

ENTROPY OF MIXING

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 2.37 - 2.38.

The entropy of an ideal gas is given by the Sackur-Tetrode formula:

$$(0.1) \quad S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

where V is the volume, U is the energy, N is the number of molecules, m is the mass of a single molecule and h is Planck's constant.

We can apply this formula to the case where we begin with two *different* ideal gases A and B , with a total number N of gas molecules divided into two volumes V_A and V_B , but at equal pressures and temperatures. Thus the number of type B molecules can be expressed as a fraction x of the total number so that $N_B = xN$, and thus $N_A = (1-x)N$. The volumes can be expressed as the same fractions of the total volume, so that $V_A = (1-x)V$ and $V_B = xV$.

We now remove the partition between the gases and allow them to mix. Because they were at the same pressure and temperature before they mixed, both P and T remain unchanged when the gases mix, so the energy of each gas $U_{A,B}$ also remains unchanged. For each species of gas, the only change is the volume, which expands to the total volume V .

From 0.1, the change in entropy in a process where only the volume changes is

$$(0.2) \quad \Delta S = S_f - S_i = Nk \ln \frac{V_f}{V_i}$$

The entropy changes for the two gases is therefore

$$(0.3) \quad \Delta S_A = (1-x)Nk \ln \frac{V}{(1-x)V} = -(1-x)Nk \ln(1-x)$$

$$(0.4) \quad \Delta S_B = xNk \ln \frac{V}{xV} = -xNk \ln x$$

Thus the total entropy change after mixing, called, appropriately, the *entropy of mixing*, is

$$(0.5) \quad \Delta S_{\text{mixing}} = -Nk [x \ln x + (1-x) \ln (1-x)]$$

[Note that both logarithms are negative since $0 < x < 1$, so $\Delta S_{\text{mixing}} > 0$.] If $x = \frac{1}{2}$ so that we start out with 2 equal quantities of gases, the formula reduces to

$$(0.6) \quad \Delta S_{\text{mixing}} = Nk \ln 2$$

This is the same result as equation 2.54 in Schroeder, since in that equation his N is the number of molecules of *each* gas, not the total number.

It's worth noting that this formula applies only if the two gases are different, that is, they are distinguishable. If the two gases are the same, there is essentially no change in entropy when we remove the partition. The situation is similar to Example 3 in our earlier post which dealt with two Einstein solids. Before we remove the partition, the gas in each portion of the volume is overwhelmingly likely to be at or near its most probable state. After removing the partition, the combined gas is also almost certain to be at or near the most probable macrostate for the overall system. Since the gas molecules are indistinguishable, it's virtually impossible to tell the difference between the states before and after the partition is removed, so the entropy of the two systems are virtually identical. [I don't understand Schroeder's explanation following his equation 2.56, where he tries to explain the difference by doubling the amount of gas in what appears to be a fixed volume. This isn't what happens if you start with a fixed amount of gas divided into two cells and then remove the partition.]

Another way of looking at it is as follows. Suppose we start with a number N of identical molecules. (This argument applies to any system in which the molecules all have similar properties and interact with each other in the same way, not just to ideal gases.) The entropy of this system is some value S_0 which may or may not be easy to calculate. Now suppose that at some point in time, we magically change N_A of these molecules to a different species (which has similar properties to the original species as mentioned). The entropy will increase by the number of distinct ways we can choose to locate these N_A molecules among the N places available. (The entropy due to the number of possible locations and momenta of the molecules won't change when we replace N_A of the molecules by a different species, since that is already accounted for by S_0 . We're interested only in the *extra* entropy generated by introducing a second species of molecule.) The number of ways of choosing N_A locations from a total of N is just $\binom{N}{N_A}$ so the entropy of mixing is

$$(0.7) \quad \Delta S_{mixing} = k \ln \binom{N}{N_A}$$

Using Stirling's approximation for large N , and taking $N_A = (1-x)N$ as before, we get

$$(0.8) \quad \Delta S_{mixing} \approx k \ln \left[\frac{\sqrt{2\pi N} N^N e^{-N}}{2\pi N \sqrt{x(1-x)} N^N x^{xN} (1-x)^{(1-x)N}} \right]$$

$$(0.9) \quad = -k \left[\frac{1}{2} \ln(2\pi N x(1-x)) - xN \ln x - (1-x)N \ln(1-x) \right]$$

$$(0.10) \quad \approx -Nk [x \ln x + (1-x) \ln(1-x)]$$

(we've neglected the first term in the second line as for large N it is negligible compared to the last two terms) which is the same as 0.5.

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