ENTROPY: A FEW EXAMPLES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 2.34 - 2.36.

The entropy of a substance is given as

$$S = k\ln\Omega \tag{1}$$

where Ω is the number of microstates accessible to the substance.

For a 3-d ideal gas, this is given by the Sackur-Tetrode formula:

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

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.

Although this formula looks a bit complicated, we can see that increasing any of V, U or N increases the entropy. For an isothermal expansion, the gas expands quasistatically so that its temperature stays constant. This means that $U = \frac{3}{2}NkT$ also stays constant, so that only the volume changes. Since the gas is doing work W by expanding, the energy for the work must be provided by an amount of heat Q input into the gas to maintain the temperature as constant. This heat is given by the formula

$$Q = NkT\ln\frac{V_f}{V_i} \tag{3}$$

where V_i and V_f are the initial and final volumes.

However, from 2, the change in entropy in a process where only the volume changes is

$$\Delta S = S_f - S_i = Nk\ln\frac{V_f}{V_i} \tag{4}$$

Combining these two equations gives

$$\Delta S = \frac{Q}{T} \tag{5}$$

This relation is valid for the case where the expanding gas does work, so that heat must be input to provide the energy for the work. In a free expansion, the gas expands into a vacuum so does no work (well, technically, after some of the gas has entered the vacuum area, it's no longer a vacuum so that *some* work is done, but we'll assume the vacuum area is very large so we can neglect this). In this case, the internal energy U still doesn't change, since the gas neither absorbs any heat nor does any work, so $\Delta U = Q + W = 0$. However, the volume occupied by the gas *does* increase (and it's the only thing that changes) so 4 is still valid, although 5 is not.

Another property of 2 is that if the energy U drops low enough, the log term can decrease below $-\frac{5}{2}$ making S negative. This isn't possible, so the Sackur-Tetrode equation must break down at low energies. For a monatomic ideal gas, $U = \frac{3}{2}NkT$, so this implies that things go wrong for low temperatures. For example, suppose we have a mole of helium and cool it (assuming it remains a gas). Then the critical temperature is found from

$$-\frac{5}{2} = \ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) \tag{6}$$

$$T_{crit} = \frac{h^2}{2\pi mk}\left(\frac{N}{V}e^{-5/2}\right)^{2/3} \tag{7}$$

If we start at room temperature $T = 300$ K and atmospheric pressure $P = 1.01 \times 10^5$ Pa, and can hold the density N/V fixed, this will give an actual temperature at which the entropy becomes zero. The density is

$$\frac{N}{V} = \frac{P}{kT} = 2.44 \times 10^{25}\ \mathrm{m}^{-3} \tag{8}$$

The mass of a helium atom is 4×10^{-3} kg mol$^{-1}/6.02 \times 10^{23}$, so plugging in the other values gives

$$T_{crit} = 0.012\ \mathrm{K} \tag{9}$$

In fact, helium liquefies at around 4 K, so it appears that 2 might actually be valid for the region where helium remains a gas.

As a final example, we can observe that the entropy of an ideal gas is Nk multiplied by a logarithm, and of an Einstein solid is also Nk multiplied by a logarithm (because $\Omega \approx (qe/N)^N$ for high-temperature solids). For any macroscopic object, N is a large number and the logarithm is much smaller, so for a rough order-of-magnitude estimate of the entropy, we can neglect the log term and take $S \sim Nk$. A few such estimates are:

For a 1 kg book, we can take it to be 1 kg of carbon, with a molar mass of 12×10^{-3} kg mol^{-1}, so the entropy of a book is around

$$S\sim\frac{6.02\times10^{23}}{12\times10^{-3}}(1)\left(1.38\times10^{-23}\right)=692\text{ J K}^{-1} \tag{10}$$

For a 400 kg moose, which we can approximate by 400 kg of water with molar mass of around 18×10^{-3} kg mol^{-1}, we have

$$S\sim\frac{6.02\times10^{23}}{18\times10^{-3}}(400)\left(1.38\times10^{-23}\right)=1.85\times10^{5}\text{ J K}^{-1} \tag{11}$$

For the sun, we can take it to be 2×10^{30} of ionized hydrogen (protons) with molar mass of 10^{-3} kg mol^{-1}. The entropy is around

$$S\sim\frac{6.02\times10^{23}}{10^{-3}}\left(2\times10^{30}\right)\left(1.38\times10^{-23}\right)=1.66\times10^{34}\text{ J K}^{-1} \tag{12}$$

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