

Lecture 5: Diffusion Coefficient (Diffusivity)

Today's topics

- Understand the general physical meaning of diffusion coefficient.
- What is chemical diffusion coefficient (D_A^C) and tracer diffusion coefficient (D_A)? How are

they inter-related as $D_A^C = D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$

- Understand the meaning of the thermodynamic factor, $\left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$, and the relationship

with the free energy gradient:

$$\left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_A^2} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_B^2}$$

In last two lectures, we learned the basics of diffusion and how to describe the diffusion flux

using Fick's first, $J = -D \cdot \frac{dc(x)}{dx}$, and second law $\frac{\partial c(x,t)}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$, where D is defined as the

diffusion coefficient, $D = \frac{a^2 \nu}{6} e^{-\Delta G^\ddagger / RT}$ (see Lecture 3), which has an SI unit of m²/s (length²/time).

Apparently, D is a proportionality constant between the diffusion flux and the gradient in the concentration of the diffusing species, and D is dependent on both temperature and pressure.

Diffusion coefficient, also called **Diffusivity**, is an important parameter indicative of the diffusion mobility. Diffusion coefficient is not only encountered in Fick's law, but also in numerous other equations of physics and chemistry.

Diffusion coefficient is generally prescribed for a given pair of species. For a multi-component system, it is prescribed for each pair of species in the system. The higher the diffusivity (of one substance with respect to another), the faster they diffuse into each other.

Now let's consider the **diffusion in a non-ideal, binary substitutional solution**

Consider two components, A and B

As we learned from thermodynamics, for the chemical potential of A and B, we have

$$\mu_A = \mu_A^0 + RT \ln a_A = \mu_A^0 + RT \ln \gamma_A + RT \ln x_A$$

$$\mu_B = \mu_B^0 + RT \ln a_B = \mu_B^0 + RT \ln \gamma_B + RT \ln x_B$$

where a is the activity, γ is the activity coefficient, and x_A and x_B is the composition fraction,

$$x_A = \frac{c_A}{c_A + c_B}, \quad x_B = \frac{c_B}{c_A + c_B}.$$

$$\text{Then, } \frac{d\mu_A}{dx} = \frac{d\mu_A}{dx_A} \frac{dx_A}{dx}, \quad x_A = \frac{c_A}{c_A + c_B},$$

Where c_A and c_B are the concentrations of A and B, and $c_A + c_B = \text{fixed}$

$$\text{Now, } \frac{dx_A}{dx} = \frac{1}{c_A + c_B} \cdot \frac{dc_A}{dx}$$

$$\text{So, } \frac{d\mu_A}{dx} = \frac{d\mu_A}{dx_A} \cdot \frac{1}{c_A + c_B} \cdot \frac{dc_A}{dx} \quad (1)$$

Also, as shown in Eq. (2) of Lecture 3, the Fick's first law can be written as

$$J = -D \cdot \frac{c(x)}{RT} \cdot \frac{d\mu}{dx}$$

Then, we have

$$J_A = c_A \frac{D_A}{RT} \left(-\frac{d\mu_A}{dx} \right)$$

Substituted with Eq. (1), we have

$$J_A = - \frac{c_A D_A}{RT} \cdot \frac{1}{c_A + c_B} \cdot \frac{d\mu_A}{dx_A} \cdot \frac{dc_A}{dx}$$

$$= - \frac{D_A}{RT} \cdot x_A \cdot \frac{d\mu_A}{dx_A} \frac{dc_A}{dx}$$

$$= - \frac{D_A}{RT} \cdot \frac{d\mu_A}{d \ln x_A} \cdot \frac{dc_A}{dx}$$

Now, as shown above, $\mu_A = \mu_A^0 + RT \ln \gamma_A + RT \ln x_A$

Then, we have

$$\frac{d\mu_A}{d \ln x_A} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$$

Then, J_A above can be re-written as

$$\begin{aligned} J_A &= -\frac{D_A}{RT} \cdot RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} \cdot \frac{dc_A}{dx} \\ &= -D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} \cdot \frac{dc_A}{dx} \\ &= -D_A^C \cdot \frac{dc_A}{dx} \end{aligned}$$

Where $D_A^C = D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$ is defined as the **chemical diffusion coefficient**

D_A is defined as the **self or tracer diffusion coefficient**

D_A^C denotes diffusion under a concentration gradient

D_A denotes diffusion of tracer A (dilute) in uniform concentration

In dilute solution, $\gamma_A = \gamma^H = \text{constant}$, $\frac{d \ln \gamma_A}{d \ln x_A} = 0$, then, $D_A^C \rightarrow D_A$

chemical diffusion coefficient (D_A^C) and tracer diffusion coefficient (D_A) are two very important parameters, please make sure you understand them well and not get confused.

- *Tracer diffusion*, which is a spontaneous mixing of molecules taking place in the absence of concentration (or chemical potential) gradient. This type of diffusion can be followed using isotopic tracers, hence the name. The tracer diffusion is usually assumed to be identical to self-diffusion (assuming no significant isotopic effect). This diffusion can take place under equilibrium.
- *Chemical diffusion* occurs in a presence of concentration (or chemical potential) gradient and it results in net transport of mass. This is the process described by the diffusion equation. This diffusion is always a non-equilibrium process, increases the system entropy, and brings the system closer to equilibrium.

The diffusion coefficients for these two types of diffusion are generally different because the diffusion coefficient for chemical diffusion is binary and it includes the effects due to the correlation of the movement of the different diffusing species.

Within the above relationship, $D_A^C = D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\}$

$\left\{1 + \frac{d \ln \gamma_A}{d \ln x_A}\right\}$ is a thermodynamic factor, and it can be expressed in terms of Gibbs free energy as

shown below:

Since, $G = x_A \mu_A + x_B \mu_B$

We have, $dG = x_A d\mu_A + \mu_A dx_A + x_B d\mu_B + \mu_B dx_B$

Now, taking the Gibbs – Duhem equation: $x_A d\mu_A + x_B d\mu_B = 0$

We have $dG = \mu_A dx_A + \mu_B dx_B$, differentiation of both sides gives

$$\begin{aligned} \frac{dG}{dx_A} &= \mu_A + \mu_B \frac{dx_B}{dx_A} = \mu_A + \mu_B \frac{d(1-x_A)}{dx_A} = \mu_A - \mu_B \\ &= \mu_A^0 + RT \ln \gamma_A + RT \ln x_A - \mu_B^0 - RT \ln \gamma_B - RT \ln x_B \end{aligned}$$

Then, we have the second order differential

$$\frac{d^2 G}{dx_A^2} = RT \frac{d \ln \gamma_A}{dx_A} + \frac{RT}{x_A} + RT \frac{d \ln \gamma_B}{dx_B} + \frac{RT}{x_B}$$

It can be re-written as:

$$\begin{aligned} x_A x_B \frac{d^2 G}{dx_A^2} &= RT \left\{ x_A x_B \frac{d \ln \gamma_A}{dx_A} + x_A x_B \frac{d \ln \gamma_B}{dx_B} + x_B + x_A \right\} \\ &= RT \left\{ 1 + x_B \frac{d \ln \gamma_A}{d \ln x_A} + x_A \frac{d \ln \gamma_B}{d \ln x_B} \right\} \end{aligned}$$

Now, taking the Gibbs – Duhem equation: $x_A d\mu_A + x_B d\mu_B = 0$

And taking $\mu_A = \mu_A^0 + RT \ln \gamma_A + RT \ln x_A$, $\mu_B = \mu_B^0 + RT \ln \gamma_B + RT \ln x_B$

We have, $x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$

$$\text{or, } x_A \frac{d \ln \gamma_A}{dx_A} - x_B \frac{d \ln \gamma_B}{dx_B} = 0 \quad (\text{note: } dx_A + dx_B = 0)$$

with little re-writing, we have

$$\frac{d \ln \gamma_A}{d \ln x_A} = \frac{d \ln \gamma_B}{d \ln x_B}$$

So, the above equation can be re-written as (note: $x_A + x_B = 1$)

$$x_A x_B \frac{d^2 G}{dx_A^2} = RT \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = RT \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\}$$

$$\text{or, } \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_A^2} = \frac{x_A x_B}{RT} \frac{d^2 G}{dx_B^2}$$

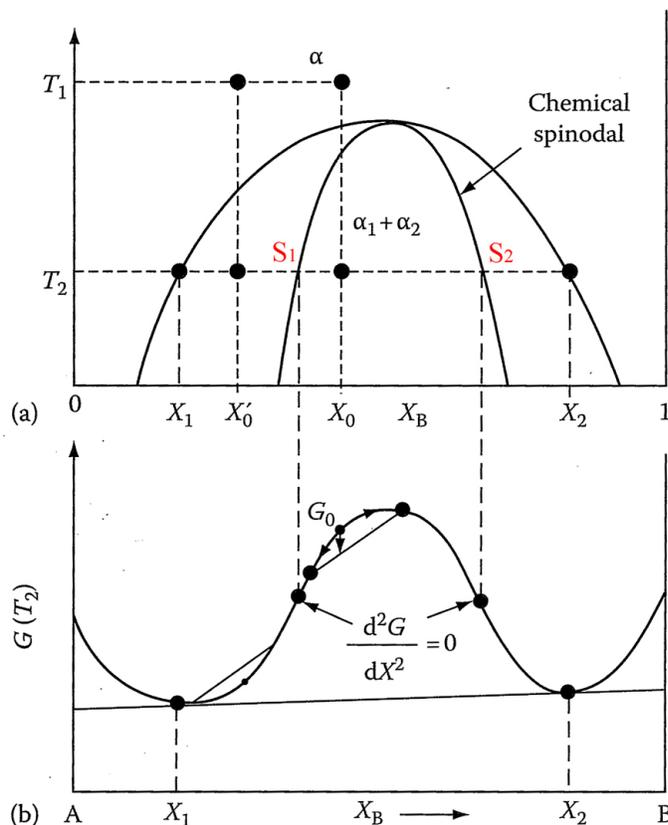
So, the relationship between **chemical diffusion coefficient** (D_A^C) and **tracer diffusion coefficient** (D_A) can now also be written as

$$\begin{aligned} D_A^C &= D_A \left\{ 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right\} = D_A \frac{x_A x_B}{RT} \frac{d^2 G}{dx_A^2} \propto \frac{d^2 G}{dx_A^2} \\ &= D_A \left\{ 1 + \frac{d \ln \gamma_B}{d \ln x_B} \right\} = D_A \frac{x_A x_B}{RT} \frac{d^2 G}{dx_B^2} \propto \frac{d^2 G}{dx_B^2} \end{aligned}$$

Please pay attention to the inter-relation above, and not be confused. A and B component are equally considered; the same equation applies to component B.

The above equation implies that the **chemical diffusion** (under concentration gradient) is proportional to the second order differential of free energy with respect to the composition.

Consider a binary solution with a miscibility gap as shown below (top: phase diagram, bottom: free energy curve).



With regard to the original solution (metastably retained) as quenched (rapidly cooled), the region inside spinodal is characterized by

$$\frac{d^2G}{dx_A^2} = \frac{d^2G}{dx_B^2} < 0$$

since D_A is always >0 , then this means $D_A^C < 0$

That is, if the original solution is cooled inside the spinodal, the chemical diffusion coefficient

D_A^C is less than zero, i.e., a negative diffusion coefficient, as $J_A = -D_A^C \cdot \frac{dC_A}{dx}$, it means the flux

of A diffuse up against concentration gradient (*though still along chemical potential or free energy gradient*). This is known as uphill diffusion, which is important for a special phase transformation, called Spinodal Decomposition (to be taught in details later in [Lectures 22-24](#)).