

Entropy of Mixing, What Does Entropy Measure?

and for gas number 2,

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2} \quad (3b)$$

The total entropy change is the sum of these two individual entropy changes,

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2} \quad (4)$$

Equation 4 could be used for calculations, but it is not in the form that we will see in other contexts. To obtain the usual form factor the R out of Equation 4 and invert the argument of the logarithms,

$$\Delta S_{\text{mix}} = -R \left(n_1 \ln \frac{V_1}{V_1 + V_2} + n_2 \ln \frac{V_2}{V_1 + V_2} \right) \quad (5)$$

Since we are doing a calculation for ideal gases, notice that the argument of the first logarithm in Equation 5 can be written,

$$\frac{V_1}{V_1 + V_2} = \frac{\frac{n_1 R T}{p}}{\frac{n_1 R T}{p} + \frac{n_2 R T}{p}} = \frac{n_1}{n_1 + n_2} = X_1, \quad (6)$$

where X_1 is the mole fraction of component 1. There is an equivalent expression for the argument of the second logarithm. The entropy of mixing becomes,

$$\Delta S_{\text{mix}} = -R (n_1 \ln X_1 + n_2 \ln X_2). \quad (7)$$

Equation 7 is also suitable for calculations, but it is not yet in the standard form. To obtain the standard form write the total number of moles $n_1 + n_2$ as n and multiply and divide equation 7 by n . The result is

$$\Delta S_{\text{mix}} = -nR (X_1 \ln X_1 + X_2 \ln X_2). \quad (8)$$

Equation 8 is the same form that we will find when we derive an expression for the entropy of mixing ideal solutions and it is the same form that Shannon found for the "entropy of a message" in his famous series of papers on information theory.

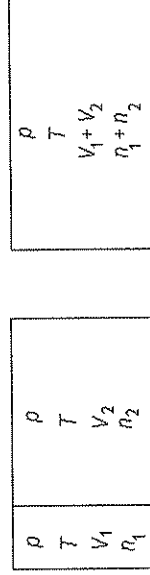
If the two gases were not at the same initial pressure you would have to introduce some extra steps. Expand or compress one of the gases to bring it to the pressure of the other gas, mix the gases, and then compress or expand the mixture to bring it to the correct final volume and pressure.

Entropy of Mixing, What Does Entropy Measure?

Second Law Applications - Equilibrium and Entropy Changes

Entropy of Mixing (Ideal Gases)

Visualize that we have a container divided into two compartments. In one compartment we have n_1 moles of an ideal gas, gas 1, at pressure, p and temperature, T . In the other compartment we have n_2 moles of another ideal gas, gas 2, at the same p and T .



If we remove the partition the gases will begin to diffuse into each other and the system will eventually reach the state where both gases are uniformly distributed throughout the container. This is clearly an irreversible process so that we would expect that the entropy would increase.

To calculate the entropy change we must find a reversible path to carry out the process, even if the path is fictitious. Imagine that we can devise a process that will expand one gas reversibly and isothermally, but leave the other gas undisturbed. We know how to calculate the change in entropy for the reversible isothermal expansion of an ideal gas.

Recall that $dU = 0$ for the isothermal expansion of an ideal gas. Then,

$$dU = TdS - pdV = 0. \quad (1)$$

So,

$$\begin{aligned} TdS &= pdV \\ dS &= \frac{p}{T} dV \\ &= \frac{nR}{V} dV, \end{aligned} \quad (2a, b, c)$$

for an ideal gas. So, for gas number 1 in our fictitious isothermal expansion we have,

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1}, \quad (3a)$$

If the two gases are not at the same temperature and pressure it is more complicated. You must find the final temperature using heat balance, reversibly cool and heat the two gases respectively to the same temperature, expand or contract on of the gases, mix them, and then expand or contract the mixture to the appropriate volume.

Equation 8 can easily be extended to more than two gases,

$$\Delta S_{\text{mix}} = -nR(X_1 \ln X_1 + X_2 \ln X_2 + X_3 \ln X_3 + \dots). \quad (9)$$

Example - The molar entropy of dry air

The composition of dry air is approximately 78% N₂, 21% O₂, and 1% Ar by volume (which is the same as mole percent). What is the molar entropy of mixing of air?

$$\begin{aligned} \Delta S_{\text{mix,air}} &= 1 \text{ mol} \times 8.314 \frac{\text{J}}{\text{K mol}} (0.78 \ln 0.78 + 0.21 \ln 0.21 + 0.01 \ln 0.01) \\ &= 4.7 \frac{\text{J}}{\text{K}}. \end{aligned}$$

What Does Entropy Measure?

Entropy measures disorder.

If we look at the processes we have seen which have positive entropy changes we can see that in each case an increase in entropy is associated with an increase in disorder.

An isothermal expansion gives the molecules more room to move around in, the molecules are less localized.

Increasing the temperature increases the average speeds of the molecules. The molecules are said to be more disordered in "velocity space" (or momentum space).

Mixing gases (or liquids) intersperses the molecules among each other increasing the disorder.

Phase changes, such as going from a solid to a liquid or a gas, or from a liquid to a gas, increase the entropy because gases are more disordered than solids or liquids and liquids are more disordered than solids.

For example, the entropy of fusion of 1.00 mol of ice at 273.15 (heat of fusion is 6.008 kJ/mol) is

$$\Delta S_{\text{fus}} = \frac{6008 \text{ J}}{273.15 \text{ K}} = 22.0 \frac{\text{J}}{\text{K}}.$$

Vaporization of liquids has a large positive entropy of vaporization because gases are greatly disordered compared to liquids. A typical value is obtained from the vaporization of benzene at its boiling point.

The heat of vaporization is 30.8 kJ at the boiling point, 353.1K. The entropy of vaporization is

$$\Delta S_{\text{vap}} = \frac{30800 \text{ J}}{353.1 \text{ K}} = 87.2 \frac{\text{J}}{\text{K}}.$$

It is interesting that the entropy of vaporization of many substances at their boiling points is close to about 86 J/K. (Water and helium are exceptions.) This phenomenon is called "Trouton's rule." It is easily understood on the basis of entropy being a measure of disorder. The vaporization process essentially "creates" a mole of disordered molecules (the gas) from a mole of highly ordered molecules (the solid or liquid). The gases are all at one atmosphere pressure because we are at their normal boiling point.

WRS

From here you can:

[Return to the local Table of Contents.](#)

[Return to the Table of Contents for the Dynamic Text, or](#)

[Return to the WRS Home Page.](#)

Copyright 2004, W. R. Salzmann
Permission is granted for individual, noncommercial use of this file.
salzmann@arizona.edu
Last updated 09 Jul 04
salzmannindex