

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

$$(1) \quad k_t = \frac{C_V}{2V} \ell \bar{v}$$

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

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

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:

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

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

$$(4) \quad \ell = \frac{1}{4\pi r^2} \frac{V}{N}$$

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

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

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

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

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

$$(7) \quad n = \frac{PV}{RT}$$

so Avogadro's number is roughly

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

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

$$(9) \quad \left(\frac{C_V}{k_t}\right)^3 \left(\frac{P}{M}\right)^{3/2} \frac{1}{\sqrt{V}} \rightarrow \left[\frac{\text{energy/K}}{\text{energy/s m K}}\right]^3 \left[\frac{\text{force/m}^2}{\text{kg}}\right]^{3/2} \frac{1}{\text{m}^{3/2}}$$

$$(10) \quad = [\text{s}^3 \text{m}^3] [\text{m}^{-1} \text{s}^{-2}]^{3/2} \text{m}^{-3/2}$$

$$(11) \quad = 1$$

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

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

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.