AVOGADRO'S NUMBER FROM THERMAL CONDUCTIVITY IN AN IDEAL GAS

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 1.65.

We can get a rough estimate of Avogadro's number from the thermal conductivity and other macroscopic quantities measurable for an ideal gas. Schroeder's derivation of the thermal conductivity formula gives the result

$$k_t = \frac{C_V}{2V}\ell\bar{v} \tag{1}$$

Suppose we set up the system so that we have a box of volume V and cross-sectional area A. We know that the average speed $\bar{v}$ is approximately the rms speed, which is

$$\bar{v} \approx v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3NkT}{Nm}} = \sqrt{\frac{3PV}{M}} \tag{2}$$

where M is the total mass of the gas. If we measure the thermal conductivity and heat capacity, we can then get the mean free path:

$$\ell = \frac{2Vk_t}{C_V\bar{v}} = \frac{2k_t}{C_V}\sqrt{\frac{MV}{3P}} \tag{3}$$

Schroeder's expression for ℓ is based on the idea that the mean path length is equal to the length of a cylinder of radius equal to the molecule's diameter and volume equal to the average volume per molecule V/N, so that

$$\ell = \frac{1}{4\pi r^2}\frac{V}{N} \tag{4}$$

where r is the radius of the molecule. To get N from this formula, we need to know r, but this is a microscopic quantity which we're assuming we don't know. I can't see any way of progressing from here unless we take a different value for ℓ. Since we're after only a rough approximation of Avogadro's number, we can take ℓ to be the average distance between molecules, rather than the average distance between collisions. That is

$$\ell \approx \left(\frac{V}{N}\right)^{1/3} \tag{5}$$

We can now combine this with 3 to get an estimate for the number of molecules N:

$$N \approx \left(\frac{C_V}{2k_t}\right)^3 \left(\frac{3P}{MV}\right)^{3/2} V = \frac{1}{\sqrt{V}} \left(\frac{C_V}{2k_t}\right)^3 \left(\frac{3P}{M}\right)^{3/2} \tag{6}$$

Assuming we know the gas constant R, we can get the number of moles from the ideal gas law

$$n = \frac{PV}{RT} \tag{7}$$

so Avogadro's number is roughly

$$N_A = \frac{N}{n} \approx RT\sqrt{P} \left(\frac{C_V}{2k_t}\right)^3 \left(\frac{3}{MV}\right)^{3/2} \tag{8}$$

As a check on this formula, we can verify that it's dimensionless. RT has the dimensions of PV, so dimensionally, the quantity is equivalent to

$$\begin{aligned} \left(\frac{C_V}{k_t}\right)^3 \left(\frac{P}{M}\right)^{3/2} \frac{1}{\sqrt{V}} &\rightarrow \left[\frac{\text{energy/K}}{\text{energy/s m K}}\right]^3 \left[\frac{\text{force/m}^2}{\text{kg}}\right]^{3/2} \frac{1}{\text{m}^{3/2}} && (9) \\ &= \left[\text{s}^3\text{m}^3\right] \left[\text{m}^{-1}\text{s}^{-2}\right]^{3/2} \text{m}^{-3/2} && (10) \\ &= 1 && (11) \end{aligned}$$

Thus the dimensions check out.

I don't know if this is the solution Schroeder had in mind, or whether it's possible to get N_A using the formula 4 for the mean free path. If we're not allowed to know a priori any microscopic quantities, that means we don't know k (Boltzmann's constant), m (the mass of a single molecule) or r (the radius of a molecule). Together with N, that makes 4 unknowns, so we need 4 independent equations to find them. Comments welcome.

Remark 1. Thanks for the quick reply. I think what he's saying is that we can take $\frac{4}{3}\pi r^3$ to be the volume per molecule in the liquid phase, so that

$$\frac{4}{3}\pi r^3 = \frac{V_{liq}}{N}$$

If we know that the volume in the gas phase is 1000 times that in the liquid, then

$$\ell \approx \frac{r}{3} \frac{V_{gas}}{N} \frac{N}{V_{liq}} = \frac{1000}{3} r$$

Hence ℓ is about 300 - 400 times larger than r. It's interesting that he doesn't actually work out the numbers, though (but of course neither did I), so it's hard to say how good an estimate of N_A this is.