Lecture 3: Diffusion: *Fick's first law*

Today's topics

- What is diffusion? What drives diffusion to occur?
- Understand why diffusion can "surprisingly" occur against the concentration gradient?
- Learn how to deduce the Fick's first law, and understand the meaning of diffusion coefficient and diffusion length.

In last two lectures, we learned the thermodynamics, concerned mainly with stable or equilibrium systems. The study of materials Kinetics, like phase transformation, concerns those mechanism by which a system attempts to reach the equilibrium state and how long it takes. *One of the most fundamental processes that control the rate at which many transformation occur is the* ***diffusion***, as we will learn in the following several lectures and use throughout the whole semester.

General review of diffusion:

Diffusion describes the spread of particles (which can also be atoms, molecules) through random motion usually (but not always) from regions of higher concentration to regions of lower concentration. The time dependence of the statistical distribution in space is given by the diffusion equation. The concept of diffusion is tied to that of mass transfer driven by a concentration gradient, but diffusion can still occur when there is no concentration gradient (but there will be no net flux).

History: The concept of diffusion emerged from physical sciences. The paradigmatic examples were heat diffusion, molecular diffusion and Brownian motion. Their mathematical description was elaborated by *Joseph Fourier* in 1822, *Adolf Fick* in 1855 and by *Albert Einstein* in 1905.

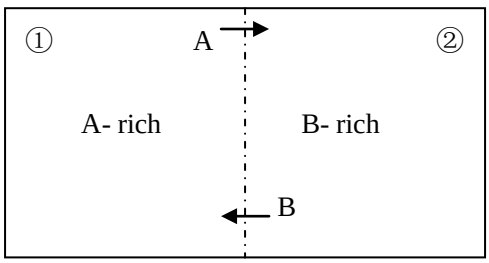
Specifically, atomic diffusion is a diffusion process whereby the random thermally-activated movement of atoms in a solid results in the net transport of atoms. For example, helium atoms inside a balloon can diffuse through the wall of the balloon and escape, resulting in the balloon slowly deflating. Other air molecules (e.g. oxygen, nitrogen) have lower mobilities and thus diffuse more slowly through the balloon wall. There is a concentration gradient in the balloon wall, because the balloon was initially filled with helium, and thus there is plenty of helium on the inside, but there is relatively little helium on the outside (helium is not a major component of air). The rate of transport is governed by the diffusivity and the concentration gradient.

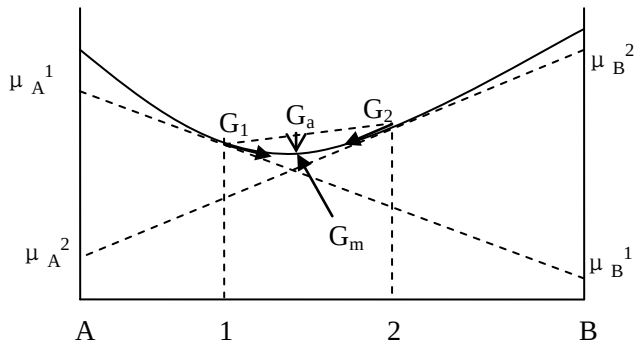
Diffusion in solid: In the crystal solid state, diffusion within the crystal lattice occurs by either *interstitial* or *substitutional* mechanisms and is referred to as lattice diffusion. In interstitial lattice diffusion, a diffusant (such as C in an iron alloy), will diffuse in between the lattice structure of another crystalline element. In substitutional lattice diffusion (self-diffusion for example), the

atom can only move by substituting place with another atom. Substitutional lattice diffusion is often contingent upon the availability of point vacancies throughout the crystal lattice. Diffusing particles migrate from point vacancy to point vacancy by the rapid, essentially random jumping about (jump diffusion). See below in this Lecture for details about *interstitial* or *substitutional.*

Diffusion is driven by decrease in Gibbs free energy or chemical potential difference.
As a simple illustration of this, consider the figure below, where two blocks of the same A-B solid solution, but with different compositions (concentrations), are welded together and held at a temperature high enough for long range diffusion to occur.

Case 1: along concentration gradient





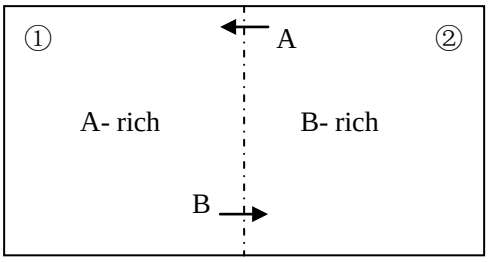
For case 1: $\mu_A^1 > \mu_A^2$ => A goes from 1 to 2
$\mu_B^2 > \mu_B^1$ => B goes from 2 to 1

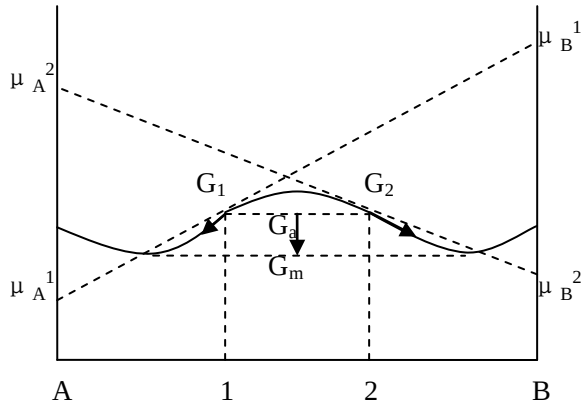
The molar free energy diagram of the A-B alloy is shown at right: the molar free energy of each part is given by G_1 and G_2, and the initial total free energy of the welded block is G_a, upon the diffusion as illustrated on the left (so as to eliminate the concentration difference), the total free energy decreases towards G_m, the free energy characteristic of a homogeneous system. *In this case, the decrease in free energy is produced by A and B diffusion along the concentration gradient.*

However, diffusion needs not always be *along the concentration gradient.* For example, in the alloy systems that contain a miscibility gap, the free energy curve can have a negative curvature at low temperature, as shown below in Case 2. In such a case, A and B atoms would diffuse against the concentration gradient (i.e., toward the regions of high concentration as shown at left below), though this diffusion is still a natural (spontaneous) process as it reduces the total free energy from G_a to G_m as shown.

For case 2: $\mu_A^2 > \mu_A^1$ => A goes from 2 to 1
$\mu_B^1 > \mu_B^2$ => B goes from 1 to 2

Case 2: against concentration gradient

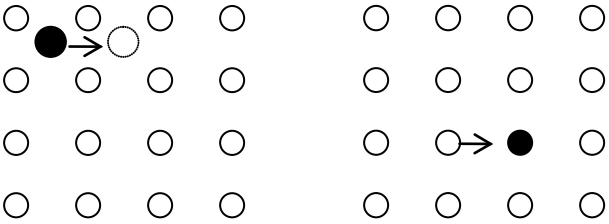




Diffusion is always along chemical potential gradient!

Diffusion stops when chemical potential of all species everywhere are same. In most cases, chemical potential increases with increasing concentration, so it is convenient to express diffusion in term of concentration.

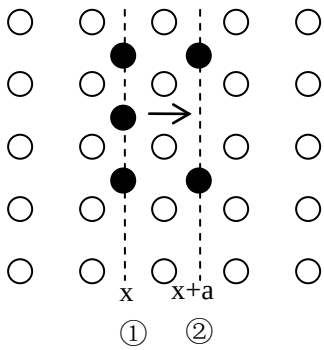
Now lets consider Interstitial diffusion vs. Substitutional diffusion:



Interstitial Substitutional (by vacancy)

<u>Considered at low concentration</u>

Now Let's deduce the Diffusion Equation for interstitial diffusion based on the following illustration, moving from position ① to ②.



c (x) ~ concentration at x, c (x+a) = c(x) + a $\frac{dc}{dx}$ ~ concentration at x+a

μ(x) ~ chemical potential at x, μ(x+a) =μ(x) + a $\frac{d\mu(x)}{dx}$ ~ chemical potential at x+a

ΔG^A ~ activation barrier

The forward rate $\propto e^{-\Delta G^A/RT}\left|\frac{\Delta G}{RT}\right|$;

--- see last Lecture for how to deduce this equation with an assumption that ΔG << RT, and this is usually true for diffusion, where the free energy change within short distance is small.

ΔG = G (x+a) - G (x) = μ(x+a) - μ(x)

(here ΔG is only contributed by the change in chemical potential)

Now $\frac{\Delta G}{RT} = \frac{\mu(x+a)}{RT} - \frac{\mu(x)}{RT} = \frac{a}{RT}\frac{d\mu}{dx}$ (as defined above, μ(x+a) =μ(x) + a $\frac{d\mu(x)}{dx}$)

Let ν be vibrational frequency, then an atom will have enough energy in unit time (per second) to overcome the barrier $\nu \cdot e^{-\Delta G^A/RT}$ times, *i.e., the number of jump of step "a" per second*, which we can define as "Γ".

$\Gamma = \nu \cdot e^{-\Delta G^A/RT}$

In a three-dimensional space (lattice), an atom can jump in six equivalent directions (±x, ±y, ±z), so the number of jumps toward right (along "x") in one second is $\frac{\nu}{6}e^{-\Delta G^A/RT}$.

So, the net forward rate for an atom to jump from x to x+a is

Rate = $\frac{\nu}{6} e^{-\Delta G^A/RT} (-\frac{a}{RT}\frac{d\mu}{dx})$ (where $\frac{d\mu}{dx} < 0$)

Let n(x) be the number of atoms (solute) per unit area at x, then the net flux along "x". (i.e., number of atom passing through unit area in unit time along "x") is

$$J = n(x)\cdot\frac{\nu}{6} e^{-\Delta G^A/RT} (-\frac{a}{RT}\frac{d\mu}{dx}) \qquad (1)$$

Since n(x) = a· c(x), Eq. (1) can be written as

$$J = -\frac{a^2\nu}{6} e^{-\Delta G^A/RT} \cdot \frac{c(x)}{RT} \cdot \frac{d\mu}{dx} \qquad (2)$$

Now let's consider the expression of chemical potential as we learned in the course of Thermodynamics:

$$\mu(x) = \mu^0 + RT\ln a(x) = \mu^0 + RT \ln \gamma c(x)$$

where a(x) is the activity of solute (atom) at x, γ is the activity coefficient, a constant.

Then, we have

$$\frac{d\mu}{dx} = \frac{RT}{c(x)} \cdot \frac{dc(x)}{dx} \qquad (3)$$

Substituting Eq. (3) into Eq. (2), we have

$$J = -\frac{a^2\nu}{6} e^{-\Delta G^A/RT} \cdot \frac{dc(x)}{dx} \qquad (4)$$

Let's define D = $\frac{a^2\nu}{6} e^{-\Delta G^A/RT}$ as the intrinsic **diffusion coefficient**

Then we have

$$J = -D\cdot\frac{dc(x)}{dx}$$ (Unit: D: cm^2/sec; J: number/cm^2/sec)

This is the Fick's first law of diffusion.

Now, let's consider diffusion in a three-dimensional space, i.e., ***random walk of an atom****:*

As defined on page 4,

$\Gamma = \nu \cdot e^{-\Delta G^A/RT}$

Combining with $D = \frac{a^2\nu}{6} e^{-\Delta G^A/RT}$

We have

$D = \frac{1}{6}\Gamma \cdot a^2 = \frac{a^2\nu}{6} e^{-\Delta G^A/RT}$

Then we have

$\Gamma = \nu e^{-\Delta G^A/RT} = 6D / a^2$ (Γ: number of jump an atom make per second)

For a random walk in three-dimensions, an atom travels an average distance of $\sqrt{n} \cdot a$ after n steps (i.e., n times of jump) with a step length of a.

Thus, after time t, the atom jumps Γ t times (steps). So it moves a distance of

$r = a\sqrt{\Gamma t} = a\sqrt{\frac{6Dt}{a^2}} = \sqrt{6Dt} \approx 2.4\sqrt{Dt}$

This is usually defined as the ***diffusion length***.