GIBBS FREE ENERGY OF A MIXTURE OF TWO IDEAL GASES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.56.

To study phase changes of mixtures of substances, rather than pure substances on their own, it's best to start by looking at the Gibbs free energy of the mixture. If we start with a collection of molecules of two types, A and B, that are initially separated but whose total number $N_A + N_B = N$ is fixed. Since the two populations are separated, the total Gibbs energy is just the sum of the energies of the two individual populations. If population B makes up a fraction x and A a fraction $1-x$ of the total, then

$$G = (1-x)\,G_A^{\circ} + xG_B^{\circ} \tag{1}$$

What happens if we now mix the two populations, but keep the pressure and temperature constant? The Gibbs energy is defined as

$$G \equiv U + PV - TS \tag{2}$$

It's possible that the energy U will change due to interactions between the two species being different than interactions between molecules of the same species. It's also possible that the volume will change, if the two species either attract or repel each other differently than molecules of the same species. The biggest change, however, is likely to come from a change in entropy, because with the two populations mixed there are now a great many more ways that the molecules can be arranged.

As we saw earlier, if the two substances are ideal gases at the same pressure and temperature and we allow them to mix so that the total volume is unchanged, the change in entropy is

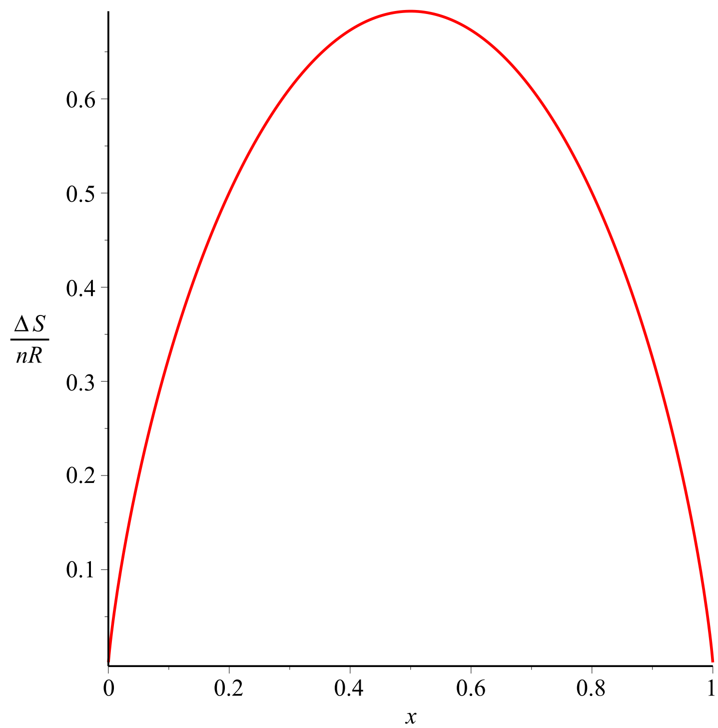
$$\begin{aligned}
\Delta S_{mixing} &= -Nk\left[x\ln x + (1-x)\ln(1-x)\right] && (3)\\
&= -nR\left[x\ln x + (1-x)\ln(1-x)\right] && (4)
\end{aligned}$$

where n is the total number of moles of both species and R is the gas constant.

If we ignore changes in U and V, then the Gibbs energy after mixing is

$$G=(1-x)G_A^\circ+xG_B^\circ+nRT\left[x\ln x+(1-x)\ln(1-x)\right] \tag{5}$$

The change in entropy looks like this:

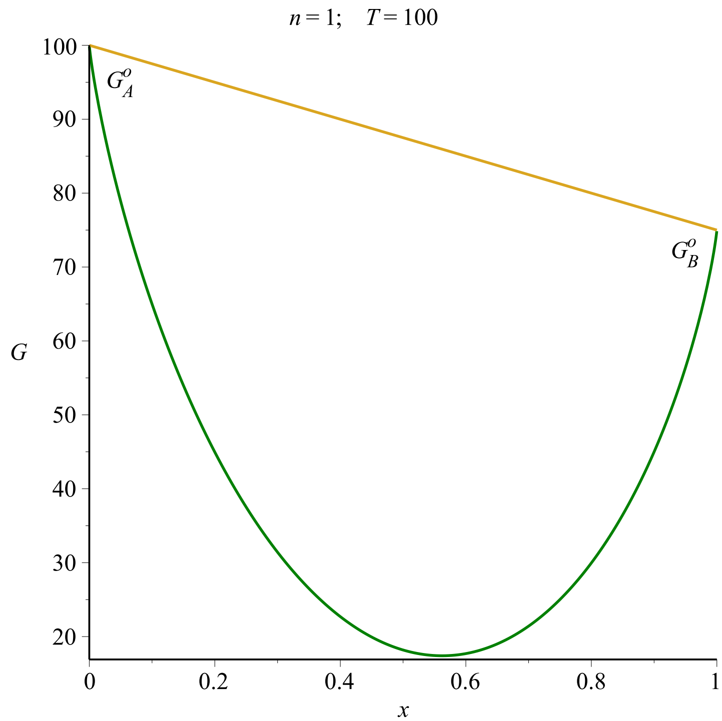


The slopes at the two ends are actually infinite, as we can see by taking the derivative of 4:

$$\frac{1}{nR}\frac{d\Delta S_{mixing}}{dx}=-\ln x+\ln(1-x)=\ln\frac{1-x}{x} \tag{6}$$

As $x\to0$, $\frac{1-x}{x}\to+\infty$ so the log also tends to $+\infty$. As $x\to1$, $\frac{1-x}{x}\to0$ and the log tends to $-\infty$.

A comparison of 1 and 5 looks like this:



Here we've taken $G_A^o = 100$, $G_B^o = 75$, $n = 1$ and $T = 100$. The yellow line shows the Gibbs energy from 1, where the two populations are unmixed. The green curve shows 5, where the two populations are mixed. Since the energy for the mixture is lower (because of the increase in entropy), it is the favoured state.

The Gibbs energy also has infinite slopes at $x = 0$ and 1:

$$\frac{dG}{dx} = -G_A^o + G_B^o + nRT\ln\frac{x}{1-x} \tag{7}$$

Because the numerator and denominator of the log have swapped places from 6, the slope at $x = 0$ is now $-\infty$ and the slope at $x = 1$ is now $+\infty$.

The infinite slopes show that even if the proportion of one of the species is very small, there is a very large increase in entropy when the two species are allowed to mix, so there is a strong tendency for this to occur.

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