

3.10: The Third Law

For entropy on the other hand, the fact that the heat capacity goes to zero as the temperature decreases has important consequences. Consider the change in the entropy of a pure substance whose heat capacity approaches some finite limiting value as its temperature decreases to absolute zero. For such a substance, C_P/T becomes arbitrarily large as the temperature decreases, and the entropy integral

$$\int_T^0 \frac{C_P}{T} dT$$

approaches minus infinity as the temperature approaches zero. For real substances, this does not occur. In the neighborhood of absolute zero, heat capacities decrease more rapidly than temperature. The entropy change approaches zero as the temperature approaches zero.

The idea that the entropy change for a pure substance goes to zero as the temperature goes to zero finds expression as the third law of thermodynamics. In 1923, Lewis and Randall¹ gave a statement of the third law that is particularly convenient in chemical applications:

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

Implicitly, the Lewis and Randall statement defines the entropy of any substance, at any temperature, T , to be the difference between the entropy of the constituent elements, at absolute zero, and the entropy of the substance at temperature T . Equivalently, we can say that it is the entropy change when the substance is formed at temperature T from its constituent elements at absolute zero. Arbitrarily, but very conveniently, the statement sets the entropy of an element to zero at absolute zero.

The distinction between perfect crystalline substances and less-than-perfect crystalline substances lies in the regularity of the arrangement of the molecules within the crystal lattice. In any lattice, each molecule of the substance is localized at a specific site in the lattice. In a perfect crystal, all of the molecules are oriented the same way with respect to the lattice. Some substances form crystals in which the molecules are not all oriented the same way. This can happen when the molecule can fit into a lattice site of the same shape in more than one way. For example, in solid carbon monoxide, the individual molecules occupy well-defined lattice sites. If the carbon monoxide crystal were perfect, all of the molecules would point in the same direction, as diagrammed in Figure 2. Instead, they point randomly in either of two possible directions.



Figure 2. A two-dimensional representation of a perfect CO crystal.

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