

15

Energy and Enthalpy in Chemical Systems

Key Concepts

15-1 Work and heat. Equivalence of heat, work, and energy.

15-2 The first law of thermodynamics. Thermodynamic systems: open, closed, and isolated. Interconversion of heat, work, and energy. PV work. Conservation of energy. State functions. Internal energy E .

15-3 Energy, enthalpy, and heat capacity. Exothermic and endothermic reactions. Enthalpy, H . Heat capacities at constant volume and at constant pressure.

15-4 The first law and chemical reactions. Hess' law and additivity of heats of reaction. Energy-level diagrams for reactions. Standard states and standard heats of formation.

15-5 Bond energies. Heats of formation and bond energies. Strain and distortion of bond angles. Electron delocalization and bond stabilization.

*Heat and cold are nature's two hands by
which she chiefly worketh.*

Francis Bacon (1627)

An old motto from the time of World War II (and probably earlier) is, "The difficult we do at once; the impossible takes a little longer." In this chapter and the next we shall discover what is *possible* in chemical reactions. This does not mean that everything that is possible by the laws of thermodynamics will take place in a short time. When the chemical thermodynamicist says that a reaction is spontaneous, he makes no predictions whatsoever about elapsed time; he only says that, given *enough* time, the reaction can happen. To the thermodynamicist, the explosion produced by dropping sodium in water and the weathering away of the entire North American continent are both spontaneous processes.

To the chemist, it is important to know whether a reaction is spontaneous in the thermodynamic sense. If it is slow but spontaneous, then some means, such as catalysis, may be found to hasten the process. If the reaction is not spontaneous, the search for an accelerator is doomed at the start; another means must be devised to force the desired reaction to occur.

By what criterion does a chemist say that a reaction is spontaneous? In Chapter 4 we discussed the ideas of spontaneity and equilibrium, but we took the numerical values of equilibrium constants on faith. Now we shall see how these constants can be related to other measurable properties of a reaction. Most spontaneous reactions release heat. Explosions and other

combustions are familiar examples. Is it a valid generalization to say that *all* spontaneous reactions release heat? Why do some reactions go to completion so thoroughly that essentially no reactants are left, whereas others appear to halt when a mixture of reactants and products is present? Can we predict in advance that a given reaction will behave in either of these two ways? What effect does the amount of a reactant or a product have on the spontaneity of a reaction?

These are some of the questions that we will answer in the course of this chapter and the next one. However, you should not forget that thermodynamics only describes what *can* happen (or better, what is not forbidden). Making it happen, and making it happen in a reasonable time, is the task of the research chemist.

15-1 WORK, HEAT, AND CALORIC

One of Lavoisier's great contributions to chemistry was to undercut the phlogiston theory, as we have seen in Chapter 6. He demonstrated that combustion was a combination with oxygen and not a loss of phlogiston. He was less perceptive in his ideas about the source of the heat, which is so prominent a feature of combustion. Lavoisier coined the term *caloric*, in 1789, for what he regarded as the "imponderable matter of heat." Heat was considered to be a fluid, probably weightless, that surrounded the atoms of substances and could be drained away in reactions that produced heat.

Dalton conceived of each atom as existing in an "atmosphere" of heat. In 1808, he wrote:

"The most probable opinion concerning the nature of caloric is that of its being an elastic fluid of great subtilty, the particles of which repel one another, but are attracted by all other bodies."

According to this generally accepted idea of Dalton's time, a gas is heated when it is compressed because the particles of caloric, repelling one another as they do, are squeezed out of the gas. Heat of friction develops when the frictional motion strips caloric away from its atoms. The caloric theory of heat was accepted by most scientists for the first half of the nineteenth century.

The Cannons of Bavaria

In 1798, Benjamin Thompson (Count Rumford) conducted some experiments with friction that, if they had been appreciated fully, would have done away with caloric as Lavoisier did away with phlogiston. Thompson was superintending the boring of cannons at the military arsenal in Munich. The process involved cast metal cannon blanks and drill bits that were turned by horses. Thompson was impressed by the considerable heat

evolved during the drilling. He tried boring the cannons under water and determined that the same length of time was always required to bring a given amount of water to the boiling point. He also observed that the generation of heat apparently could be continued indefinitely. He interpreted what he saw correctly; the work provided by the horses was being converted into heat. Thompson wrote:

“It is hardly necessary to add that anything which any insulated body or system of bodies can continually be furnished without limitation cannot possibly be a material substance, and it appears to me to be extremely difficult if not quite impossible to form any distinct ideas of anything capable of being excited and communicated in the manner the *Heat* was excited and communicated in these experiments except it be *Motion*.”

His experiments failed to convince others. Those who believed in the caloric theory were ready with the explanation that the friction of the drill bit rubbed caloric away from the metal atoms and brought it to the surface. They failed to appreciate the significance of Count Rumford’s ability to continue to produce heat indefinitely. According to the caloric theory, after the supply of caloric had been rubbed away from the metal, further boring should not produce heat. Unfortunately, scientists were not accustomed to thinking of heat in quantitative terms, just as they were not accustomed to thinking of matter in quantitative terms before Lavoisier’s proposal. Rumford’s work had little impact.

Blood, Sweat, and Gears

The men who finally convinced scientists *that heat and work were equivalent, and that both were forms of energy*, were Julius Mayer (1814–1878) and Hermann von Helmholtz (1821–1894), both German physicians, and James Joule (1818–1889). In 1840, Mayer signed onto a ship bound for Java as ship’s doctor. He noted that the blood from the veins of the Javanese and from his own ship’s crew was a brighter red than that he had seen from patients in Germany. He interpreted this correctly as indicating that more oxygen remained in the veins of inhabitants from the tropics than in the veins of people from cold climates, because less combustion of foods was required to maintain a constant body temperature in the tropics. This train of thought led him to the further conclusion that the heat of combustion of foods was used both to maintain body temperature and to carry out the work done by an individual. Heat could be converted into work, and both were forms of the same thing, energy. On his return to Germany he tried to calculate the conversion factor between heat and work by using stirring devices for water and expanding gases into chambers. The experiments were difficult to perform accurately, because the temperature increases were fractions of a degree. Nevertheless, he obtained an approximate value for

the mechanical equivalent of heat and submitted an account of his work to the *Annalen der Physik*. The *Annalen der Physik* rejected his paper as unfit for publication. He reworked it and submitted it to the *Annalen der Chemie und Pharmacie* instead. It was published in 1842, and aroused no comment whatever. Like Newlands with his classification of the elements, Mayer had expected controversy, but encountered only indifference.

At the same time, Joule, in England, was doing virtually the same experiments and meeting the same indifference and disbelief. Joule was a student of Dalton and the son of a Lancashire brewer. At the age of 19, he began building electric motors and generators with the intention of converting the brewery from steam power to electricity. These attempts were abortive, but Joule became interested in the relationship among the work of cranking the dynamo, the electricity generated, and the heat produced by electricity. Later he dropped the electricity from the sequence and studied the heat produced by stirring water mechanically with paddles driven by a falling weight (Figure 15-1). Like Mayer, Joule found the experiments difficult because of the small temperature changes produced. In spite of this, he obtained a conversion factor that, expressed in calories, is $42.4 \text{ kg cm cal}^{-1}$, with 1% of the currently accepted value of $42.67 \text{ kg cm cal}^{-1}$. That is, a 1-kg weight, falling through a distance of 42.67 cm, can do enough work (by turning a stirring paddle, for example) to add 1 cal of heat to the water. If the experiment is performed with an insulated 1-liter container of water, then, since the heat capacity of water is $1 \text{ cal deg}^{-1} \text{ g}^{-1}$, the temperature will increase only by one-thousandth of a degree. It was a remarkable achievement of Joule's to come so close to the best modern value with home-made and home-calibrated thermometers.

The connection between heat and work is much more straightforward in SI units. If a mass of m kilograms is lifted a distance h against the acceleration of gravity, $g = 9.806 \text{ m sec}^{-2}$, the work done is

$$w = mgh \text{ joules}$$

From this and Joule's experiment we can find the conversion between calories and joules. For $m = 1.000 \text{ kg}$ and $h = 0.4267 \text{ m}$:

$$\begin{aligned} w &= 1.000 \text{ cal} = 1.000 \times 9.806 \times 0.4267 \text{ kg m}^2 \text{ sec}^{-2} \\ 1.000 \text{ cal} &= 4.184 \text{ J} \end{aligned}$$

In 1843, Joule submitted his results to the British Association. They were received with disbelief and general silence. A year later a paper on the subject was rejected by the Royal Society. In 1845, Joule again presented his ideas on the equivalence of work and heat to the British Association. He suggested that the water at the bottom of Niagara Falls should be 0.2°F warmer than the water at the top because of the energy gained in the fall. He also proposed the idea of an absolute zero of temperature, based on the thermal expansion of gases, at -480°F (-284°C).

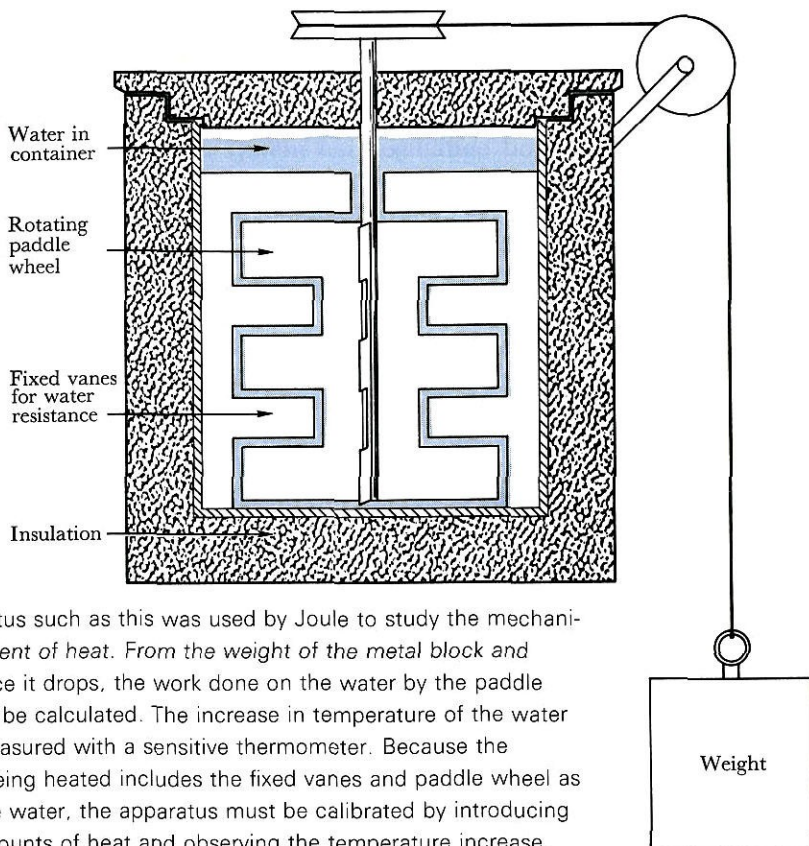


Figure 15-1

An apparatus such as this was used by Joule to study the mechanical equivalent of heat. From the weight of the metal block and the distance it drops, the work done on the water by the paddle wheel can be calculated. The increase in temperature of the water can be measured with a sensitive thermometer. Because the material being heated includes the fixed vanes and paddle wheel as well as the water, the apparatus must be calibrated by introducing known amounts of heat and observing the temperature increase.

No one listened. He tried again in 1847, and in Joule's own words, written in 1885:

“The communication would have passed without comment if a young man had not risen in the section, and by his intelligent observations created a lively interest in the new theory. The young man was William Thomson, who had two years previously passed the University of Cambridge with the highest honour, and is now probably the foremost scientific authority of the age.”

Thomson, later to become Lord Kelvin, was 26 years old at the time. Neither he nor Faraday, who was also at the meeting, was convinced by Joule's case, which depended on temperature increases of hundredths of a degree; but at long last, Joule had forced his peers to discuss his ideas. Thomson wrote later that, two weeks after the 1847 meeting, he was walking from Chamonix to begin a tour of Mont Blanc when . . .

“whom should I meet walking up but Joule, with a long thermometer in his hand, and a carriage with a lady in it not far off. He told me that he had been married since we parted at Oxford! and he was going to try for elevation of temperatures in waterfalls.”

In 1849, a paper by Joule entitled “On the Mechanical Equivalent of Heat” was communicated to the Royal Society by Faraday, and it appeared in their *Philosophical Transactions* the next year.

Mayer suffered the same pangs that Newlands did; he saw what he regarded as his own ideas being acclaimed by others but attributed to Joule. Mayer’s despondency led him to attempt suicide in 1850, and he was committed to a mental asylum for two years thereafter. He continued to receive little credit or attention until late in his life, when John Tyndall, in England, and Rudolf Clausius and Hermann von Helmholtz, in Germany, made a concerted effort to secure proper recognition for Mayer.

The man who finally convinced scientists of the validity of the equivalence of heat and work was Helmholtz. In 1847, he submitted a paper to the *Annalen der Physik* that outlined the principles of the *conservation of energy* and the *equivalence of heat and work* in more general terms than either Mayer or Joule had done. The paper was rejected. Helmholtz presented the paper at a meeting in Berlin and had it published privately.

Helmholtz’ analysis of heat, work, and energy convinced Faraday and Thomson. Joule’s experiments gradually began to be accepted. Ultimately, the German physicist Rudolf Clausius (1822–1888) stated, in 1850, the first law of thermodynamics as it usually is given today:

Heat and work are both forms of energy. In any process, energy can be changed from one form to another (including heat and work), but it is never created or destroyed.

Helmholtz’ conservation of energy joined Lavoisier’s conservation of mass as one of the great generalizations of science.

15-2 THE FIRST LAW OF THERMODYNAMICS

Thermodynamicists talk continually about **thermodynamic systems** and their **surroundings**; so will we. We shall look at the work that a system does on its surroundings, or the work that the surroundings do on the system. We shall note the loss or gain of heat of a system to or from its surroundings. What is a thermodynamic system?

A thermodynamic system is any part of the universe that we want to focus attention upon, and its surroundings are that part of the universe with which it can exchange energy, heat, or work. A suitable system could be a balloon full of gas, or a flask with reacting chemicals, or a locomotive engine, or just the cylinders and pistons of the engine. If we are looking at the energy balance on our planet, then the earth itself would be a thermo-

dynamic system, and the sun would be part of its surroundings. An **isolated system** is one that does not exchange energy, heat, or work with its surroundings. So far as thermodynamics is concerned, it has no surroundings. A **closed system** has walls that permit heat and energy, but not matter, to flow in and out. An **open system** can exchange both matter and energy with its surroundings. The word *system* is a pointing finger on an old-fashioned signboard; it calls attention to whatever region of space we want to examine.

Example 1

What kind of thermodynamic systems are the following: (a) a beaker half full of chemicals; (b) the same chemicals in a screw-top jar with the lid on; (c) the same chemicals in a sealed vacuum bottle; (d) a human being; (e) a tin can of beans; (f) the planet earth; (g) the solar system; (h) the Andromeda galaxy; (i) the entire material universe?

Solution

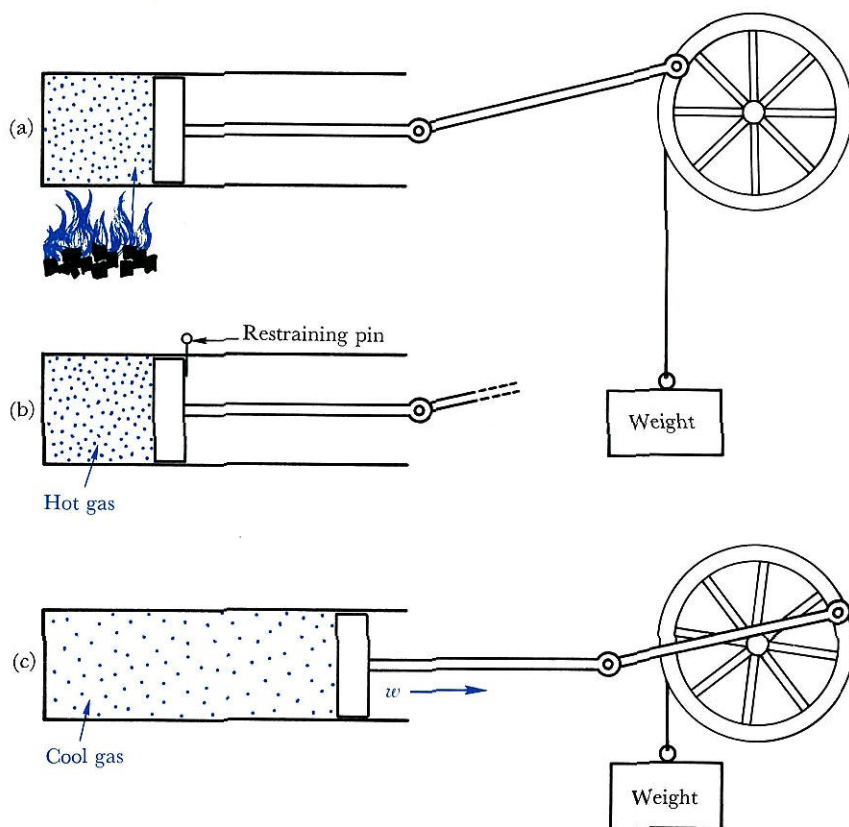
(a) Open; (b) closed; (c) isolated, if the bottle is a good one; (d) open (how could someone turn you into a closed system, and what would happen to you then?); (e) closed; (f) open (the earth receives energy from the sun, and exchanges astronauts and other forms of matter with its neighbors); (g) an open system (think of starlight and comets); (h) very nearly isolated; (i) isolated, by definition.

It is often easiest to think of an ideal gas in some type of enclosure as a typical thermodynamic system. Many of the thermodynamic properties common to all systems are comprehended most readily in such a simple system. When we heat a gas, it expands unless it is constrained. As it expands, it pushes against the pressure of the atmosphere and therefore does work against this pressure. We say that heat, q , has been added to the gas from its surroundings, and that the gas has done work on the surroundings. If we add heat to the gas but constrain it so it cannot expand, the temperature and pressure increase as given by the ideal gas law, derived in Chapter 3,

$$PV = nRT \quad (3-8)$$

Heat again has been added to the gas, but no work has been done by the gas. If the gas is initially at a high pressure, we can allow it to expand without heating it. In this case, the gas does work against its environment or surroundings, without having heat added to it. However, the gas at the conclusion of the expansion is cooler than it was initially.

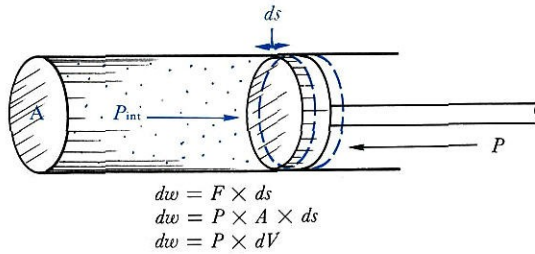
A variation of this experiment is shown in Figure 15-2. In this experiment, the way in which the expanding gas can be made to do work is

**Figure 15-2**

If the gas in the cylinder is heated (a), but the gas is prevented from expanding (b), its temperature increases. Conversely, if the gas is allowed to expand (c), it can do mechanical work, and its final temperature will not be so high. In the first example, heat is converted into internal energy; in the second example, it is converted into work.

somewhat more obvious. Heat, q , can be added to the gas with or without its doing work, and work, w , can be obtained from the gas if heat is added and sometimes even if it is not.

How is work measured in an expanding gas? Work is defined in physics as the product of the force against which motion takes place times the distance moved. Endless motion of an object produces no work if there is no resisting force to the motion. Moreover, no matter how large the resisting force to the motion of an object might be, no work is done unless the object moves against that force. For an infinitesimal movement, ds , against an opposing force, F , the infinitesimal amount of work done is $dw = F ds$. If the

**Figure 15-3**

The work done by the gas in the cylinder when it moves the piston an infinitesimal distance, ds , against an opposing pressure, P , is: $dw = F ds = P A ds = P dV$. (A is the area over which the pressure is exerted.) The pressure in the work expression is the external pressure against which the motion takes place, not the internal pressure (P_{int}) of the expanding gas. However, for an expansion to occur, P_{int} must be greater than the external pressure.

object moves through a finite distance, s , against a constant force, F , the work done is $w = F s$, as we saw in Chapter 2.

Let's suppose that the gas is enclosed in a cylinder with a piston (Figure 15-3) and that the pressure inside the cylinder, P_{int} , is greater than the constant atmospheric pressure outside, P . As the gas expands and moves the piston an infinitesimal distance, ds , the force against the piston from the outside remains constant and equal to the product of the pressure, P , and the area, A , over which this pressure is exerted. The work done, as shown in the figure, is the product of the volume increase times the external pressure against which the expansion takes place: $dw = P dV$. For an expansion such as this one, in which the resisting pressure remains constant, the work done in a measurable volume change of ΔV is $w = P \Delta V$. These relationships, although derived here only for gas expanding in a cylinder, are generally true in gas expansions. This kind of work is commonly called *expansion work*, or *PV work*. Other kinds of work are possible. We can do gravitational work by lifting a weight to a position where it has greater potential energy and can fall to its original position. We can do electrical work by moving charged ions or other objects in an electrical potential field. We can do magnetic work by pulling a compass needle away from the direction to which it points if undisturbed. All of these types of work are included in the generalization known as the **first law of thermodynamics**.

In a thermodynamic system, heat can go in or out, and work can be done on or by the system. The first law states that in all of these processes *energy in the system is neither created nor destroyed*. The energy of the system is not necessarily constant; it can rise or fall, depending on what we do to or with the system. But the *change* in energy of the system is equal to the *net* heat added to the system less the *net* work done by the system on its surroundings:

$$\Delta E = q - w \quad (15-1)$$

A Different View of the First Law

Another way of looking at the first law of thermodynamics is especially meaningful for chemists. In this view we think of equation 15-1 as no more than a definition of a bookkeeping function known as the **internal energy**, E . Recall from the discussion of Figure 15-1 that we can heat a gas and do work with it. We can also reverse the process. We can do work on a gas by compressing it, and we can drain away the heat produced. We can heat a gas without letting it do work, in which case the temperature increases. Conversely, we can let a gas at high pressure expand and do work without being heated, but we will find that the gas cools in the process. With the right conditions, q and w can be manipulated independently. It's easier to keep track of what's happening if we define change in the internal energy, ΔE , as the *difference* between the heat added and the work done, as in equation 15-1. If heat is added and an exactly equivalent amount of work is done, the internal energy of the system is unchanged. If we heat the gas but constrain it so it cannot expand and do work, the internal energy increases by an amount equal to the heat added. Finally, if we use the gas to do work without adding heat, the internal energy decreases by an amount equal to the work done. Our common-sense observations in this paragraph about when the gas is heated and cooled suggest that internal energy and temperature should be related.

Thus far, we have done nothing remarkable. From this viewpoint, equation 15-1 is not the first law; it is only the definition of a bookkeeping device or a fudge factor. The first law is the statement that *this new bookkeeping function is a state function*.

State Functions

State functions are extremely important in thermodynamics, especially to chemists. A **state function** is a property whose value is determined completely by the state of a system at a given instant; it is not dependent on the past history of the system.

To illustrate what this means, imagine the following Cold War scenario. Suppose that a river flows from West Germany into East Germany at Einstadt and reemerges to West Germany many miles further at Ausdorf (Figure 15-4). West German observers are not allowed behind the Iron Curtain. The East German authorities are suspected of building an atomic power station by the banks of the river and of using the river water as a coolant and working medium for their steam turbines. Can the presence of the reactor be detected by the West German observers?

First, let's suppose that the heat from the reactor converts river water to steam, which then drives steam turbines and generates electricity. The river water is now the thermodynamic system. The water is heated and vaporized by the heat supplied by the atomic pile; then it is cooled as it expands in the turbine and does work to turn the turbine rotor. The East

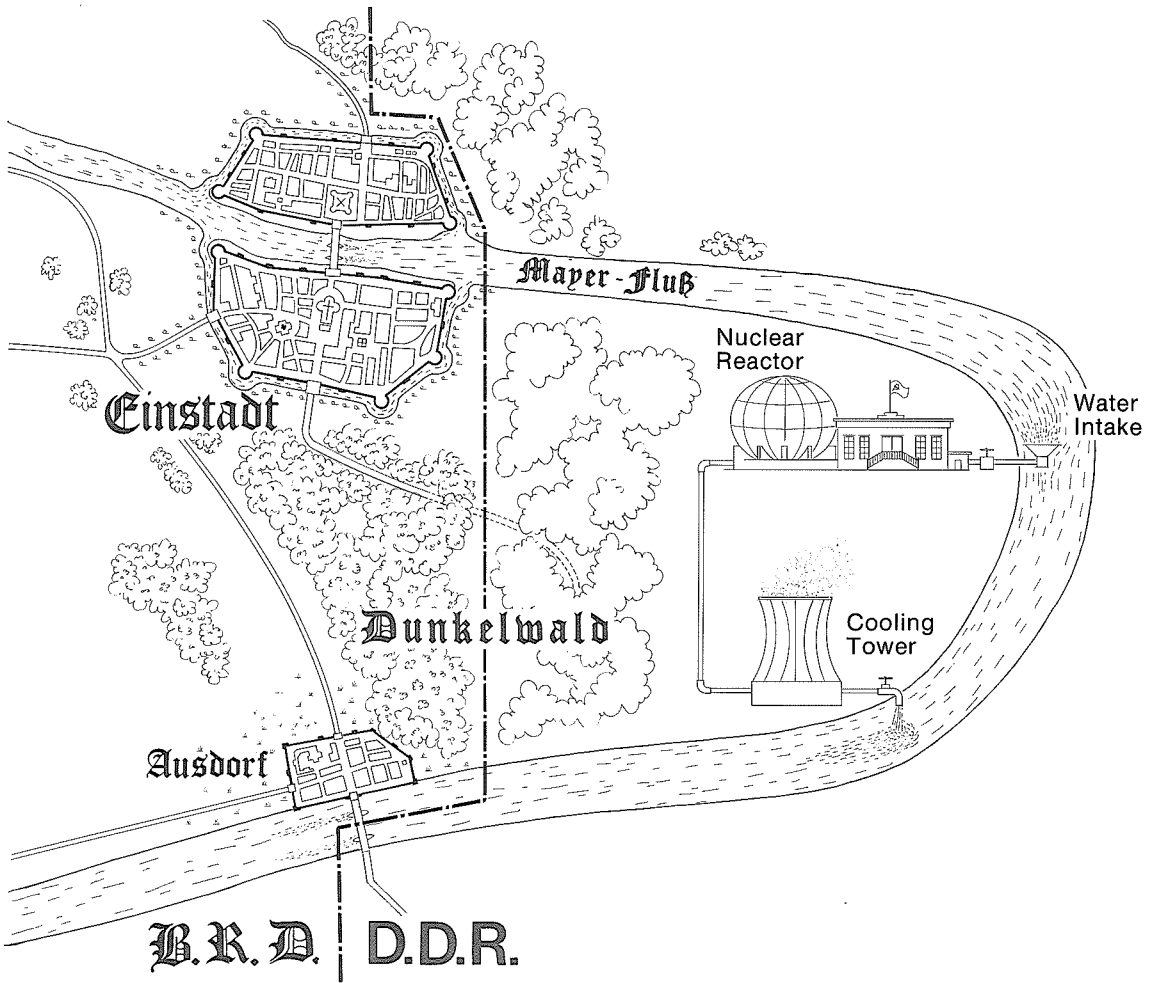


Figure 15-4

State functions of the river water (or any other thermodynamic system) are functions whose value depends only on the present state of the water and not upon its history. A scientist at Einstadt and Ausdorf cannot tell, by measurements on the water as it flows into or out of East Germany, whether the nuclear reactor is operating or not, as long as the effluent water is carefully recooled. For analogies with the first law of thermodynamics, see text.

German power authorities suspect that their West German colleagues are investigating, so they take care to cool the water to the same temperature as it had at the intake channel before they dump it back in the river.

Next, suppose that May Day is a holiday at the reactor, and that on May 1 of every year the engineers shut down the reactor and close the intake channel at the river. Can the West German observers detect the presence

of the power station by taking measurements on the river at Einstadt and Ausdorf?

Unfortunately for the peace of mind of West German intelligence, they cannot. What physical measurements might be made on the thermodynamic system (the river)? They could measure the temperature of the water, its density, viscosity, molar volume, electrical conductivity, ratio of ^{16}O to ^{18}O , melting and boiling points, chemical purity, and many other properties. All these properties are state functions. The temperature of the water depends on its present state and not on its past history. (That is, the present temperature may be a consequence of what happened in the past, but we do not need to know that history to measure the temperature.) The change in temperature of the water as it flows from Einstadt to Ausdorf can be determined by measuring the temperature at the two towns:

$$\Delta T = T_{\text{Aus}} - T_{\text{Ein}} = T_2 - T_1$$

Similarly, the change in density, viscosity, or any other state function is obtained by taking the difference between the density, or viscosity, or other property at Einstadt and at Ausdorf. We do not need to know what happened to the river in East Germany.

All of this may seem trivial until you realize that we cannot do the same thing with heat or work. There is no such thing as a "heat content" that we can measure at Einstadt and Ausdorf to indicate how much heat has been added to the water during its route through East Germany. Similarly, there is no property known as "work content" that can be measured at the two towns to determine how much work the East Germans obtained from the water. So long as the power authorities are careful to make the temperature of the exit water from the reactor match the temperature of the intake water, there will be no difference in the water at Ausdorf when the reactor is running, or on May Day when it is not. The existence or nonexistence of the power station will be a mystery to the West German observers, at least from their measurements on the river water.

If we observe that the change in water temperature at Einstadt and Ausdorf is the same on May Day as on any other day, then we can say that whatever amount of heat was added to the water in the reactor must have been balanced precisely by the work done in the turbines (or by the cooling done before the water was dumped back into the river). Conversely, every bit of work obtained in the turbines must have been compensated by heat from the reactor or else the water would have been cooler at Ausdorf. No information about the water at the two towns will suggest the amount of heat, q , added to the water or the amount of work done, w . Neither heat nor work is a state function, *but their difference is*. If the quantity $q - w$ is not kept constant, differences will appear in measurable properties of the water at Ausdorf. The most obvious such property is temperature, but molar volume, density, electrical conductivity, and other properties will change as well. Turning this statement around, if we specify the state of the water at Einstadt and Ausdorf, then we have specified the quantity $q - w$ during

the transit to East Germany, even though we have not specified q and w individually. Their difference is the *change in a state function*, E .

For an ideal gas, this internal energy, E , is the same function as the mean molar kinetic energy, $E_{k\text{c}}$, that we encountered in Chapter 3. The internal energy is directly proportional to temperature:

$$E = \frac{3}{2}PV = \frac{3}{2}RT \quad (\text{for 1 mole of ideal monatomic gas}) \quad (3-26)$$

For nonideal gases, E will be approximately proportional to temperature; and for substances in general, an increase in temperature accompanies an increase in internal energy.

State functions are useful to chemists precisely because they do not depend on the history of a chemical system. Energy is a state function. So are pressure, temperature, volume, and all the other quantities that we commonly think of as properties of a substance. The very term *property* suggests something that a substance has, independent of any factors other than its present condition. We never speak of the work that a substance has, and should not speak of the heat that it possesses. If the final state of a system is identified by a subscript 2, and the initial state is given the subscript 1, then equation 15-1 becomes the first law of thermodynamics if we expand it to

$$\Delta E = E_2 - E_1 = q - w \quad (15-2)$$

The state-function properties are implicit in the middle term.

Example 2

A traveler goes from Pasadena, California, to Aspen, Colorado. Which of the following are state functions of the trip, and which are not: (a) distance traveled; (b) latitude change; (c) altitude change; (d) gasoline consumed; (e) elapsed time; (f) longitude change; (g) work done to move the vehicle; (h) oxygen consumed by passengers and vehicle?

Solution

Only b, c, and f are state functions, independent of the way the trip was carried out.

15-3 ENERGY, ENTHALPY, AND HEAT CAPACITY

When chemists first began to study heats of reaction systematically they discovered that a particularly convenient type of reaction was one constrained to a fixed volume in a **bomb calorimeter** (Figure 2-4). This is a sturdy steel container with a tight lid, immersed in a water bath and provided with electrical leads to detonate the reaction inside. The heat evolved in such a reaction at constant volume is measured by the increase in temperature of the water bath.

If the chemical system inside the metal container is not allowed to change in volume, then it cannot do PV work. If no other types of work are involved, the heat liberated by the reaction is equal to the decrease in internal energy:

$$\Delta E = q_v \quad (\text{at constant volume}) \quad (15-3)$$

In the absence of any work effects, the gain or loss of heat by the contents of the container is a direct measure of the increase or decrease of internal energy of the reacting substances. If the reaction releases heat, it is called an **exothermic** reaction; if it absorbs heat, it is **endothermic**.

Most reactions take place at constant pressure rather than at constant volume, and it would be useful to have a thermodynamic function that behaves at constant pressure as E does at constant volume; that is, a measure of the heat of the reaction under those conditions. Such a function is the **enthalpy**, H , defined by

$$H \equiv E + PV \quad (15-4)$$

At constant pressure, the change in enthalpy of a system is

$$\Delta H = \Delta E + P \Delta V \quad (15-5)$$

From the first law, we can write this as

$$\Delta H = q - w + P \Delta V$$

If we rule out electrical, gravitational, magnetic, and all kinds of work other than PV work, then $w = P \Delta V$ and the last two terms cancel in the preceding equation. We then have the statement that the heat of a reaction at constant pressure is equal to the change in enthalpy of the system:

$$\Delta H = q_P \quad (15-6)$$

(The subscript P indicates that the transfer of heat takes place at constant pressure.) At constant pressure, enthalpy *increases* in an endothermic reaction as heat flows into the system, and enthalpy *decreases* in an exothermic process as heat flows out of the system.

All the functions on the right of the equivalence sign in equation 15-4 are state functions, so H is a state function as well. The change in enthalpy of a system depends on the enthalpy of the system before and after a process and not at all on the path by which the system went from the initial state to the final state; thus

$$\Delta H = H_2 - H_1 \quad (15-7)$$

In summary, internal energy, E , and enthalpy, H , are complementary functions because they both measure the transfer of heat in a process under certain conditions: E at constant volume, and H at constant pressure. Both E and H are state functions, so the change in E , for example, is the same

whether the process is carried out at absolutely constant volume, or whether the volume is merely brought back to its original value at the end. Similarly, the enthalpy change during a reaction is the same if the reaction is carried out at constant pressure, or if the pressure is allowed to vary but is brought back to its starting value at the end. Hence the expressions *constant volume* or *constant pressure* in connection with state functions need only mean “no net change in volume or pressure.” This is an advantage of state functions.

The heat that must be added to a specified amount of any substance in order to increase the temperature by one kelvin is defined as the **heat capacity** of the substance, C . Heat capacities are expressed in units of joules per mole per kelvin. Since the heat capacity is the rate of addition of heat with temperature change, it can be written as*

$$C = \frac{dq}{dT} \quad (15-8)$$

Under constant-pressure conditions (or at least with no net change in pressure), transfer of heat is measured by change in enthalpy, so the heat capacity at constant pressure is the rate of change of enthalpy with temperature:

$$C_P = \left(\frac{dH}{dT} \right)_P \quad (15-9)$$

*For those for whom differential notation is unfamiliar, the *average* heat capacity when a quantity of heat, Δq , is added over a temperature change, ΔT , is

$$C_{av} = \frac{\Delta q}{\Delta T}$$

The heat capacity at a specific temperature, T , is the limit of this average as the size of the temperature interval ΔT goes to zero:

$$C_T = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta q}{\Delta T} \right) = \frac{dq}{dT}$$

Differential notation may be easier to understand with speed, v , which is the rate of change of position, x , with time, t . Here v_{av} corresponds to an average speed over a time interval Δt :

$$v_{av} = \frac{\Delta x}{\Delta t}$$

whereas v_t corresponds to an instantaneous speed at time t :

$$v_t = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta x}{\Delta t} \right) = \frac{dx}{dt}$$

Energy plays the corresponding role under constant volume conditions, and the heat capacity at constant volume is

$$C_V = \left(\frac{dE}{dT} \right)_V \quad (15-10)$$

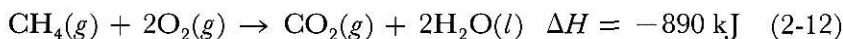
As we saw in Chapter 3, the energy per mole of an ideal monatomic gas is $E = \frac{3}{2}RT$. Hence the heat capacity at constant volume is $C_V = \frac{3}{2}R = \frac{3}{2} \times 8.314 \text{ J mole}^{-1} = 12.47 \text{ J mole}^{-1}$. It is a test of the validity of ideal gas theory that the measured heat capacity of monatomic gases such as helium or neon at room temperature is extremely close to this figure. Moreover, the heat capacity at constant pressure is expected to be

$$C_P = \frac{5}{2}R \quad (15-11)$$

since $H = E + PV = E + RT$ for 1 mole of an ideal gas. The fact that C_P for real monatomic gases is very close to $\frac{5}{2}R$ or $20.79 \text{ J mole}^{-1}$, and approaches this value most closely under conditions of low pressure or high temperature, gives us confidence in the essential correctness of the kinetic molecular theory of gases outlined in Chapter 3.

15-4 THE FIRST LAW AND CHEMICAL REACTIONS

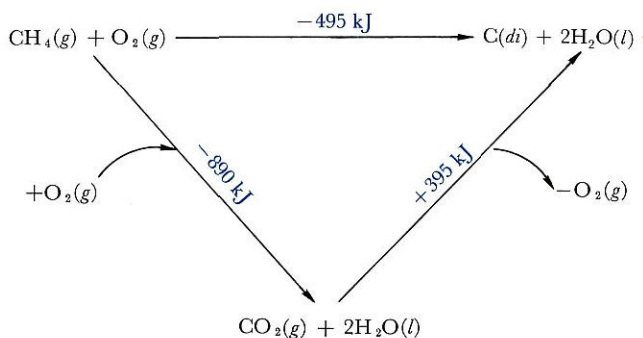
Equation 15-7 is the most important single consequence of the first law of thermodynamics for chemistry. It tells us that the heat of a reaction carried out at constant pressure is a state function. The heat of reaction is the difference between the enthalpy of the products and the enthalpy of the reactants. It is the same whether the actual reaction occurs in one step, or in half a dozen intermediate steps. This principle of the additivity of heats of reaction was introduced in Chapter 2 without proof, but now we can see why it is so. In our example from Section 2-6 on the synthesis of diamond, the heat of preparation of diamond from methane is the same, regardless of whether diamond is made directly from methane or the methane is oxidized to CO_2 , which is then used to make diamond:



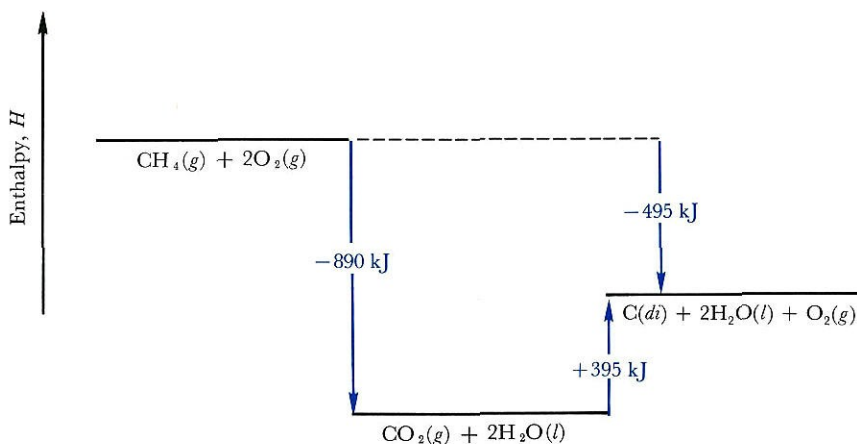
Because enthalpy, H , is a state function, *heats of reactions are additive* in the same way that the reactions to which they pertain are additive. This statement is sometimes called Hess' law, although it is really only a consequence of the first law of thermodynamics.

Figure 15-5

The heat of preparation of diamond from methane is the same whether the reaction occurs in one step or whether CO_2 is made from methane, and then diamond is made from CO_2 . Such a statement can be made only because the heat of a reaction at constant pressure and temperature is equal to the change in enthalpy, H , and enthalpy is a state function.



The independence of enthalpy change of the path of a reaction can be diagrammed for the diamond synthesis reactions by a cycle, as in Figure 15-5. The first law states that either way around the cycle (the one- or two-step path) leads to the same ΔH and heat of reaction. The enthalpy changes also can be represented on an energy-level diagram (Figure 15-6). Note that the absolute numerical value of the enthalpy is not defined, but only the changes in going from one state of reactants or products to another. In the past, every time that we drew an energy-level diagram we were unconsciously using the state function properties of energy. Neither heat nor work can be represented on such a diagram (except for the special cases in which one or the other of these is equal to a state function).

**Figure 15-6**

For the same reasons that the reactions of Figure 15-5 can be drawn as a cycle, the enthalpies can be represented in an energy-level diagram such as this one. The enthalpy change in going from one state to another depends only on the levels of the two states in this diagram and not on the manner of going from one state to the other.

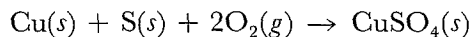
All of the earlier discussion of Section 2-6 is valid because H is a state function. It is unnecessary to tabulate the heats of all reactions; we need to list only those from which all other reactions can be obtained by a proper combination of reactions. The reactions chosen are the reactions for the formation of compounds from their elements in standard states. The **standard state** of a gas at a chosen temperature is 1 atm partial pressure; that of a liquid or solid is the pure liquid or solid at 1 atm external pressure. The chosen temperature is usually 298 K for most thermodynamic tabulations. Standard heats of formation for many substances are listed in Appendix 3.

Example 3

What is the standard heat of the reaction for the formation of anhydrous crystalline copper sulfate from its elements in their standard states?

Solution

The reaction is



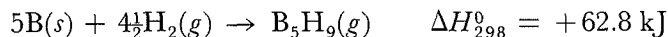
This is the reaction for which the heat of formation is tabulated in Appendix 3. For this reaction, $\Delta H_{298}^{\circ} = -769.9 \text{ kJ mole}^{-1}$.

Example 4

The standard heat of formation of gaseous B_5H_9 is given in Appendix 3 as $+62.8 \text{ kJ mole}^{-1}$. Of what reaction is this the heat of reaction?

Solution

The reaction is that of synthesis of B_5H_9 from elemental solid boron and hydrogen gas at 1 atm and 298 K:



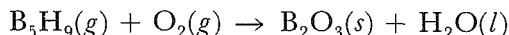
When a heat term is written after a reaction, as in the preceding equation, the units are understood to be kilojoules *per stoichiometric unit* of reaction as written. The heat of the reaction here is 62.8 kJ per mole of B_5H_9 , but only 12.6 kJ per mole of boron used, or 62.8 kJ for every $4\frac{1}{2}$ moles of hydrogen gas used. Heats of formation are always tabulated per mole of the compound formed.

Example 5

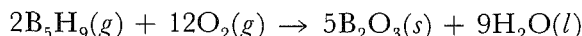
The compound B_5H_9 ignites spontaneously in air with a green flash to produce B_2O_3 and water. What is the heat of the reaction under standard conditions?

Solution

The reaction in unbalanced form is



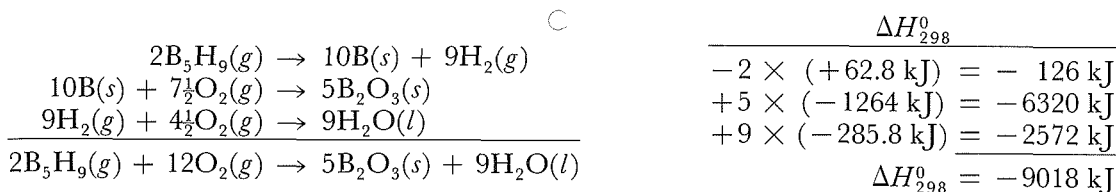
Two moles of B_5H_9 are needed for every 5 moles of B_2O_3 to account for the boron. Hence, the 18 hydrogen atoms must appear as 9 water molecules. The balanced reaction is



The tabulated standard heats of formation of reactants and products are

Substance	ΔH_{298}^0
$\text{B}_5\text{H}_9(g)$	+62.8 kJ mole ⁻¹
$\text{O}_2(g)$	0.0 kJ mole ⁻¹
$\text{B}_2\text{O}_3(s)$	-1264 kJ mole ⁻¹
$\text{H}_2\text{O}(l)$	-285.8 kJ mole ⁻¹

The three reactions of formation that when added produce the desired reaction are



Boron hydrides were once considered as rocket fuels because of their extremely high heats of combustion.

We can take a shortcut with these tables of enthalpies or heats of formation by treating the numbers as though they were absolute enthalpies of the compounds, rather than enthalpies of formation from elements. The result is the same, since reactants and products must be composed of the same number and same kind of atoms. Then for the reaction



the enthalpy of reaction is nine times the standard enthalpy of liquid water, plus five times the standard enthalpy of solid B_2O_3 , less two times the standard enthalpy of gaseous B_5H_9 . The standard enthalpy of elemental O_2 is zero.

Example 6

The compound B_5H_9 can be prepared from diborane, B_2H_6 , which reacts at

the proper temperature to give B_5H_9 and H_2 . Is the reaction exothermic or endothermic? What is the heat of reaction at 298 K per mole of diborane consumed?

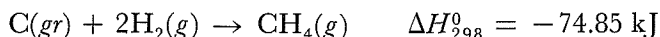
Solution

The reaction is exothermic; $\Delta H_{298}^0 = -29 \text{ kJ mole}^{-1}$ of B_2H_6 .

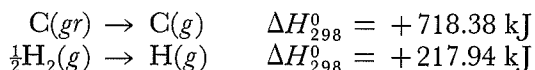
15-5 BOND ENERGIES

In the language of localized bond models, we say that a molecule of methane, CH_4 , is held together by four equivalent C—H single bonds. If this idea is valid, the heat of decomposition of methane to isolated carbon and hydrogen atoms should be four times the bond energy of a C—H bond. (Although we shall work consistently with enthalpies, we shall adopt the common but loose terminology and refer to our results as bond energies rather than bond enthalpies. The difference is small and is within the limits of accuracy of the bond-energy approach itself.)

The heat of formation of methane is

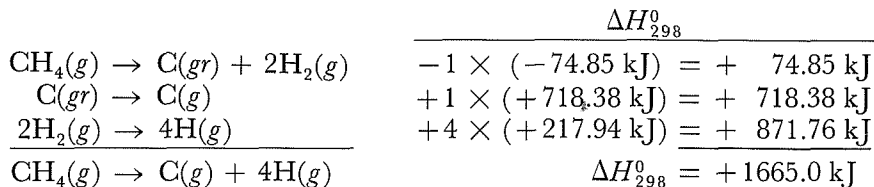


But to calculate bond energies we need the decomposition to atomic gaseous carbon and hydrogen, not solid graphite and diatomic H_2 . The atomization reactions are



These are the standard heats of formation of the gaseous atoms from the elements in their standard states, and are tabulated in Appendix 3 along with the other heats of formation.

The desired reaction for decomposing methane into isolated atoms can be constructed from the preceding reactions:

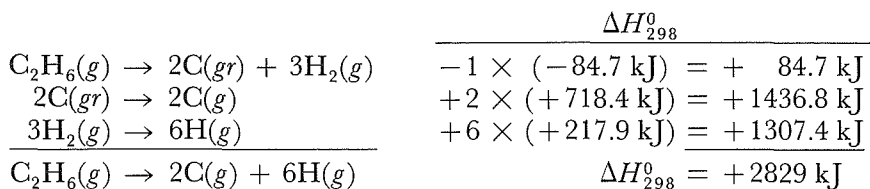


If this is the heat needed to break four C—H bonds, then the bond energy (strictly speaking, the bond enthalpy) of one C—H bond is one-fourth this figure. The bond energy of a C—H bond in methane is 416 kJ mole^{-1} of bonds.

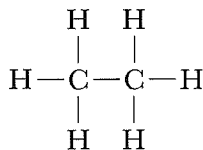
Bond Energy of a C—C Single Bond

From the heat of formation of ethane, C_2H_6 , we can obtain a value for the

bond energy of a carbon-carbon single bond. From Appendix 3,

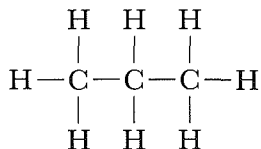


In the localized bond model of ethane, the molecule has six C—H bonds and one C—C bond:

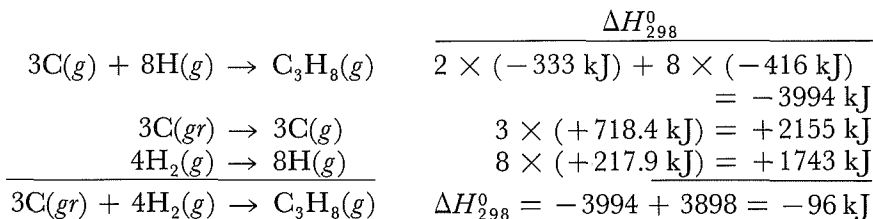


If the value of 416 kJ mole^{-1} is accepted for the C—H bonds in methane, the six C—H bonds in ethane will account for $2496 \text{ kJ mole}^{-1}$. The remaining 333 kJ must be the bond energy of a mole of C—C single bonds.

We can test the validity of this entire approach by calculating the expected heat of formation of propane, C_3H_8 , from graphite and hydrogen gas. In the localized bond model, propane has two C—C bonds and eight C—H bonds:

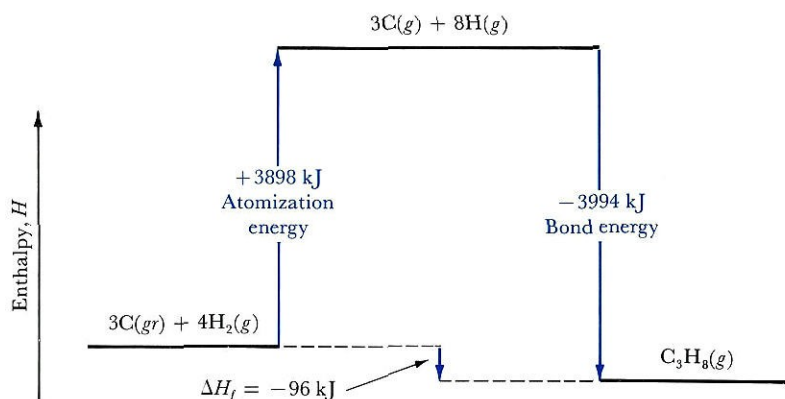


The heat of formation is calculated as follows:



The observed heat of formation of propane is $-104 \text{ kJ mole}^{-1}$, which gives you some idea of the degree of accuracy of bond-energy calculations. We are unfortunately in the difficult position of wanting the small difference between two large numbers. Errors and approximations in the data and in the assumption of localized bonds contribute to an error of 8 kJ mole^{-1} .

The calculations for propane can be diagrammed on an energy scale, as in Figure 15-7. The addition of 3898 kJ to atomize graphite and dis-

**Figure 15-7**

An energy-level diagram representing the formation of propane, C_3H_8 , from graphite and hydrogen gas. Bond-energy calculations involve a hypothetical intermediate high-energy state in which all atoms are isolated from one another in the gas phase. The difference between the energy required to turn reactants into gaseous atoms and that given off when products are made from these same atoms is the heat of formation.

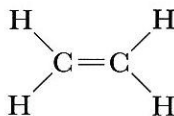
sociate hydrogen gas represents a move from a lower to a higher energy level, that of separated atoms. The combination of those atoms into a molecule of C_3H_8 then represents a drop in energy of 3994 kJ, to a still lower state. The difference between initial and final energy levels, of graphite and H_2 as reactants and C_3H_8 as product, is the calculated heat of formation, $\Delta H_{298} = -96$ kJ.

Tabulation of Bond Energies

Now we can proceed to calculate the bond energies of bonds of all types.

Example 7

From the data for ethene in Appendix 3, calculate the bond energy of a $C=C$ double bond. The bond structure of ethene is



Solution

The bond energy is 592 kJ mole^{-1} .

Example 8

From the data for water in Appendix 3, calculate the bond energy of an O—H bond.

Solution

The bond energy is 463 kJ mole^{-1} . Note that you need the heat of atomization of oxygen and that you must use the heat of formation of water vapor, not of liquid water.

The most useful bond energies are obtained not from the heats of formation of individual compounds like methane or ethane, but by averaging the values obtained from entire classes of compounds, such as the hydrocarbons for C—H and C—C bond energies. These adjusted best values for several types of bonds are given in Table 15-1. Note that the adjusted value for a C—H bond differs by 3 kJ mole^{-1} from the value obtained from methane alone. Errors of 5 or 10 kJ mole^{-1} are considered acceptable in bond-energy calculations.

Table 15-1**Approximate Molar Heats of Atomization and Bond Energies^a at 298 K**

	Molar heat of atomization (kJ mole^{-1})	Bond energy ^b (kJ mole^{-1})								
		H—	C—	C=	C≡	N—	N=	N≡	O—	O=
H	217.9	436	413			391			463	
C	718.4	413	348	615	812	292	615	891	351	728
N	472.6	391	292	615	891	161	418	946		
O	247.5	463	351	728					139	485
F	76.6	563	441			270			185	
Si	368.4	295	290						369	
P	314.5	320								
S	222.8	339	259	477						
Cl	121.4	432	328			200			203	
Br	111.8	366	276							
I	106.6	299	240							

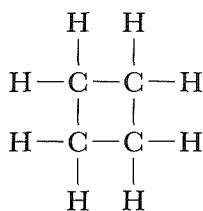
^aValues from L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y., 1960, 3rd ed. See also T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworths, London, 1958, 2nd ed.

^bThis is an example of loose but convenient terminology. These are actually bond enthalpies at 298 K, in the sense that they were obtained from enthalpies of formation.

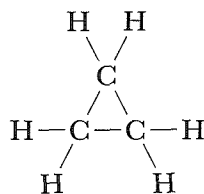
Applications of Bond-Energy Calculations

Using the best mean values for bond energies given in Table 15-1, we can calculate the expected heat of formation of a molecule from its elements. This is useful in cases where the method works; but paradoxically it is even more useful in cases where the method does not work, or where the calculated heat of formation differs sharply from the experimentally measured value. When this occurs, it is a sign that our simple picture of bonds between pairs of atoms is not good enough. Bond-energy calculations can be a tool for learning about bonding in molecules.

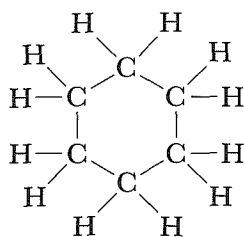
As an example, small hydrocarbon molecules are known in which the carbon atoms are in a ring, and each carbon has two hydrogens bonded to it. The simplest of these cyclic hydrocarbons have the structures:



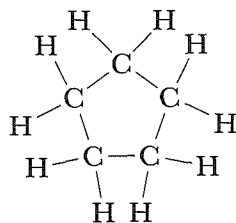
cyclobutane



cyclopropane



cyclohexane



cyclopentane

Let's compare the expected heats of formation of these molecules with the observed values. In Table 15-2, line A gives the total bond energy of each molecule, or the energy given off when the molecule is made from isolated carbon and hydrogen atoms. Line B gives the energy needed to make the requisite number of C and H atoms from graphite and H_2 gas. The difference, in line C, is the calculated heat of formation, and the measured value is in line D. Agreement is quite good for cyclohexane, but becomes progressively worse as the molecules become smaller. The cyclopropane molecule is expected to be 60 kJ mole^{-1} more stable than its component elements, but is actually 53 kJ mole^{-1} less stable. The molecule is 113 kJ mole^{-1} less stable than it is expected to be on the basis of three

Table 15-2

Strain Energy in Cyclic Hydrocarbon Molecules (kilojoules per mole)

	Cyclopropane, C ₃ H ₆	Cyclobutane, C ₄ H ₈	Cyclopentane, C ₅ H ₁₀	Cyclohexane, C ₆ H ₁₂
No. C—C bonds	3	4	5	6
No. C—H bonds	6	8	10	12
C—C bond energy	1044	1392	1740	2088
C—H bond energy	<u>2478</u>	<u>3304</u>	<u>4130</u>	<u>4956</u>
A. Total bond energy	3522	4696	5870	7044
No. C atoms	3	4	5	6
No. H atoms	6	8	10	12
C vaporization energy	2155	2874	3592	4310
H ₂ dissociation energy	<u>1307</u>	<u>1743</u>	<u>2179</u>	<u>2615</u>
B. Total atomization energy	3462	4617	5771	6925
C. ΔH , calculated (B - A)	-60	-79	-99	-119
D. ΔH , measured	<u>+53</u>	<u>+27</u>	<u>-77</u>	<u>-123</u>
E. Instability of molecule (D - C)	+113	+106	+22	-4

C—C bonds and six C—H bonds. These energy levels are diagrammed in Figure 15-8.

The reason for the unexpected instability of the cyclopropane molecule is that it is highly strained. The three-carbon ring must have bond angles of 60° rather than the preferred tetrahedral 109.5°. In terms of molecular orbitals, the overlap between atomic sp^3 orbitals on the carbon atoms is poor, so the bonds are weak. Cyclobutane has somewhat less strain or bond distortion, and cyclopentane has even less. Table 15-2 shows that cyclohexane is essentially an unstrained molecule. If you try to build models using tetrahedrally bonded carbon atoms, cyclopropane and cyclobutane cannot be built without bending the bonds, cyclopentane requires only a warping of bond angles from 109.5° to the 108° of a pentagon, and the cyclohexane molecule is loose and free to adopt more than one configuration.

The Heat of Formation of Benzene

The bond-energy method is a conspicuous failure again in predicting the heat of formation of benzene. As before, this failure suggests a great deal

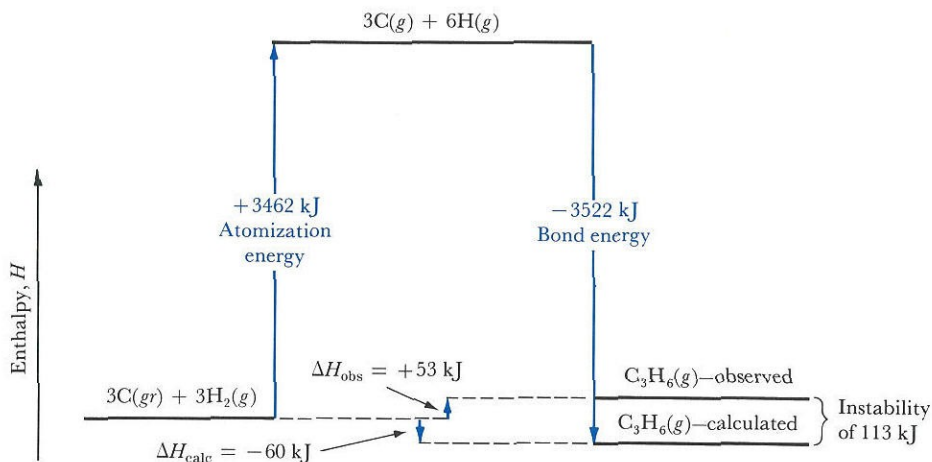
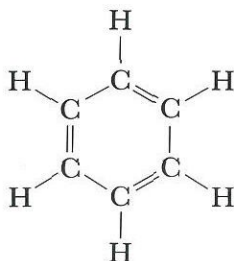


Figure 15-8

Energy-level diagram for the formation of cyclopropane from graphite and hydrogen gas. Bond strain makes the product molecule 113 kJ mole^{-1} less stable than would be expected from simple bond-energy calculations.

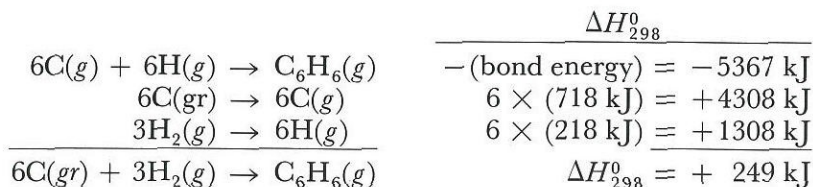
about the benzene molecule. Let us assume that benzene has one of the structures proposed for it by the organic chemist Kekulé.



From this model, benzene would contain six C—H single bonds, three C—C single bonds, and three C=C double bonds. Hence per mole of benzene the total bond energy is (using values from Table 15-1)

Six C—H bonds:	$6 \times 413 \text{ kJ} = 2478 \text{ kJ}$
Three C—C bonds:	$3 \times 348 \text{ kJ} = 1044 \text{ kJ}$
Three C=C bonds:	$3 \times 615 \text{ kJ} = 1845 \text{ kJ}$
Total bond energy:	5367 kJ

The heat of formation reaction then is constructed:



There is a flaw somewhere, because the standard heat of formation of gaseous benzene, as measured in the laboratory, is not 249 kJ mole^{-1} of benzene, but only 83 kJ mole^{-1} . The benzene molecule is more stable by 166 kJ mole^{-1} than predicted for a molecule with the Kekulé structure. These energy levels are shown in Figure 15-9.

The flaw lies in the assumption of the Kekulé structure. In Chapter 13 we discovered that the Kekulé structure failed to explain the six equal bond lengths between carbon atoms in the benzene ring, but that a delocalized-molecular-orbital theory could satisfactorily account for bonding. In Chapter 21, we shall look at the large class of aromatic compounds—compounds with just such delocalized electrons. In general, delocalization makes the molecule more stable by lowering the energy of the delocalized electrons. Bond energies provide a way to calculate this stabilization from measurements of heats of formation of aromatic compounds.

Example 9

Calculate the standard heat of formation of carbon dioxide, $\text{O}=\text{C}=\text{O}$. Assume the presence of two double $\text{C}=\text{O}$ bonds. Compare your value with the measured value in Appendix 3. Do your figures predict delocalization in CO_2 ?

Solution

The calculated heat of formation is $-243 \text{ kJ mole}^{-1}$. Yes; the stabilization energy is 151 kJ mole^{-1} .

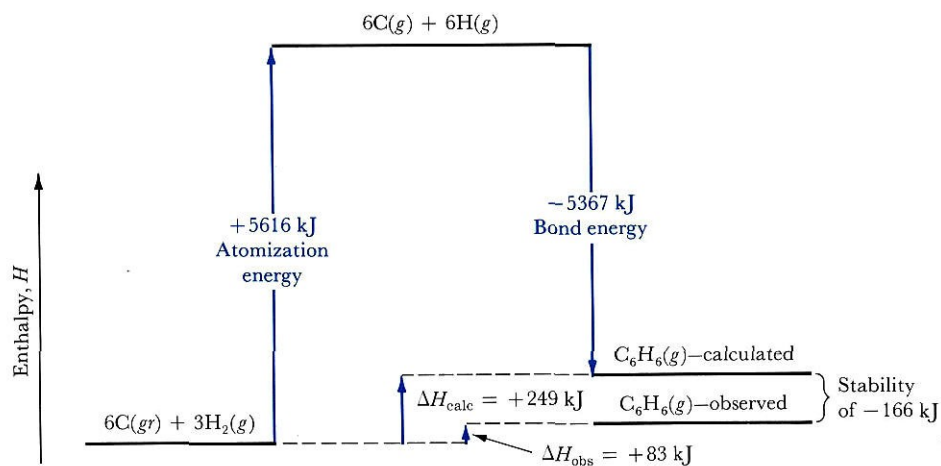


Figure 15-9

Energy-level diagram for formation of benzene. The expected heat of formation, ΔH_{calc} , is $+249 \text{ kJ}$, but the observed value, ΔH_{obs} , is only $+83 \text{ kJ}$. Hence the benzene molecule is 166 kJ more stable than the bond structure suggested by Kekulé would predict.

Summary

This chapter has provided the foundation for the treatment of energy in chemical reactions that was introduced in Chapter 2. There are many ways in which the first law of thermodynamics can be viewed, but we have confined our discussion to the aspects that are most useful to a chemist interested in heats of reaction and bond energies.

Heat and work are alternative forms of energy and, within limits, they can be interconverted. In any such process, energy is conserved. The difference between the heat fed into a system and the work done by the system on its surroundings is defined as the change in **internal energy**, E :

$$\Delta E = q - w$$

A **state function** is a function for which we can calculate the change during any process, knowing only the starting and ending states, without information about how the process was carried out. In short, state functions depend only on the state of a system and not on its past history. Neither q nor w by itself is a state function, but the **first law of thermodynamics** asserts that the *difference* between heat added and work done is a state function. If the initial state is represented by the subscript 1 and the final state is represented by 2, then the first law is

$$\Delta E = E_2 - E_1 = q - w$$

The internal energy then is a property that a substance exhibits under a certain set of conditions. From intuition we know that internal energy is somehow correlated with temperature, and the simple kinetic molecular theory of gases introduced in Chapter 3 tells us that for ideal, monatomic gases, $E = \frac{3}{2}RT$.

The work done when a gas increases in volume by dV against an opposing pressure of P is $dw = P dV$. If the volume is kept constant, $w = 0$, and the internal energy increase is simply equal to the amount of heat fed in: $\Delta E_V = q_V$. The heat of a reaction carried out at constant volume is measured by the change in internal energy.

Most reactions are carried out at constant pressure, not constant volume. If the **enthalpy**, H , is defined by $H = E + PV$, then the heat of a reaction carried out at constant pressure is ΔH , or $\Delta H_P = q_P$. Because E , P , and V are state functions, H also is a state function. This has important consequences for heats of reaction. Because only the initial and final states of a reaction are important for ΔH , the term *constant pressure* need only mean that the pressure at the end of the reaction is brought back to its original value. Furthermore, the heat of a reaction that can be written as a sum of several reactions is found by summing the individual heats of those reactions. Heats of reaction are additive because H is a state function.

This additivity results in a great simplification in data handling. In-

stead of tabulating heats of all possible reactions, we need list only those for the formation of each molecule from its elements in agreed-upon standard states. The heat of any other reaction can be found by combining heats of formation in the same way that the formation reactions are combined to make the reaction in question.

The heat required to cause a 1 K temperature increase per mole of a substance is the **molar heat capacity**, C . At constant volume, $C_V = \frac{3}{2}R$ for an ideal monatomic gas, and at constant pressure, $C_P = \frac{5}{2}R$. The extent to which real monatomic gases approach these relationships is a measure of the validity of the ideal gas model.

The simplest picture of chemical bonding imagines that a molecule is held together by individual two-electron bonds connecting pairs of atoms. For the great majority of molecules, standard bond energy values can be set up that reproduce the experimental heats of formation of molecules within 5 or 10 kJ. For some molecules, however, the bond-energy calculations appear to fail. The molecules are more stable, or less stable, than calculations using simple bond models predict. This is a sign that the simple bond model is wrong. Molecules with strained geometries may be less stable than predicted, and molecules with delocalization of electrons may be more stable.

Self-Study Questions

1. What is the difference between a spontaneous process and a rapid process? Give an example of a reaction that is either spontaneous or rapid, but not both.
2. Give an example of the conversion of (a) heat into work; (b) kinetic energy into heat; (c) work into heat; (d) work into kinetic energy; (e) potential energy into work; (f) work into potential energy; (g) kinetic energy into work; (h) heat into kinetic energy.
3. Characterize the following thermodynamic systems as open, closed, or isolated: (a) an astronaut in the briefing room at the Houston space center; (b) the same astronaut in a space capsule without a window; (c) the same astronaut in Skylab, with a hydroponic garden; (d) Dracula in his Transylvanian castle; (e) Dracula sealed in a lead coffin.
4. What will happen to any living organism if steps are taken to turn it into an isolated thermodynamic system?
5. How is work related to pressure, volume, and temperature in the expansion of a gas?
6. In what way is a state function different from any other type of function? Are pressure and volume state functions? Why are state functions particularly convenient to work with?

7. A careless driver keeps putting dents into his Porsche, but he has a skilled repairman who smooths them out with creative bodywork almost as fast as they occur. On the first of each month, his friendly banker, who really owns the car, tallies the net number of dents present in the car body, as an estimate of the market value of the vehicle. Show that this market value is a state function, whereas the number of dents incurred in a given month and the amount of bodywork done are not. Why would the number of dents received become a state function if the auto mechanic went on vacation for a month?
8. In the analogy in Question 7, which quantities correspond to work, heat, and energy? Why is a repairman on vacation like a closed steel container?
9. What is the first law of thermodynamics, and how do state functions enter it?
10. When we define the molar energy of a monatomic ideal gas as the sum of the kinetic energies of the individual molecules, or as Avogadro's number times the average molecular energy as in Chapter 3, unconsciously we are saying that E is a state function. Why is this so?
11. Under what conditions will the following functions be state functions: (a) internal energy; (b) heat; (c) volume; (d) work; (e) enthalpy?
12. What is Hess' law? How is it only a special case of the first law of thermodynamics?
13. Suppose that you take two identical clock springs, leave one slack, wind the other tightly and tie it with catgut (acid-impervious), and then dissolve each spring in a beaker of acid. What do you think happens to the work that you exerted to wind the second spring?
14. What is heat capacity? For an ideal monatomic gas, what is the difference between heat capacity at constant volume and heat capacity at constant pressure? Why, from a molecular viewpoint, would you expect C_P to be greater than C_V ? What heat-compensating abilities does the gas have at constant pressure that it does not have at constant volume?
15. Why does the first law of thermodynamics permit us to add heats of reaction along with the reactions themselves, as we did in Chapter 2?
16. Why does the first law of thermodynamics make it unnecessary for us to tabulate the heat of each and every chemical reaction?
17. What is a standard heat of formation? Formation from what? And why "standard"? What is the heat of combustion of a substance? Can you think of two substances for which a heat of formation is also a heat of combustion?
18. How does an energy-level diagram such as Figure 15-6 imply that the energy function plotted is a state function?
19. What important assumption lies behind a table of bond energies such as Table 15-1? Why is this assumption valid for methane, ethane, and propane, but not for benzene or cyclopropane?

- Suppose that you wanted to calculate an experimental C—O single-bond energy in methanol, $\text{CH}_3\text{—OH}$, but had *only* the information contained in Appendix 3. How would you go about it?
- What effects do strain and electron delocalization have on the stability of a molecule? How can bond-energy calculations reveal these two effects?
- What would be the effect on the petroleum industry if work were a state function?

Problems

First law

- When a bottle containing copper shot is shaken, its temperature increases. Explain this phenomenon in terms of the first law of thermodynamics.
- What interconversion of quantities measured in joules is involved when a moving automobile skids to a braking stop? What happens to the kinetic energy of motion that the vehicle once had?

Heat of formation

- The standard heat of formation of liquid water is $-285.8 \text{ kJ mole}^{-1}$. (a) Write a balanced equation for this reaction. Is heat absorbed or given off? (b) What is the heat of combustion of hydrogen gas per mole?
- (a) What is the standard heat of formation of liquid benzene, from Appendix 3? (b) Write a balanced equation for this reaction. Is heat emitted or absorbed? (c) What is the heat of combustion of liquid benzene?

Heat of combustion

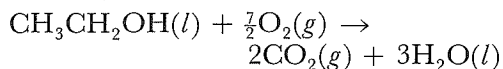
- The heat of combustion of a mole of liquid acetaldehyde, CH_3CHO , to car-

bon dioxide and liquid water is -1164 kJ . (a) Write a balanced equation for the combustion reaction. (b) How much heat is evolved per mole of acetaldehyde burned? Per mole of liquid water produced? Per mole of oxygen used? (c) How much heat is released when a gram of acetaldehyde is burned? (d) Use the data you have obtained plus data on carbon dioxide and water from Appendix 3 to calculate the standard heat of formation of acetaldehyde. Compare your answer with that tabulated in Appendix 3.

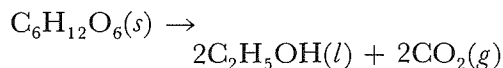
- The heat of combustion of solid urea, $(\text{NH}_2)_2\text{CO}$, to CO_2 , N_2 , and liquid water is -632.2 kJ per mole of urea burned. (a) Write a balanced equation for the reaction. (b) How much heat is given off per mole of oxygen used? (c) Use the data you have obtained plus data for CO_2 and water from Appendix 3 to calculate the standard heat of formation of urea. Compare your figure with the value tabulated in Appendix 3.
- (a) Write a balanced equation for the combustion of liquid methanol, CH_3OH , in an ample supply of oxygen to produce liquid water. (b) From data

in Appendix 3, calculate the heat given off during this reaction.

8. (a) Calculate the heat of combustion of ethanol,



- (b) Do the same for glucose, $\text{C}_6\text{H}_{12}\text{O}_6(s)$.
 (c) How do the heats of combustion of ethanol and glucose compare on a joule-per-gram basis? By this calculation, which is a better energy source, gin or candy? (Assume gin to be 45% ethanol by weight, and candy 100% glucose.)
 (d) Many microorganisms, including yeast, obtain their energy by fermenting glucose to ethanol, which they give off as a waste product:



We use the ethanol in wine, and even use the carbon dioxide in champagne and other sparkling wines. Calculate the energy that the yeast obtains per mole of glucose. What can you deduce from this calculation and part b about the advantages of combustion of glucose with O_2 , over simple fermentation without O_2 ?

Fuel combustion

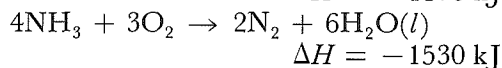
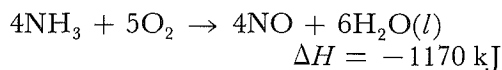
9. (a) How much heat is released when a mole of gasoline, C_8H_{18} , is burned in the open air? Write a balanced equation for the reaction that produces liquid water. (b) How much heat is obtained if the gasoline is burned with a restricted oxygen supply, so CO is produced instead of CO_2 ? (c) How much heat results if this CO is oxidized to CO_2 ? (d) How do your answers to parts b and c compare with that to part a? What principle does this represent?

Heat of condensation

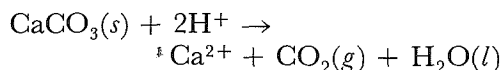
10. When an inch of rain falls on New York City, it results in a rainfall of 19.7×10^9 liters over the city's 300-square-mile area. (a) Assume a density of liquid water of 1.00 g cm^{-3} , how much heat is released when this quantity of water condenses from vapor in the rain clouds? (Think of condensation as a chemical reaction: $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$, and use thermodynamic data from Appendix 3.) (b) A ton of TNT releases around 4000 kJ of energy. How many megatons of TNT (1 megaton = 10^6 tons) would be needed for an explosion that released as much energy as the inch of rain in part a?

Heat of reaction

11. Use the following heats of reaction to calculate the heat of formation of NO. Compare your answer with that given in Appendix 3.

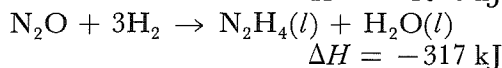
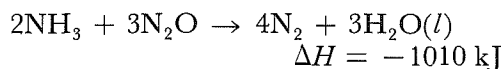


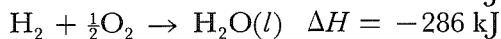
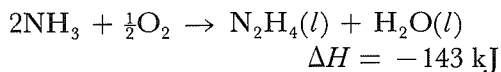
12. From data in Appendix 3, calculate the heat given off when limestone is dissolved by acid:



Rocket fuels

13. Calculate the heat of formation of liquid hydrazine, N_2H_4 , from the following data:



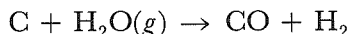


Write the balanced equation for the combustion of N_2H_4 in oxygen to form nitrogen gas and liquid water. What is the heat of combustion of hydrazine?

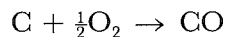
14. (a) In liquid-fuel rockets, such as the lunar module of the Apollo moon missions, the fuel is liquid hydrazine, N_2H_4 , and the oxidant is N_2O_4 . Write a balanced equation for the reaction of these two substances to form liquid water and N_2 gas. (b) How much heat is given off in this reaction per mole of hydrazine? (c) Would more, or less, heat be given off if the oxidant were O_2 instead of dinitrogen tetroxide? How much?

Industrial fuel gas

15. In the manufacture of water gas, a commercial heating gas, steam is passed through hot coke, and the following reaction occurs:



- (a) What is the standard enthalpy of this reaction per mole of carbon in the coke? How much heat is stored per mole of carbon? (b) Write the reactions that occur when water gas (the mixture of CO and H_2) is burned in air. How much energy is released when water gas containing a mole each of CO and H_2 is burned to CO_2 and liquid water? (c) How much heat is given off when 100 liters of water gas (measured at 1 atm pressure and 298 K) are burned?
16. Another way of storing the energy of coke in a combustible gas is by passing dry air (20% O_2 and 80% N_2 by volume or moles) through hot coke so the following reaction occurs:



- (a) If 100 liters of air are passed through the furnace, how many liters of O_2 are used up? How many liters of CO are formed? How many liters of N_2 go through the furnace unchanged? What volume of CO gas is obtained from 100 liters of air? (b) How much heat is given off when 100 liters of CO gas (1 atm and 298 K) are burned?

Bond energies

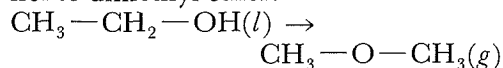
17. The heat of combustion of gaseous dimethyl ether, $\text{CH}_3\text{—O—CH}_3$, to carbon dioxide and liquid water is $-1461 \text{ kJ mole}^{-1}$ of ether. (a) Calculate the standard heat of formation of dimethyl ether and compare your value with that tabulated in Appendix 3. (b) Use the table of bond energies to calculate the standard heat of formation of dimethyl ether. Illustrate your calculation with an energy-level diagram similar to Figure 15-7, labeling all energy levels and energy transitions. How does your answer compare with that of part a?
18. Use bond energies to calculate the heat of formation of acetaldehyde vapor, $\text{CH}_3\text{CHO}(g)$, at 25°C from graphite and O_2 and H_2 gases. Illustrate your calculations with an energy-level diagram. Compare your answer with the thermodynamic value in Appendix 3. How good is the bond-energy method, according to this calculation?
19. From bond energies and atomic heats of formation, calculate the standard heat of formation of the following gases: (a) C_2H_6 ; (b) CH_3SH ; (c) CH_3NH_2 . How do these heats compare with the measured values in Appendix 3?
20. The following are some of the gas reactions that take place in our atmosphere.

Use bond-energy information to calculate the enthalpy for each reaction:

- $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$
- $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$
- $\text{N} + \text{N} \rightarrow \text{N}_2$
- $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$

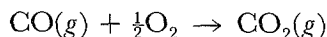
Bond energies and molecular structure

21. (a) From data in Appendix 3, calculate the heat of isomerization of liquid ethanol to dimethyl ether:



- (b) Calculate the corresponding heat of isomerization beginning with ethanol vapor. Explain the difference between this value and the answer to part a. (c) Calculate the heat of the reaction in part b from bond energies. How different are the bond energy and thermodynamic values? (d) Account for the heat of isomerization of ethanol vapor in terms of the bonding in each molecule.
22. (a) Assume that the bond structure of carbon monoxide is $\text{C}=\text{O}$; of carbon

dioxide, $\text{O}=\text{C}=\text{O}$. Calculate the standard enthalpy of the following reaction from bond-energy tables:



Compare this enthalpy with the thermodynamically measured value. How big is the error, and how good do your assumptions about the bond structures of these two molecules appear to be? (b) Select two other chemical reactions from the data in Appendix 3, one involving CO but not CO_2 , and the other involving CO_2 but not CO. Calculate the enthalpies of these two reactions from bond energies, compare them with thermodynamic values, and decide which bond assumption of part a is worse, that of $\text{C}=\text{O}$ or that of $\text{O}=\text{C}=\text{O}$.

23. The heat of combustion of gaseous isoprene, $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ or C_5H_8 , to carbon dioxide gas and liquid water is $-3186 \text{ kJ mole}^{-1}$. Calculate the heat of formation, and, by comparison with a bond-energy calculation, estimate the resonance energy of isoprene. Can you draw several possible resonance structures?

Postscript: Count Rumford versus the World

In *Order and Chaos*, S. W. Angrist and L. G. Hepler remark:

“It is well established that people with widely differing backgrounds and positions have made significant contributions to the theory of heat and energy. Consider the following list of contributors to the science and practice of heat: (1) a spy for the British government in the employ of General Gage, who was British Commandant in Boston at the time of the American Revolution, (2) the Secretary of the Province of Georgia in the British Foreign Office in 1779, (3) The Undersecretary of State for the Northern Department in the British Foreign Office in 1780, (4) a lieutenant colonel in the King’s American Dragoons, (5) a Knight in the court of George III, (6) a British spy in the court of the Elector of Bavaria, (7) the founder of the Munich Military Workhouse, (8) the designer of Munich’s English

Gardens, (9) a lieutenant general in the service of the Elector of Bavaria, (10) a member of the Polish Order of St. Stanislaus with the rank of White Eagle, (11) a Count of the Holy Roman Empire, (12) the founder of the Royal Institution, (13) a foreign associate of the French Academy of Sciences, and (14) Lavoisier's widow's second husband. ♪*

As the authors point out, all these people are really only one individual, Benjamin Thompson, later Count Rumford.

To this list they could have added: the inventor of the combustion calorimeter, the comparative photometer with the International Standard Candle, the kitchen range or cookstove, the double boiler, the baking oven, the portable stove and army field kitchen, the drip coffee maker, the modern steam heating system, the smoke shelf and damper system now used in all fireplaces, an improved oil study lamp of unprecedented illumination, a naval signaling system used by Great Britain, and an improved ballistic pendulum for measuring the force of gunpowder; the discoverer of convection currents in gases and liquids, the maximum density of water at 4°C, and the superior absorption and emission of radiation by black instead of polished objects; one of the earliest investigators of the tensile strength of fibers and the insulating properties of cloth; the founder of one of the earliest public schools, and of the first international scientific medal and prize (still awarded); and the intended first head of West Point (declined by prearrangement for political reasons). The list is still incomplete. Thompson was a practical genius and inventor in the same league with Thomas Edison. He revolutionized nutrition in Europe in the late 1700s in the same way that Edison revolutionized life, a century later, with the practical use of electricity. He was certainly a more prolific inventor than Franklin, and probably a better scientist. Why, then, is he virtually unknown except to historians of science and students of thermodynamics?

The reason lies largely in the personality of the man. Thompson was ambitious and utterly without scruples or principles. He toadied to his superiors, was caustic and treacherous to his peers, and tyrannical to his subordinates. No one could work with him, and he made a host of enemies wherever he went. He was, in short, an intolerable genius.

Thompson was born in Woburn, Massachusetts, in 1753. He was a member of a large farm family. He appears to have been a compulsive organizer and student. Notebooks from his youth give a daily schedule of subjects to be studied ("Munday—Anatomy, Tewsday—Anatomy, Wednesday—Institutes of Physick, Thursday—Surgery, Fryday—Chimistry with the Materia Medica, Saturday—Physick $\frac{1}{2}$ and Surgery $\frac{1}{2}$ ") as well as hourly schedules for each day. He was first apprenticed to a dry-goods dealer, then to a local doctor. Neither apprenticeship was satisfactory, and he became a schoolteacher in Concord, New Hampshire (originally called Rumford, N.H.). Here Thompson made his first—and in many respects typical—step

*S. W. Angrist and L. G. Hepler, *Order and Chaos: Laws of Energy and Entropy*, Basic Books, New York, 1967, p. 9.

upward in life. In 1772, he married the young widow of a wealthy New Hampshire landowner.

Thompson's natural autocratic leanings and the connections of his wife and her late husband led him to become a favorite of the British Royal Governor of New Hampshire. He became an informer and spy for the British, who needed information on caches of arms and supplies that the Colonial Militia and Minuteman groups were secreting about the New England countryside. He was suspected of being an informer, and the New Hampshire Committee of Public Safety called him before them to answer charges that he was "unfriendly to the cause of freedom." Nothing could be proved against him. But a week before Christmas, 1774, Thompson learned that a group of "patriots" was coming for him that evening with tar and feathers. He left his wife, baby daughter, and elderly father-in-law to face the mob alone and rode for Boston. He never came back.

Thompson continued to spy for the British in Massachusetts, and had another brush with the Committee of Public Safety in that state. Again, he was too clever for anything to be proved against him, but thereafter he was watched carefully and lost his advantage as a spy. When the British army was forced out of Boston in March, 1776, Thompson went with them. He soon arrived in London, where he found employment, first as an expert on the Revolutionary War (the equivalent of our "Kremlinologists"), then in several governmental posts. After seven years, during which time he made several important inventions, was suspected of slipping British naval intelligence to the French in the La Motte case, and made innumerable personal enemies, he felt obliged to seek employment elsewhere. He soon appeared in Munich as a colonel and military advisor to the Elector Karl Theodore of Bavaria. (He sent several military intelligence reports on the state of the army of his new employer back to England in cipher.)

The Bavarian army was in wretched shape. It had no discipline, training, decent equipment, supply procedures, or morale, and was ridden with graft, corruption, and inefficiency. Thompson was given the responsibility for whipping it into a decent fighting force. His situation in Munich was similar to Lavoisier's in the *Ferme Générale*, or Tax Farm. The businessmen of the *Ferme Générale* contracted with the French Crown to deliver a certain amount in tax revenues to the treasury each year. Any taxes that they collected over and above this amount, they could keep. Colonel Thompson was given a fixed sum of money each year to run the Bavarian army. If the operation of the army became more effective and Thompson simultaneously found ways to cut expenses, the money saved was his own. It paid both Lavoisier and Thompson to carry out their duties in the most efficient possible manner. Thompson's experiments with clothing, nutrition, cannon boring and the Munich military workhouses were all part of his plan to make the Bavarian army efficient. When conservative manufacturers refused to weave cloth and construct equipment to his specifications, he used the army to round up the thousands of street beggars of Munich in one night's sweep and set up the military workhouses as his factories. He gave



Figure 15-10

Count Rumford supervising a public lecture at his Royal Institution in London, in 1802. Rumford is the hook-nosed figure smiling benignly at the upper right. The lecturer is Thomas Young, a Professor of Natural Philosophy at the Royal Institution, and his assistant with the bellows and an evil leer is the young Humphrey Davy. The "victim" of the demonstration is Sir John Hippisley, manager of the Royal Institution. Davy worked extensively with the physiological effects of various gases. He had almost killed himself inhaling methane two years before, and caused a sensation at a lecture in 1801 by giving laughing gas (nitrous oxide) to volunteers from the audience. James Gillray, the artist, was the Herblock or Mauldin of his era and was famous for his devastating political cartoons. He considered these Royal Institution lectures a sham because, although intended as an education for working people, they had become the fashionable entertainment of the wealthy, as caricatured here. Davy and Michael Faraday continued a tradition of public lectures which has been maintained to the present day. One of us [R.E.D.] gave a Royal Institution lecture in 1970 in what was recognizably the same lecture hall as shown here in 1802. (Photograph of the original etching courtesy The Fisher Collection.)

each worker room and board, and set up free schools for their children (until they were old enough to work). He built the famous Munich “English Gardens” as demonstration gardens for his innovations in agriculture and nutrition. His “Rumford soup,” developed for the workhouses, was an attempt to provide a complete food at the lowest possible cost. He introduced potatoes to Bavaria, although he had to smuggle the first ones into his kitchens by stealth because the Bavarians considered them unfit to eat. He propagandized coffee as a stimulating substitute for alcohol and invented the drip percolator to make it popular. Soldiers in European armies of the time found food where they could get it, and cooked it themselves over open fires in camp. Thompson first designed a collapsible one-man field stove and then conceived the idea of a traveling field kitchen to cook for the army. His cannon-boring experiments, virtually the only achievement for which he is still remembered, were only an incident in a colorful career in Munich.

From a colonel in the Bavarian army, Thompson rose to be minister of war, minister of police, major general, chamberlain of the Bavarian Court, and state councillor. He held all these offices simultaneously and was the second most powerful man in Bavaria, after the elector himself. His ultimate title was that of count of the Holy Roman Empire. Thompson chose as his title the original name of Concord, New Hampshire, and, after 1792, insisted on being addressed as “Count Rumford” rather than as Benjamin Thompson. The choice of “Rumford” may have been a belated acknowledgment of his wife and child, whom he had deserted 18 years earlier, or it might have derived from his pretensions that he had come from a wealthy landowning family in the Colonies.

By 1795, his intensive work had begun to damage his health, and his many enemies in the Court of Bavaria were becoming too powerful. He left Munich and returned in triumph to London. He was given almost overwhelming adulation, by both governmental figures and the general public, as a great philanthropist, philosopher, and benefactor. No matter what his difficulties in getting along with people and his personal defects might have been, Rumford’s improvements in housing, lighting, clothing, and nutrition had made a real difference to the average citizen of Europe of the time. The Royal Institution of Great Britain, now a respected research laboratory, was initially created as a showcase for Thompson’s inventions and innovations. He brought in a young country boy by the name of Humphry Davy (the Sir Humphry Davy of the Dalton postscript to Chapter 6) to assist in giving public demonstrations and lectures (Figure 15-10). Typically, Thompson conceived of the Royal Institution as a place where the uninformed would come to ask Count Rumford how their lives should be run. The fact that he was so often right made little difference to those who were put off by his arrogance. Within two years, he was forced out of active control of the Royal Institution, although the Institution went on to be the brilliant showcase and laboratory for Humphry Davy, Michael Faraday, and a continuing procession of noted scientists.

At this point in his career, Rumford was only 49 years old. We must leave him, except to remark that he began a new career in France by marrying the widow of Lavoisier. His first wife had conveniently died by this time. The new marriage was notoriously stormy and lasted only two years. But by the end of this time, he was as firmly established in French affairs as he had been in those of Munich and London.

Rumford died suddenly in 1814. He managed his death as efficiently as he had his life. In a curious will, he left all his possessions to Harvard University, which still looks after his grave in France. Upon his death, he sank into obscurity as rapidly as he had risen from it. He was not remembered, as were Lavoisier, or Dalton, or Franklin. People who tried to live and work with him found it so difficult to give him credit for his real achievements that when his life was over they simply forgot him as fast as possible. He had proclaimed so often in life what a great man he was, that people were content to let the issue rest after his death.

In a funeral eulogy before the French Academy, the naturalist Baron Cuvier summarized the flaws in this remarkable man:

“He considered the Chinese government as the nearest to perfection, because in delivering up the people to the absolute power of men of knowledge alone, and in raising each of these in the hierarchy according to the degree of his knowledge, it made in some measure so many millions of hands the passive organs of the will of a few good heads. An empire such as he conceived would not have been more difficult for him to manage than his barracks and poorhouses. . . . The world requires a little more freedom and is so constituted that a certain height of perfection often appears to it a defect, when the person does not take as much pains to conceal his knowledge as he has taken to acquire it.”

Suggested Reading

- S. C. Brown, *Count Rumford, Physicist Extraordinary*, Anchor, New York, 1962. An entertaining biography of one of the greatest practical geniuses and blackguards in the annals of science.
- I. M. Klotz and R. M. Rosenberg, *Introduction to Chemical Thermodynamics*, W. A. Benjamin, Menlo Park, Calif., 1972, 2nd ed.
- B. H. Mahan, *Elementary Chemical Thermodynamics*, W. A. Benjamin, Menlo Park, Calif., 1963. A good introduction to classical thermodynamics (that is, without the statistical interpretation of entropy). Moderate use of calculus, which is mostly explained as it is introduced.
- L. Nash, *Introduction to Chemical Thermodynamics*, Addison-Wesley, Reading, Mass., 1963.
- J. Waser, *Basic Chemical Thermodynamics*, W. A. Benjamin, Menlo Park, Calif., 1966. Both this and Nash's book are at a level similar to Mahan and this chapter. Highly recommended.