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# BASIC THERMODYNAMICS



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# ENERGY AND THE FIRST LAW OF THERMODYNAMICS

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## 1.1. FUNDAMENTAL CONCEPTS

***Temperature and the Zeroth Law.*** The concept of temperature is so familiar to us that we may not comprehend why scientists two centuries ago tended to confuse temperature with heat. We will start with the notion that temperature corresponds to “degree of hotness” experienced as a sensation. Next we assign a number to the temperature based on the observation that material objects (gases and liquids in particular) respond to “degree of hotness” through variations in their volumes. Thus we should be able to associate a number (its temperature) with the volume of a specified amount of material. We call the instrument designed for this purpose a thermometer.

The first requirement in setting up a scale of temperatures is to choose a zero point. In the common *Celsius* or *centigrade* scale we set the freezing point of water (which is also the melting point of ice) at  $0^{\circ}\text{C}$  [more precisely,  $0^{\circ}\text{C}$  corresponds to the freezing point of water (called the “ice point”) in the presence of air at a pressure of 1 atmosphere (atm)]. The second requirement is that we must define the size of the degree, which is done for this scale by setting the boiling point of water (the “steam point”) at  $100^{\circ}\text{C}$ . The intervening portion of the scale is then divided linearly into 100 segments. We will let  $t$  signify temperature on the Celsius scale.

Experience shows that different substances may give different temperature readings under identical conditions even though they agree perfectly at 0 and  $100^{\circ}\text{C}$ . For example, a mercury thermometer and an alcohol thermometer will not give precisely the same readings at (say) room temperature. In very careful work it would be advantageous to have available an “absolute” temperature scale that does not depend on the identity of the thermometer substance. Again we appeal to laboratory

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experience, which has shown that the dependence of the volume of a fixed amount of a gas on temperature, at very low pressures of the gas, is independent of the chemical nature of the gas. Later we will study the behavior of gases at low pressures in more detail; for the present we can call such gases “ideal gases” and use them to define an *absolute ideal-gas temperature scale*. We define the absolute temperature as directly proportional to the volume of a given mass of ideal gas at constant pressure (i.e., letting  $T$  be the absolute temperature and  $V$  the gas volume):

$$T \propto V$$

For convenience we define the size of the absolute temperature to be identical to the Celsius degree. If  $V_0$  and  $V_{100}$  are the volumes of the ideal gas at the ice and steam points of water, respectively, the size of the degree is given by

$$\frac{V_{100} - V_0}{100}$$

Then our absolute temperature scale is defined by

$$T = \frac{V}{(V_{100} - V_0)/100} \quad (1.1)$$

Now suppose that we apply our ideal-gas thermometer to water at the ice point. In this special case Eq. (1.1) becomes

$$T_0 = \frac{V_0}{(V_{100} - V_0)/100}$$

Careful experimental work with numerous gases has revealed that  $T_0 = 273.15$  K. Thus the Celsius and absolute scales are related by

$$T = t + 273.15 \quad (1.2)$$

The absolute temperature scale is also called the *thermodynamic scale* or the *Kelvin scale*, and temperatures on this scale are denoted K (pronounced Kelvin, with no degree symbol or word).

According to Eq. (1.1), when  $T = 0$  K,  $V = 0$ ; the volume of the ideal gas goes to zero at the *absolute zero*. Modern experimental techniques have achieved temperatures within microdegrees of the absolute zero, but  $T = 0$  K appears to be an unattainable condition.

The concept and practical use of temperature scales and thermometers is based on the experimental fact that if two bodies are each in thermal equilibrium with a third body, they are in thermal equilibrium with each other. This is the *zeroth law of thermodynamics*.

**Work and Energy.** Let us begin with the mechanical concept of *work* as the product of a force and a displacement:

$$\text{Work} = \text{force} \times \text{displacement} \quad (1.3)$$

The units of work are consequently those of force and length. Now from Newton's laws of motion,

$$\text{Force} = \text{mass} \times \text{acceleration} \quad (1.4)$$

In SI units, force therefore has the units  $\text{kg m s}^{-2}$ , which is also called a newton, N. Hence the units of work are either  $\text{kg m}^2 \text{s}^{-2}$  or N m.

Energy is defined as any property that can be produced from or converted into work (including work itself). Therefore work and energy have the same dimensions, although different units may be used to describe different manifestations of energy and work. For example,  $1 \text{ Nm} = 1 \text{ J}$  (joule), and energy is often given in joules or kilojoules. Here are relationships to earlier energy units:

$$1 \text{ J} = 10^7 \text{ erg}$$

$$4.184 \text{ J} = 1 \text{ cal (calorie)}$$

Note from the definition (1.3) that work is a product of an intensive property (force) and an extensive property (displacement). In general, work or energy can be expressed as this product:

$$\text{Work (energy)} = \text{intensity factor} \times \text{capacity factor} \quad (1.5)$$

Here are several examples of Eq. (1.5):

Mechanical work = mechanical force  $\times$  distance

Work of expansion = pressure  $\times$  volume change

Electrical work = electric potential  $\times$  charge

Surface work = surface tension  $\times$  area change

All forms of work are, at least in principle, completely interconvertible. For example, one could use the electrical energy provided by a battery to drive a (frictionless) piston that converts the electrical work to an equivalent amount of work of expansion.

**Heat and Energy.** Heat has been described as *energy in transit* (Glasstone 1947, p. 7) or as a *mode of energy transfer* (Denbigh 1966, p. 18). Heat is that form of energy that is transferred from one place to another as a consequence of a difference in temperature between the two places. Numerically heat is expressed in joules (J) or calories (cal). Heat is not "degree of hotness," which, as we have seen, is measured by temperature.<sup>1</sup>

**Table 1.1. The energy of a thermodynamic system**

Total energy of a body			
Thermodynamic energy ( $U$ )		Mechanical energy	
Kinetic energy (translational energy)	Internal energy (vibrational, rotational, and electronic energy)	Kinetic energy as a result of the body's motion as a whole	Potential energy as a result of the body's position

Since both work and heat are forms of energy, they are closely connected. Work can be completely converted into an equivalent amount of heat (e.g., through friction). The converse is not possible, however; it is found experimentally that heat cannot be completely converted into an equivalent amount of work (without producing changes elsewhere in the surroundings). This point will be developed later; for the present we observe that this finding is the basis for the impossibility of a “perpetual-motion machine.”

We find it convenient to divide energy into categories. This is arbitrary, but there is nothing wrong with it provided we are careful to leave nothing out. Now, we have seen that thermodynamics is not built on the atomic theory; nevertheless, we can very usefully invoke the atomic and molecular structure of matter in our interpretation of energy. In this manner we view heat as thermal energy, equivalent to, or manifesting itself as, motions of atoms and molecules. The scheme shown in Table 1.1 clarifies the several “kinds” of energy that a body (the “system”) can possess.<sup>2</sup>

Chemical thermodynamics is concerned with the energy  $U$ . This energy is a consequence of the *electronic* distribution within the material, and of three types of atomic or molecular motion: (1) *translation*, the movement of individual molecules in space; (2) *vibration*, the movement of atoms or groups of atoms with respect to each other within a molecule; and (3) *rotation*, the revolution of molecules about an axis. If a material object is subjected to an external source of heat, so that the object absorbs heat and its temperature rises, the atoms and molecules increase their translational, vibrational, and rotational modes of motion. Energy is not a “thing”; it is rather one way of describing and measuring these molecular and atomic distributions and motions, as well as the electronic distribution within atoms and molecules.

**Systems and States.** In order to carry out experimental studies and to interpret the results, we must focus on some part of the universe that interests us. In thermodynamics this portion of the universe is called a *system*. The system typically consists of a specified amount of chemical substance or substances, such as a given

mass of a gas, liquid, or solid. Whatever exists outside of the system is called the *surroundings*. Certain conditions give rise to several types of systems:

*Isolated Systems.* These systems are completely uninfluenced by their surroundings. This means that neither matter nor energy can flow into or out of the system.<sup>3</sup>

*Closed Systems.* Energy may be exchanged with the surroundings, but there can be no transfer of matter across the boundaries of the system.

*Open Systems.* Both energy and matter can enter or leave the system.

We can also speak of a *homogeneous* system, which is completely uniform in composition; or a *heterogeneous* system, which consists of two or more phases.

The *state* of a system, experiment has shown, can be completely defined by specifying four observable thermodynamic variables: the composition, temperature, pressure, and volume. If the system is homogeneous and consists of a single chemical substance, only three variables suffice. Moreover, it is known that these three variables are not all independent; if any two are known, the third is thereby fixed. Thus the thermodynamic state of a pure homogeneous system is completely defined by specifying any two of the variables pressure ( $P$ ), volume ( $V$ ), and temperature ( $T$ ). The quantitative relationship, for a given system, among  $P$ ,  $V$ , and  $T$  is called an *equation of state*. Generally the equation of state of a system must be established experimentally.

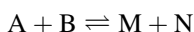
The fact that the state of a system can be completely defined by specifying so few (two or three) variables constitutes a vast simplification in the program of describing physicochemical systems, for this means that all the other macroscopic physical properties (density, viscosity, compressibility, etc.) are fixed. We don't know their values, but we know that they depend only on the thermodynamic variables, and therefore are not themselves independent. With this terminology we can now say that thermodynamics deals with changes in the energy  $U$  of a system as the system passes from one state to another state.

***Thermodynamic Processes and Equilibrium.*** A system whose observable properties are not undergoing any changes with time is said to be in *thermodynamic equilibrium*. Thermodynamic equilibrium implies that three different kinds of equilibrium are established: (1) *thermal equilibrium* (all parts of the system are at the same temperature), (2) *chemical equilibrium* (the composition of the system is not changing), and (3) *mechanical equilibrium* (there are no macroscopic movements of material within the system).

Many kinds of processes can be carried out on thermodynamic systems, and some of these are of special theoretical or practical significance. *Isothermal processes* are those in which the system is maintained at a constant-temperature. (This is easy to do with a constant-temperature bath or oven.) Since it is conceivable that heat is given off or taken up by the system during the process, maintaining a constant temperature requires that the heat loss or gain be offset by heat absorbed from or given up to the surroundings. Thus an isothermal process requires either a

closed or an open system, both of these allowing energy to be exchanged with the surroundings. An *adiabatic process* is one in which no heat enters or leaves the system. An adiabatic process requires an isolated system. Obviously if the process is adiabatic, the temperature of the system may change.

A *spontaneous process* is one that occurs “naturally”; it takes place without intervention. For example, if a filled balloon is punctured, much of the contained gas spontaneously expands into the surrounding atmosphere. In an equilibrium chemical reaction, which we may write as



it is conventional to consider the reaction as occurring from left to right as written. Thus if the position of equilibrium favors  $M + N$  (the products), the reaction is said to be spontaneous. If the reactants ( $A + B$ ) are favored, the reaction is nonspontaneous as written. (Obviously we can change these designations simply by writing the reaction in the reverse direction.)

It is the business of thermodynamics to tell us whether a given process is spontaneous or nonspontaneous. However, thermodynamics, which deals solely with systems at equilibrium, cannot tell us how fast the process will be. For example, according to thermodynamic results, a mixture of hydrogen and oxygen gases will spontaneously react to yield water. This is undoubtedly correct—but it happens that (in the absence of a suitable catalyst) the process will take millions of years.

There is one more important type of thermodynamic process: the *reversible process*. Suppose we have a thermodynamic system at equilibrium. Now let an infinitesimal alteration be made in one of the thermodynamic variables (say,  $T$  or  $P$ ). This will cause an infinitesimal change in the state of the system. If the alteration in the variable is reversed, the process will reverse itself exactly, and the original equilibrium will be restored. This situation is called *thermodynamic reversibility*. Reversibility in this sense requires that the system always be at, or infinitesimally close to, equilibrium, and that the infinitesimally small alterations in variables be carried out infinitesimally slowly. Because of this last factor, thermodynamically reversible processes constitute an idealization of real processes, but the concept is theoretically valuable. One feature of a reversible process is that it can yield the maximum amount of work; any other (irreversible) process would generate less work, because some energy would be irretrievably dissipated (e.g., by friction).

Now suppose that a system undergoes a process that takes it from state A to state B:



We define a change in some property  $Q$  of the system by

$$\Delta Q = Q_B - Q_A \quad (1.6)$$

In other words, the incremental change in the property is equal to its value in the final state minus its value in the initial state.

Next consider this series of processes, which constitute a *thermodynamic cycle*:

$$\begin{array}{rcl}
 \text{A} & \xrightarrow{1} & \text{B} & \Delta Q_1 = Q_B - Q_A \\
 4 \uparrow & & \downarrow 2 & \Delta Q_2 = Q_C - Q_B \\
 \text{D} & \xleftarrow{3} & \text{C} & \Delta Q_3 = Q_D - Q_C \\
 & & & \Delta Q_4 = Q_A - Q_D \\
 & & & \hline
 & & & \text{Sum: } \Delta Q = 0
 \end{array}$$

In any cycle in which the system is restored exactly to its original state, the total incremental change is zero.

## 1.2. THE FIRST LAW OF THERMODYNAMICS

**Statement of the First Law.** To this point we have been establishing a vocabulary and some basic concepts, and now we are ready for the first powerful thermodynamic result. This result is solidly based on extensive experimentation, which tells us that although energy can be converted from one form to another, it cannot be created or destroyed [this statement is completely general in the energy regime characteristic of chemical processes; relativistic effects (i.e., the famous equation  $E = mc^2$ ) do not intrude here]. This is the great *conservation of energy* principle, which is expressed mathematically as Eq. (1.7), the *first law of thermodynamics*.

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

Here  $\Delta U$  is the change in thermodynamic energy of the system,  $q$  is the amount of energy gained by the system as heat, and  $w$  is the amount of energy lost by the system by doing work on its surroundings. These are the sign conventions that we will use:

$q$  is positive if the heat is taken up by the system (i.e., energy is gained by the system).

$w$  is positive if work is done by the system (i.e., energy is lost by the system).<sup>4</sup>

Equation (1.7) is the incremental form of the first law. The differential form is

$$dU = dq - dw \quad (1.8)$$

But now we must make a very clear distinction between the quantity  $dU$  and the quantities  $dq$  and  $dw$ .  $U$  is a *state function* and  $dU$  is an *exact differential*. This terminology means that the value of  $\Delta U$ , which is obtained by integrating  $dU$  over the limits from the initial state to the final state, is independent of the path (i.e., the process or mechanism) by which the system gets from the initial state to the final

state. A state function depends only on the values of the quantity in the initial and final states.

It is otherwise with  $q$  and  $w$ , for these quantities may be path-dependent. For example, the amount of work done depends on the path taken (e.g., whether the process is reversible or irreversible). Therefore  $dq$  and  $dw$  are not exact differentials, and some authors use different symbols to indicate this. Nevertheless, although  $q$  and  $w$  individually may be path-dependent, the combination  $q-w$  is independent of path, for it is equal to  $\Delta U$ .<sup>5</sup>

**The Ideal Gas.** Experimental measurements on gases have shown that, as the pressure is decreased, the volume of a definite amount of gas is proportional to the reciprocal of the pressure:

$$V \propto \frac{1}{P}$$

As  $P$  is decreased toward zero, all gases (at constant temperature) tend to behave in the same way, such that Eq. (1.9) is satisfied:

$$PV = \text{constant} \quad (1.9)$$

This result can be generalized as Eq. (1.10), which is called the *ideal-gas equation* (or the ideal-gas law):

$$PV = nRT \quad (1.10)$$

where  $P$ ,  $V$ , and  $T$  have their usual meanings;  $n$  is the number of moles of gas; and  $R$  is a proportionality constant called the *gas constant*. Equation (1.10) is the equation of state for an ideal gas (sometimes called the “perfect gas”), and it constitutes a description of real-gas behavior in the limit of vanishingly low pressure.

**Example 1.1.** Experiment has shown that 1 mol of an ideal gas occupies a volume of 22.414 L at 1 atm pressure when  $T = 273.15$  K. Calculate  $R$ :

$$\begin{aligned} R &= \frac{PV}{nT} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} \\ &= 0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1} \end{aligned}$$

We can use a dimensional analysis treatment to convert to other energy units, as described in Appendix B:

$$\begin{aligned} R &= \left( \frac{0.082057 \text{ L atm}}{\text{mol K}} \right) \left( \frac{101325 \text{ Pa}}{1 \text{ atm}} \right) \left( \frac{1 \text{ N m}^{-2}}{1 \text{ Pa}} \right) \left( \frac{10^3 \text{ cm}^3}{1 \text{ L}} \right) \left( \frac{1 \text{ J}}{1 \text{ N m}} \right) \left( \frac{1 \text{ m}}{10^2 \text{ cm}} \right)^3 \\ &= 8.3144 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

and since  $1 \text{ cal} = 4.184 \text{ J}$ ,  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Notice that, in this calculation of  $R$ , its units are energy per mol per K. That is, since  $R = PV/nT$ , the units of the product  $PV$  are energy, which we expressed in the particular units L atm, J, or cal. These several values of  $R$  are widely tabulated, and they can serve as readily accessible conversion factors among these energy units.

We earlier mentioned a type of work called *work of expansion*. This is the work done by a gas when it expands against a resisting pressure, as happens when a piston moves in a cylinder. We can obtain a simple expression for work of expansion. Suppose a piston of cross-sectional area  $A$  moves against a constant pressure  $P$ . We know that mechanical work is the product of force ( $F$ ) and distance, or

$$w = F(L_2 - L_1)$$

where  $L_1$  is the initial position of the piston and  $L_2$  is its final position. Pressure is force per unit area ( $A$ ), so  $F = PA$ , giving

$$w = PA(L_2 - L_1)$$

But  $A(L_2 - L_1) = V_2 - V_1$ , where  $V_1$  and  $V_2$  are volumes, so

$$w = P(V_2 - V_1) = P \Delta V \quad (1.11)$$

where  $\Delta V$  is the volume displaced. Thus work of expansion is the product of the (constant) pressure and the volume change; in fact, we often refer to work of expansion as  $P \Delta V$  work.

Now, if the process is carried out reversibly, so that the pressure differs only infinitesimally from the equilibrium pressure, the volume change will be infinitesimal, and Eq. (1.11) can be written

$$dw = P dV \quad (1.12)$$

We can integrate this between limits:

$$w = \int_{V_1}^{V_2} P dV \quad (1.13)$$

(In the case of an isothermal, reversible expansion,  $w$  does not depend upon the path, but this is a special case.) Now suppose that the gas is ideal and that the process is carried out isothermally. From the ideal gas law,  $P = nRT/V$ , so

$$w = nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad (1.14)$$

$$w = nRT \ln \frac{V_2}{V_1} \quad (1.15)$$

If  $V_2 > V_1$ , the system does work on the surroundings, and  $w$  is positive. If  $V_1 > V_2$ , the surroundings do work on the system, and  $w$  is negative.

In developing Eq. (1.15) we saw an example of thermodynamic reasoning, and we obtained a usable equation from very sparse premises. Here is another example, again based on the ideal gas. Suppose that such a gas expands into a vacuum. Since the resisting pressure is zero, Eq. (1.11) shows that  $w = 0$ ; that is, no work is done. Careful experimental measurements by Joule and Kelvin in the nineteenth century showed that there is no heat exchange in this process, so  $q = 0$ . The first law therefore tells us that  $\Delta U = 0$ . Since the energy depends on just two variables, say, volume and temperature, we can express the result as

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad (1.16)$$

which says that the energy of an ideal gas is independent of its volume at constant temperature. We can interpret this thermodynamic result in molecular terms as follows. A gas behaves ideally when the intermolecular forces of attraction and repulsion are negligible. (This is why real gases approach ideality at very low pressures, for then the molecules are so far apart that they do not experience each others' force fields.) If there are no forces between the molecules, no energy is required to change the intermolecular distances, and so expansion (or compression) results in no energy change.

### 1.3. THE ENTHALPY

**Definition of Enthalpy.** In most chemical studies we work at constant pressure. (The reaction vessel is open to the atmosphere, and  $P = 1$  atm, approximately.) Consequently the system is capable of doing work of expansion on the surroundings. From the first law we can write  $q = \Delta U + w$ , and since  $w = P \Delta V$ ,

$$q = \Delta U + P \Delta V$$

at constant  $P$ . Writing out the increments, we obtain

$$q = (U_2 - U_1) + P(V_2 - V_1)$$

and rearranging, we have

$$q = (U_2 + PV_2) - (U_1 + PV_1) \quad (1.17)$$

where  $U$ ,  $P$ , and  $V$  are all state functions. We define a new state function  $H$ , the *enthalpy*, by

$$H = U + PV \quad (1.18)$$

giving, from Eq. (1.17), the following:

$$q = \Delta H \quad (1.19)$$

Although Eq. (1.18) defines the enthalpy, it is usually interpreted according to Eq. (1.19), because we can only measure changes in enthalpy (as with all energy quantities). The enthalpy change is equal to the heat gained or lost in the process, at constant pressure (there is another restriction, viz., that work of expansion is the only work involved in the process). Since enthalpy is an energy, it is measured in the usual energy units.

From Eq. (1.18) we can write

$$\Delta H = \Delta U + P \Delta V \quad (1.20)$$

For chemical processes involving only solids and liquids,  $\Delta V$  is usually quite small, so  $\Delta H \approx \Delta U$ , but for gases, where  $\Delta V$  may be substantial,  $\Delta H$  and  $\Delta U$  are different. We can obtain an estimate of the difference by supposing that 1 mol of an ideal-gas is evolved in the process. From the ideal gas law we write

$$P \Delta V = (\Delta n)RT$$

For 1 mol,  $\Delta n = 1$ , so from Eq. (1.20), we have

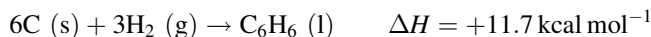
$$\Delta H = \Delta U + RT$$

At 25°C, this gives

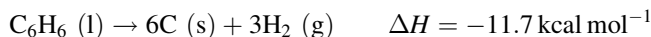
$$\begin{aligned} \Delta H &= \Delta U + (1.987 \text{ cal mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \\ &= \Delta U + 592 \text{ cal mol}^{-1} \end{aligned}$$

which is a very appreciable difference.

When a chemical process is carried out at constant pressure, the heat evolved or absorbed, per mole, can be identified as  $\Delta H$ . Specific symbols and names have been devised to identify  $\Delta H$  with particular processes. For example, the heat absorbed by a solid on melting is called the *heat of fusion* and is labeled  $\Delta H_m$  or  $\Delta H_f$ . The *heat of solution* is the enthalpy change per mole when a solute dissolves in a solvent. For a chemical reaction  $\Delta H$  is called a *heat of reaction*. The heat of reaction may be positive (heat is absorbed) or negative (heat is evolved). By writing a reaction on paper in reverse direction its  $\Delta H$  changes sign. For example, this reaction absorbs heat:



This reaction, its reverse, therefore evolves heat:



We will later see how enthalpy changes for chemical processes can be measured.

**Heat Capacity.** A quantity  $C$ , called the *heat capacity*, is defined as

$$C = \frac{dq}{dT} \quad (1.21)$$

where  $C$  is a measure of the temperature change in a body produced by an increment of heat. The concept of the heat capacity is essential in appreciating the distinction between heat and temperature.

Chemical processes can be carried out at either constant volume or constant pressure. First consider constant volume. If only work of expansion is possible, at constant volume  $\Delta V = 0$ , so  $w = 0$ , and from the first law  $dq = dU$ . We therefore define the heat capacity at constant volume by

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (1.22)$$

At constant pressure, on the other hand, we have, from Eq. (1.19),  $dq = dH$ , and we define the heat capacity at constant pressure by

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad (1.23)$$

In the preceding section we had obtained, for one mole of an ideal gas, Eq. (1.24).

$$\Delta H = \Delta U + RT \quad (1.24)$$

Let us differentiate this with respect to temperature. Using Eqs. (1.22) and (1.23), we get

$$C_P = C_V + R \quad (1.25)$$

For argon, at room temperature,  $C_P = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_V = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ; hence  $C_P - C_V = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is  $R$ .

For most compounds only  $C_P$  has been measured. Values of  $C_P$  for typical organic compounds lie in the range  $15\text{--}50 \text{ cal K}^{-1} \text{ mol}^{-1}$ . As seen here, heat capacity is expressed on a per mole basis, and is sometimes called the *molar heat capacity*. When the heat capacity is expressed on a per gram basis it is called the *specific heat*.

Taking the constant-pressure condition of Eq. (1.23) as understood, we can write  $C_P = dH/dT$ , or  $dH = C_P dT$ . If we suppose that  $C_P$  is essentially constant over the temperature range  $T_1$  to  $T_2$ , integration gives

$$\Delta H = C_P \Delta T \quad (1.26)$$

**Example 1.2.** The mean specific heat of water is  $1.00 \text{ cal g}^{-1} \text{ K}^{-1}$ . Calculate the heat required to increase the temperature of 1.5 L of water from  $25^\circ\text{C}$  to the boiling point.<sup>6</sup>

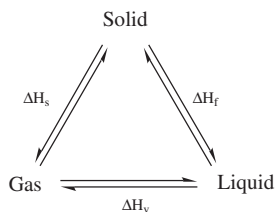
As a close approximation we may take the density of water as  $1.00 \text{ g mL}^{-1}$  and the boiling point as  $100^\circ\text{C}$ , so, from Eq. (1.26), we obtain

$$\Delta H = \left( \frac{1.00 \text{ cal}}{\text{g K}} \right) (1500 \text{ g})(75 \text{ K}) = 112,500 \text{ cal}$$

or 112.5 kcal.

## PROBLEMS

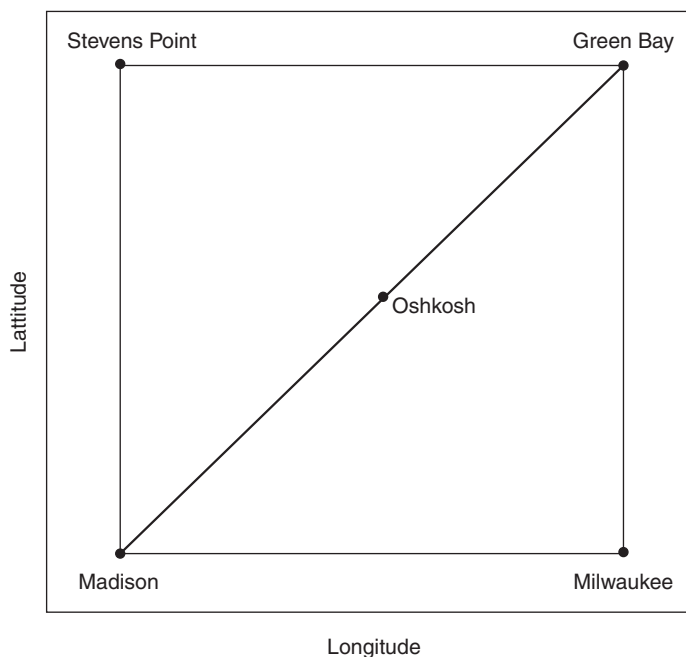
- 1.1. A piston 3.0 in. in diameter expands into a cylinder for a distance of 5.0 in. against a constant pressure of 1 atm. Calculate the work done in joules.
- 1.2. What is the work of expansion when the pressure on 0.5 mol of ideal gas is changed reversibly from 1 atm to 4 atm at 25°C? (*Hint*: For an ideal gas  $P_1V_1 = P_2V_2$ .)
- 1.3. Derive an equation giving the heat change in the isothermal reversible expansion of an ideal gas against an appreciable pressure. [*Hint*: Make use of Eq. (1.16) and the first law.]
- 1.4. What is the molar heat capacity of water? (See Example 1.2 for the specific heat.)
- 1.5. The molar heat capacity of liquid benzene is  $136.1 \text{ J mol}^{-1} \text{ K}^{-1}$ . What is its specific heat?
- 1.6. The specific heat of solid aluminum is  $0.215 \text{ cal g}^{-1} \text{ K}^{-1}$ . If a 100-g block of aluminum, initially at 25°C, absorbs 1.72 kcal of heat, what will be its final temperature?
- 1.7. A 500-g piece of iron, initially at 25°C, is plunged into 0.5 L of water at 75°C in a Dewar flask. When thermal equilibrium has been reached, what will the temperature be? The specific heat of iron is  $0.106 \text{ cal g}^{-1} \text{ K}^{-1}$ .
- 1.8. In the following thermodynamic cycle,  $\Delta H_f$ ,  $\Delta H_v$ , and  $\Delta H_s$  are, respectively, molar heats of fusion, vaporization, and sublimation for a pure substance. Obtain an equation connecting these three quantities. (*Hint*: Pay careful attention to the directions of the arrows.)



## NOTES

1. Note that temperature is an intensive property, whereas heat is an extensive property. Two hot potatoes differing in size may have the same temperature, but the larger potato possesses more heat than the smaller one.
2. This scheme is consistent with the usage of most authors, but some variation is found in the literature. The thermodynamic energy  $U$  may also be symbolized  $E$ , and some authors label the thermodynamic energy the internal energy. The internal energy shown Table 1.1 may be identified with the potential energy of the molecules (to be distinguished from the potential energy of the body as a whole).

3. A truly isolated system is an idealization, but a very close approximation can be achieved inside a closed thermos (derived from the original trade name *Thermos* in 1907) bottle. (The laboratory version is called a *Dewar flask*.)
4. This is the sign convention used by most authors, but the International Union of Pure and Applied Chemistry (IUPAC) reverses the convention for  $w$ , giving as the first law  $\Delta U = q + w$ .
5. This analogy will clarify the difference between path-dependent and path-independent quantities. Suppose we wish to drive from Madison (WI) to Green Bay. Obviously there are numerous routes we might take. We could drive via Milwaukee, or via Oshkosh, or via Stevens Point, and so on. Graphically the possibilities can be represented on a map, as shown in the accompanying figure. Now, no matter which path we take, the changes in latitude,  $\Delta\text{Lat}$ , and in longitude,  $\Delta\text{Lon}$ , will be exactly the same for each route; for example,  $\Delta\text{Lat} = \text{Lat}(\text{GB}) - \text{Lat}(\text{MAD})$ , and this quantity is independent of the route. Thus latitude and longitude are state functions. But the amount of gasoline consumed, the time spent driving, and the number of miles driven all depend on the path taken; these are not state functions. This analogy is taken from Smith (1977).



6. It is not a coincidence that the specific heat of water is  $1.00 \text{ cal g}^{-1} \text{ K}^{-1}$ , for this is how the calorie was originally defined: one calorie was the amount of heat required to raise the temperature of one gram of water by  $1^\circ\text{C}$ . Actually the specific heat of water varies slightly with the temperature.