

5.7: The Third Law of Thermodynamics

One important consequence of Boltzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible to have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**.

The entropy of a perfectly ordered crystal at 0 K is zero.

This also suggests that absolute molar entropies can be calculated by

$$S = \int_0^T \frac{C}{T} dT$$

where C is the heat capacity. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change. Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3 . Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

✓ Example 5.7.1

SiO_2 is found to have a molar heat capacity of $0.777 \text{ J mol}^{-1} \text{ K}^{-1}$ at 15 K (Yamashita, et al., 2001). Calculate the molar entropy of SiO_2 at 15 K.

Solution

Using the Debye model, the heat capacity is given by



The value of a can be determined by



The entropy is then calculated by

Calculating a third Law Entropy

Start at 0 K, and go from there!

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