Lecture 7: How to determine the binary interdiffusion coefficient in real experiments

Today's topics

- Continue to understand the interdiffusion coefficient, $\tilde{D}$, as defined in Darken's equation (see Lecture 6).
- Learn how to experimentally measure the value of $\tilde{D}$: understanding the mathematic methods and how to apply the math in the data analysis.

Following what we learned in last lecture, we will learn in this lecture how to measure the interdiffusion coefficient in real experiments, which was first carried out by Kirkendall and published in 1942 (E.O. Kirkendall, "Diffusion of Zinc in Alpha Brass," Trans. AIME, 147 (1942), pp. 104-110). See the additional reading for detailed description of the experiment and data analysis.

Darken's equation: $\tilde{D} = x_A D_B^C + x_B D_A^C$

D_A^C, D_A^C are in general functions of (or dependent on) composition:

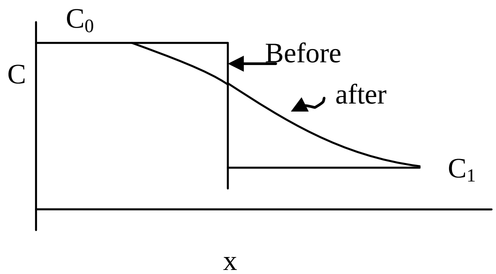
$$D_A^C = D_A \{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \} = D_A \{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \}$$

$$D_B^C = D_B \{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \} = D_B \{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \}$$

Therefore, $\tilde{D}$ is difficult to measure. It can only be determined (estimated) by graphical or numerical method (but no analytical solution).

$J_A = -\tilde{D} \frac{dc_A}{dx}$, $\qquad J_B = -\tilde{D} \frac{dc_B}{dx}$

The experimental procedure usually used for determining $\tilde{D}$ follows:
form a diffusion couple → anneal with a given time → measure composition profile, which can be done by electron probe microanalysis (EPMA) or other solid composition analysis method like XPS.



Rate of changing composition

$$\frac{\partial c_A}{\partial t} = -\frac{\partial J_A}{\partial x} = \frac{\partial}{\partial x}[\tilde{D}\frac{\partial c_A}{\partial x}]$$

$$\frac{\partial c_B}{\partial t} = -\frac{\partial J_B}{\partial x} = \frac{\partial}{\partial x}[\tilde{D}\frac{\partial c_B}{\partial x}]$$

For given Δt, c(x) can be measured, but not $\frac{\partial c}{\partial t}$

The mathematic approach to be introduced herein for determining $\tilde{D}$ was first suggested by Boltzmann, and then demonstrated by Matano --- now called **Boltzmann-Matano method**, which is based on ***graphical integration*** of diffusion equation (Fick's second law).

Fick's second law: $\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x}[\tilde{D}\frac{\partial c_A}{\partial x}]$

Let's introduce, $\lambda = \frac{x}{\sqrt{t}}$,

where x and t are independent, representing the space and time term.

Then, $d\lambda = (\frac{\partial \lambda}{\partial x})_t\, dx + (\frac{\partial \lambda}{\partial t})_x\, dt$

now, $(\frac{\partial \lambda}{\partial x})_t = \frac{1}{\sqrt{t}}$, $(\frac{\partial \lambda}{\partial t})_x = -\frac{x}{2t^{3/2}} = -\frac{\lambda}{2t}$

re-write: $$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \lambda}\cdot\frac{\partial \lambda}{\partial t} = -\frac{\lambda}{2t}\cdot\frac{\partial c}{\partial \lambda} \qquad (1)$$

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial \lambda}\cdot\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}}\cdot\frac{\partial c}{\partial \lambda}$$

Similarly, we can re-write the right term of Fick's second law above as

$$\frac{\partial}{\partial x}[\tilde{D}\frac{\partial c}{\partial x}] = \frac{\partial[\tilde{D}\frac{\partial c}{\partial x}]}{\partial \lambda}\frac{\partial \lambda}{\partial x}$$

Substituting $(\frac{\partial \lambda}{\partial x})_t = \frac{1}{\sqrt{t}}$ (as we deduced above) into above equation, we have

$$\frac{\partial}{\partial x}[\tilde{D}\frac{\partial c}{\partial x}] = \frac{\partial[\tilde{D}\frac{\partial c}{\partial x}]}{\partial \lambda}\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}}\frac{\partial}{\partial \lambda}[\tilde{D}\frac{\partial c}{\partial x}],$$

Then substituting $\frac{\partial c}{\partial x} = \frac{1}{\sqrt{t}}\cdot\frac{\partial c}{\partial \lambda}$ (as we deduced above) into above equation, we have

$$\frac{\partial}{\partial x}[\tilde{D}\frac{\partial c}{\partial x}] = \frac{\partial[\tilde{D}\frac{\partial c}{\partial x}]}{\partial \lambda}\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}}\frac{\partial}{\partial \lambda}[\tilde{D}\frac{\partial c}{\partial x}] = \frac{1}{\sqrt{t}}\cdot\frac{\partial}{\partial \lambda}[\frac{\tilde{D}}{\sqrt{t}}\cdot\frac{\partial c}{\partial \lambda}] \qquad (2)$$

Thus, using Eq. (1) and (2) to replace the left and right term of the Fick' second law equation above, we have

$$-\frac{\lambda}{2t}\frac{\partial c}{\partial \lambda} = \frac{1}{\sqrt{t}}\cdot\frac{\partial}{\partial \lambda}[\frac{\tilde{D}}{\sqrt{t}}\cdot\frac{\partial c}{\partial \lambda}]$$

For a fixed time period of annealing, t = const, the above equation can be re-written as

$$-\frac{\lambda}{2t}\frac{\partial c}{\partial \lambda} = \frac{1}{t}\cdot\frac{\partial}{\partial \lambda}[\tilde{D}\cdot\frac{\partial c}{\partial \lambda}]$$

Then,

$$-\frac{\lambda}{2}\partial c = \partial[\tilde{D}\cdot\frac{\partial c}{\partial \lambda}]$$

Integrate from C_0 to C, we have

$$\tilde{D}\left.\frac{\partial c}{\partial \lambda}\right|_c - \tilde{D}\left.\frac{\partial c}{\partial \lambda}\right|_{c_0} = -\frac{1}{2}\int_{c_0}^{c}\lambda dc$$

C_0 is far away from diffusion zone, c_0 is constant. $\left.\frac{\partial c}{\partial \lambda}\right|_{c_0} = 0$

Then, we have,

$$\tilde{D}\left.\frac{\partial c}{\partial \lambda}\right|_c = -\frac{1}{2}\int_{c_0}^{c}\lambda dc$$

So, $\tilde{D} = -\frac{1}{2}(\frac{\partial \lambda}{\partial c})_c \int_{c_0}^{c} \lambda dc$

substituting back $\lambda = \frac{x}{\sqrt{t}}$, and now t (as a fixed annealing time) is a constant, we have

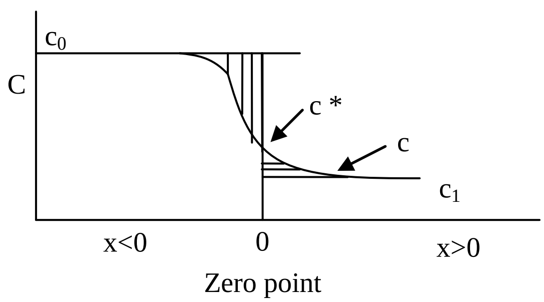
$\tilde{D}(\mathrm{c}) = -\frac{1}{2t}(\frac{\partial x}{\partial c})_c \int_{c_0}^{c} x dc$ --- *$\tilde{D}$ is a function of concentration, c.*

This is Boltzmann - Matano equation.

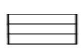
By measuring c(x) experimentally, we will be able to give $(\frac{\partial x}{\partial c})_c$ (we no longer needs to know $\frac{\partial c}{\partial t}$!)

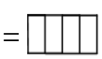
However $\int x dc$ depends on origin of x, so one must determine where to measure x from

Arbitrarily choose x in the diffusion zone

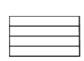


Now consider a composition to the both sides of the chosen origin:

$\int_{c_0}^{c} x dc =$  + 

First, considering the top part, $\int_{c_0}^{c^*} x dc =$ 

Since x<0, c<c_0 (or dc<0), so, $\int_{c_0}^{c^*} x dc > 0$

Second, considering the lower part, $\int_{c^*}^{c} x dc =$ 

Since x>0, c<c* (or dc<0), so, $\int_{c^*}^{c} x dc < 0$

Also note, $(\frac{\partial x}{\partial c})_c < 0$, c ↑, and x ↓

Then,

$$\tilde{D} = -\frac{1}{2t}\left(\frac{\partial x}{\partial c}\right)_c \cdot \int_{c_0}^{c} x\,dc$$

$$= -\frac{1}{2t}\left(\frac{\partial x}{\partial c}\right)_c \{ \quad (>0) + \quad (<0) \}$$

As long as { + } > 0, then $\tilde{D}$ >0

As a boundary condition, when c → c_1 (the final equilibrium concentration), $\left(\frac{\partial x}{\partial c}\right)_c$ → ∞, to have $\tilde{D}$ still to be finite, { + } must go to zero.

--- That's to say, ***x origin must be chosen to have left and right intergral equal*** --- this is referred as the ***Matano interface***.

Then, we can determine $\tilde{D} = -\frac{1}{2t}\frac{\partial x}{\partial c}\cdot\int_{c_0}^{c} x\,dc$, where x is measured from *Matano interface* that needs to be determined first.