16.6: Getting Acquainted with Entropy

You can experience directly the mass, volume, or temperature of a substance, but you cannot experience its entropy. Consequently you may have the feeling that entropy is somehow less real than other properties of matter. We hope to show in this section that it is quite easy to predict whether the entropy under one set of circumstances will be larger than under another set of circumstances, and also to explain why. With a little practice in making such predictions in simple cases you will acquire an intuitive feel for entropy and it will lose its air of mystery.

The entropy of a substance depends on two things: first, the *state* of a substance—its temperature, pressure, and amount; and second, how the substance is *structured* at the molecular level. We will discuss how *state* properties affect entropy first.

Temperature As we saw in the last section, there should be only one way of arranging the energy in a perfect crystal at 0 K. If $W = 1$, then $S = k \ln W = 0$; so that the *entropy should be zero at the absolute zero of temperature*. This rule, known as the **third law of thermodynamics**, is obeyed by all solids unless some randomness of arrangement is accidentally “frozen” into the crystal. As energy is fed into the crystal with increasing temperature, we find that an increasing number of alternative ways of dividing the energy between the atoms become possible. W increases, and so does S. Without exception the entropy of any pure substance *always increases with temperature*.

Volume and Pressure We argued earlier that when a gas doubles its volume, the number of ways in which the gas molecules can distribute themselves in space is enormously increased and the entropy increases by 5.76 J K^{-1}. More generally the entropy of a gas always *increases with increasing volume* and *decreases with increasing pressure*. In the case of solids and liquids the volume changes very little with the pressure and so the entropy also changes very little. **Amount of Substance** One of the main reasons why the entropy is such a convenient quantity to use is that its magnitude is *proportional to the amount of substance*. Thus the entropy of 2 mol of a given substance is twice as large as the entropy of 1 mol. Properties which behave in this way are said to be **extensive properties**. The mass, the volume, and the enthalpy are also extensive properties, but the temperature, pressure, and thermodynamic probability are not.