

6.1: Entropy and the 3rd Law

Of all the thermodynamic variables, entropy is the only one that can be quantified with certainty due to the 3rd Law:

The absolute value of the entropy of a perfect crystal at 0 K is 0 J/K

A little dry, isn't it? What is important is that the 3rd Law gives us a starting point for measuring the entropy of a real chemical, that being a frozen, perfect crystal of the substance at 0 K. Next, the material is heated to room temperature, all the while constantly measuring how much energy is added. All this heat energy is translated into entropy using the various equations we developed in Chapter 4 and further here. We assume that we have 1 mole of a pure, perfectly crystalline chemical in a calorimeter. As we efficiently add heat, we must know whether the conditions are those of constant volume or pressure given that the heat capacity depends on these factors. As it isn't easy to keep a solid at a constant volume, we make these measurements at a constant pressure. Recalling that: $\partial q = C_P \partial T$, and assuming the heat is added reversibly: $\partial S = \frac{\partial q_{rev}}{T}$, the absolute entropy is:

$$S(T_f) = S(0\text{ K}) + \int_{T_i}^{T_f} C_P \frac{\partial T}{T} = S(0\text{ K}) + C_P \cdot \ln\left(\frac{T_f}{T_i}\right)$$

where $S(0\text{ K})$ is 0 J/K due to the 3rd Law. From this, can you see how the 3rd Law allows us to determine the actual entropy of a chemical is at room temperature and pressure? If we didn't know $S(0\text{ K})$, then we could never calculate the absolute value of S at any temperature!

As an example, we will determine the entropy of nitrogen gas at 25 °C starting from 0 K. First, you may be tempted to use the value of $C_{P,m}$ that we determined in Chapter 2: $C_{P,m} = C_{V,m} + R = \frac{5}{2}R + R = 29.1\text{ J/K/mol}$. The problem is that this is the per molar heat capacity of N_2 gas near room temperature, not the heat capacity of solid nitrogen near 0 K! These heat capacities are not the same, in fact, they are very different as heat capacity of N_2 is dependent on both the phase and temperature as shown in Figure 6.1A. We can see that the per molar heat capacity of the solid at $\sim 0\text{ K}$ is $\sim 0\text{ J/K/mol}$, and quickly rises with temperature until $T = \sim 36\text{ K}$. Next the heat capacity suddenly decreases, which is due to a solid-solid phase transition. What this means is that N_2 remains a solid, but the internal structure changes from cubic to hexagonal close-packed. This is still a change of phase, just like ice melting into water. There is also an associated heat of transition per mole, $\Delta_{h \leftarrow c} H_m$, which is the energy added to 1 mole of N_2 in the cubic phase to transform it into a hexagonal solid (" $h \leftarrow c$ " refers to the solid phase transition from cubic to hexagonal). Since the addition of heat will always increase entropy, this must be added in as:

$$[S_m = S_m(0\text{ K}) + C_{P,m} \ln\left(\frac{T_{h \leftarrow c}}{T_i}\right) + \frac{\Delta_{h \leftarrow c} H_m}{T_{h \leftarrow c}}]$$

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where $T_{h \leftarrow c}$ is the temperature at which this phase change occurs ($\sim 36\text{ K}$). Next, we heat the hexagonal solid phase of nitrogen to 63 K, at which point the N_2 begins to melt. As before, the heat added to allow this phase transition to occur increases the entropy and is added to the total: $[S_m = S_m(0\text{ K}) + C_{P,m} \ln\left(\frac{T_{h \leftarrow c}}{T_i}\right) + \frac{\Delta_{h \leftarrow c} H_m}{T_{h \leftarrow c}}]$

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$$+ C_{P,m} \ln\left(\frac{T_{fus}}{T_{h \leftarrow c}}\right) + \frac{\Delta_{fus} H_m}{T_{fus}}]$$

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where "fus" is fusion (the IUPAC word for melting) and T_{fus} is the melting temperature ($\sim 64\text{ K}$). We repeat this process using additional terms to account for warming the liquid to the vaporization temperature, and then vaporizing to liquid to form a gas, etc., until we reach 298.15 K:

$$S_m(298.15\text{ K}) = S_m(0\text{ K}) + C_{P,m}(T) \ln \left(\frac{T_h}{T_i} \right) + \frac{C_{P,m}}{T_i} \ln \left(\frac{T_h}{T_i} \right)$$

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$$+ C_{P,m}(T) \ln \left(\frac{T_h}{T_i} \right) + \frac{C_{P,m}}{T_i} \ln \left(\frac{T_h}{T_i} \right)$$

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$$+ C_{P,m}(T) \ln \left(\frac{T_h}{T_i} \right) + \frac{C_{P,m}}{T_i} \ln \left(\frac{T_h}{T_i} \right) \text{ \label{6.1}}$$

When we do this calculation using the $C_{P,m}(T)$ data shown in Figure 6.1A, including the enthalpies of all the various phase transformations, we determine that 1 mole of gaseous N_2 at this temperature and 1 bar of pressure has 190.1 J/K of entropy. This value then gets placed in standard thermodynamic tables along with the data on every other chemical that has been measured the same way.

6.1.1 Standard Temperature and Pressure

The above example demonstrates that thermodynamic values depend on the conditions at which they are reported. In the example above entropy is always increasing with temperature. Thus, we must designate a single, standard temperature (such as room temperature) that we use at the stopping point for the calculation in Equation 6.1. If we need to know the thermodynamic data at a different temperature, we can simply take the value from this standard state and then adjust it appropriately. This happens frequently, and we will show how to do so later in this chapter.

Before we get ahead of ourselves, we must define the standard state at which all thermodynamic data are tabulated. Furthermore, we have to define what variables comprise the standard state! To this end, we use pressure and temperature because these are intensive variables, and intensive variables are the deciding factors that determine equilibrium (this is explored in Chapter 8). For example, water and ice at equilibrium have the same temperature at the same pressure, whereas they do not have the same entropy and volume. Thus, we choose to define the standard state using temperature and pressure; specifically at 25 °C (298.15 K) and 1 bar (100 kPa).

6.2 Energy, it's all relative. 6.3 Enthalpy and Gibbs Energy of Formation: Hess's Law examples.

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