6.1: The Zero of Entropy

There is no theoretical relation between the entropies of different chemical elements. We can arbitrarily choose the entropy of every pure crystalline element to be zero at zero kelvins. Then the experimental observation expressed by Eq. 6.0.1 requires that the entropy of every pure crystalline *compound* also be zero at zero kelvins, in order that the entropy change for the formation of a compound from its elements will be zero at this temperature.

A classic statement of the third law principle appears in the 1923 book *Thermodynamics and the Free Energy of Chemical Substances* by G. N. Lewis and M. Randall (McGraw-Hill, New York, p. 448):

> "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature: *every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances*."

According to this principle, every substance (element or compound) in a pure, perfectly-ordered crystal at $0\,\mathrm{K}$, at any pressure, has a molar entropy of zero:

$$S_{\mathrm{m}}(0\,\mathrm{K}) = 0 \tag{6.1.1}$$
$$\text{(pure, perfectly-ordered crystal)}$$

This convention establishes a scale of absolute entropies at temperatures above zero kelvins called **third-law entropies**, as explained in Sec. 6.2.

> The entropy becomes independent of pressure as T approaches zero kelvins. This behavior can be deduced from the relation $(\partial S/\partial p)_T = -\alpha V$ (Table 7.1) combined with the experimental observation that the cubic expansion coefficient α approaches zero as T approaches zero kelvins.