</sub> H <sub>8</sub> (g)	-2220
Pyruvic acid, CH <sub>3</sub> (CO)COOH(l)	-950
Sucrose, C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)	-5645
Urea, CO(NH <sub>2</sub> ) <sub>2</sub> (s)	-632

\*2,2,4-Trimethylpentane.

**ILLUSTRATION 1.6** Converting between  $\Delta_c H$  and  $\Delta_c U$ 

The energy released as heat by the combustion of the amino acid glycine is  $969.6 \text{ kJ mol}^{-1}$  at  $298.15 \text{ K}$ , so  $\Delta_c U = -969.6 \text{ kJ mol}^{-1}$ . From the chemical equation



we find that  $\Delta \nu_{\text{gas}} = (2 + \frac{1}{2}) - \frac{9}{4} = \frac{1}{4}$ . Therefore,

$$\begin{aligned} \Delta_c H &= \Delta_c U + \frac{1}{4}RT = -969.6 \text{ kJ mol}^{-1} \\ &+ \frac{1}{4} \times (8.3145 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \\ &= -969.6 \text{ kJ mol}^{-1} + 0.62 \text{ kJ mol}^{-1} = -969.0 \text{ kJ mol}^{-1} \blacksquare \end{aligned}$$

We shall see in Chapter 2 that the best assessment of the ability of a compound to act as a fuel to drive many of the processes occurring in the body makes use of the ‘‘Gibbs energy.’’ However, a useful guide to the resources provided by a fuel, and the only one that matters when energy transferred as heat is being considered, is the enthalpy, particularly the enthalpy of combustion. The thermochemical properties of fuels and foods are commonly discussed in terms of their *specific enthalpy*, the enthalpy of combustion per gram of material, or the *enthalpy density*, the magnitude of the enthalpy of combustion per liter of material. Thus, if the standard enthalpy of combustion is  $\Delta_c H^\ominus$  and the molar mass of the compound is  $M$ , then the specific enthalpy is  $\Delta_c H^\ominus / M$ . Similarly, the enthalpy density is  $\Delta_c H^\ominus / V_m$ , where  $V_m$  is the molar volume of the material.

Table 1.6 lists the specific enthalpies and enthalpy densities of several fuels. The most suitable fuels are those with high specific enthalpies, as the advantage of a high molar enthalpy of combustion may be eliminated if a large mass of fuel is to be transported. We see that H<sub>2</sub> gas compares very well with more traditional fuels such as methane (natural gas), octane (gasoline), and methanol. Furthermore, the

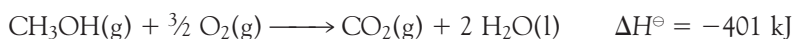
**Table 1.6** Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\circ / (\text{kJ mol}^{-1})$	Specific enthalpy/ ( $\text{kJ g}^{-1}$ )	Enthalpy density*/ ( $\text{kJ L}^{-1}$ )
Hydrogen	$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$	-286	142	13
Methane	$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-890	55	40
iso-Octane <sup>†</sup>	$2 \text{C}_8\text{H}_{18}(\text{l}) + 25 \text{O}_2(\text{g}) \rightarrow 16 \text{CO}_2(\text{g}) + 18 \text{H}_2\text{O}(\text{l})$	-5461	48	$3.3 \times 10^4$
Methanol	$2 \text{CH}_3\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$	-726	23	$1.8 \times 10^4$

\*At atmospheric pressures and room temperature.  
<sup>†</sup>2,2,4-Trimethylpentane.

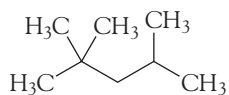
combustion of  $\text{H}_2$  gas does not generate  $\text{CO}_2$  gas, a pollutant implicated in the mechanism of global warming. As a result,  $\text{H}_2$  gas has been proposed as an efficient, clean alternative to fossil fuels, such as natural gas and petroleum. However, we also see that  $\text{H}_2$  gas has a very low enthalpy density, which arises from the fact that hydrogen is a very light gas. So, the advantage of a high specific enthalpy is undermined by the large volume of fuel to be transported and stored. Strategies are being developed to solve the storage problem. For example, the small  $\text{H}_2$  molecules can travel through holes in the crystalline lattice of a sample of metal, such as titanium, where they bind as metal hydrides. In this way it is possible to increase the effective density of hydrogen atoms to a value that is higher than that of liquid  $\text{H}_2$ . Then the fuel can be released on demand by heating the metal.

We now assess the factors that optimize the enthalpy of combustion of carbon-based fuels, with an eye toward understanding such biological fuels as carbohydrates, fats, and proteins. Let's consider the combustion of 1 mol  $\text{CH}_4(\text{g})$ . The reaction involves changes in the oxidation numbers of carbon from  $-4$  to  $+4$ , an oxidation, and of oxygen from  $0$  to  $-2$ , a reduction. From the thermochemical equation, we see that 890 kJ of energy is released as heat per mole of carbon atoms that are oxidized. Now consider the oxidation of 1 mol  $\text{CH}_3\text{OH}(\text{g})$ :



This reaction is also exothermic, but now only 401 kJ of energy is released as heat per mole of carbon atoms that undergo oxidation. Much of the observed change in energy output between the reactions can be explained by noting that the carbon atom in  $\text{CH}_3\text{OH}$  has an oxidation number of  $-2$ , and not  $-4$  as in  $\text{CH}_4$ . That is, the replacement of a C-H bond by a C-O bond renders the carbon in methanol more oxidized than the carbon in methane, so it is reasonable to expect that less energy is released to complete the oxidation of carbon in methanol to  $\text{CO}_2$ . In general, we find that the presence of partially oxidized carbon atoms (that is, carbon atoms bonded to oxygen atoms) in a material makes it a less suitable fuel than a similar material containing more highly reduced carbon atoms.

Another factor that determines the enthalpy of combustion reactions is the number of carbon atoms in hydrocarbon compounds. For example, from the value of the standard enthalpy of combustion for methane we know that for each mole of  $\text{CH}_4$  supplied to a furnace, 890 kJ of heat can be released, whereas for each mole of iso-octane ( $\text{C}_8\text{H}_{18}$ , 2,2,4-trimethylpentane, **5**, a typical component of gasoline)



5 2,2,4-Trimethylpentane

**COMMENT 1.10** See Appendix 4 for a review of oxidation numbers. ■

supplied to an internal combustion engine, 5471 kJ of energy is released as heat (Table 1.6). The much larger value for iso-octane is a consequence of each molecule having eight C atoms to contribute to the formation of carbon dioxide, whereas methane has only one.

### (b) Biological fuels

A typical 18- to 20-year-old man requires a daily energy input of about 12 MJ (1 MJ =  $10^6$  J); a woman of the same age needs about 9 MJ. If the entire consumption were in the form of glucose, which has a specific enthalpy of  $16 \text{ kJ g}^{-1}$ , meeting energy needs would require the consumption of 750 g of glucose by a man and 560 g by a woman. In fact, the complex carbohydrates (polymers of carbohydrate units, such as starch, as discussed in Chapter 11) more commonly found in our diets have slightly higher specific enthalpies ( $17 \text{ kJ g}^{-1}$ ) than glucose itself, so a carbohydrate diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fiber, the indigestible cellulose that helps move digestion products through the intestine.

The specific enthalpy of fats, which are long-chain esters such as tristearin, is much greater than that of carbohydrates, at around  $38 \text{ kJ g}^{-1}$ , slightly less than the value for the hydrocarbon oils used as fuel ( $48 \text{ kJ g}^{-1}$ ). The reason for this difference lies in the fact that many of the carbon atoms in carbohydrates are bonded to oxygen atoms and are already partially oxidized, whereas most of the carbon atoms in fats are bonded to hydrogen and other carbon atoms and hence have lower oxidation numbers. As we saw above, the presence of partially oxidized carbons lowers the energy output of a fuel.

Fats are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply. In Arctic species, the stored fat also acts as a layer of insulation; in desert species (such as the camel), the fat is also a source of water, one of its oxidation products.

Proteins are also used as a source of energy, but their components, the amino acids, are also used to construct other proteins. When proteins are oxidized (to urea,  $\text{CO}(\text{NH}_2)_2$ ), the equivalent enthalpy density is comparable to that of carbohydrates.

We have already remarked that not all the energy released by the oxidation of foods is used to perform work. The energy that is also released as heat needs to be discarded in order to maintain body temperature within its typical range of 35.6 to 37.8°C. A variety of mechanisms contribute to this aspect of **homeostasis**, the ability of an organism to counteract environmental changes with physiological responses. The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When energy needs to be dissipated rapidly by heating, warm blood is allowed to flow through the capillaries of the skin, so producing flushing. Radiation is one means of heating the surroundings; another is evaporation and the energy demands of the enthalpy of vaporization of water.

#### ILLUSTRATION 1.7 Dissipation of energy through perspiration

From the enthalpy of vaporization ( $\Delta_{\text{vap}}H^\ominus = 44 \text{ kJ mol}^{-1}$ ), molar mass ( $M = 18 \text{ g mol}^{-1}$ ), and mass density ( $\rho = 1.0 \times 10^3 \text{ g L}^{-1}$ ) of water, the energy removed as heat through evaporation per liter of water perspired is

$$q = \frac{\rho \Delta_{\text{vap}}H^\ominus}{M} = \frac{(1.0 \times 10^3 \text{ g L}^{-1}) \times (44 \text{ kJ mol}^{-1})}{18 \text{ g mol}^{-1}} = 2.4 \text{ MJ L}^{-1}$$

where we have used  $1 \text{ MJ} = 10^6 \text{ J}$ . When vigorous exercise promotes sweating (through the influence of heat selectors on the hypothalamus), 1 to 2 L of perspired water can be produced per hour, corresponding to a loss of energy of approximately  $2.4$  to  $5.0 \text{ MJ h}^{-1}$ . ■

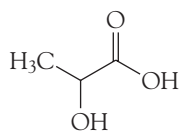
### 1.13 The combination of reaction enthalpies

*To make progress in our study of bioenergetics, we need to develop methods for predicting the reaction enthalpies of complex biochemical reactions.*

It is often the case that a reaction enthalpy is needed but is not available in tables of data. Now the fact that enthalpy is a state function comes in handy, because it implies that we can construct the required reaction enthalpy from the reaction enthalpies of known reactions. We have already seen a primitive example when we calculated the enthalpy of sublimation from the sum of the enthalpies of fusion and vaporization. The only difference is that we now apply the technique to a sequence of chemical reactions. The procedure is summarized by **Hess's law**:

The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.

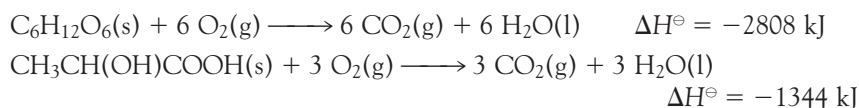
Although the procedure is given the status of a law, it hardly deserves the title because it is nothing more than a consequence of enthalpy being a state function, which implies that an overall enthalpy change can be expressed as a sum of enthalpy changes for each step in an indirect path. The individual steps need not be actual reactions that can be carried out in the laboratory—they may be entirely hypothetical reactions, the only requirement being that their equations should balance. Each step must correspond to the same temperature.



6 Lactic acid

#### EXAMPLE 1.3 Using Hess's law

In biological cells that have a plentiful supply of  $\text{O}_2$ , glucose is oxidized completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Section 1.12). Muscle cells may be deprived of  $\text{O}_2$  during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid (6) by the process of glycolysis (Section 4.9). Given the thermochemical equations for the combustions of glucose and lactic acid:



calculate the standard enthalpy for glycolysis:



Is there a biological advantage of complete oxidation of glucose compared with glycolysis? Explain your answer.

**Strategy** We need to add or subtract the thermochemical equations so as to reproduce the thermochemical equation for the reaction required.

**Solution** We obtain the thermochemical equation for glycolysis from the following sum:

	$\Delta H^\ominus/\text{kJ}$
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \longrightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$	−2808
$6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l}) \longrightarrow 2 \text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s}) + 6 \text{O}_2(\text{g})$	$2 \times (+1344 \text{ kJ})$
Overall: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \longrightarrow 2 \text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s})$	−120

It follows that the standard enthalpy for the conversion of glucose to lactic acid during glycolysis is  $-120 \text{ kJ mol}^{-1}$ , a mere 4% of the enthalpy of combustion of glucose. Therefore, full oxidation of glucose is metabolically more useful than glycolysis, because in the former process more energy becomes available for performing work.

**SELF-TEST 1.5** Calculate the standard enthalpy of the fermentation  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2 \text{C}_2\text{H}_5\text{OH}(\text{l}) + 2 \text{CO}_2(\text{g})$  from the standard enthalpies of combustion of glucose and ethanol (Table 1.5).

Answer:  $-72 \text{ kJ}$  ■

## 1.14 Standard enthalpies of formation

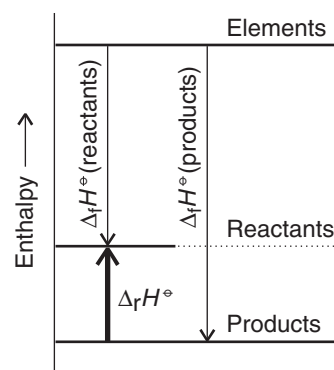
*We need to simplify even further the process of predicting reaction enthalpies of biochemical reactions.*

The **standard reaction enthalpy**,  $\Delta_r H^\ominus$ , is the difference between the standard molar enthalpies of the reactants and the products, with each term weighted by the stoichiometric coefficient,  $\nu$  (nu), in the chemical equation

$$\Delta_r H^\ominus = \sum \nu H_{\text{m}}^\ominus(\text{products}) - \sum \nu H_{\text{m}}^\ominus(\text{reactants}) \quad (1.21)$$

where  $\Sigma$  (uppercase sigma) denotes a sum. Because the  $H_{\text{m}}^\ominus$  are molar quantities and the stoichiometric coefficients are pure numbers, the units of  $\Delta_r H^\ominus$  are kilojoules per mole. The standard reaction enthalpy is the change in enthalpy of the system when the reactants in their standard states (pure, 1 bar) are completely converted into products in their standard states (pure, 1 bar), with the change expressed in kilojoules per mole of reaction as written.

The problem with eqn 1.21 is that we have no way of knowing the absolute enthalpies of the substances. To avoid this problem, we can imagine the reaction as taking place by an indirect route, in which the reactants are first broken down into the elements and then the products are formed from the elements (Fig. 1.23). Specifically, the **standard enthalpy of formation**,  $\Delta_f H^\ominus$ , of a substance is the standard enthalpy (per mole of the substance) for its formation from its elements in their reference states. The **reference state** of an element is its most stable form under the prevailing conditions (Table 1.7). Don't confuse "reference state" with "standard state": the reference state of carbon at  $25^\circ\text{C}$  is graphite (not diamond); the standard state of carbon is any specified phase of the element at 1 bar. For

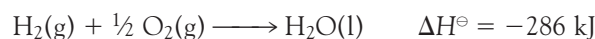


**Fig. 1.23** An enthalpy of reaction may be expressed as the difference between the enthalpies of the products and the reactants.

**Table 1.7** Reference states of some elements at 298.15 K

Element	Reference state
Arsenic	gray arsenic
Bromine	liquid
Carbon	graphite
Hydrogen	gas
Iodine	solid
Mercury	liquid
Nitrogen	gas
Oxygen	gas
Phosphorus	white phosphorus
Sulfur	rhombic sulfur
Tin	white tin, $\alpha$ -tin

example, the standard enthalpy of formation of liquid water (at 25°C, as always in this text) is obtained from the thermochemical equation



and is  $\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l}) = -286 \text{ kJ mol}^{-1}$ . Note that enthalpies of formation are molar quantities, so to go from  $\Delta H^\ominus$  in a thermochemical equation to  $\Delta_f H^\ominus$  for that substance, divide by the amount of substance formed (in this instance, by 1 mol  $\text{H}_2\text{O}$ ).

With the introduction of standard enthalpies of formation, we can write

$$\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{products}) - \sum \nu \Delta_f H^\ominus(\text{reactants}) \quad (1.22)$$

**COMMENT 1.11** The text's web site contains links to online databases of thermochemical data, including enthalpies of combustion and standard enthalpies of formation. ■

The first term on the right is the enthalpy of formation of all the products from their elements; the second term on the right is the enthalpy of formation of all the reactants from their elements. The fact that the enthalpy is a state function means that a reaction enthalpy calculated in this way is identical to the value that would be calculated from eqn 1.21 if absolute enthalpies were available.

The values of some standard enthalpies of formation at 25°C are given in Table 1.8, and a longer list is given in the *Data section*. The standard enthalpies of formation of elements in their reference states are zero by definition (because their formation is the null reaction: element  $\rightarrow$  element). Note, however, that the standard enthalpy of formation of an element in a state other than its reference state is not zero:



Therefore, although  $\Delta_f H^\ominus(\text{C, graphite}) = 0$ ,  $\Delta_f H^\ominus(\text{C, diamond}) = +1.895 \text{ kJ mol}^{-1}$ .

#### EXAMPLE 1.4 Using standard enthalpies of formation

Glucose and fructose (7) are simple carbohydrates with the molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . Sucrose (8), or table sugar, is a complex carbohydrate with molecular

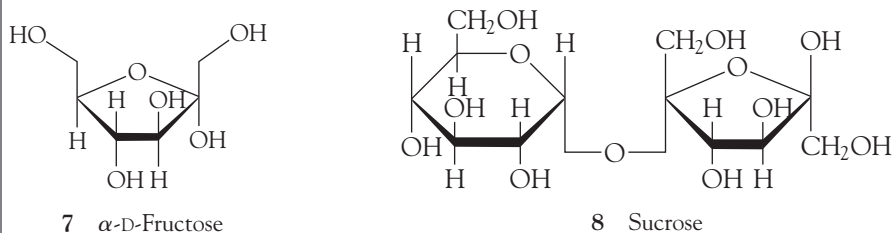


**Table 1.8** Standard enthalpies of formation at 298.15 K\*

Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
<i>Inorganic compounds</i>		<i>Organic compounds</i>	
Ammonia, $\text{NH}_3(\text{g})$	-46.11	Adenine, $\text{C}_5\text{H}_5\text{N}_5(\text{s})$	+96.9
Carbon monoxide, $\text{CO}(\text{g})$	-110.53	Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}(\text{s})$	-604.0
Carbon dioxide, $\text{CO}_2(\text{g})$	-393.51	Benzene, $\text{C}_6\text{H}_6(\text{l})$	+49.0
Hydrogen sulfide, $\text{H}_2\text{S}(\text{g})$	-20.63	Butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}(\text{l})$	-533.8
Nitrogen dioxide, $\text{NO}_2(\text{g})$	+33.18	Ethane, $\text{C}_2\text{H}_6(\text{g})$	-84.68
Nitrogen monoxide, $\text{NO}(\text{g})$	+90.25	Ethanoic acid, $\text{CH}_3\text{COOH}(\text{l})$	-484.3
Sodium chloride, $\text{NaCl}(\text{s})$	-411.15	Ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69
Water, $\text{H}_2\text{O}(\text{l})$	-285.83	$\alpha$ -D-Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1268
$\text{H}_2\text{O}(\text{g})$	-241.82	Guanine, $\text{C}_5\text{H}_5\text{N}_5\text{O}(\text{s})$	-183.9
		Glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}(\text{s})$	-528.5
		N-Glycylglycine, $\text{C}_4\text{H}_8\text{N}_2\text{O}_3(\text{s})$	-747.7
		Hexadecanoic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}(\text{s})$	-891.5
		Leucine, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}(\text{s})$	-637.4
		Methane, $\text{CH}_4(\text{g})$	-74.81
		Methanol, $\text{CH}_3\text{OH}(\text{l})$	-238.86
		Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	-2222
		Thymine, $\text{C}_5\text{H}_6\text{N}_2\text{O}_2(\text{s})$	-462.8
		Urea, $(\text{NH}_2)_2\text{CO}(\text{s})$	-333.1

\*A longer list is given in the *Data section* at the end of the book.

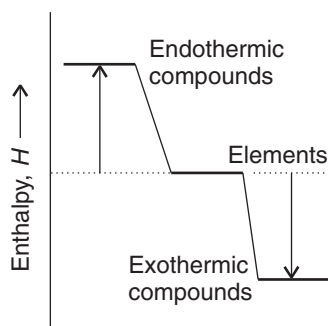
formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  that consists of a glucose unit covalently linked to a fructose unit (a water molecule is released as a result of the reaction between glucose and fructose to form sucrose). Estimate the standard enthalpy of combustion of sucrose from the standard enthalpies of formation of the reactants and products.



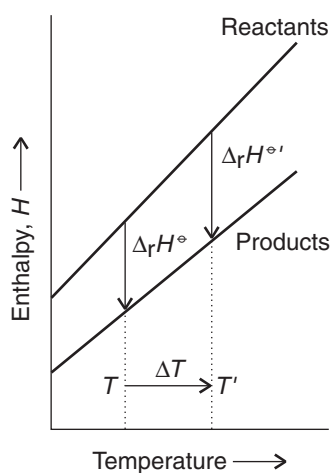
**Strategy** We write the chemical equation, identify the stoichiometric numbers of the reactants and products, and then use eqn 1.22. Note that the expression has the form “products – reactants.” Numerical values of standard enthalpies of formation are given in the *Data section*. The standard enthalpy of combustion is the enthalpy change per mole of substance, so we need to interpret the enthalpy change accordingly.

**Solution** The chemical equation is





**Fig. 1.24** The enthalpy of formation acts as a kind of thermochemical “altitude” of a compound with respect to the “sea level” defined by the elements from which it is made. Endothermic compounds have positive enthalpies of formation; exothermic compounds have negative enthalpies of formation.



**Fig. 1.25** The enthalpy of a substance increases with temperature. Therefore, if the total enthalpy of the reactants increases by a different amount from that of the products, the reaction enthalpy will change with temperature. The change in reaction enthalpy depends on the relative slopes of the two lines and hence on the heat capacities of the substances.

It follows that

$$\begin{aligned}\Delta_r H^\ominus &= \{12\Delta_f H^\ominus(\text{CO}_2, \text{g}) + 11\Delta_f H^\ominus(\text{H}_2\text{O}, \text{l})\} \\ &\quad - \{\Delta_f H^\ominus(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{g}) + 12\Delta_f H^\ominus(\text{O}_2, \text{g})\} \\ &= \{12 \times (-393.51 \text{ kJ mol}^{-1}) + 11 \times (-285.83 \text{ kJ mol}^{-1})\} \\ &\quad - \{(-2222 \text{ kJ mol}^{-1}) + 0\} \\ &= -5644 \text{ kJ mol}^{-1}\end{aligned}$$

Inspection of the chemical equation shows that, in this instance, the “per mole” is per mole of sucrose, which is exactly what we need for an enthalpy of combustion. It follows that the estimate for the standard enthalpy of combustion of sucrose is  $-5644 \text{ kJ mol}^{-1}$ . The experimental value is  $-5645 \text{ kJ mol}^{-1}$ .

*A note on good practice:* The standard enthalpy of formation of an element in its reference state (oxygen gas in this example) is written 0, not  $0 \text{ kJ mol}^{-1}$ , because it is zero whatever units we happen to be using.

**SELF-TEST 1.6** Use standard enthalpies of formation to calculate the enthalpy of combustion of solid glycine to  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$ , and  $\text{N}_2(\text{g})$ .

**Answer:**  $-969.7 \text{ kJ mol}^{-1}$ , in agreement with the experimental value (see the Data section) ■

The reference states of the elements define a thermochemical “sea level,” and enthalpies of formation can be regarded as thermochemical “altitudes” above or below sea level (Fig. 1.24). Compounds that have negative standard enthalpies of formation (such as water) are classified as **exothermic compounds**, for they lie at a lower enthalpy than their component elements (they lie below thermochemical sea level). Compounds that have positive standard enthalpies of formation (such as carbon disulfide) are classified as **endothermic compounds** and possess a higher enthalpy than their component elements (they lie above sea level).

## 1.15 The variation of reaction enthalpy with temperature

*We need to know how to predict reaction enthalpies of biochemical reactions at different temperatures, even though we may have data at only one temperature.*

Suppose we want to know the enthalpy of a particular reaction at body temperature,  $37^\circ\text{C}$ , but have data available for  $25^\circ\text{C}$ , or suppose we to know whether the oxidation of glucose is more exothermic when it takes place inside an Arctic fish that inhabits water at  $0^\circ\text{C}$  than when it takes place at mammalian body temperatures. In precise work, every attempt would be made to measure the reaction enthalpy at the temperature of interest, but it is useful to have a rapid way of estimating the sign and even a moderately reliable numerical value.

Figure 1.25 illustrates the technique we use. As we have seen, the enthalpy of a substance increases with temperature; therefore the total enthalpy of the reactants and the total enthalpy of the products increases as shown in the illustration. Provided the two total enthalpy increases are different, the standard reaction enthalpy (their difference) will change as the temperature is changed. The change in the enthalpy of a substance depends on the slope of the graph and therefore on the constant-pressure heat capacities of the substances (recall Fig. 1.17). We can there-

fore expect the temperature dependence of the reaction enthalpy to be related to the difference in heat capacities of the products and the reactants. We show in the following *Derivation* that this is indeed the case and that, when the heat capacities do not vary with temperature, the standard reaction enthalpy at a temperature  $T'$  is related to the value at a different temperature  $T$  by a special formulation of **Kirchhoff's law**:

$$\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \Delta_r C_p^\ominus \times (T' - T) \quad (1.23)$$

where  $\Delta_r C_p^\ominus$  is the difference between the weighted sums of the standard molar heat capacities of the products and the reactants:

$$\Delta_r C_p^\ominus = \sum \nu C_{p,m}^\ominus(\text{products}) - \sum \nu C_{p,m}^\ominus(\text{reactants}) \quad (1.24)$$

Values of standard molar constant-pressure heat capacities for a number of substances are given in the *Data section*. Because eqn 1.23 applies only when the heat capacities are constant over the range of temperature of interest, its use is restricted to small temperature differences (of no more than 100 K or so).

#### DERIVATION 1.5 Kirchhoff's law

To derive Kirchhoff's law, we consider the variation of the enthalpy with temperature. We begin by rewriting eqn 1.15b to calculate the change in the standard molar enthalpy  $H_m^\ominus$  of each reactant and product as the temperature of the reaction mixture is increased:

$$dH_m^\ominus = C_{p,m}^\ominus dT$$

where  $C_{p,m}^\ominus$  is the standard molar constant-pressure heat capacity, the molar heat capacity at 1 bar. We proceed by integrating both sides of the expression for  $dH_m^\ominus$  from an initial temperature  $T$  and initial enthalpy  $H_m^\ominus(T)$  to a final temperature  $T'$  and enthalpy  $H_m^\ominus(T')$ :

$$\int_{H_m^\ominus(T)}^{H_m^\ominus(T')} dH = \int_T^{T'} C_{p,m}^\ominus dT$$

It follows that for each reactant and product (assuming that no phase transition takes place in the temperature range of interest):

$$H_m^\ominus(T') = H_m^\ominus(T) + \int_T^{T'} C_{p,m}^\ominus dT$$

Because this equation applies to each substance in the reaction, we use it and eqn 1.22 to write the following expression for  $\Delta_r H^\ominus(T')$ :

$$\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \int_T^{T'} \Delta_r C_p^\ominus dT$$

where  $\Delta_r C_p^\ominus$  is given by eqn 1.24. This equation is the exact form of Kirchhoff's law. The special case given by eqn 1.23 can be derived readily from it by

making the approximation that  $\Delta_r C_p^\ominus$  is independent of temperature. Then the integral on the right evaluates to

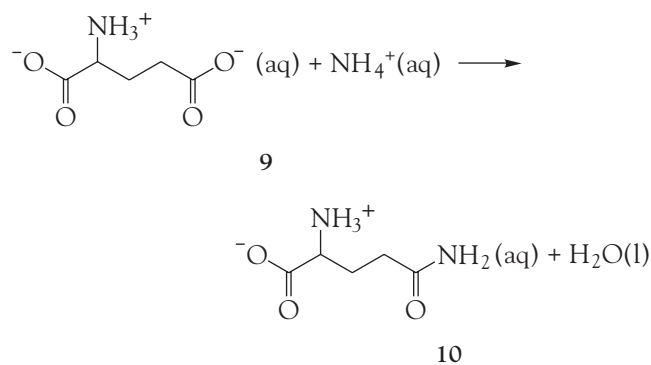
$$\int_T^{T'} \Delta_r C_p^\ominus dT = \Delta_r C_p^\ominus \int_T^{T'} dT = \Delta_r C_p^\ominus \times (T' - T)$$

and we obtain eqn 1.23.

*A note on good practice:* Because heat capacities can be measured more accurately than some reaction enthalpies, the exact form of Kirchhoff's law, with numerical integration of  $\Delta_r C_p^\ominus$  over the temperature range of interest, sometimes gives results more accurate than a direct measurement of the reaction enthalpy at the second temperature.

### EXAMPLE 1.5 Using Kirchhoff's law

The enzyme glutamine synthetase mediates the synthesis of the amino acid glutamine (Gln, **10**) from the amino acid glutamate (Glu, **9**) and ammonium ion:



$$\Delta_r H^\ominus = +21.8 \text{ kJ mol}^{-1} \text{ at } 25^\circ\text{C}$$

The process is endothermic and requires energy extracted from the oxidation of biological fuels and stored in ATP (Section 1.3). Estimate the value of the reaction enthalpy at  $60^\circ\text{C}$  by using data found in this text (see the *Data section*) and the following additional information:  $C_{p,m}^\ominus(\text{Gln, aq}) = 187.0 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_{p,m}^\ominus(\text{Glu, aq}) = 177.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Strategy** Calculate the value of  $\Delta_r C_p^\ominus$  from the available data and eqn 1.24 and use the result in eqn 1.23.

**Solution** From the *Data section*, the standard molar constant-pressure heat capacities of  $\text{H}_2\text{O(l)}$  and  $\text{NH}_4^+(\text{aq})$  are  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $79.9 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. It follows that

$$\begin{aligned}
 \Delta_r C_p^\ominus &= \{C_{p,m}^\ominus(\text{Gln, aq}) + C_{p,m}^\ominus(\text{H}_2\text{O, l})\} \\
 &\quad - \{C_{p,m}^\ominus(\text{Glu, aq}) + C_{p,m}^\ominus(\text{NH}_4^+, \text{aq})\} \\
 &= \{(187.0 \text{ J K}^{-1} \text{ mol}^{-1}) + (75.3 \text{ J K}^{-1} \text{ mol}^{-1})\} \\
 &\quad - \{(177.0 \text{ J K}^{-1} \text{ mol}^{-1}) + (79.9 \text{ J K}^{-1} \text{ mol}^{-1})\} \\
 &= +5.4 \text{ J K}^{-1} \text{ mol}^{-1} = +5.4 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

Then, because  $T' - T = +35$  K, from eqn 1.23 we find

$$\begin{aligned}\Delta_r H^\ominus(333 \text{ K}) &= (+21.8 \text{ kJ mol}^{-1}) + (5.4 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (35 \text{ K}) \\ &= (+21.8 \text{ kJ mol}^{-1}) + (0.19 \text{ kJ mol}^{-1}) \\ &= +22.0 \text{ kJ mol}^{-1}\end{aligned}$$

**SELF-TEST 1.7** Estimate the standard enthalpy of combustion of solid glycine at 340 K from the data in Self-test 1.6 and the *Data section*.

**Answer:**  $-973 \text{ kJ mol}^{-1}$  ■

The calculation in Example 1.5 shows that the standard reaction enthalpy at 60°C is only slightly different from that at 25°C. The reason is that the change in reaction enthalpy is proportional to the *difference* between the molar heat capacities of the products and the reactants, which is usually not very large. It is generally the case that provided the temperature range is not too wide, enthalpies of reactions vary only slightly with temperature. A reasonable first approximation is that standard reaction enthalpies are independent of temperature. However, notable exceptions are processes involving the unfolding of macromolecules, such as proteins (*Case study* 1.1). The difference in molar heat capacities between the folded and unfolded states of proteins is usually rather large, on the order of a few kilojoules per mole, so the enthalpy of protein unfolding varies significantly with temperature.

## Checklist of Key Ideas

You should now be familiar with the following concepts:

- 1. A system is classified as open, closed, or isolated.
- 2. The surroundings remain at constant temperature and either constant volume or constant pressure when processes occur in the system.
- 3. An exothermic process releases energy as heat,  $q$ , to the surroundings; an endothermic process absorbs energy as heat.
- 4. The work of expansion against constant external pressure is  $w = -p_{\text{ex}}\Delta V$ .
- 5. Maximum expansion work is achieved in a reversible change.
- 6. The change in internal energy can be calculated from  $\Delta U = w + q$ .
- 7. The First Law of thermodynamics states that the internal energy of an isolated system is constant.
- 8. The enthalpy is defined as  $H = U + pV$ .
- 9. A change in internal energy is equal to the energy transferred as heat at constant volume ( $\Delta U = q_V$ ); a change in enthalpy is equal to the energy transferred as heat at constant pressure ( $\Delta H = q_p$ ).
- 10. The constant-volume heat capacity is the slope of the tangent to the graph of the internal energy of a constant-volume system plotted against temperature ( $C_V = dU/dT$ ) and the constant-pressure heat capacity is the slope of the tangent to the graph of the enthalpy of a constant-pressure system plotted against temperature ( $C_p = dH/dT$ ).
- 11. The standard state of a substance is the pure substance at 1 bar.
- 12. The standard enthalpy of transition,  $\Delta_{\text{trs}}H^\ominus$ , is the change in molar enthalpy when a substance in one phase changes into another phase, both phases being in their standard states.
- 13. The standard enthalpy of the reverse of a process is the negative of the standard enthalpy of the forward process,  $\Delta_{\text{reverse}}H^\ominus = -\Delta_{\text{forward}}H^\ominus$ .
- 14. The standard enthalpy of a process is the sum of the standard enthalpies of the individual processes into which it may be regarded as divided, as in  $\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus$ .
- 15. Differential scanning calorimetry (DSC) is a useful technique for the investigation of phase transitions, especially those observed in biological macromolecules.

- 16. Hess's law states that the standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction can be divided.
- 17. The standard enthalpy of formation of a compound,  $\Delta_f H^\ominus$ , is the standard reaction enthalpy for the formation of the compound from its elements in their reference states.
- 18. The standard reaction enthalpy,  $\Delta_r H^\ominus$ , is the difference between the standard enthalpies of formation of the products and reactants, weighted by their stoichiometric coefficients  $\nu$ :  $\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{products}) - \sum \nu \Delta_f H^\ominus(\text{reactants})$ .
- 19. At constant pressure, exothermic compounds are those for which  $\Delta_f H^\ominus < 0$ ; endothermic compounds are those for which  $\Delta_f H^\ominus > 0$ .
- 20. Kirchhoff's law states that the standard reaction enthalpies at different temperatures are related by  $\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \Delta_r C_p^\ominus \times (T' - T)$ , where  $\Delta_r C_p^\ominus = \sum \nu C_{p,m}^\ominus(\text{products}) - \sum \nu C_{p,m}^\ominus(\text{reactants})$ .

## Discussion questions

- 1.1 Provide molecular interpretations of work and heat.
- 1.2 Explain the difference between the change in internal energy and the change in enthalpy of a chemical or physical process.
- 1.3 Explain the limitations of the following expressions: (a)  $w = -nRT \ln(V_f/V_i)$ ; (b)  $\Delta H = \Delta U + p\Delta V$ ; (c)  $\Delta_r H^\ominus(T') = \Delta_r H^\ominus(T) + \Delta_r C_p^\ominus \times (T' - T)$ .
- 1.4 A primitive air-conditioning unit for use in places where electrical power is not available can be made by hanging up strips of linen soaked in water. Explain why this strategy is effective.
- 1.5 In many experimental thermograms, such as that shown in Fig. 1.22, the baseline below  $T_1$  is at a different level from that above  $T_2$ . Explain this observation.
- 1.6 Describe at least two calculational methods by which standard reaction enthalpies can be predicted. Discuss the advantages and disadvantages of each method.
- 1.7 Distinguish between (a) standard state and reference state of an element; (b) endothermic and exothermic compounds.

## Exercises

Assume all gases are perfect unless stated otherwise. All thermochemical data are for 298.15 K.

- 1.8 How much metabolic energy must a bird of mass 200 g expend to fly to a height of 20 m? Neglect all losses due to friction, physiological imperfection, and the acquisition of kinetic energy.
- 1.9 Calculate the work of expansion accompanying the complete combustion of 1.0 g of glucose to carbon dioxide and (a) liquid water, (b) water vapor at 20°C when the external pressure is 1.0 atm.
- 1.10 We are all familiar with the general principles of operation of an internal combustion reaction: the combustion of fuel drives out the piston. It is possible to imagine engines that use reactions other than combustions, and we need to assess the work they can do. A chemical reaction takes place in a container of cross-sectional area 100 cm<sup>2</sup>; the container has a piston at one end. As a result of the reaction, the piston is pushed out through 10.0 cm against a constant external pressure of 100 kPa. Calculate the work done by the system.
- 1.11 A sample of methane of mass 4.50 g occupies 12.7 L at 310 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 30.0 kPa until its volume has increased by 3.3 L. (b) Calculate the work that would be done if the same expansion occurred isothermally and reversibly.
- 1.12 Derivation 1.2 showed how to calculate the work of reversible, isothermal expansion of a perfect gas. Suppose that the expansion is reversible but not isothermal and that the temperature decreases as the expansion proceeds. (a) Find an expression

for the work when  $T = T_i - c(V - V_i)$ , with  $c$  a positive constant. **(b)** Is the work greater or smaller than for isothermal expansion?

- 1.13** Graphical displays often enhance understanding. Take your result from Exercise 1.12 and use an electronic spreadsheet to plot the work done by the system against the final volume for a selection of values of  $c$ . Include negative values of  $c$  (corresponding to the temperature rising as the expansion occurs).
- 1.14** The heat capacity of air is much smaller than that of water, and relatively modest amounts of heat are needed to change its temperature. This is one of the reasons why desert regions, though very hot during the day, are bitterly cold at night. The heat capacity of air at room temperature and pressure is approximately  $21 \text{ J K}^{-1} \text{ mol}^{-1}$ . How much energy is required to raise the temperature of a room of dimensions  $5.5 \text{ m} \times 6.5 \text{ m} \times 3.0 \text{ m}$  by  $10^\circ\text{C}$ ? If losses are neglected, how long will it take a heater rated at  $1.5 \text{ kW}$  to achieve that increase given that  $1 \text{ W} = 1 \text{ J s}^{-1}$ ?
- 1.15** The transfer of energy from one region of the atmosphere to another is of great importance in meteorology for it affects the weather. Calculate the heat needed to be supplied to a parcel of air containing  $1.00 \text{ mol}$  air molecules to maintain its temperature at  $300 \text{ K}$  when it expands reversibly and isothermally from  $22 \text{ L}$  to  $30.0 \text{ L}$  as it ascends.
- 1.16** A laboratory animal exercised on a treadmill, which, through pulleys, raised a mass of  $200 \text{ g}$  through  $1.55 \text{ m}$ . At the same time, the animal lost  $5.0 \text{ J}$  of energy as heat. Disregarding all other losses and regarding the animal as a closed system, what is its change in internal energy?
- 1.17** The internal energy of a perfect gas does not change when the gas undergoes isothermal expansion. What is the change in enthalpy?
- 1.18** A sample of a serum of mass  $25 \text{ g}$  is cooled from  $290 \text{ K}$  to  $275 \text{ K}$  at constant pressure by the extraction of  $1.2 \text{ kJ}$  of energy as heat. Calculate  $q$  and  $\Delta H$  and estimate the heat capacity of the sample.
- 1.19** (a) Show that for a perfect gas,  $C_{p,m} - C_{V,m} = R$ . (b) When  $229 \text{ J}$  of energy is supplied as heat at constant pressure to  $3.00 \text{ mol CO}_2(\text{g})$ , the temperature of the sample increases by  $2.06 \text{ K}$ .
- Calculate the molar heat capacities at constant volume and constant pressure of the gas.
- 1.20** Use the information in Exercise 1.19 to calculate the change in **(a)** molar enthalpy, **(b)** molar internal energy when carbon dioxide is heated from  $15^\circ\text{C}$  (the temperature when air is inhaled) to  $37^\circ\text{C}$  (blood temperature, the temperature in our lungs).
- 1.21** Suppose that the molar internal energy of a substance over a limited temperature range could be expressed as a polynomial in  $T$  as  $U_m(T) = a + bT + cT^2$ . Find an expression for the constant-volume molar heat capacity at a temperature  $T$ .
- 1.22** The heat capacity of a substance is often reported in the form  $C_{p,m} = a + bT + c/T^2$ . Use this expression to make a more accurate estimate of the change in molar enthalpy of carbon dioxide when it is heated from  $15^\circ\text{C}$  to  $37^\circ\text{C}$  (as in Exercise 1.20), given  $a = 44.22 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $b = 8.79 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$ , and  $c = -8.62 \times 10^5 \text{ J K mol}^{-1}$ . *Hint:* You will need to integrate  $dH = C_p dT$ .
- 1.23** Exercise 1.22 gives an expression for the temperature dependence of the constant-pressure molar heat capacity over a limited temperature range. **(a)** How does the molar enthalpy of the substance change over that range? **(b)** Plot the molar enthalpy as a function of temperature using the data in Exercise 1.22.
- 1.24** Classify as endothermic or exothermic **(a)** a combustion reaction for which  $\Delta_r H^\ominus = -2020 \text{ kJ mol}^{-1}$ , **(b)** a dissolution for which  $\Delta H^\ominus = +4.0 \text{ kJ mol}^{-1}$ , **(c)** vaporization, **(d)** fusion, **(e)** sublimation.
- 1.25** The pressures deep within the Earth are much greater than those on the surface, and to make use of thermochemical data in geochemical assessments, we need to take the differences into account. **(a)** Given that the enthalpy of combustion of graphite is  $-393.5 \text{ kJ mol}^{-1}$  and that of diamond is  $-395.41 \text{ kJ mol}^{-1}$ , calculate the standard enthalpy of the  $\text{C}(\text{s, graphite}) \rightarrow \text{C}(\text{s, diamond})$  transition. **(b)** Use the information in part (a) together with the densities of graphite ( $2.250 \text{ g cm}^{-3}$ ) and diamond ( $3.510 \text{ g cm}^{-3}$ ) to calculate the internal energy of the transition when the sample is under a pressure of  $150 \text{ kbar}$ .

- 1.26 A typical human produces about 10 MJ of energy transferred as heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?
- 1.27 Use the information in Tables 1.1 and 1.2 to calculate the total heat required to melt 100 g of ice at 0°C, heat it to 100°C, and then vaporize it at that temperature. Sketch a graph of temperature against time on the assumption that the sample is heated at a constant rate.
- 1.28 The mean bond enthalpies of C–C, C–H, C=O, and O–H bonds are 348, 412, 743, and 463 kJ mol<sup>-1</sup>, respectively. The combustion of a fuel such as octane is exothermic because relatively weak bonds break to form relatively strong bonds. Use this information to justify why glucose has a lower specific enthalpy than the lipid decanoic acid (C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>) even though these compounds have similar molar masses.
- 1.29 Use bond enthalpies and mean bond enthalpies to estimate (a) the enthalpy of the anaerobic breakdown of glucose to lactic acid in cells that are starved of O<sub>2</sub>, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(aq) → 2 CH<sub>3</sub>CH(OH)COOH(aq), (b) the enthalpy of combustion of glucose. Ignore the contributions of enthalpies of fusion and vaporization.
- 1.30 Glucose and fructose are simple sugars with the molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. Sucrose (table sugar) is a complex sugar with molecular formula C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> that consists of a glucose unit covalently bound to a fructose unit (a water molecule is eliminated as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25% of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a tablet provides assuming 25% of the energy is available for work?
- 1.31 Camping gas is typically propane. The standard enthalpy of combustion of propane gas is –2220 kJ mol<sup>-1</sup> and the standard enthalpy of vaporization of the liquid is +15 kJ mol<sup>-1</sup>. Calculate (a) the standard enthalpy and (b) the standard internal energy of combustion of the liquid.
- 1.32 Ethane is flamed off in abundance from oil wells, because it is unreactive and difficult to use commercially. But would it make a good fuel? The standard enthalpy of reaction for 2 C<sub>2</sub>H<sub>6</sub>(g) + 7 O<sub>2</sub>(g) → 4 CO<sub>2</sub>(g) + 6 H<sub>2</sub>O(l) is –3120 kJ mol<sup>-1</sup>. (a) What is the standard enthalpy of combustion of ethane? (b) What is the specific enthalpy of combustion of ethane? (c) Is ethane a more or less efficient fuel than methane?
- 1.33 Estimate the difference between the standard enthalpy of formation of H<sub>2</sub>O(l) as currently defined (at 1 bar) and its value using the former definition (at 1 atm).
- 1.34 Use information in the *Data section* to calculate the standard enthalpies of the following reactions:
- (a) the hydrolysis of a glycine-glycine dipeptide:
- $$^+\text{NH}_3\text{CH}_2\text{CONHCH}_2\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2 ^+\text{NH}_3\text{CH}_2\text{CO}_2^-(\text{aq})$$
- (b) the combustion of solid β-D-fructose
- (c) the dissociation of nitrogen dioxide, which occurs in the atmosphere:
- $$\text{NO}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{O}(\text{g})$$
- 1.35 During glycolysis, glucose is partially oxidized to pyruvic acid, CH<sub>3</sub>COCOOH, by NAD<sup>+</sup> (see Chapter 4) without the involvement of O<sub>2</sub>. However, it is also possible to carry out the oxidation in the presence of O<sub>2</sub>:
- $$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{CH}_3\text{COCOOH}(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$$
- $$\Delta_r H^\ominus = -480.7 \text{ kJ mol}^{-1}$$
- From these data and additional information in the *Data section*, calculate the standard enthalpy of combustion and standard enthalpy of formation of pyruvic acid.
- 1.36 At 298 K, the enthalpy of denaturation of hen egg white lysozyme is +217.6 kJ mol<sup>-1</sup> and the change in the constant-pressure molar heat capacity resulting from denaturation of the protein is +6.3 kJ K<sup>-1</sup> mol<sup>-1</sup>. (a) Estimate the enthalpy of denaturation of the protein at (i) 351 K, the “melting” temperature of the



macromolecule, and (ii) 263 K. State any assumptions in your calculations. (b) Based on your answers to part (a), is denaturation of hen egg white lysozyme always endothermic?

1.37 Estimate the enthalpy of vaporization of water at 100°C from its value at 25°C (+44.01 kJ mol<sup>-1</sup>) given the constant-pressure heat capacities of 75.29 J K<sup>-1</sup> mol<sup>-1</sup> and 33.58 J K<sup>-1</sup> mol<sup>-1</sup> for liquid and gas, respectively.

1.38 Is the standard enthalpy of combustion of glucose likely to be higher or lower at blood temperature than at 25°C?

1.39 Derive a version of Kirchhoff's law (eqn 1.23) for the temperature dependence of the internal energy of reaction.

1.40 The formulation of Kirchhoff's law given in eqn 1.23 is valid when the difference in heat capacities is independent of temperature over the temperature range of interest. Suppose instead that  $\Delta_r C_p^\ominus = a + bT + c/T^2$ . Derive a more accurate form of Kirchhoff's law in terms of the parameters  $a$ ,  $b$ , and  $c$ . *Hint*: The change in the reaction enthalpy for an infinitesimal change in temperature is  $\Delta_r C_p^\ominus dT$ . Integrate this expression between the two temperatures of interest.

## Project

1.41 It is possible to see with the aid of a powerful microscope that a long piece of double-stranded DNA is flexible, with the distance between the ends of the chain adopting a wide range of values. This flexibility is important because it allows DNA to adopt very compact conformations as it is packaged in a chromosome (see Chapter 11). It is convenient to visualize a long piece of DNA as a *freely jointed chain*, a chain of  $N$  small, rigid units of length  $l$  that are free to make any angle with respect to each other. The length  $l$ , the *persistence length*, is approximately 45 nm, corresponding to approximately 130 base pairs. You will now explore the work associated with extending a DNA molecule.

(a) Suppose that a DNA molecule resists being extended from an equilibrium, more compact conformation with a *restoring force*  $F = -k_F x$ , where  $x$  is the difference in the end-to-end distance of the chain from an equilibrium value and  $k_F$  is the *force constant*. Systems showing this behavior are said to obey *Hooke's law*. (i) What are the limitations of this model of the DNA molecule? (ii) Using this model, write an expression for the work that must be done to extend a DNA molecule by  $x$ . Draw a graph of your conclusion.

(b) A better model of a DNA molecule is the *one-dimensional freely jointed chain*, in which a rigid unit of length  $l$  can only make an angle of 0° or 180° with an adjacent unit. In this case, the restoring force of a chain extended by  $x = nl$  is given by

$$F = \frac{kT}{2l} \ln\left(\frac{1+\nu}{1-\nu}\right) \quad \nu = n/N$$

where  $k = 1.381 \times 10^{-23}$  J K<sup>-1</sup> is *Boltzmann's constant* (not a force constant). (i) What are the limitations of this model? (ii) What is the magnitude of the force that must be applied to extend a DNA molecule with  $N = 200$  by 90 nm? (iii) Plot the restoring force against  $\nu$ , noting that  $\nu$  can be either positive or negative. How is the variation of the restoring force with end-to-end distance different from that predicted by Hooke's law? (iv) Keeping in mind that the difference in end-to-end distance from an equilibrium value is  $x = nl$  and, consequently,  $dx = l d\nu = Nl d\nu$ , write an expression for the work of extending a DNA molecule. (v) Calculate the work of extending a DNA molecule from  $\nu = 0$  to  $\nu = 1.0$ . *Hint*: You must integrate the expression for  $w$ . The task can be accomplished easily with mathematical software.

(c) Show that for small extensions of the chain, when  $\nu \ll 1$ , the restoring force is given by

$$F \approx \frac{\nu kT}{l} = \frac{nkT}{Nl}$$

*Hint*: See Appendix 2 for a review of series expansions of functions.

(d) Is the variation of the restoring force with extension of the chain given in part (c) different from that predicted by Hooke's law? Explain your answer.