Diffusion in Solids and Fick's Laws

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Diffusion refers to the phenomenon of one species (compound, element, etc.) moving into and through another in order to minimize some chemical potential gradient. This is clearly visible in gases, where they expand to fill the available volume almost instantly, and mix very readily with other gases. With gases in solids the process takes longer, and with solids diffusing into other solids, even longer.

Fick's first and second laws of diffusion are named for Adolf Eugen Fick, a German physiologist who also invented contact lenses. The two laws describe solid state diffusion in one dimension, such as the concentration of one species in another, given a specific amount of time. This can be very useful, for example, for the case-hardening of steel. By diffusing carbon into steel via diffusion, a hardened layer (maybe only a few micrometers thick) can be created without too much trouble. Fick's first law describes diffusion at steady state, this means the source concentration never changes. Imagine having two chambers separated by a sheet of metal foil, one with with a high concentration of some gas, the other with a very low concentration. The first law would only apply if you were able to constantly supply additional more gas to the high concentration side, and move it out of the low concentration side, as it diffused through the foil, keeping both concentrations constant. The most significant impact of this situation, is that the concentration gradient is constant and progress linearly from the high concentration on the high side, to the low concentration on the low side.

Fick's second law governs non-steady state diffusion, where the gas may not pass entirely through the material, and the concentration gradient will not be linear.

Fick's First Law:

$$J = -D\left(\frac{\partial C}{\partial x}\right) \tag{1}$$

J is flux, having units of mass per length squared per second. If one were to count the cars that passed a specific point on the freeway, you'd get a flux of cars per square meter per second. For this application, we usually use atoms per square meter per second. The D term represents the ease with which the the species in question diffuses into another species, and it is also a function of temperature. The partial derivative of concentration with respect to x represents how the concentration changes with position within a material. In steady state problems this term becomes a constant.

$$J = -D\left(\frac{\Delta C}{\Delta x}\right) \tag{2}$$

Fick's Second Law:

$$\left(\frac{\partial c}{\partial t}\right) = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{3}$$

This second order differential applies to non-steady state situations, where the concentration cannot be considered to be infinite, or the material is so thick (more than a few millimeters) that the concentration on the opposite side is no longer of interest on small time scales. There are two specific solutions to this differential that are of interest, as they use boundary conditions indicating the most common conditions. First is constant surface concentration (denoted C_s).

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{4}$$

C_0 is the preexisting concentration of the diffusing species, ideally zero, but clearly not for applications like case-hardening steel with more carbon. erf is the error function, shown below. It normalizes inputs between 0 and 2.8 to values between 0 and 1, and has many other applications, and such can be called directly within some calculators and software packages.

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy \tag{5}$$

The second significant solution to the differential represents a depleting source, as if you allowed carbon to diffuse into steel for 10 hours, but did not provide additional carbon as it diffused into the material. A consequence of this is that surface concentration is not constant, and that the total amount of diffusing atoms cannot change. The term before the error function does exactly this, ensuring that the area under the curve remains constant.

$$C(x,t) - C_0 = \frac{C_0}{\sqrt{\pi Dt}} erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{6}$$

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Temperature Dependence of D

The diffusion coefficient D depends upon temperature, as energy is required for atoms to shift position. This movement has a specific activation energy (E_A), usually in electron-volt per atom, or joules per mole. D_0, the pre-exponential, is an experimentally established value for different material pairs (like Ni into Cu, or H into BCC Fe). Lastly, k is Boltzmann's constant, which must have units matching with the units of the activation energy.

$$D(t) = D_0 e^{\frac{-E_A}{kT}} \tag{7}$$

Example

Suppose we have the situation mentioned above, wherein a piece of BCC iron foil, 0.001 inches thick, separates two chambers filled with hydrogen. On one side, the concentration is $5 * 10^8$ atoms per cubic centimeter, and on the other side, $2 * 10^3$ atoms per cubic centimeter. The system is allowed to reach steady state at 650 C. Find the concentration gradient, and the flux through the foil. It is given that the standard state diffusion pre-exponential is 0.0012 square centimeters per second, and the activation energy is 3600 calories per mole. Before we begin, we need to get everything into similar units. 0.001

Inches becomes 0.00254 centimeters. 650 degrees Celsius must be expressed as 923 Kelvin. As it is stated that it has reached steady state, we can simply use Fick's first law.

$$\frac{\partial C}{\partial x} = \frac{\Delta C}{\Delta x} = \frac{5 * 10^8 - 2 * 10^3}{0.00254} \tag{8}$$

$$\frac{\partial C}{\partial x} = 1.968 * 10^{11} \tag{9}$$

To find the flux through the foil, we use the rest of Fick's first law.

$$J = -D \left(\frac{\Delta C}{\Delta x} \right) \tag{10}$$

$$J = -D * 1.968 * 10^{11} \tag{11}$$

To find the diffusion coefficient, we need to make use of the temperature and the activation energy. Note that we must also divide by Avagadro's number to change calories per mole into calories per atom, and we use the appropriate form of Boltzman's constant.

$$D(t) = D_0 e^{\frac{-E_A}{kT}} \tag{12}$$

$$D(923K) = 0.0012 * e^{\frac{-3600}{3.298*10^{-24}*923*6.023*10^{23}}} \tag{13}$$

$$D(923K) = 0.000168 \tag{14}$$

Plugging both of these in, we find the flux, with units of atoms per centimeter squared second.

$$J = -0.000168 * 1.968 * 10^{11} = 3.31 * 10^7 \tag{15}$$