

ENTROPY OF DISTINGUISHABLE MOLECULES

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

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (1)$$

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.

One of the assumptions made in deriving this formula is that the molecules are indistinguishable, so for any configuration of the molecules in position and momentum space, interchanging any of the molecules makes no difference. This assumption introduces the factor of $N!$ in the denominator of the multiplicity function (Schroeder's equation 2.40):

$$\Omega \approx \frac{V^N (2\pi mU)^{3N/2}}{h^{3N} N! (3N/2)!} \quad (2)$$

The Sackur-Tetrode formula is obtained from this by applying Stirling's approximation to the two factorials in the denominator and throwing away small factors. If we now assume that the molecules are all distinguishable, we can follow through the derivation, but without the $N!$. We start with

$$\Omega \approx \frac{V^N (2\pi mU)^{3N/2}}{h^{3N} (3N/2)!} \quad (3)$$

We find that the $\frac{5}{2}$ term in 1 changes to $\frac{3}{2}$ and the $\frac{V}{N}$ factor in the logarithm loses its N , so we get

$$S_{\text{dist}} = Nk \left[\ln \left(V \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{3}{2} \right] \quad (4)$$

To see what difference this would make, we can compute the entropy of a mole of *distinguishable* helium atoms at room temperature (300 K) and 1 atmosphere ($1.01 \times 10^5 \text{ N m}^{-2}$) and compare it with the value of 126 J K^{-1} for real, indistinguishable helium atoms given in Schroeder's book. We

can use most of the numbers from our earlier calculation of the entropy of argon:

$$V = \frac{nRT}{P} = \frac{(1)(8.31)(300)}{1.01 \times 10^5} = 0.025 \text{ m}^3 \quad (5)$$

The internal energy of a monatomic gas is $\frac{1}{2}kT$ per molecule per degree of freedom, so for one mole we have

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT = 3739 \text{ J} \quad (6)$$

The mass of a mole of helium is 4.0026×10^{-3} kg, so with $N = 6.02 \times 10^{23}$ we have

$$m = \frac{4.0026 \times 10^{-3}}{6.02 \times 10^{23}} = 6.65 \times 10^{-27} \text{ kg} \quad (7)$$

We get

$$S_{\text{dist}} = (6.02 \times 10^{23}) (1.38 \times 10^{-23}) \left(67.45 + \frac{3}{2} \right) = 573 \text{ J K}^{-1} \quad (8)$$

As we'd expect, the entropy is significantly higher if the molecules are distinguishable, since there are many more microstates available to the system.