

DIFFUSION IN AN IDEAL GAS - FICK'S LAW

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Diffusion is the process by which the concentration of some substance varies over time by means of the drifting of molecules through a volume. We must distinguish between diffusion and other methods by which molecular concentrations can vary, such as convection (macroscopic motion of large chunks of the material due to such things as temperature differences) and mechanical stirring.

We can treat diffusion in ideal gases in a similar way to that used for thermal conductivity and viscosity. In diffusion, we are interested in the movement of molecular concentration, rather than energy transport (as in thermal conductivity) or momentum transport (as in viscosity). The derivation of a crude formula for diffusion, however, follows the same steps as in the other two cases.

Consider a thin slab of gas of cross-sectional area A . We divide the box in half so that the number of molecules on one side of the partition is N_1 and on the other side is N_2 . We're assuming that the whole box is at a constant temperature T , and that Schroeder's approximations for the mean free path ℓ and average speed \bar{v} are valid:

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

$$\bar{v} \approx \sqrt{\frac{3kT}{m}} \quad (2)$$

where r is the molecular radius and m the mass of one molecule. Since only half the molecules will, on average, be moving towards the partition, the net number ΔN of molecules that cross the partition in a time Δt , which is the time it takes a molecule to move distance ℓ , is

$$\Delta N = \frac{1}{2} (N_1 - N_2) \quad (3)$$

If the gradient in molecule number is dN/dx then we have

$$\Delta N = \frac{1}{2} \ell \frac{dN}{dx} \quad (4)$$

and the net rate at which molecules cross the partition per unit area, known as the *flux* J_x , is

$$|J_x| = \frac{\Delta N}{A\Delta t} = \frac{1}{2} \frac{\ell}{A\Delta t} \frac{dN}{dx} = \frac{1}{2} \frac{\ell^2}{\ell A\Delta t} \frac{dN}{dx} = \frac{1}{2} \frac{\ell}{V} \bar{v} \frac{dN}{dx} = \frac{1}{2} \ell \bar{v} \frac{dn}{dx} \quad (5)$$

where $n = N/V$ is the molecular concentration. The absolute value indicates that this is the magnitude of the flux. As the flux is in the opposite direction to the gradient, we will have

$$J_x = -\frac{1}{2} \ell \bar{v} \frac{dn}{dx} \quad (6)$$

The quantity $\frac{1}{2} \ell \bar{v}$ is an approximation for the *diffusion constant* D for an ideal gas, and has units of m^2s^{-1} . The more general form of this equation

$$J_x = -D \frac{dn}{dx} \quad (7)$$

is known as *Fick's law*.

Example 1. For air at room temperature, using the values from Schroeder's book,

$$D \approx \frac{1}{2} (1.5 \times 10^{-7}) (500) = 3.75 \times 10^{-5} \text{m}^2\text{s}^{-1} \quad (8)$$

The measured value is around 2×10^{-5} so this isn't too far off for a rough estimate.

From the values for ℓ and \bar{v} above, we have

$$D = \frac{1}{2} \ell \bar{v} = \frac{1}{8\pi r^2} \frac{V}{N} \sqrt{\frac{3kT}{m}} = \frac{1}{8\pi r^2} \frac{(kT)^{3/2}}{P} \sqrt{\frac{3}{m}} \quad (9)$$

At fixed pressure, $D \propto T^{3/2}$.

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