Phys 335:

Problem 2.35. According to the Sackur-Tetrode equation, the entropy of a monatomic ideal gas can become *negative* when its temperature (and hence its energy) is sufficiently low. Of course this is absurd, so the Sackur-Tetrode equation must be invalid at very low temperatures. Suppose you start with a sample of helium at room temperature and atmospheric pressure, then lower the temperature holding the density fixed. Pretend that the helium remains a gas and does not liquefy. Below what temperature would the Sackur-Tetrode equation predict that S is negative? (The behavior of gases at very low temperatures is the main subject of Chapter 7.)

Phys 335:
Problem 2.35

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

$S = k\ln\Omega$ is always ≥ 0.

But the term in $\ln(\ )$ could get negative for small enough argument.

What conditions would give $S = 0$? Consider Helium - a monatomic ideal gas, initially at $p_i = 1$ atm and room temperature $T_i \approx 300$ K. Suppose you keep the density $\frac{N}{V}$ fixed but lower T.

At what temperature will $S = 0$?

Want $\ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\right)^{3/2}\left(\frac{U}{N}\right)^{3/2}\right) = -5/2$

$$\frac{V}{N}\left(\frac{4\pi m}{3h^2}\right)^{3/2}\left(\frac{U}{N}\right)^{3/2} = e^{-5/2}$$

recall

$U = \frac{3}{2}NkT$, so $\frac{U}{N} = \frac{3}{2}kT$. Also,

$\frac{V}{N} = \frac{V_i}{N_i} = \frac{kT_i}{p_i}$, since the density is constant and the system follows the ideal gas law.

$$\therefore \left(\frac{kT_i}{p_i}\right)\left(\frac{4\pi m}{3h^2}\right)^{3/2}\left(\frac{3}{2}kT\right)^{3/2} = e^{-5/2}$$

solve for T.

$$\left(\frac{3}{2}kT\right)^{3/2} = \left(\frac{p_i}{kT_i}\right)\left(\frac{3h^2}{4\pi m}\right)^{3/2} e^{-5/2}$$

$$\frac{3}{2}kT = \left(\frac{p_i}{kT_i}\right)^{2/3}\left(\frac{3h^2}{4\pi m}\right) e^{-5/3}$$

$$T = \frac{2}{3k}\left(\frac{p_i}{kT_i}\right)^{2/3}\left(\frac{3h^2}{4\pi m}\right) e^{-5/3}$$

$$T = \left(\frac{p_i}{kT_i}\right)^{2/3}\frac{h^2}{2\pi m k} e^{-5/3}$$

There are no obvious clever units shortcuts here. It might be simplest to convert everything to the usual SI basic units.

(See the Mathematica notebook for how to incorporate units into Mathematica.)

$p_i = 1\,\text{atm} = 1.01\times10^5\ \text{N/m}^2$
$T_i = 300\ \text{K}$
$k = 1.381\times10^{-23}\ \text{J/K}$

$$\frac{p_i}{kT_i} = 2.438\times10^{25}\ \frac{\text{N}}{\text{m}^2\,\text{J}}$$

units: $\frac{\text{N}}{\text{m}^2\text{J}} = \frac{\text{N}}{\text{m}^2(\text{N}\cdot\text{m})} = \frac{1}{\text{m}^3}$

This was the original density: $2.438\times10^{25}/\text{m}^3$

$h = 6.626\times10^{-34}\ \text{J}\cdot\text{s}$

$$m = 4.0\times10^{-3}\frac{\text{kg}}{\text{mole}}\times\frac{1\,\text{mole}}{6.022\times10^{23}\,\text{atoms}} = 6.64\times10^{-27}\,\text{kg}$$

$$T = \left(\frac{P_i}{kT_i}\right)^{2/3} \frac{h^2}{2\pi m k} e^{-5/3}$$

$$T = \left(2.438 \times 10^{25}/m^3\right)^{2/3} \frac{(6.626\times10^{-34}\ J\cdot s)^2}{(2\cdot\pi)(6.64\times10^{-27}\ kg)(1.381\times10^{-23}\ J/k)} e^{-5/3}$$

$$\boxed{T = 0.012\ K}$$

Helium actually liquifies around 4K, so this negative entropy doesn't happen. At these low temperatures, the ideal gas law no longer applies. The weak interactions between He atoms can no longer be ignored.