

4

The Third Law and Free Energies

In a certain city the cold was so intense that words were congealed as soon as spoken.

Plutarch

Because a real engine operating with a cold reservoir at 0 K violates the second law, a third law, *it is impossible to reach 0 K in a finite number of steps*, is invoked. Thus, a real engine cannot employ such a reservoir. Practical methods of achieving very low temperatures are discussed. With the use of heat diagrams, the third law is then restated in the chemically useful form that *the entropies of all pure, perfectly crystalline materials approach zero as the temperature approaches 0 K*. This statement permits the calculation of absolute entropies. The definitions of the Helmholtz and Gibbs free energies allow thermodynamic criteria to be developed based only on properties of the system. Many important differential relations, including those of Maxwell, are developed from these functions, and the relations are utilized in considering heat capacities and entropies of mixing. Standard states for tabulating thermodynamic data are discussed. Finally, the thermodynamic equations are applied to the stretching of elastomeric materials.

4.1 Absolute Zero and the Third Law of Thermodynamics

Because the entropy increase of a heat reservoir is the heat added to the reservoir divided by its absolute temperature, as the temperature of the reservoir becomes very low, just a little heat added to it produces a very large entropy increase. A reversible heat engine operating with such a reservoir becomes more and more efficient ($\varepsilon = 1 - T_c/T_h$) until, with a cold reservoir at 0 K, a heat engine could convert heat into work with 100% efficiency! Is this a contradiction of the second law, which requires net energy degradation in any real process? Once again we must look to the little word “real” to remove this difficulty. There must be something “unreal” about a heat engine operating with a reservoir at 0 K (in addition to its using reversible processes for maximum efficiency). The third law of thermodynamics provides us with a way out of this dilemma by asserting that it is infinitely difficult to reach 0 K. A real engine thus cannot have one of its reservoirs at this temperature. We will state the third law as follows:

It is impossible to reach 0 K in a finite number of steps.¹

In addition to being necessary for the consistency of the second law, the third law is a summary of our experience in attempting to achieve lower and lower temperatures. The third law also allows us to discuss *absolute entropies*, rather than just entropy changes. To see how this comes about, let us digress a bit and discuss how scientists actually attempt to reach very low temperatures.

We have already seen how gases below their Joule–Thomson inversion temperature (T_i) cool upon rapid expansion. By Joule–Thomson expansion, N_2 can be liquefied (77 K). Liquid N_2 can be used to cool H_2 below its T_i (195 K), and then further Joule–Thomson expansion can produce liquid H_2 (20.4 K), which can be used to cool He below its T_i (44.8 K). Joule–Thomson expansion of this cooled He can produce liquid He (4.2 K), and reducing the pressure above the liquid can conveniently produce temperatures as low as about 1 K.

To achieve temperatures lower than 1 K, the process of *adiabatic demagnetization* is usually employed. The best way to describe this process is by the T – S (reversible heat) diagram shown in Fig. 1a. In the presence of a magnetic field, it is energetically favorable for unpaired electrons of paramagnetic salts (usually of transition or lanthanide metals) to have their spins aligned with the field. Such a state also has a lower entropy than the state with randomly aligned spins in the absence of the field at the same temperature. The magnetization is carried out in contact with a thermal reservoir (liquid He, using gaseous He for heat transfer), which absorbs the energy released as the spins adopt their lower-energy orientation. Although it is not necessary in practice, we will assume that the isothermal magnetization is carried out reversibly, so that it can be represented by a horizontal line on the heat diagram. After magnetization, contact with the

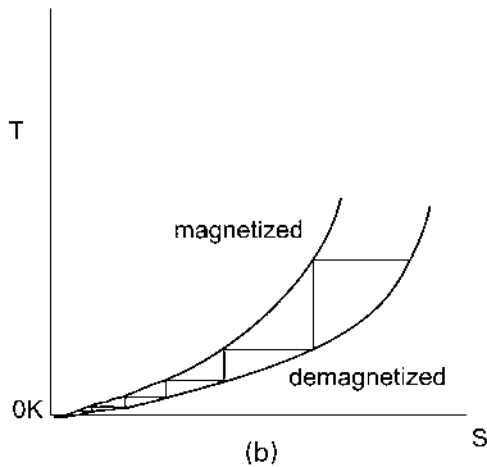
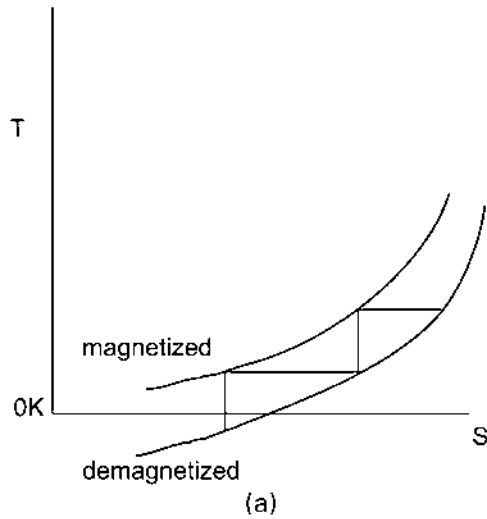


Figure 1 (a) Adiabatic demagnetization; (b) adiabatic demagnetization in agreement with the third law.

reservoir is removed by pumping away the gaseous He, thermally isolating the sample, and slowly reducing the magnetic field. Assuming that this step is reversible, it is isoentropic and is represented by a vertical line on the diagram. As the field is reduced, the spins randomly align, and the energy for this is taken from the thermal energy of the sample, with the resulting temperature drop shown

on the diagram. The lower-temperature sample can now be used to reduce the temperature of the reservoir and the process is repeated, achieving an even lower temperature. Temperatures below 10^{-7} K have been achieved by this method, although it becomes necessary to use nuclear rather than electron spins, in order to obtain a less hindered reorientation at lower temperatures.²

It would appear that by a finite number of successive applications of the magnetization–demagnetization process shown in Fig. 1a, 0 K could be achieved. The only thing that could prevent this goal, as required by the third law, is if, as the temperature is reduced, the two curves approach each other, as shown in Fig. 1b. In this case, the temperature change for the isentropic demagnetization approaches zero as T approaches 0 K:

$$\left(\frac{\Delta T}{\Delta \mathbf{H}}\right)_S \rightarrow 0 \quad \text{as } T \rightarrow 0 \quad (1)$$

where \mathbf{H} is the magnetic field. In this situation, it takes an infinite number of steps to achieve 0 K. Also obvious in Fig. 1b is that the two curves also approach each other along the direction of the S axis, giving

$$\left(\frac{\Delta S}{\Delta \mathbf{H}}\right)_T \rightarrow 0 \quad \text{as } T \rightarrow 0 \quad (2)$$

The choice of magnetic field variation as the process that distinguishes the two curves in Figs. 1a and 1b is of practical, but not of theoretical, significance. If we could find *any* reversible isothermal process whose entropy change remained finite as 0 K was approached, it would be described by a diagram similar to Fig. 1a and theoretically permit the attainment of 0 K in a finite number of steps. The third law therefore requires the following:

The entropy change of any reversible isothermal process must approach zero as T approaches 0 K.

$$\left(\frac{\Delta S}{\Delta \beta}\right)_T \rightarrow 0 \quad \text{as } T \rightarrow 0 \quad (3)$$

where β is the parameter whose variation determines the process.

One such process that we could consider is the chemical reaction $A + B \rightarrow C + D$, with $\beta = \xi$, the extent of the reaction, which will be introduced in Chapter 7. Equation (3) then indicates that the entropy change of *every* reversible³ chemical reaction must approach zero at 0 K. This can be achieved if the entropy of every compound approaches the same value at 0 K. In Chapter 5, we will see that for conformity with the microscopic definition of entropy, we should call this common value of entropy zero.⁴ The requirement that the considered reactions are all reversible demands that all reactants and products

have sufficient time to achieve their equilibrium states, which, generally, will be the perfectly ordered crystalline state of lowest energy. A corollary of the third law is therefore as follows:

The entropies of all pure, perfectly crystalline materials approach zero as temperature approaches 0 K.

As the temperature is reduced, the thermal energy available to overcome kinetic barriers to the lowest-energy state is reduced and, in some cases, *residual entropy* is difficult to remove at low temperatures. In other words, in the low-temperature cooling of these substances, reversibility cannot be approached. An example of a substance with residual entropy is solid CO. Carbon monoxide has a very small dipole moment, which indicates that there is a preferential orientation of molecules at low temperature. The magnitude of the dipole is so small, however, that at temperatures at which the preference becomes appreciable, there is insufficient thermal energy to overcome kinetic barriers for rotation of the molecules in the solid.

4.2 Absolute Entropies

The third law gives us a reference point for entropy and allows us to calculate absolute entropies as

$$S^\circ(T) = S^\circ(T) - S^\circ(0) = \int_0^T \left(\frac{\partial S^\circ}{\partial T} \right)_P dT \quad (4)$$

The integral has contributions from phase transitions as well as from heating:

$$S^\circ(T) = \int_0^{T_m} \frac{C_{P, \text{sol}}^\circ}{T'} dT' + \frac{\Delta H_f^\circ}{T_m} + \int_{T_m}^{T_b} \frac{C_{P, \text{liq}}^\circ}{T'} dT' + \frac{\Delta H_v^\circ}{T_b} + \int_{T_b}^T \frac{C_{P, \text{gas}}^\circ}{T'} dT' \quad (5)$$

The superscript $^\circ$ indicates that this equation is for a gas at the standard state of 1 bar. Standard states will be discussed in greater detail later in this chapter. For a solid, the calculation just includes the first integral (to T), and for a liquid, the first two terms plus the second integral (to T). If there are any solid-phase transformations at temperatures T_ϕ , with heats of transformation $\Delta_\phi H$, additional terms of the form $\Delta_\phi H/T_\phi$ must be included.

One problem that arises in calculating absolute entropies is that heat capacities of solids are not known to 0 K; thus, the first integral in Eq. (5) cannot be performed. The T' in the denominator of this integrand suggests that this contribution to the entropy might be very large. However, heat capacities also

go to zero as $T \rightarrow 0$. The usual procedure is to make use of the Debye theory of solids, which predicts that for nonmetallic materials, heat capacities vary as T^3 at low temperatures. This theory has been verified by many measurements. (For metals, an additional term proportion to T must be included to account for the heat capacity of the electrons.)

Some values for standard entropies at 298 K are given in Table 1.

The following generalizations can be made concerning absolute entropies:

1. In a given phase, molar entropies are larger for molecules that are heavier and contain more atoms.
2. For molecules of similar mass and complexity, entropies are larger for gases than for liquids than for solids.

These trends are explained by the larger heat capacities of more complex molecules and heavier species (except for monatomic gases) and the large latent heat contributions introduced upon melting and vaporization.

4.3 Helmholtz and Gibbs Free Energies

The first and second laws of thermodynamics tell us what type of processes occur in nature, namely those that conserve energy but result in net energy degradation (entropy increase). For isolated systems, where there are no interactions between the system and its surroundings, the energy of the system must remain constant and its entropy must increase in any real process. For closed systems, however, the second law is somewhat inconvenient to use, because it forces us to consider entropy changes in both the system and its surroundings. In processes that occur at constant volume and constant temperature or at constant pressure and constant temperature, the surroundings interact with the system in very restricted ways. In this section, we will see that for such processes, it is possible to reformulate our

TABLE 1 Standard Entropies at 298.15 K (J/mol K)

Substance	S_m°	Substance	S_m°
C (graph)	5.74	N ₂	191.61
PbO (solid)	68.70	Cl ₂	223.08
Hg (liq)	76.03	Br ₂ (liq)	152.21
He	126.15	CO ₂	213.80
Ne	146.33	SO ₂	248.21
Ar	154.84	NH ₃	192.77
H ₂	130.68	CH ₄	186.25

Source: Data from NIST-JANAF Thermochemical Tables, 4th ed., Am Inst Physics, New York, 1998.

thermodynamics so that the criteria for real processes consider only properties of the system.

4.3.1 Constant-Volume and Temperature Processes: The Helmholtz Free Energy

In order to explore the tendency of a system to change in one direction or another, it will be sufficient to consider infinitesimal changes in these directions. If, for one of these changes, the energy remains constant and there is net entropy increase, the change can occur. At constant volume, expansion work is zero. Assuming that no other forms of work are done on the system, $dU = \delta q$. The net entropy change for a real process is then

$$dS_{\text{univ}} = dS - \frac{\delta q}{T} \stackrel{\text{const. } V}{=} dS - \frac{dU}{T} > 0 \quad (6)$$

Multiplying by T and adding $S dT$ (which is zero for a constant temperature process) gives

$$T dS + S dT - dU = -d(U - TS) \stackrel{\text{const. } V, T}{>} 0 \quad (7)$$

We define a new thermodynamic state function of the system:

$$A \equiv U - TS \quad (8)$$

the *Helmholtz free energy*. (A is sometimes called the Helmholtz function, the Helmholtz energy, or the work function.) We see that in any real process at constant volume and constant temperature

$$-dA \stackrel{\text{const. } V, T}{>} 0 \quad \text{or} \quad dA \stackrel{\text{const. } V, T}{<} 0 \quad (9)$$

A is a state function of the system because U , T , and S are all state functions of the system. We have thus remarkably transformed our criteria for real processes (at constant T and V) so that we do not have to consider the surroundings at all! We can say that a system with constant T and V will *spontaneously* undergo a process if it lowers the system's Helmholtz free energy.

A is sometimes called the *work function* because the decrease in A is the maximum work that the system can perform in any isothermal process. To see this, we calculate $-\delta w_{\text{rev}}$, which is the maximum work done by the system, because no energy is lost by friction in a reversible process:

$$-\delta w_{\text{rev}} = \delta q_{\text{rev}} - dU \stackrel{\text{isoth.}}{=} T dS + S dT - dU = -d(U - TS) = -dA \quad (10)$$

Note that we can add a $S dT$ term because we are considering constant-temperature processes. Likewise, if A increases in a constant-temperature process,

dA is the minimum amount of work (δw_{rev}) that must be done on the system in the process.

If an analysis of a process at constant V and T shows that $dA > 0$, then that process will not occur. However, because A is a state function, the reverse process will have a negative dA and therefore be real. Only if $dA = 0$ will there be no tendency for a process to occur in either direction. We then say that the system is in *equilibrium* with respect to the process. Equilibrium corresponds to a reversible process, which has no driving force in either direction. Much of the interest in thermodynamics is in determining the conditions under which various processes are at equilibrium.

4.3.2 Constant Pressure and Temperature Processes: The Gibbs Free Energy

When dealing with condensed phases, it is more usual to employ systems exposed to the atmosphere, keeping pressure constant, than systems confined in vessels of fixed volume.⁵ We are therefore particularly interested in transforming the equations dealing with constant P and T processes. Under such conditions, assuming that there is no work other than expansion work, $\delta q = dH$, and

$$dS_{\text{univ}} = dS - \frac{\delta q}{T} \stackrel{\text{const. } P}{=} dS - \frac{dH}{T} > 0 \quad (11)$$

Multiplying by T and adding $S dT$, which is zero at constant T , gives

$$T dS + S dT - dH = -d(H - TS) \stackrel{\text{const. } P, T}{>} 0 \quad (12)$$

We now define the state function,

$$G \equiv H - TS = U + PV - TS \quad (13)$$

the *Gibbs free energy* (sometimes just called the free energy). From Eq. (12),

$$dG \stackrel{\text{const. } P, T}{<} 0 \quad (14)$$

for any real process at constant T and P . G is a property only of the system; we no longer have to consider the surroundings, even though the system interacts with the surroundings. A process will spontaneously occur in a system at constant T and P , if it lowers the system's Gibbs free energy. If for a given process $dG > 0$, the reverse process will be spontaneous. Only if $dG = 0$ will a system held at constant T and P be at equilibrium for the considered change. We will make repeated use of this criterion for equilibrium in our applications of thermodynamics.

We can see another important use of the Gibbs free energy by writing the first law in the form

$$-\delta w_{\text{rev}} = P dV - \delta w_{\text{oth, rev}} = \delta q_{\text{rev}} - dU \quad (15)$$

At constant T and P , this becomes

$$\begin{aligned} -\delta w_{\text{orth, rev}} &\stackrel{\text{const. } P, T}{=} -dU + T dS - P dV + S dT - V dP \\ &= -d(U + PV - TS) = -dG \end{aligned} \quad (16)$$

However, $-\delta w_{\text{orth, rev}}$ is the maximum (because reversible means that no energy is lost to friction) amount of useful work (because expansion against the atmosphere is not usually useful) that can be done by the system. This amount of work could be obtained from a chemical reaction, for example, if it is run in an electrochemical cell, with an opposing voltage that makes the reaction proceed infinitely slowly. This is a reversible (equilibrium) situation, because slight changes in the opposing voltage can make the reaction run in either direction. More commonly, the free energy decrease of one reaction drives another reaction for which $\Delta G > 0$. This commonly occurs in biochemical systems (which operate at constant T and P).

4.4 Partial Derivatives of Energy-like Quantities

As we have seen from our previous discussions of heat capacities, thermal expansion coefficients, and compressibilities, partial derivatives are the key to discussing changes in thermodynamic systems. In a single-component system of fixed size, the specification of two state variables completely determines the state of the system. Calling one of the molar energy quantities Z , we can write $Z = Z(X, Y)$, where X and Y are any two state variables, such as T and P , or T and V . Using the general mathematical properties of functions of two variables that are discussed in [Appendix A](#),

$$dZ = \left(\frac{\partial Z}{\partial X} \right)_Y dX + \left(\frac{\partial Z}{\partial Y} \right)_X dY = M dX + N dY \quad (17)$$

where $M = (\partial Z / \partial X)_Y$ and $N = (\partial Z / \partial Y)_X$ are, in general, both functions of X and Y . The cross-derivative rule [Eq. (17) in [Appendix A](#)] gives

$$\left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial N}{\partial X} \right)_Y \quad (18)$$

which is a useful route for deriving important partial derivative relationships.

The starting point for our derivation is the first law, which we will write in the following manner:

$$dU = \delta q + \delta w = \delta q_{\text{rev}} + \delta w_{\text{rev}} \quad (19)$$

Equation (19) acknowledges that U is a state function and, thus, the (differential) change in U between any two states can be calculated for any process that goes between the two states. In particular, we can choose a reversible process connecting the two states. However, an important restriction applies to the use of Eq. (19). In a reversible process, internal and external equilibria are maintained at all times. Because the symbol dU refers to specific states of the real process, these must be states that can also be initial and final states of the reversible process. Thus, Eq. (19) can only apply if the initial and final states are in internal equilibrium.

For a process in which the only work is expansion work, Eq. (19) becomes

$$dU \stackrel{\text{m.e.}}{=} T dS - P dV \quad (20)$$

Because Eq. (20) is of great importance and can be a source of considerable confusion, it will be discussed in detail. As we have stated, the initial and final states must be in internal equilibrium. Internal equilibrium requires mechanical equilibrium, thermal equilibrium, and material equilibrium. Because Eq. (20) contains P and T , these variables must be uniform throughout the system, ensuring internal mechanical and thermal equilibria. Because internal material equilibrium is not explicitly required by any of the variables in the final equation, it is indicated by “m.e.” above the equals sign. Thus, if chemical reactions or phase transformations can occur in the system, they must be at equilibrium. The designation “m.e.” is also appropriate for systems not in material equilibrium, if constraints result in transformation processes being negligibly slow. Thus, Eq. (20) could be used to treat the expansion of a mixture of H_2 and O_2 , as long as no catalysts or initiators of the water-forming reaction are present. For single-component, single-phase systems, the designation “m.e.” can be ignored.

For a single-component, single-phase system or a system at material equilibrium, the change of internal energy is completely determined by the change in two state variables. Thus, Eq. (20) is valid for any process that goes between the initial and final states of the infinitesimal process; its application is not limited to reversible processes. It would, for example, apply to a Joule–Thomson expansion, a distinctly nonreversible process.

From the definitions of H , A , and G , three more differential relationships are immediately obtained:

$$\begin{aligned} dH &= d(U + PV) \stackrel{\text{m.e.}}{=} T dS - P dV + P dV + V dP \\ &\stackrel{\text{m.e.}}{=} T dS + V dP \end{aligned} \quad (21)$$

$$\begin{aligned} dA &= d(U - TS) \stackrel{\text{m.e.}}{=} T dS - P dV - T dS - S dT \\ &\stackrel{\text{m.e.}}{=} -P dV - S dT \end{aligned} \quad (22)$$

$$\begin{aligned} dG &= d(H - TS) \stackrel{\text{m.e.}}{=} T dS + V dP - T dS - S dT \\ &\stackrel{\text{m.e.}}{=} V dP - S dT \end{aligned} \quad (23)$$

To this can be added a differential relationship for S derived from Eq. (20):

$$dS \stackrel{\text{m.e.}}{=} \frac{1}{T} dU + \frac{P}{T} dV \quad (24)$$

Because of the simplicity of these relationships, we sometimes say that the *natural variables* of U are S and V , of H are S and P , of A are V and T , of G are P and T , and of S are U and V . It is noteworthy that the natural variables of U are both extensive variables and those of G are both intensive variables; the natural variables of H and A are mixed—one extensive and one intensive variable for each. Because Eqs. (20)–(24) only hold for systems at material equilibrium, they will become our criteria for material equilibrium under each set of conditions. For example, at constant T and P , for a system to be at material equilibrium for a process, dG must equal zero for the (infinitesimal) process.

Applying Eq. (18) to the first four differential relationships gives

$$\left(\frac{\partial T}{\partial V} \right)_S \stackrel{\text{m.e.}}{=} - \left(\frac{\partial P}{\partial S} \right)_V \quad \text{from Eq. (20)} \quad (25)$$

$$\left(\frac{\partial T}{\partial P} \right)_S \stackrel{\text{m.e.}}{=} \left(\frac{\partial V}{\partial S} \right)_P \quad \text{from Eq. (21)} \quad (26)$$

$$\left(\frac{\partial S}{\partial V} \right)_T \stackrel{\text{m.e.}}{=} \left(\frac{\partial P}{\partial T} \right)_V \quad \text{from Eq. (22)} \quad (27)$$

$$\left(\frac{\partial S}{\partial P} \right)_T \stackrel{\text{m.e.}}{=} - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{from Eq. (23)} \quad (28)$$

Equations (25)–(28) are known as the Maxwell relations. We will find the latter two equations to be particularly useful. They give the surprising result that the volume and pressure dependence of entropy are determined by equations of state, from which the temperature derivatives of P and V can be calculated.

An additional useful relationship is

$$\left(\frac{\partial(T^{-1}G)}{\partial T^{-1}}\right)_P \stackrel{\text{m.e.}}{=} T^{-1} \left(\frac{\partial G}{\partial T}\right)_P \left(\frac{\partial T}{\partial T^{-1}}\right)_P + G \stackrel{\text{m.e.}}{=} H \quad (29)$$

which is known as the Gibbs–Helmholtz equation.

In considering changes in U , H , A , G , and S , all of which are extensive state functions with units of energy, it is usually convenient to divide each of these functions by the number of moles in the system, giving the intensive properties: molar energy, U_m ; molar enthalpy, H_m ; molar Helmholtz free energy, A_m ; molar Gibbs free energy, G_m . All of the above equations hold for the corresponding molar quantities.

4.4.1 Internal Pressure

In [Chapter 2](#), we called the quantity $(\partial U/\partial V)_T$ the internal pressure. An equation can be found for the internal pressure by writing Eq. (20) for a constant-temperature process and dividing by dV_T :

$$\left(\frac{\partial U}{\partial V}\right)_T \stackrel{\text{m.e.}}{=} T \left(\frac{\partial S}{\partial V}\right)_T - P \stackrel{\text{m.e.}}{=} T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (30)$$

where the last step follows from Eq. (27). In a similar manner, we can write, from Eqs. (21) and (28),

$$\left(\frac{\partial H}{\partial P}\right)_T \stackrel{\text{m.e.}}{=} T \left(\frac{\partial S}{\partial P}\right)_T + V \stackrel{\text{m.e.}}{=} -T \left(\frac{\partial V}{\partial T}\right)_P + V = V(1 - \alpha T) \quad (31)$$

Because the right-hand sides of Eqs. (30) and (31) can be evaluated from equations of state, we see that such equations plus heat capacity data allow us to completely calculate changes of U and H . Equations (30) and (31) are known as the *thermodynamic equations of state*.

Example 1. Find an expression for the internal pressure of an ideal gas.

Solution: For an ideal gas $P = nRT/V$; therefore, $(\partial P/\partial T)_V = nR/V$ and

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - P = 0$$

This shows that for an ideal gas, the energy does not depend on how far apart the molecules are, and the forces between molecules must be zero. This was previously taken as a postulate of the Bernoulli model of the ideal gas. Example 1 shows that the result does not depend on a particular model, but follows directly

from the equation of state of the ideal gas. [In Problem 9, you show that in addition $(\partial H/\partial P)_T = 0$ for an ideal gas.]

For real gases, due to forces between molecules, the internal energy does depend on how far apart the molecules are. We define the difference between the internal energies of real and ideal gases at given volume and temperature as the *molecular interaction energy*, U_{int} . Because the internal energy of a real gas approaches that of an ideal gas as volume becomes infinite, we can write

$$U_{\text{int}}(V) = U(V) - U_{\text{id}}(V) = U(V) - U(\infty) = \int_{\infty}^V \left(\frac{\partial U}{\partial V} \right)_T dV \quad (32)$$

Example 2. Find an expression for the internal pressure and the molecular interaction energy of a van der Waals gas. For He at 298 K and 1.0 atm pressure, compare the molecular interaction energy with the kinetic energy of the atoms.

Solution: For a van der Waals gas,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

therefore,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V - nb}$$

and the internal pressure is

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{an^2}{V^2}$$

$$U_{\text{int}}(V) = \int_{\infty}^V \frac{an^2}{V'^2} dV' = -\frac{an^2}{V}$$

Note that for a van der Waals gas, only the attractive interactions contribute to the internal pressure. The molar interaction energy is

$$U_{\text{int}, m} = \frac{U_{\text{int}}}{n} = -\frac{an}{V} \approx -\frac{aP}{RT}$$

where we used the ideal gas approximation for the molar volume in the last step.

For He, $a = 0, 0.00345 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$; therefore,

$$U_{\text{int}, m} = -\frac{0.00345 (\text{Pa} \cdot \text{m}^6/\text{mol}^2) \times 10^5 \text{ Pa}}{(8.314 \text{ J/mol K})(298 \text{ K})} = -0.14 \frac{\text{J}}{\text{mol}}$$

This has to be compared with the total internal energy, which is very close to

$$\frac{3}{2}RT = 3716 \frac{\text{J}}{\text{mol}}$$

4.5 Heat Capacities

Because we have found the variation of U and H with V and P , we can do the same for the heat capacities, C_V and C_P :

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T \quad (33)$$

Reversing the order of differentiation gives

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V \quad (34)$$

Substituting for the internal pressure from Eq. (30),

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (35)$$

In a similar manner, it can be shown that (Problem 10)

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (36)$$

We can also write Eq. (32) of [Chapter 2](#) for the difference in C_P and C_V as

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \quad (37)$$

4.6 Generalization to Additional Displacements

It will be useful to generalize these ideas to cases in which the system can have additional displacement coordinates, l_i . This will give rise to terms in δw_{oth} of the form $L_{i, \text{ext}} dl_i$, where $L_{i, \text{ext}}$ is the external driving force conjugate to the coordinate l_i . For example, l_i could be the length of a wire and $L_{i, \text{ext}}$ could be the force on the wire. Equation (20) then becomes

$$dU = \delta q_{\text{rev}} + \delta w_{\text{rev}} \stackrel{\text{m.e.}}{=} T dS - P dV + \sum_i L_i dl_i \quad (38)$$

As mentioned in [Chapter 2](#), we choose to define enthalpy as

$$H = U + PV - \sum_i L_i l_i \quad (39)$$

The corresponding relation for the Gibbs free energy is

$$G = U - TS + PV - \sum_i L_i l_i \quad (40)$$

We then obtain

$$dH \stackrel{\text{m.e.}}{=} T dS + V dP - \sum_i l_i dL_i \quad (41)$$

$$dG \stackrel{\text{m.e.}}{=} -S dT + V dP - \sum_i l_i dL_i \quad (42)$$

We also have

$$dA \stackrel{\text{m.e.}}{=} -S dT - P dV + \sum_i L_i dl_i \quad (43)$$

$$dS \stackrel{\text{m.e.}}{=} \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_i L_i dl_i \quad (44)$$

These equations give criteria for equilibrium similar to those obtained from Eqs. (20)–(24). For example, at constant T , P , and generalized driving forces L_i , a process is at equilibrium if $dG = 0$ and proceeds spontaneously if $dG < 0$.

We will always choose G so that it is a criterion for spontaneity under conditions of constant *intensive* variables, T , P , and conjugate driving forces, L_i . It should be realized, however, that new displacement coordinates introduce the possibility of a number (see Question 9) of other new energy-like functions, and consideration of some of these may provide useful thermodynamic relationships. In particular, we will have some use for the function

$$F = U + PV - TS \quad (45)$$

(like G , but without the additional displacement variable terms). We will call this function the *F function*.

4.7 Standard States

Above all, thermodynamics is a useful subject. Its usefulness is largely dependent on the tabulation of thermodynamic quantities in an efficient and convenient form. Because it takes at least two variables to determine the state of a pure material, tables could get rather unwieldy. To avoid this, properties are tabulated at a standard (pressure) state and then converted to the pressure that is desired. For liquids and solids, the standard state is just that of the pure material at 1.0 bar pressure.

The properties of matter in so-called “ideal states” vary in ways that are mathematically much simpler than those of matter in real states. We have seen an example of this in [Chapter 1](#), which dealt with ideal and real gases, and a similar result will be seen when we consider solutions in [Chapters 8 and 9](#). Because of this mathematical simplicity, it will often be advantageous to use ideal states for tabulations. In particular, properties of gases are tabulated in the ideal gas state, where all intermolecular interactions are zero.

For the standard state of gaseous substances, we want to calculate thermodynamic properties in the 1.0-bar ideal gas state from measured values of properties at the measurement pressure, P . The calculation consists of the following three steps:

1. The thermodynamic property of the real gas is extrapolated to zero pressure.
2. At zero pressure, intermolecular interactions are removed, and the real gas becomes an ideal gas.
3. The ideal gas is then extrapolated to 1.0 bar pressure.

In general, thermodynamic properties are not changed by step 2, because at zero pressure, there are no intermolecular interactions.

For enthalpy, the calculation is

$$\Delta H = \Delta_a H + \Delta_c H = \int_P^0 \left(\frac{\partial H}{\partial P} \right)_T dP + \int_0^{1.0} \left(\frac{\partial H}{\partial P} \right)_{T, \text{i.g.}} dP \quad (46)$$

where the subscript i.g. represents ideal gas. The second integral is zero because enthalpies of ideal gases do not depend on pressure. For the first integral, we use Eq. (31), giving

$$\Delta H = \int_P^0 V(1 - \alpha T) dP \quad (47)$$

The conversion from a tabulated value at 1.0 bar pressure to a real gas value at pressure P is, of course, the reverse of process 1–2–3, and so its enthalpy change is the negative of that given in Eq. (47).

For entropy, the calculation is

$$\Delta S = \Delta_a S + \Delta_c S = \int_P^0 \left(\frac{\partial S}{\partial P} \right)_T dP + \int_0^{1.0} \left(\frac{\partial S}{\partial P} \right)_{T, \text{i.g.}} dP \quad (48)$$

$(\partial S/\partial P)_T$ is obtained from Eq. (28) and becomes $-nR/P$ for an ideal gas. Equation (48) then becomes

$$\Delta S = - \int_P^0 \left(\frac{\partial V}{\partial T} \right)_P dP - \int_0^{1.0} \frac{nR}{P} dP = \int_{1.0}^P \left(\frac{\partial V}{\partial T} \right)_P dP + \int_0^{1.0} \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{nR}{P} \right] dP \quad (49)$$

Note the method of dealing with two integrals, each of which is infinite. A difference of the two integrands is taken and this difference goes to zero as the pressure goes to zero. Standard Gibbs free energies can be calculated from standard enthalpies and entropies. Because real gases behave quite ideally up to 1.0 bar, Eqs. (47) and (49) show that negligible error is made by just correcting the real gas H and S to 1.0 bar.

4.8 Entropy of Mixing of Ideal Gases

So far, our discussion of entropy has been concerned with pure substances. In order to calculate the entropy of mixtures, we can first calculate the entropies of the pure components of the mixture and then add the entropy change of mixing to the sum of these. Entropy of mixing is most easily calculated for ideal gas mixtures. Because ideal gas molecules do not interact, their mixing is at constant temperature. Probably the simplest way of thinking about mixing two ideal gases is to have them in separate containers at the same pressure and then open a valve connecting the two containers. In this case, we are mixing the components from their partial molar volumes in the final mixture to the total volume of the mixture. Because this process involves no heat, we might think that it has no entropy change. However, this is not correct, because this “mixing at constant pressure” is not reversible, and the entropy change for this process cannot be directly calculated.

The same change of state can be achieved in the following manner: First, we expand each gas from its partial molar volume, V_j , to the final volume of the gas mixture, $V_f = V_j(n_{\text{tot}}/n_j)$. This gives for each gas, from Eq. (11) of [Chapter 3](#), an entropy increase of expansion of

$$n_j R \ln \left(\frac{V_f}{V_j} \right) = n_j R \ln \left(\frac{n_{\text{tot}}}{n_j} \right) = -n R X_j \ln X_j$$

where X_j is the mole fraction of component j and we have used n for n_{tot} . The total entropy of expansion is then

$$\Delta_{\text{exp}}S = -nR \sum_j X_j \ln X_j \quad (50)$$

To the entropy of expansion, we add the entropy change on reversible mixing at constant temperature in a manner such that the final volume is equal to the initial volume of each of the component gases. In other words, we mix the gases from their partial pressures in the final mixture to the total pressure of the mixture. However, if the temperature is constant, so is the energy for an ideal gas, and Eq. (24) shows that there is no entropy change for each component of the mixture for this process. (This assumes that the process can be carried out with the system in material equilibrium.) The entropy change for this “mixing at constant volume” is thus zero. (In Question 6, a device for reversible mixing at constant volume is shown.) The entropy of mixing therefore is just

$$\Delta_{\text{mix}}S = -nR \sum_j X_j \ln X_j \quad (51)$$

Because we have achieved the same change of state as for “mixing at constant pressure” and entropy is a state function, this must be the entropy change for opening the valve between bulbs at the same pressure. Note that, as expected, entropy of mixing is always positive.

4.9 Thermodynamics of Stretching Rubbers

The change of internal energy upon stretching a rubber is

$$dU = \delta q_{\text{rev}} + \delta w_{\text{rev}} \stackrel{\text{m.c.}}{=} T dS + f dl - P dV \quad (52)$$

Material equilibrium is not an issue and this designation will be dropped. The change in the Helmholtz free energy is

$$dA = d(U - TS) = -S dT + f dl - P dV \quad (53)$$

from which a Maxwell relationship

$$\left(\frac{\partial f}{\partial T}\right)_{l, V} = -\left(\frac{\partial S}{\partial l}\right)_{T, V} \quad (54)$$

can be obtained. Also, from Eq. (53),

$$f = \left(\frac{\partial A}{\partial l}\right)_{T, V} = \left(\frac{\partial U}{\partial l}\right)_{T, V} - T \left(\frac{\partial S}{\partial l}\right)_{T, V} = \left(\frac{\partial U}{\partial l}\right)_{T, V} + T \left(\frac{\partial f}{\partial T}\right)_{l, V} \quad (55)$$

which gives

$$\left(\frac{\partial U}{\partial l}\right)_{T, V} = f - T\left(\frac{\partial f}{\partial T}\right)_{l, V} \quad (56)$$

Equations (54) and (56) suggest that measurements of the force required to keep a rubber at constant length as a function of temperature would determine the thermodynamic properties of the rubber. However, due to thermal expansion, very large changes in pressure would be required to keep the polymer volume constant as its temperature is varied. Thus, measurements of $(\partial f/\partial T)_l$ are usually made at constant pressure. Extending Eq. (10) of [Appendix A](#) to an additional variable gives

$$\left(\frac{\partial f}{\partial T}\right)_{l, V} = \left(\frac{\partial f}{\partial T}\right)_{l, P} + \left(\frac{\partial f}{\partial P}\right)_{l, T} \left(\frac{\partial P}{\partial T}\right)_{l, V} \quad (57)$$

Using the chain rule for partial derivatives [Eq. (7) of [Appendix A](#)], Eq. (57) can be written as

$$\left(\frac{\partial f}{\partial T}\right)_{l, V} = \left(\frac{\partial f}{\partial T}\right)_{l, P} - \left(\frac{\partial f}{\partial P}\right)_{l, T} \left(\frac{\partial V}{\partial T}\right)_{l, P} \left(\frac{\partial V}{\partial P}\right)_{l, T}^{-1} = \left(\frac{\partial f}{\partial T}\right)_{l, P} + \left(\frac{\partial f}{\partial P}\right)_{l, T} \frac{\alpha_l}{\kappa_l} \quad (58)$$

$(\partial f/\partial P)_{l, T}$ is small. However, the ratio of the thermal expansion coefficient to the isothermal compressibility in SI units of solid materials is so large (see [Table 3](#) of [Chapter 1](#)) that $(\partial f/\partial T)_{l, V}$ is not well approximated by $(\partial f/\partial T)_{l, P}$. It can be shown,⁶ however, that to a good approximation, $(\partial f/\partial T)_{l, V}$ is well approximated by $(\partial f/\partial T)_{l, \alpha}$

$$\left(\frac{\partial f}{\partial T}\right)_{l, V} \approx \left(\frac{\partial f}{\partial T}\right)_{l, \alpha} \quad (59)$$

where α , the *elongation* of the rubber, is defined by $\alpha \equiv l/l_0$. l_0 is the unstretched length of the polymer. Using Eq. (59) for estimating $(\partial f/\partial T)_{l, V}$ requires slight adjustments of l as the temperature is varied, to account for changes of l_0 with temperature due to bulk thermal expansion.

An ideal rubber is defined as one for which

$$\left(\frac{\partial U}{\partial l}\right)_{T, V} \stackrel{\text{id. rub.}}{=} 0 \quad (60)$$

which, from Eq. (55), means that

$$f \stackrel{\text{id. rub.}}{=} -T\left(\frac{\partial S}{\partial l}\right)_{T, V} = T\left(\frac{\partial f}{\partial T}\right)_{l, V} \quad (61)$$

The force resisting extension for an ideal rubber is completely entropically derived. Because it certainly requires a positive force to stretch a rubber,

$$\left(\frac{\partial f}{\partial T}\right)_{l, v}^{\text{id. rub.}} > 0 \quad (62)$$

This is in contrast with most other solid materials, which weaken as temperature is increased. In addition,

$$\left(\frac{\partial S}{\partial l}\right)_{T, v}^{\text{id. rub.}} < 0 \quad (63)$$

This result will be discussed in [Chapter 5](#).

We can also write

$$\left(\frac{\partial T}{\partial l}\right)_{S, v} = -\left(\frac{\partial S}{\partial l}\right)_{T, v} \left(\frac{\partial S}{\partial T}\right)_{l, v}^{-1} \quad (64)$$

By analogy to other heat capacities, we identify $(\partial S/\partial T)_{l, v}$ as $C_{l, v}/T$, where $C_{l, v}$ is the heat capacity at constant extension and volume, definitely a positive quantity. We then have

$$\left(\frac{\partial T}{\partial l}\right)_{S, v} = -\frac{T}{C_{l, v}} \left(\frac{\partial S}{\partial l}\right)_{T, v} \quad (65)$$

With Eq. (63), we see that

$$\left(\frac{\partial T}{\partial l}\right)_{S, v} > 0 \quad (66)$$

(i.e., the rubber gets warm when it is stretched adiabatically and reversibly). (When stretching with different constraints, the magnitude, but not the sign, of the temperature change would vary.)

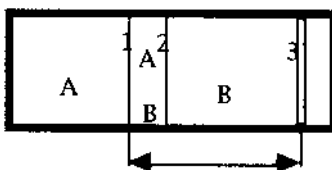
Questions

1. In order to make use of a heat reservoir at 0 K, we need to be able to add some heat to the reservoir while maintaining its temperature. Show that the second law precludes this, in that an infinite amount of work would be necessary to maintain a heat reservoir at 0 K against any heat addition.

2.* Consider how you might use a chemical reaction in a *gedanken* experiment to reduce temperature by a process described by [Fig. 1](#). One suggestion is to use an exothermic reaction, such as $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ ($\Delta S_{\text{eq}} < 0$), and vary the extent of the reaction by changing the amount of H_2 in contact with Cl_2 . This could be done by using a piston through which H_2 , but not Cl_2 , could pass. The apparatus would be used in a reversible cycle, with alternating isothermal and adiabatic steps. Of course, the availability of an

appropriate apparatus and reaction catalyst would have to be assumed.

3. Why are heat capacities at constant pressure used in Eq. (5)?
4. Is $-dA$ the maximum work that can be obtained in a constant- T process if volume is allowed to change in the process?
5. Show by both a mathematical and by a physical argument that if $dS = 0$ for a process at constant U and V with no “other work,” the system is at equilibrium for that process.
6. A *gedanken* device is shown in the following diagram whereby two gases, each at volume V_i could be mixed to give a mixture that also has volume V .



Movable partition 1 is permeable only to A , stationary partition 2 is permeable only to B , and partition 3 is impermeable and rigidly attached to partition 1 through the handle. Show that as the handle is moved to the left, the gases are mixed, and as it is moved to the right, they are unmixed. Moreover, show that the gases exert no net force on the device, so that in the absence of friction, it can be moved in either direction with negligible force, and thus reversibly.

7. In mixing ideal gases at constant pressure by opening a stopcock between bulbs containing them, T and U remain constant and $q = 0$. Why is not $\Delta S = 0$ for this process?
8. From the form of Eq. (28), why would a zero-pressure ideal gas state be inconvenient for tabulation of standard molar entropies?
9. Show that a system that has one additional displacement variable, l , in addition to V and S , can be described by a total of eight energylike functions (i.e., four in addition to U , H , A , and G).
10. Show that the first law of thermodynamics requires that heat be evolved when an ideal rubber is stretched.
11. At large elongation, attractive interaction between extended polymer chains in many rubbers occurs. These interactions are called strain-induced crystallization. What would be the effect of these interactions on $(\partial U/\partial l)_{T, V}$ and $(\partial S/\partial l)_{T, V}$?
12. Verify that each term in each of Eqs. (5), (29), (37), (43), and (54) has the same units.
13. Give all the Maxwell-type relationships that can be derived from the equation $dG = V dP - S dT + l dL$.

Problems

1. Show that in order to use the third law to calculate entropies, the heat capacity must approach zero as $T \rightarrow 0$ at least as quickly as does T .
2. Prove the equation for U analogous to the Gibbs–Helmholtz equation, Eq. (48), namely

$$\left(\frac{\partial(T^{-1}A)}{\partial T^{-1}} \right)_V = U$$

3. Show that for a nonmetallic crystalline substance at low temperature, in the range where the heat capacity varies as T^3 , the entropy is given as $S = C_p/3$.
- 4.^M Some heat capacity data for benzene is given in the following table. Estimate the entropy of liquid benzene at 298 K and compare your estimate with the literature value of 173 J/K mol.

T (K)	$C_{P, m}$ (J/K mol)	T (K)	$C_{P, m}$ (J/K mol)
13	2.87	160	67.9
15	4.16	180	75.4
20	8.37	200	83.7
25	13.16	220	93.4
30	18.0	240	104.1
40	26.5	260	116.1
50	33.0	278.7	128.7 (solid)
60	37.9	$\Delta_{\text{fus}}H^\circ = 9866 \text{ J/mol at } 278.7 \text{ K}$	
80	45.0	278.7	131.7 (liquid)
100	50.4	298	136
120	55.7		
140	61.5		

Source: Data from GD Oliver, M Eaton, HM Huffman. J Am Chem Soc 70:1502, 1948.

5. The heat capacity of a nonmetal at 7 K is 1.5 J/K mol. Assuming that the Debye theory holds up to this temperature, what is the molar entropy of the substance at 5 K?
6. Find an expression for the entropy change resulting from the expansion of a van der Waals gas from a molar volume of V_{m1} to a molar volume of V_{m2} at temperature T .
7. Find a formula for the change of Gibbs free energy of 1 mol of a gas that expands from a volume V_1 to a volume V_2 at constant temperature T . Use terms in the virial expansion up to and including the second virial coefficient to describe the equation of state of the gas.
8. Show that $\mu_{JT} = (V_m/C_{P, m})(\alpha T - 1)$.
9. Show that $(\partial H/\partial P)_T = 0$ for an ideal gas.

10. Derive Eq. (36).
- 11.* For a van der Waals gas find $(\partial C_V/\partial V)_T$ and $(\partial C_P/\partial P)_T$. You do not have to simplify your results.
12. For a Redlich–Kwong gas, find $(\partial C_V/\partial V)_T$.
13. Find an expression for the internal pressure of a Berthelot gas.
14. Show that for a two-component mixture, the entropy of mixing is a maximum when $X_1 = 0.5$.
15. Bromine has two isotopic forms of isotopic mass 79 and 81 and almost equal isotopic abundance. Calculate $\Delta_{\text{mix}}S^\circ$ (0 K) for forming 1 mol of the random mixture of Br_2 isotopomers from 0.5 mol of each of the isotopically pure Br_2 isotopomers.
- 16.* Show that the Gibbs free energy of 1 mol of a mixture of components A and B, with individual molar free energies $G_{m, A}$ and $G_{m, B}$ is a minimum when

$$\frac{x_A}{1 - x_A} = \exp\left(\frac{-(G_{m, A} - G_{m, B})}{RT}\right)$$

Because molar free energies are finite, this minimum will occur at any real temperature when both A and B are present in the mixture.

17. Show that $(\partial S/\partial V)_P = C_P/TV\alpha$.
18. Calculate ΔG_f° of liquid methanol from enthalpies and entropies given in [Appendix C](#). Compare your answer with the value given in this table.
19. Show that a rubber for which the force required to achieve a given elongation (at a particular pressure) is proportional to the temperature is an ideal rubber.
20. Show that from measurements of the stress versus strain curve and the force required to keep a rubber at constant extension as temperature is varied (and pressure is held constant) $(\partial H/\partial l)_{T, P}$, $(\partial S/\partial l)_{T, P}$, and $(\partial G/\partial l)_{T, P}$ can be obtained. (Hint: the F function is useful for this problem.)
21. Show that for a system at constant T and P and subject to constant driving forces L_i , processes proceed spontaneously if they lower the Gibbs free energy, with G defined as in Eq. (40).
- 22.* Show that the Joule coefficient can be obtained from the equation of state of a gas by

$$\mu_J = \frac{1}{C_P} \left(P - T \left(\frac{\partial P}{\partial T} \right)_V \right)$$

and that the Joule coefficient of an ideal gas is zero.

23.* Show that the Joule–Thomson coefficient can be obtained from the equation of state of a gas by

$$\mu_{JT} = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_p - V \right)$$

and that the Joule–Thomson coefficient of an ideal gas is zero.

24. Find the change in entropy when 1 mol of a van der Waals gas is expanded from a volume of 5 L to a volume of 10 L at a temperature T . (Express your answer in terms of the van der Waals constants of the gas and the temperature.)

Notes

1. Some authors have argued that because this is required for the validity of the second law, it should not be considered a separate law of thermodynamics. For a discussion of this point, see AB Pippard, *Elements of Classical Thermodynamics*. Cambridge: Cambridge University Press, 1957, p 48.
2. Comparable low temperatures have also been obtained by trapping gaseous particles in magnetic fields and lowering their velocity by absorption and reemission of laser energy. Using these methods, a new state of matter, the Bose–Einstein condensate has been created.
3. We can think of chemical reactions occurring reversibly in electrochemical cells, where the driving force of the reaction is opposed by an electrical force. The difficulty of constructing electrochemical cells at 0 K is a practical, not a theoretical limitation.
4. If, at 0 K, entropies of compounds are the sum of nonzero values assigned to each atom, conservation of atoms would ensure that the entropy change for all chemical reactions would be zero. This way of satisfying the third law would not be in agreement with the microscopic interpretation of entropy given in [Chapter 5](#).
5. Condensed phase systems can be studied at constant volume by using very strong cells, such as those made of diamonds, which can withstand the very high pressure buildup that occurs as these systems are heated.
6. PJ Flory, *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press, 1953.