CRYSSTALLINE SOLIDS

One can think of a solid as a giant molecule with a great many vibrations. Translations and rotations can be ignored except for extremely small particles. In three dimensions there will be $3N$ vibrations where $N$ is the number of atoms. While the heat capacity over the full range of temperature is of importance, we are particularly interested in the behavior at very low temperatures where a crystal might fall into a single quantum state.

The idea that the lattice vibrations of a crystal might be quantized was proposed by Einstein\textsuperscript{9} soon after Planck\textsuperscript{10} had shown that there were quanta of electromagnetic radiation. Einstein assumed that the frequencies of all atomic vibrations were the same and he adopted Planck's expression for the energy $\varepsilon = nh\nu$. We now know that this energy expression is correct for a harmonic oscillator and the resulting heat capacity follows directly from Eq. (5-44). For three directions of vibration, this yields $3N_A$ vibrations per gram-atom and

\[ \frac{C}{R} = \frac{3\hbar^2 e^u}{(e^u - 1)^2}, \quad u = \frac{h\nu}{kT} \quad (5-45) \]

At high temperatures, this equation gives the value $C = 3R$, which is the magnitude noted many years earlier by Dulong and Petit\textsuperscript{11} from experiment and explained in classical statistical mechanics by Boltzmann.\textsuperscript{12}

Equation (5-45) yields a heat capacity that decreases with decrease in temperature. At that time, this behavior had already been noted for diamond, and Einstein showed that there was reasonable agreement between his calculated values and the experimental measurements, which then extended from 1200 K down to 220 K. About this same time, refrigeration methods were being developed for lower temperatures, and heat capacity measurements were extended below 200 K, first by Dewar,\textsuperscript{13} and soon by others. It then became apparent that the assumption of a single frequency for all vibrations in a solid was not correct.

A crystal has many different modes of vibration and each mode has its own frequency. Most of these modes depend in detail on the masses and interatomic forces in a complex manner. But for long-wavelength motions where several atoms move together, the modes and frequencies of a real crystal approach those of a continuous material. This pattern was well known, and Debye\textsuperscript{14} recognized that it would be the dominant contribution at low temperature. In particular, the number of modes of frequency from $\nu$ to $\nu + d\nu$ is proportional to $\nu^2 d\nu$. Debye adopted this distribution, known to be correct for the low frequencies, and then extended it to higher frequencies until the total number $3N_A$ were included for $N_A$ atoms in three-dimensional space.

It is convenient to define a temperature $\theta_D$ by the maximum frequency of the Debye distribution,

\[ \theta_D = \frac{h\nu_{\text{max}}}{k} \quad (5-46) \]
Each substance will have a different $\theta_D$. Then the heat capacity is

$$\frac{C}{R} = f(T/\theta_D) = 9 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \left( e^u - 1 \right)^2 e^u u^4 \, du \tag{5.47}$$

At high temperatures, the integral approaches $\frac{1}{2}(\theta_D/T)^3$ and $C/R$ becomes 3 as expected from the law of Dulong and Petit. At low temperatures, the integral approaches a constant value and

$$\frac{C}{R} \approx \left( \frac{12\pi^4}{5} \right) \left( \frac{T}{\theta_D} \right)^3 = \text{constant} \times T^3 \tag{5.48}$$

This proportionality of $C$ to $T^3$ is verified approximately for many substances and there is every reason to believe it is exact for crystal vibrations (phonons) in the limit as $T$ approaches zero. At intermediate temperatures, the Debye function is complex to express analytically but readily calculated numerically; tables are given in Appendix 2 for the heat capacity, the entropy, and other functions.

One important feature of the Debye formula, which arises from the form of the equation, is the property that $C_v$ is a general function of $\log T - \log \theta_D$. Consequently, if we plot $C_v$ for various elements as a function of $\log T$, we should obtain curves of the same shape but displaced from one another horizontally by the differences in $\log \theta_D$ for the various substances. Figure 5-1 presents such a plot for several solid elements. The quantity $\theta_D$ is proportional to the frequency of atomic vibration which in turn increases with the strength of interatomic forces and decreases with atomic mass. One notes the large increase in $\theta_D$ from lead with softly bound heavy atoms to $C$ (diamond) with tightly bound light atoms.

In addition to the vibrations of the atomic nuclei in a crystal, there may be other contributions to the heat capacity. One of rather general interest is that of free conduction electrons in a metal. Although electrons are free to move through the metal to conduct electricity, their contribution to the heat capacity is so small that it was unnoticed for many years. This peculiar situation is now explained by the quantum theory of a degenerate Fermi–Dirac gas. This theory predicts that at low temperatures the electronic heat capacity will rise with the first power of the absolute temperature.

$$\frac{C}{R} = \gamma T \tag{5.49}$$

The proportionality constant $\gamma$ is a property of each metal. It is interesting to note that the electronic heat capacity can best be detected at either high or very low temperatures. At high temperatures [although Eq. (5.49) is no longer strictly valid], one finds a small linear increment over the theoretical value of $3R$ for $C_e$, due to anharmonicity of lattice vibrations as well as the electronic effect, while at very low temperatures the normal atomic vibrational heat capacity drops off more rapidly (as $T^3$) than the electronic term. Table 5-2 indicates the relative magnitude of the electronic term at 2 K and 30 K.

The discussion of solids to this point has emphasized the heat capacity. The integration to the entropy and other thermodynamic functions is straightforward. If in the region of very low temperatures, only the lattice vibrations (phonons) and conduction electrons, if present, contribute, one has

$$C = aT^3 + \gamma T \tag{5.50}$$

where $a$ is the coefficient of the Debye contribution and $\gamma$ that for metallic electrons. If this expression is integrated to yield the entropy, the result is

$$S = \left( \frac{a}{3} \right) T^3 + \gamma T \tag{5.51}$$

In the case that the electronic term is absent or negligible, one has the simple result that, at a given low temperature, $S = C/3$. We shall use the results just derived to estimate the entropy increment from 0 K up to the lowest temperature of measurement.

There are a number of other phenomena that yield heat-capacity contributions in certain solids. Examples include the change from an ordered to a disordered arrangement of certain atoms or the beginning of rotation of a group of atoms. If any atom or ion in the solid has a magnetic moment, then heat-capacity effects can arise.

---

**TABLE 5-2**

**Electronic contribution to heat capacity, $C/R$**

<table>
<thead>
<tr>
<th></th>
<th>$\gamma \times 10^4$</th>
<th>At 2 K</th>
<th>At 30 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{el}$</td>
<td>$C_{total}$</td>
<td>$C_{el}$</td>
</tr>
<tr>
<td>Copper</td>
<td>0.90</td>
<td>0.00018</td>
<td>0.00023</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1.73</td>
<td>0.00035</td>
<td>0.00038</td>
</tr>
</tbody>
</table>
from the reorientation of these magnetic moments. Nonzero nuclear spin yields significant effects for most substances only at extremely low temperatures, but for H₂ this temperature is much higher, as discussed in Chapter 22. Similarly, special effects occasionally arise from reorientation of molecules with electric-dipole moments. Several of these effects will be considered in later chapters.

**PRACTICAL ZERO OF ENTROPY**

In addition to the various contributions to the multiplicity \( W \) and to the entropy discussed above, there may be other multiplicities that have no practical effect and are best ignored for practical chemical thermodynamics. The first is nuclear spin, which is nonzero for some isotopes. Except for hydrogen itself, methane, and possibly a few other hydrogen compounds, any thermal effects of nuclear spin occur at such extremely low temperatures (microkelvins) that there is no overlap with the thermal effects of present interest. Furthermore, the spin multiplicity of a given isotope remains the same in the gas, liquid, or solid element and in any chemical compound. Thus, the entropy associated with nuclear spin multiplicity would cancel for any physical or chemical process, and it is best simply to omit that term.

Although various isotopes of hydrogen and methane show effects due to nuclear spin in the solid at temperatures where the lattice heat capacity is still significant, the two contributions can be separately evaluated. Also, the molecular properties are very well known; hence, we can calculate entropies on a basis excluding nuclear spin multiplicity.

A second phenomenon to be discussed is the mixing of isotopes. Here, one may wish specifically to consider isotopic separation processes. Then, one wishes thermodynamic properties for pure isotopes or molecules of defined isotopic structure. Such values are available for H₂, HD, D₂, HT, and T₂, and can readily be calculated whenever the structural data are known.

With the exception again of hydrogen, for many purposes the isotopes of each element remain randomly mixed. Thus, the inclusion of the entropy of mixing would serve no useful purpose; it would cancel in chemical reactions and in vaporization and other processes. In principle, we note that there may also be undiscovered multiplicities that do not show any thermal effects even in the millikelvin range of temperatures. If so, they will cancel for all of our purposes and would be omitted even if known.

In summary, the multiplicity due to nuclear spin is always omitted in the calculation of thermodynamic properties for practical purposes and, correspondingly, the entropy of nuclear spin is likewise omitted from the practical zero. Thermodynamic functions are calculated both for pure isotopes and for the natural mixture of isotopes, but in the latter case the entropy of isotopic mixing is omitted.

**REFERENCES**


**PROBLEMS**

5-1. Calculate the Gibbs energy function \(-G = H/T + RT\) for CO at 2000 K for the harmonic oscillator rigid rotator approximation. The rotational constant \( B = 1.931 \times 10^{-4} \text{ cm}^{-1} \), and the vibration frequency is \( \omega = 2167 \text{ cm}^{-1} \). Compare this result with the more accurate value in Appendix 6, and note the magnitude of the effects of anharmonicity, stretching, etc., at this temperature.

5-2. Calculate \( C_P \) for Br₂(g) at 600 K. The vibration frequency is \( \omega = 322 \text{ cm}^{-1} \).

5-3. Calculate \( C_P \) for aluminum at 25 K and 100 K from Eq. (5-48)* with the value 389 K for \( \theta_D \). Compare with the values interpolated from the table in Appendix 2. What do you conclude about the range of applicability of Eq. (5-48)*?

5-4. Estimate the value of \( C_P \) for rhodium at 300 K. Give your reasoning.
CHAPTER 6

THE THIRD LAW OF THERMODYNAMICS; ENTROPY CALCULATIONS

For the application of thermodynamics to various substances and processes, a database of enthalpies and chemical potentials is needed. These quantities are usually given for the process of formation from the component elements in defined standard states. The required measurements for enthalpies are straightforward; the heat evolved or absorbed is measured for one or a chain of spontaneous processes connecting the substance of interest with its elements. For example, any hydrocarbon, alcohol (or similar organic compound) can be burned in oxygen. Then this heat of combustion is subtracted from the heats of combustion of the corresponding amounts of hydrogen and carbon to obtain the desired enthalpy of formation. Corresponding methods are available for other types of compounds. Indeed, a comprehensive array of enthalpy data had been measured by Thomsen, Berthelot, and others before the end of the nineteenth century.

For the prediction of the direction of chemical reactions and their points of equilibrium, however, it is the chemical potential—the molar (or partial molar) Gibbs energy—that is required. This can be obtained at ordinary temperatures only from processes that come to a measurable equilibrium either directly or in an electrical cell or similar situation. It is not always possible to find such processes. Their discovery and measurement, even if successful, is a difficult task that will differ from one compound to another and may require the development of new catalysts, etc.

An alternate approach to Gibbs energies arises if entropy values can be obtained. Thus, when it became apparent that for a single substance the entropy difference above the value at 0 K was finite and readily measurable, there was an immediate interest in the possibility that entropy changes for formation from the elements might be zero at $T = 0$. This would correspond, of course, to unit probability on a quantum basis for the compound and for its constituent elements at 0 K. Before testing this principle experimentally, we discuss practical calculations of entropy.

### NUMERICAL CALCULATIONS OF ENTROPY

As a starting point we may recall that in any reversible process a system, or any part of a system, undergoes an increase of entropy just as far as it absorbs heat from the surroundings, resulting in an equal decrease of the entropy of the surroundings, and that the increase in entropy is equal to the heat so absorbed divided by the absolute temperature,

$$dS = \frac{\delta q_{rev}}{T}$$  \hspace{1cm} (2-22)

### Heat-Capacity and Enthalpy Measurements

Since it is heat absorbed that yields an entropy increase, calorimetric measurements are important. Flow calorimeters for fluids were discussed briefly in Chapter 4. For heat-capacity measurements for solids, the sample is normally enclosed in a container carrying an electrical heater and a thermometer. Electrical resistance thermometers are excellent. A small electrical energy input $q$ yields a small temperature increase $\Delta T$, whereupon the heat capacity is obtained as $q/\Delta T$. The heat capacity of the empty container must be subtracted, of course. The difficulty lies primarily in avoiding or measuring extraneous heat transfer by radiation, through lead-in wires, etc. One method is to surround the measuring unit with a shield that is maintained by heaters and thermostatic controls at exactly the same temperature. Such adiabatic calorimeters are very successful.

For isothermal processes, melting, solid–solid transitions, and vaporization, the problem is simplified by the absence of a temperature change but may be complicated by other aspects such as sluggishness for a transition or transfer and control of the vapor for vaporization.

An excellent book is available that discusses calorimeter design and operation in detail and presents examples.\(^1\)

### Entropy Change in Fusion

Let us use this basic equation, Eq. (2-22), to calculate the change of entropy when a substance changes from one phase to another at constant temperature and under conditions of equilibrium. We shall consider the fusion of 1 mole of solid mercury at
its melting point, which (at atmospheric pressure) is 234.29 K. At the melting point the
two phases are in equilibrium. That is to say, there is a state of balance such that if the
external temperature is raised by an infinitesimal amount the solid will melt and if it
is diminished by an infinitesimal amount the liquid will freeze. So also, at constant
temperature, if the pressure is lowered or raised by any amount, the process will occur
in the one direction or the other. Hence the process of fusion at the melting point is a
reversible one.

In the case of a pure substance like mercury the temperature remains constant
during fusion, and we have from Eq. (2-22)

$$\Delta S = \frac{\Delta H}{T}$$  \hspace{1cm} (6-1)

If $\Delta_{\text{fus}} H$ is the heat of fusion of 1 mole, namely 2295 J, and $T$ is 234.29 K, we may
write

$$Hg(s) = Hg(l) \quad \frac{\Delta_{\text{fus}} S}{R} = \frac{2295}{8.3145 \times 234.29} = 1.178$$

It is convenient to divide molar entropies and heat capacities by the gas constant
$R$ since the resulting ratio is dimensionless. This follows the pattern in Chapter 5.

It must be borne in mind that such a calculation is based upon the fact that we
have a state of equilibrium in which every process is reversible. If, on the other hand, we
consider the difference in entropy between ice at -10°C and supercooled water at
the same temperature, that difference cannot be obtained by dividing the difference in
enthalpy by the absolute temperature, 263 K.

### Entropy Change in Vaporization

In vaporization the change of entropy is usually much larger than in fusion. Ethyl ether
at its boiling point, 307.7 K, absorbs 27 200 J mol$^{-1}$ by evaporation. Hence we write for
the vaporization,

$$\frac{\Delta_{\text{vap}} S}{R} = \frac{27200}{8.3145 \times 307.7} = 10.63$$

Similarly, for benzene, cyclohexane, and toluene at their respective boiling
points, the corresponding values of $\Delta_{\text{vap}} S/R$ are 10.47, 10.22, and 10.47.

It will be noted that the four values are nearly equal. An empirical principle,
known as Trouton's rule,$^2$ states that the entropy increase per mole is the same for all
so-called normal, or nonpolar, liquids at their boiling points. The constant of Trouton's
rule is usually given as about 10.5 for $\Delta_{\text{vap}} S/R$.

### Entropy Change with Pressure or Volume

The general equations for the change of entropy with pressure or volume at constant
temperature were derived in Chapter 3:

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$  \hspace{1cm} (3-11)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$  \hspace{1cm} (3-12)

For a perfect gas these integrate to the equations from Chapter 2:

$$S_B - S_A = nR \ln \left(\frac{V_B}{V_A}\right) = nR \ln \left(\frac{P_A}{P_B}\right)$$  \hspace{1cm} (2-21)*

In the case of solids or dense liquids this entropy change is very small unless the
pressure change is large. But for gases the entropy change is large. At low pressures a
gas is nearly perfect and Eq. (2-21)* is often a good approximation. Corrections for
gas imperfection are considered in Chapter 9.

### Change of Entropy with Temperature

We have seen in Eqs. (3-26) and (3-28) how the entropy of a substance changes with
the temperature. The equations read

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Thus, if a substance is heated at constant pressure, the change of entropy is given by
the equation

$$\int dS = \int \frac{C_P}{T} dT = \int C_P d\ln T$$  \hspace{1cm} (6-2)

If, therefore, $C_P$ is known at various temperatures, we may perform the integration by
analytical or graphical methods and find the change in entropy of a substance between
two temperatures.

The simplest case is the one in which $C_P$ is constant, when we find, between the
temperatures $T$ and $T'$,

$$S' - S = C_P \ln \left(\frac{T'}{T}\right)$$  \hspace{1cm} (6-3)*
carefully considered. The pertinent theory was presented in Chapter 5 together with simple examples. One often finds that the measured points at the lowest temperatures fit the $T^3$ law, Eq. (5-48)*, or, for metals, the slightly more complex equation

$$ C = aT^3 + yT $$

(5-50)*

which integrates to

$$ S = \frac{a}{3}T^3 + yT $$

(5-51)*

A graph of $C_p/RT$ vs. $T^2$ is very convenient since the function of Eq. (5-50)* becomes a straight line with a slope $a/R$ and intercept $y/R$ on the $T^2 = 0$ axis. Figures 6-2 to 6-4 present data for a number of substances on this basis, and in all cases the curves approach the behavior predicted by Eq. (5-50)* at the lowest temperatures. Also the intercept is at the origin ($y = 0$) except for metals.

In our opinion a plot of the heat-capacity data on the $C_p/RT$ versus $T^2$ basis along with the available data extending to lower temperatures for similar substances provides the best basis for extrapolation to 0 K. The already substantial and rapidly growing body of data extending to very low values of $C_p$ makes this a feasible procedure. One then draws an extrapolated curve similar to the observed curves for similar substances and in a manner consistent with Eq. (5-51)* in the limit at 0 K. The two curves for (CH$_3$)$_2$S in Fig. 6-3 illustrate the probable limits within which the correct extrapolation should lie. Finally, the extrapolated values of $C_p$ may be transferred to a plot of $C_p/T$ versus $T$ for the calculation of the entropy by graphical integration.

Extrapolation of Heat Capacity to 0 K

While the heat capacity of graphite was so small at the lowest measured temperature that the extrapolation to 0 K was trivial, for many cases this extrapolation must be

For liquid mercury in the small temperature range between $T' = 298.15$ K and the freezing point $T = 234.29$ K, we may regard the molar heat capacity as approximately constant and with $C_p/R = 3.40$. Hence

$$ \frac{S' - S}{R} = 3.40 \ln \frac{298.15}{234.29} = 0.820 $$

At moderate and high temperatures, the heat capacity can often be represented by a simple empirical equation, and this can be integrated to yield entropy, enthalpy, etc. This will be illustrated in Chapter 8. For our consideration of entropies at 0 K, however, we must evaluate Eq. (6-2) over the full range of temperature from zero upward. In this range the variation of $C_p$ is very complex, and graphical methods have been widely used. Alternatively, one can use numerical integration with a large number of smoothed values of $C_p$. Either method can be used for the actual evaluations in the following examples.

Figure 6-1 shows that the atomic heat capacity of graphite is plotted as $C_p/RT$ vs. $T$. It is evident from Fig. 6-1 that the total entropy above 0 K is a finite quantity. From the total area under the curve up to the point A one obtains $(S_{298} - S_0)/R = 0.690$, where $S_0$ represents the entropy at absolute zero.

---

**FIGURE 6-1**

$C_p/RT$ for graphite.

**FIGURE 6-2**

Absolute Entropies

We now assume that the entropy at 0 K, \( S_0 \), is zero and proceed to calculate the total entropy of substances at the standard temperature 298.15 K, the boiling point of a liquid, or another desired temperature. If there are solid–solid transitions, each entropy contribution is exactly like that for fusion. Liquid and gas heat capacities have simple temperature dependencies that are readily handled.

Oxygen constitutes a relatively complex example for which there are the measurements of Giauque and Johnston. The results are presented in Fig. 6-5 and Table 6-1. In this case there are three solid forms as well as the liquid and gas.

![Graph showing heat-capacity curves for three molecular crystals](image)

**FIGURE 6-3**
Heat-capacity curves for three molecular crystals. The pair of dashed lines for \((CH_2)_2S\) indicate the range of reasonable extrapolation curves. [J. E. Ahlberg et al., J. Chem. Phys., 6, 539 (1937), and G. O. Oliver et al., J. Am. Chem. Soc., 70, 1502 (1948), for \(C_6H_6\); D. W. Scott et al., ibid., 75, 2795 (1953), for \((CH_2)_2S\); N. E. Levitin et al., ibid., 81, 3547 (1959) for \((CH_2)_2NB_2H_7\)]

![Graph showing heat-capacity curves for KCl, Ag, and Ni](image)

**FIGURE 6-4**

![Graph showing entropy of oxygen](image)

**FIGURE 6-5**
The molal heat capacity of oxygen. The areas in the graph are terms in the entropy calculation.

**TABLE 6-1**
The entropy of oxygen

| Values of \( S/R \) and \( (\Delta H/R)/K \) |
|-----------------|-----------|
| 0–14 K, extrapolation | 0.27       |
| 14–23.66 K, solid III, graphical | 0.755      |
| Transition, 11.28/23.66 | 0.477      |
| 23.66–43.76 K, solid II, graphical | 2.345      |
| Transition, 89.36/43.76 | 2.042      |
| 43.76–54.39 K, solid I, graphical | 1.206      |
| Fusion, 53.48/54.39 | 0.983      |
| 54.39–90.13 K, liquid, graphical | 3.252      |
| Vaporization 819.690.13 | 9.094      |
| Total, \( S_{0,13} \) (gas, 1 atm.) | 20.42      |
Tests of Entropy Equality at 0 K

We now calculate the absolute entropies of a given substance by different routes and thereby test the validity of the postulate that entropies at 0 K ($S_0$) may be taken to be zero. For the present, we consider only simple cases where there are no special disorders or multiplicities present. Then the calculations for measured properties follow the methods just described.

As a first example, we consider the entropy of formation of solid AgCl:

$$\text{Ag}^{\text{cr}} + \frac{1}{2}\text{Cl}_2^{\text{g}} = \text{AgCl}^{\text{cr}}$$

The Gibbs energy, entropy, and enthalpy changes for this reaction were measured by Gerke$^5$ using a Galvanic cell with Ag, AgCl, and Cl$_2$ electrodes, and aqueous HCl electrolyte. (Galvanic cells are discussed briefly in Chapter 8 and in detail in Chapter 19.) Cell potentials were measured very precisely at 15°C, 25°C, and 35°C, and the value $\Delta_f S/R = -6.91 \pm 0.1$ was determined from the temperature coefficient. The entropy of Cl$_2$ (g) is accurately calculated from molecular properties. Values for Ag(cr)$^6$ and AgCl(cr)$^7$ are available from heat-capacity measurements extending down to 15 K or below, from which point the extrapolation to 0 K is unambiguous. Table 6-2 shows the results, which yield $\Delta_f S/R = -6.98 \pm 0.06$, in good agreement.

The entropy of chlorine is also available from measurements of the heat capacity, heat of fusion, and heat of vaporization by Giauque and Powell.$^8$ Their results are given in Table 6-3 with a comparison between calorimetric and calculated values at the boiling point. The agreement is exact, well within an uncertainty of about 0.05 for the calorimetric value.

It is interesting to see from Figure 6-6 how the $\Delta S$ of formation of AgCl from the elements changes as the temperature is reduced. The large changes occur on condensation and freezing of the chlorine; indeed, $\Delta_f S$ happens to change sign at the freezing point. Finally, $\Delta_f S$ approaches zero with zero slope as $T \to 0$.

Another type of test of the equality of entropies at 0 K is a comparison of two crystalline forms of the same substance, one of which can be supercooled. Phosphine provides an excellent example of this type, with precise data from Stephenson and Giauque$^9$ shown in Table 6-4.

The comparison of the difference in entropies of rhombic and monoclinic sulfur obtained by integration of $C_p/T$ from 0 K with that for their direct transition at 368.5 K provides another check of the same type as that of phosphine. Montgomery$^{10}$ reports that these two $\Delta S/R$ values agree exactly with an uncertainty of only 0.01.

### TABLE 6-2

<table>
<thead>
<tr>
<th>S/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
</tr>
<tr>
<td>-Ag</td>
</tr>
<tr>
<td>$\frac{1}{2}\text{Cl}_2$</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

### TABLE 6-3

<table>
<thead>
<tr>
<th>S/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–15 K, Debye function $\Theta_D = 115$</td>
</tr>
<tr>
<td>15–172.15 K integral of $C_p$</td>
</tr>
<tr>
<td>Fusion at 172.12 K</td>
</tr>
<tr>
<td>172.12–239.05 K integral of $C_p$</td>
</tr>
<tr>
<td>Vaporization at 239.05 K</td>
</tr>
<tr>
<td>Correction to ideal gas</td>
</tr>
<tr>
<td>Ideal gas, calorimetric</td>
</tr>
<tr>
<td>Ideal gas, calculated statistically</td>
</tr>
</tbody>
</table>

### TABLE 6-4

<table>
<thead>
<tr>
<th>S/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form stable above 49.43 K</td>
</tr>
<tr>
<td>0–15 K, Debye extrapolation</td>
</tr>
<tr>
<td>Integration of $C_p$</td>
</tr>
<tr>
<td>Transitions</td>
</tr>
<tr>
<td>Integration of $C_p$</td>
</tr>
<tr>
<td>Entropy, $S/R$ at 49.43 K</td>
</tr>
</tbody>
</table>
Third Law of Thermodynamics

There are many examples of the types just illustrated, although the uncertainties are somewhat larger in most cases. This body of information about the macroscopic properties, heat capacities and entropies, is the basis for the third law of thermodynamics, which states that, for any substance in a perfect crystalline state, the entropy is zero in the limit $T \to 0$. This is interpreted to be the practical zero of entropy defined in the last chapter, which excludes effects of nuclear spin and of isotopic mixing whenever the consideration is of a natural mixture of isotopes.

There remains the matter of definition of a perfect crystalline state. Some solids are obviously disordered, such as glasses, and can be excluded. In other cases, the substance is clearly crystalline but might have an internal disorder such as random magnetic moments or orientations of molecules. There is no simple test of crystalline perfection; one must consider the possibilities of residual disorder for each case.

There are many crystals, however, for which there is no plausible disorder, and one can adopt the entropy values based on the third law with full confidence. The monatomic gases neon, argon, krypton and xenon have a very simple structure in the solid state, and no rotational disorder is possible. Their entropies from low-temperature heat capacities agree accurately with the statistical values as shown in Table 6-5. The possibility of disorder in solid Cl$_2$ is most unlikely, and the agreement between statistical and calorimetric entropies in Table 6-3 is excellent. Whenever the structural pattern is very simple and the interparticle forces are strong, randomness in structure is most improbable. Entropies based on the third law have been widely adopted for such substances without any indication of discrepancy.

There are several types of crystals, however, where randomness or disorder are known to occur at room temperature. In some cases there is a transition or other thermal anomaly where the disorder is removed and the crystal then meets the perfection requirement as $T \to 0$. But in other cases, the disorder is removed only at extremely low temperature or becomes "frozen" and remains as $T \to 0$. The disorder may relate to orientation of molecules, to orientation of electronic magnetic moments, or to other phenomena. Chapter 21 describes several cases of frozen disorder.

For small molecules and some larger ones, there is adequate information about molecular properties; hence statistically calculated entropies for the ideal gas are available and should be adopted. Calorimetric measurements on the condensed phases and the vaporization process then yield entropies related to the practical zero without ambiguity. The possibility of residual disorder at $T = 0$ is an interesting structural question, but it does not affect thermodynamic properties at higher temperatures when calculated by this procedure. Some examples of this type are considered in Chapter 21. For H$_2$ and the other isotopic forms of hydrogen, there are interesting complications related to nuclear spin that are described in Chapter 22. Again, the properties for these species as gases are given accurately and reliably by the statistical calculations, and those values should be used wherever applicable.

### Table 6-5

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S^0/R$ (ideal gas)</th>
<th>$P$/bar</th>
<th>Calorimetric</th>
<th>Statistical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>12.20</td>
<td>0.4335</td>
<td>12.19</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>15.80</td>
<td>0.6870</td>
<td>15.83</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>17.69</td>
<td>0.7319</td>
<td>17.68</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>19.09</td>
<td>0.8160</td>
<td>19.08</td>
<td></td>
</tr>
</tbody>
</table>

### Figure 6-7

The heat capacity of NiCl$_2$(cr), showing the magnetic anomaly.
susceptibility\(^\text{13}\) (Figure 6-8) shows the typical Curie's law behavior with \(\chi\) approximately proportional to \(1/T\). Below the transition, the susceptibility decreases with decrease in temperature and then becomes approximately constant. This indicates that all of the magnetic moments are ordered antiferromagnetically, i.e., in an antiparallel pattern with zero net magnetization except for thermal excitations. Thus, we expect that the entropy of NiCl\(_2\) approaches the practical zero as \(T\to0\).

There is the alternative of ferromagnetic behavior below the transition with the magnetic moments adopting a parallel pattern. Again, this is an ordered pattern that should yield zero magnetic entropy as \(T\to0\). Metallic iron, cobalt, and nickel provide examples of ferromagnetism; their transition temperatures are above room temperature at 1033, 1400, and 633 K, respectively.

There are many salts that are similar to NiCl\(_2\) with paramagnetic behavior above a transition and antiferromagnetic properties below it. Presumably, the magnetic entropy approaches zero as \(T\to0\) in all such cases. There are few thermodynamic checks for these magnetic salts, but there is a verification for NiCl\(_2\). Busey and Giauque\(^\text{14}\) measured the equilibrium for the reaction

\[
\text{NiCl}_2(\text{cr}) + H_2(g) = 2\text{HCl}(g) + \text{Ni}(\text{cr})
\]

over the range 630–737 K. The entropies of H\(_2\) and HCl are accurately known from statistical calculations and those of NiCl\(_2\) and Ni from experimental heat-capacity measurements. The entropy change calculated on the basis of the third law agrees with that measured for the chemical reaction to 0.05R.

As the magnetic ions are separated more widely by nonmagnetic material, their interaction decreases and the temperature of the ordering transition is lowered.

Indeed, if these interactions are very weak, the most effective method of removing the magnetic disorder is a strong external magnetic field. One can take the double limit \(T\to0\), \((1/H)\to0\) as the method of extrapolation to the practical zero of entropy.

An important method of attainment of very low temperatures is that of adiabatic demagnetization. This is described in Chapter 24; it requires a magnetic material with extremely weak interactions.

We conclude this section with a consideration of CuSO\(_4\)·5H\(_2\)O as an example of a case with weak but not extremely weak magnetic interactions. It is interesting in that it shows two thermal anomalies; one has a very broad maximum in the range 1–2 K, and the other is very sharp at 0.035 K (see Figure 6-9). The magnetic susceptibility increases steadily with reduction in temperature through the 1–2 K range, which indicates that much of the magnetic disorder remains below 1 K. The susceptibility reaches a peak at 0.035 K and then decreases with further decrease in \(T\). This is consistent with full ordering as \(T\to0\).

The crystal structure of CuSO\(_4\)·5H\(_2\)O is triclinic, i.e., without any axes or planes of symmetry, and has two nonequivalent cupric ions per unit cell. The presence of two magnetic anomalies is undoubtedly related to this nonequivalence and the absence of symmetry. It appears that half of the magnetic entropy is associated with the transition at 0.035 K and the other half with the region of high heat capacity that extends to 5 K. However, we are not aware of a detailed theory yielding quantitatively the properties of CuSO\(_4\)·5H\(_2\)O. The very thorough experimental investigations of copper sulfate pentahydrate are summarized by Giauque et al.,\(^\text{15}\) who discuss many additional features of this interesting system.
The Entropies of Particular Substances

The heat capacity has been measured down to very low temperatures for most of the chemical elements and for a substantial number of compounds. While various types of possible disorder have been discussed in the sections above, they represent special cases that can readily be excluded for most particular substances. Then the entropy above the practical zero defined in Chapter 5 is given by

\[ S_T = \int T C_P \, d \ln T' \]  \hspace{1cm} (6-4)

Many entropy values have been calculated by the method described above. It is convenient to tabulate the entropy for a substance in a standard state. For solids and liquids, the standard state is taken at 1 bar. Since the entropy of a gas does not approach a constant value as the pressure is reduced, one cannot choose a low-pressure perfect-gas standard state for the tabulation of the entropy of a gas. The standard state for the tabulation of the entropy of a gas will be the hypothetical perfect gas at a designated pressure of 1 bar. Standard-state entropies are indicated by a superscript, \( S^o \).

To obtain this standard entropy of a gas, we first note the entropy difference between the entropy of a perfect gas at some low pressure \( P \) and at 1 bar by Eq. (2-21),

\[ S^o = S_P + R \ln \left( \frac{P}{1} \right) \]  \hspace{1cm} (6-5)*

<table>
<thead>
<tr>
<th>TABLE 6-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entropies of some common substances at 298.15 K, values of ( S^o_{298K}/R^* )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solids</th>
<th>Liquids</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.401</td>
<td>Hg</td>
</tr>
<tr>
<td>C(gr)</td>
<td>0.690</td>
<td>H(_2)O</td>
</tr>
<tr>
<td>Ca</td>
<td>5.002</td>
<td>Hg</td>
</tr>
<tr>
<td>CaO</td>
<td>4.596</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2.840</td>
<td>F(_2)</td>
</tr>
<tr>
<td>Cu</td>
<td>3.989</td>
<td>H(_2)</td>
</tr>
<tr>
<td>Fe</td>
<td>3.286</td>
<td>HCl</td>
</tr>
<tr>
<td>I(_2)</td>
<td>13.969</td>
<td>H(_2)S</td>
</tr>
<tr>
<td>Mg</td>
<td>3.929</td>
<td>N(_2)</td>
</tr>
<tr>
<td>MgO</td>
<td>3.238</td>
<td>NO</td>
</tr>
<tr>
<td>NaCl</td>
<td>8.673</td>
<td>O(_2)</td>
</tr>
<tr>
<td>Ni</td>
<td>3.925</td>
<td></td>
</tr>
<tr>
<td>Si(gr)</td>
<td>3.855</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>2.264</td>
<td></td>
</tr>
<tr>
<td>SiO(_2)(g)</td>
<td>4.987</td>
<td></td>
</tr>
</tbody>
</table>


If one now takes the limit \( P \to 0 \), the real gas approaches the ideal-gas state and the quantity \( S_P + R \ln P \) will approach a constant independent of pressure. Thus one has the equation for the standard entropy,

\[ S^o = \lim_{P \to 0} (S_P + R \ln P) \]  \hspace{1cm} (6-6)

Convenient methods of dealing with gas imperfection effects are discussed in Chapter 9.

Table 6-6 gives a brief list of entropy values at 298.15 K (\( \approx 25^\circ C \)); a more extensive table is given in Appendix 6. Note that the values of \(- (G^F - H_{298}^F)/RT\) , which are tabulated in Appendix 6 at 298.15 K, are values of \( S_{298}^o/R \). For most gases the values calculated by the methods described in Chapters 5 and 20 are more precise than those obtained by calorimetry and the third law. The values in Table 6-6 are those given by the most precise method in each case.

REFERENCES

2. F. Trauttm, Phil. Mag., 18 (5), 54 (1884).

PROBLEMS

6-1. Taking \( C_P = 3.50 \) for gaseous oxygen and the entropy of vaporization from Table 6-1, show that for the process \( O_2(g, 298.15K) \rightarrow O_2(1, 90.13K) \), \( \Delta S = -13.28 \).

6-2. Calculate the minimum amount of work required to convert 1 mole of oxygen gas at 298.15 K and 1 bar to the liquid state at 90.13 K in a reversible process in which heat is transferred to a heat reservoir at 289.15 K. Note that the entropy decrease of the oxygen was calculated in Problem 6-1 and that the entropy increase of the heat reservoir must be equal so that the net entropy change will be zero. The first law may then be used to calculate the work.