6.3 Fick's Second Law: Non-Steady-State Diffusion

Steady-state diffusion is clearly a very special case, and in general you have to deal with the concentration C being a function of both time t and position x: $C = C(x, t)$. Again, we will confine ourselves to one-dimensional problems. In the most general situation, C would be a function of all three coordinates and time: $C = C(x, y, z, t)$.

The equation that describes the one-dimensional non-steady-state case is known as **Fick's Second Law**:

$$\frac{\partial C}{\partial T} = D\,\frac{\partial^2 C}{\partial x^2} \tag{6.11}$$

You will note that this equation involves so-called partial derivatives of $C(x, t)$ with respect to x and t. If you are not familiar with them, the recipe to take a partial derivative of a function is to just think of it as taking a normal derivative with respect to one variable while treating the other variable as a constant. Also, in Eq. 6.11 the assumption is made that D itself does not depend on $C(x)$, or indirectly on x, but is only a function of T as in Eq. 6.6.

Fick's Second Law is in essence an expression of the continuity of particles (or continuity of mass): It amounts to stating mathematically that the time rate of change in concentration in a small volume element is due to the sum total of particle fluxes into and out of the volume element.

Solving Eq. 6.11 is not simple, even in only one dimension. Most importantly, there is not just one solution, i.e. THE solution. Instead, there are many possible solutions, depending on the particulars of the situation. In general, a solution to Eq. 6.11 depends on the so-called initial condition, i.e. the form of $C(x, t)$ at $t = 0$, when your observation starts, and on the boundary conditions, i.e. on how the solution must behave at the physical boundaries of your observations.

We will not get into technical details of finding solutions to Eq. 6.11. Rather, we will examine the solution and its consequences for a certain important case of diffusion in materials. Based upon this discussion, we will be able to make a few further comments about non-steady-state diffusion in general.

6.3.1 Carburizing: An Approximate Solution

The case of interest involves the process of **carburizing**, which is a form of **case-hardening**. In case-hardening, the outermost layer of a workpiece is hardened selectively by local modification of the material. Carburizing realizes this effect in steel by increasing the carbon concentration in the near-surface region via diffusion. The advantage of performing this type of material modification only in the near-surface region is that the workpiece is strengthened where it is needed, at the surface, while the interior remains at its original strength thus maintaining higher toughness.

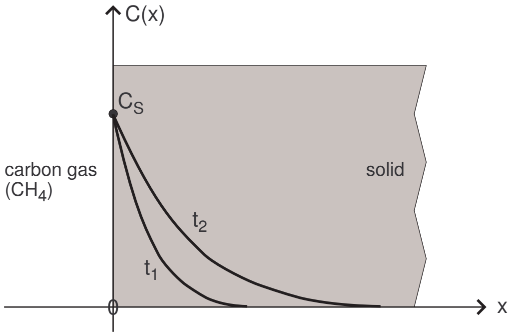

Figure 6.7: Schematic experimental setup for the carburizing process. The surface of the workpiece is at $x = 0$ and extends to very large x.

The experimental setup for the carburizing process is sketched in Fig. 6.7. The surface of the piece of iron exposed to the carbon-containing gas is located at $x = 0$, and the thickness of the piece of steel is large. (Mathematically speaking, the solid is assumed to be semi-infinite.) Most importantly, the pressure of the gas and the temperature of the iron are maintained constant, such that the concentration of carbon just inside the surface has a constant value C_S. For simplicity, we also assume that at the beginning of the process, the interior of the piece of iron does not contain any carbon. (It will be easy to relax this assumption later).

Under these conditions, carbon atoms are dissolved into the surface of the iron sample and are present at a constant concentration C_S at $x = 0$. Thus a gradient in $C(x)$ exist near the surface, so that carbon atoms diffuse gradually into the bulk of the sample. The longer we wait, the more extended the concentration profile $C(x)$ becomes, as the carbon atoms move farther and farther into the sample. Representative shapes of $C(x)$ at times t_1 and t_2 (with $t_1 < t_2$) are displayed in Fig. 6.7, .

An exact analytical solution for $C(x)$ in this problem can be given and will be discussed later, but we will examine first an approximate solution: We will assume that $C(x)$ is a straight line just as in the steady state case, except that now the slope of this line is allowed to vary with time. Fig. 6.8 suggests that this may be a reasonable approximation near the surface.

This amounts to assuming that $C(x)$ can be specified by the surface concentration C_S and the increasing length $l(t)$, which is a measure of the progress of the diffusion process. $l(t)$ can be determined as follows.

Let $C(x)$ here refer to diffusing solute atoms. Thus the total number $N(t)$ of these atoms in the sample per unit area is given by the area of the triangle with base $l(t)$ and height C_S (see Fig. 6.8).

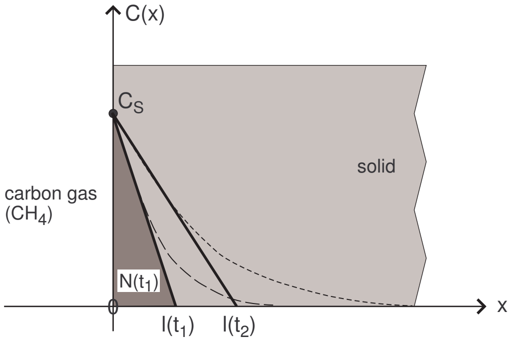

Figure 6.8: Linear approximation for $C(x)$ in the carburizing process. The change of the length l with t indicates the progress of diffusion.

$$N(t) = \frac{1}{2} C_S\, l(t) \tag{6.12}$$

$N(t)$ changes continually because more atoms are moving into the solid. Specifically, the rate of change of $N(t)$ is equal to the flux J of diffusing atoms:

$$\frac{dN}{dt} = J = -D\frac{dC}{dx} \tag{6.13}$$

where we have used Fick's First Law for the flux J. The gradient of $C(x)$ can be expressed in terms of C_S and l from Fig. 6.8, and the rate of change of $N(t)$ from Eq. 6.12:

$$\frac{1}{2} C_S \frac{dl}{dt} = -D(-\frac{C_S}{l}) \tag{6.14}$$

which can be simplified to

$$\frac{1}{2}\frac{dl}{dt} = \frac{D}{l} \tag{6.15}$$

This last equation is equivalent to

$$\frac{1}{2}\, l\, dl = D dt \tag{6.16}$$

Eq. 6.16 can be integrated easily to yield

$$\frac{1}{4} l^2 = Dt \tag{6.17}$$

and, solving for $l(t)$:

$$l(t) = 2\sqrt{Dt} \tag{6.18}$$

This is the final result for our approximate treatment of the carbonizing diffusion process: It says that the distance over which the diffusing species move into the solid with time increases as $\sqrt{t}$. In addition, $\sqrt{Dt}$ is a characteristic length for the diffusion process: It indicates the distance at which $C(x)$ has fallen off to half its value at the surface and thus denotes the width of $C(x)$.

If you are interested in the entire concentration profile $C(x)$ as a function of time t, this can be written down as

$$C(x,t) = C_S(1 - \frac{x}{l(t)}) = C_S(1 - \frac{x}{2\sqrt{Dt}}) \tag{6.19}$$

Of course it is understood that this equation is only valid for $0 \leqslant x \leqslant l(t)$. Note that in principle x and t in Eq. 6.19 are independent variables, yet they occur only as the special combination $x/2\sqrt{Dt}$ in the expression for $C(x,t)$.

6.3.2 Carburizing: The Exact Solution

Now you are ready for the exact solution of our problem. I will simply present it and discuss its consequences. The initial condition and the boundary conditions are the same as spelled out above: In essence, $C(0,t)$ remains constant at C_S for all t, and $C(x,t)$ must taper off to 0 as x becomes very large. Again, for the time being we assume that the sample contains no carbon at the start of the diffusion process.

The exact solution cannot be given as an algebraic formula, but only in the form:

$$C(x,t) = C_S(1 - \mathrm{erf}(\frac{x}{2\sqrt{Dt}})) \tag{6.20}$$

where

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du \tag{6.21}$$

The function $\mathrm{erf}(z)$ is known as the Gaussian error function. As you apply it to Eq. 6.20 and a diffusion problem, you need to set $z = \frac{x}{2\sqrt{Dt}}$.

You can see that x and t enter into the solution $C(x,t)$ as parts of the upper limit of an integral. Furthermore, and most interestingly, again they occur only in the combination of $x/2\sqrt{Dt}$! Also, note the remarkable similarity between Eqs. 6.19 and 6.20.

Let us now compare the approximate and the exact solution for $C(x,t)/C_0$, as per Eqs. 6.19 and 6.20, and using $z = x/2\sqrt{Dt}$ as a generalized independent