

21.8: The Third Law of Thermodynamics

In [Section 21.7](#), we obtain the entropy by a definite integration. We take the lower limits of integration, at $T = 0$, as $P_1(0) = 1$ and $P_i(0) = 0$, for $i > 1$. In doing so, we apply the third law of thermodynamics, which states that the entropy of a perfect crystal can be chosen to be zero when the temperature is at absolute zero. The idea behind the third law is that, at absolute zero, the molecules of a crystalline substance all are in the lowest energy level that is available to them. The probability that a molecule is in the lowest energy state is, therefore, $P_1 = 1$, and the probability that it is any higher energy level, $i > 1$, is $P_i = 0$.

While the fact is not relevant to the present development, we note in passing that the energy of a perfect crystal is not zero at absolute zero. While all of the constituent particles will be in their lowest vibrational energy levels at absolute zero, the energies of these lowest vibrational levels are not zero. In the harmonic oscillator approximation, the lowest energy possible for each oscillator is $h\nu/2$. (See [Section 18.5](#)).

By a perfect crystalline substance we mean one in which the lowest energy level is non-degenerate; that is, for which $g_1 = 1$. We see that our entropy equation conforms to the third law when we let

$$S_0 = Nk \ln g_1$$

so that $S_0 = 0$ when $g_1 = 1$.

Let us consider a crystalline substance in which the lowest energy level is degenerate; that is, one for which $g_1 > 1$. This substance is not a perfect crystal. In this case, the temperature-zero entropy is

$$S_0 = Nk \ln g_1 > 0$$

The question arises: How can we determine whether a crystalline substance is a perfect crystal? In [Chapter 11](#), we discuss the use of the third law to determine the absolute entropy of substances at ordinary temperatures. If we assume that the substance is a perfect crystal at zero degrees when it is not, our theory predicts a value for the absolute entropy at higher temperatures that is too small, because it does not include the term $S_0 = Nk \ln g_1$. When we use this too-small absolute entropy value to calculate entropy changes for processes involving the substance, the results do not agree with experiment.

Absolute entropies based on the third law have been experimentally determined for many substances. As a rule, the resulting entropies are consistent with other experimentally observed entropy changes. In some cases, however, the assumption that the entropy is zero at absolute zero leads to absolute entropy values that are not consistent with other experiments. In these cases, the absolute entropies can be brought into agreement with other entropy measurements by assuming that, indeed, $g_1 > 1$ for such substances. In any particular case, the value of g_1 that must be used is readily reconciled with other information about the substance.

For example, the third law entropy for carbon monoxide must be calculated taking $g_1 = 2$ in order to obtain a value that is consistent with other entropy measurements. This observation is readily rationalized. In perfectly crystalline carbon monoxide, all of the carbon monoxide molecules point in the same direction, as sketched in [Figure 11-2](#). However, the two ends of the carbon monoxide molecule are very similar, with the consequence that the carbon monoxide molecules in the crystal point randomly in either of two directions. Thus there are two (approximately) equally energetic states for a carbon monoxide molecule in a carbon monoxide crystal at absolute zero, and we can take $g_1 = 2$. (We are over-simplifying here. We explore this issue further in [Section 22-7](#).)

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