ENTROPY OF AN IDEAL GAS; SACKUR-TETRODE EQUATION

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 2.31 - 2.33.

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 Schroeder's equation 2.40:

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

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. We can further approximate this formula by using Stirling's approximation for the factorials:

$$N! \approx \sqrt{2\pi N} N^N e^{-N} \tag{3}$$

$$(3N/2)! \approx \sqrt{3\pi N} \left(\frac{3N}{2}\right)^{3N/2} e^{-3N/2} \tag{4}$$

We get

$$\Omega \approx \frac{V^N (\pi mU)^{3N/2}}{h^{3N}} \frac{2^{3N} e^{5N/2}}{\sqrt{6} 3^{3N/2} \pi N^{5N/2+1}} \tag{5}$$

When N is large, we can throw away a couple of factors and take the logarithm:

$$\Omega \approx \frac{V^N (\pi m U)^{3N/2}}{h^{3N}} \frac{2^{3N} e^{5N/2}}{3^{3N/2} N^{5N/2}} \tag{6}$$

$$\ln \Omega = N \ln \left(V \left(\frac{\pi m U}{3} \right)^{3/2} \left(\frac{2}{h} \right)^3 \frac{1}{N^{5/2}} \right) + \frac{5N}{2} \tag{7}$$

$$= N \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{8}$$

This gives the entropy of an ideal gas as

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \tag{9}$$

which is known as the Sackur-Tetrode equation.

Example 1. A variant of this equation can be derived in a similar way for the 2-d ideal gas considered earlier. In that case we had

$$\Omega \approx \frac{(\pi A)^N}{(N!)^2 h^{2N}} \left(\sqrt{2mU} \right)^{2N} \tag{10}$$

where A is the area of the gas. Using Stirling's approximation as before, we get

$$\Omega \approx \frac{(\pi A)^N}{2\pi N^{2N+1} e^{-2N} h^{2N}} \left(\sqrt{2mU} \right)^{2N} \tag{11}$$

$$\approx \frac{(\pi A)^N}{N^{2N} e^{-2N} h^{2N}} (2mU)^N \tag{12}$$

$$S = k \ln \Omega = Nk \left[\ln \frac{2\pi m A U}{(hN)^2} + 2 \right] \tag{13}$$

Example 2. Schroeder gives the entropy of a mole of helium at room temperature and atmospheric pressure as $S = 126 \text{ J K}^{-1}$. For another monatomic gas such as argon, we can work out the same thing. From the ideal gas law, at a pressure of $1.01 \times 10^5 \text{ N m}^{-2}$ and temperature of 300 K, one mole occupies a volume of

$$V = \frac{nRT}{P} = \frac{(1)(8.31)(300)}{1.01 \times 10^5} = 0.025 \text{ m}^3 \tag{14}$$

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

$$U = \frac{3}{2}NkT = \frac{3}{2}nRT = 3739 \text{ J} \tag{15}$$

The mass of a mole of argon is 39.948×10^{-3} kg, so with $N = 6.02 \times 10^{23}$ we have

$$m = \frac{39.948 \times 10^{-3}}{6.02 \times 10^{23}} = 6.64 \times 10^{-26} \text{ kg} \tag{16}$$

Plugging these values into 9, the entropy comes out to

$$\begin{aligned} S &= \left(6.02 \times 10^{23}\right)\left(1.38 \times 10^{-23}\right)\left(\ln 1.02 \times 10^{7} + 2.5\right) && (17) \\ &= 155 \text{ J K}^{-1} && (18) \end{aligned}$$

This is a bit higher than the value for helium because of argon's higher mass.

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