Lecture 18: Kinetics of Phase Growth in a Two-component System:

general kinetics analysis based on the dilute-solution approximation

Today's topics:

- In the last 2 Lectures, we learned three different ways to describe the diffusion flux of B atoms across the α/β interface around the β particle, and these three fluxes should be equal each other.
- For the *two-component* phase transformation (particularly in the case of dilute solution of β phase dispersed in α phase), growth of the β phase (particle) usually requires long-range diffusion of B atoms towards to the β particle. In this case, the growth rate can be determined by two different rate-limiting processes: *Interface Limited Growth and Diffusion Limited Growth.* Both of these two processes are temperature dependent --- typically the growth rate is Arrhenius type with growth becoming very slow at low temperatures.
- When rM >> D, then $C_r \approx C_\alpha$ --- The growth falls into the ***diffusion limited case,*** where there is very small buildup of B atoms near the β particles.
- When D >> rM, then $C_r \approx C_t$ --- The growth falls into the ***interface limited case,*** where there is large buildup of B atoms near the β particles.
- However, in a more general case, rM ~ D, the phase growth is determined by both the long-range diffusion of B atoms from the α matrix towards to the β particle and the diffusion across the α/β interface. *Today's topic is to learn how to describe the kinetics of such a general phase growth.*

The following kinetics treatment applies only to the dilute-solution of α phase containing small molar fraction of β phase, i.e., molar fraction of B (X_B) << molar fraction of A (X_A).

In last Lecture, we derived the diffusion flux of B atoms across the α/β interface in 3 equations:

J = M $(C_r - C_\alpha)$ **(1)**

Where M = $\dfrac{M'RT}{C_\alpha}$ defined as an interface parameter, a measure of the transport kinetics of atoms across the α/β interface, C has the unit of #/cm^3, M has the unit of cm/sec.

J' = $\left| D\left(\dfrac{dc}{d\rho}\right)_{\rho=r} \right| = \dfrac{D(C_t - C_r)}{r}$ **(2)**

J'' = $\dfrac{C_\beta 4\pi r^2 dr}{4\pi r^2 dt} = C_\beta \dfrac{dr}{dt}$ **(3)**

In a quasi-steady state, all three fluxes J, J', J'' as deduced above in Eqs. (1)(2)(3) are equal,
J = J' = J''
or

$$C_\beta \frac{dr}{dt} = \frac{D(C_t - C_r)}{r} = M(C_r - C_\alpha)$$

First, from $\frac{D(C_t - C_r)}{r} = M(C_r - C_\alpha)$, we have

$$C_r = \frac{DC_t + rMC_\alpha}{D + rM} \qquad \textbf{(i)}$$

From this equation we have two limiting cases:

- When rM >> D, then $C_r \approx C_\alpha$ --- The growth falls into the ***diffusion limited case,*** where there is very small buildup of B atoms near the β particles.
- When D >> rM, then $C_r \approx C_t$ --- The growth falls into the ***interface limited case,*** where there is large buildup of B atoms near the β particles.

Now let's deal with the general case, where both the long-range diffusion of B atoms from the α matrix towards to the β particle and the diffusion across the α/β interface will be considered.

At t = 0, before the phase transformation begins, the matrix concentration of B atoms is C_0;
When the transformation is complete, the matrix concentration of B atoms will be C_α.
As assumed at the very beginning, the original α solution is dilute, or the volume fraction of β is much less than 1.0.

Now, we define the fraction transformed, x(t), as

$$x(t) = \frac{V_\beta(t)}{V_\beta(t=\infty)}, \qquad V_\beta(t=0) << 1.0$$

where V_β is the **unit volume** of β phase.

Now, $V_\beta(t)(C_\beta - C_0) = (1 - V_\beta(t))(C_0 - C_t)$ **(ii)**

--- *increased # of B atoms within the β phase (particles) equals to the decreased # of B atoms within the α phase (now with a volume of 1- $V_\beta(t)$)*

Since $C_\beta >> C_0$, and $V_\beta(t) << 1.0$ (the dilute solution assumption)

We have $V_\beta(t)\, C_\beta \approx (C_0 - C_t) \Rightarrow V_\beta(t) = \frac{C_0 - C_t}{C_\beta}$

V_β (t=∞) = $\dfrac{C_0 - C_\alpha}{C_\beta}$

Thus, x(t) = $\dfrac{C_0 - C_t}{C_0 - C_\alpha}$ **(iii)**

Now, assuming there are **'n'** β particles (of radius of r) per **unit volume**, then,

$V_\beta(t) = \dfrac{4\pi r^3}{3} n$

Then, Eq. (ii) →

$$\frac{4\pi n r^3}{3}(C_\beta - C_0) = (C_0 - C_t)(1 - V_\beta(t))$$

Again, Since $C_\beta >> C_0$, and $V_\beta(t) << 1.0$ (the dilute solution assumption), we have

$$\frac{4\pi n r^3}{3} C_\beta \approx C_0 - C_t \qquad \textbf{(iv)}$$

Differentiation of Eq. (iv) with respect to 't' leads to

$$4\pi n r^2 C_\beta \frac{dr}{dt} = -\frac{dC_t}{dt} \qquad \textbf{(v)}$$

Also, Differentiation of Eq. (iii) with respect to 't' leads to

$$\frac{dx(t)}{dt} = -\frac{1}{C_0 - C_\alpha}\frac{dC_t}{dt}$$

or

$$-\frac{dC_t}{dt} = (C_0 - C_\alpha)\frac{dx(t)}{dt} \qquad \textbf{(vi)}$$

Combining Eq. (v) and (vi) gives,

$$4\pi n r^2 C_\beta \frac{dr}{dt} = (C_0 - C_\alpha)\frac{dx(t)}{dt} \qquad \textbf{(vii)}$$

Also, we have J = J' = J''

or

$$C_\beta \frac{dr}{dt} = \frac{D(C_t - C_r)}{r} = M(C_r - C_\alpha)$$

So, we can re-write Eq. (vii) as

$$4\pi nr^2 \cdot M(C_r - C_\alpha) = (C_0 - C_\alpha) \cdot \frac{dx}{dt}$$

Submitting C_r with Eq. (i), we have

$$\frac{4\pi nr^2 M}{C_0 - C_\alpha}\{\frac{DC_t + rMC_\alpha}{D + rM} - C_\alpha\} = \frac{dx}{dt}$$

Or

$$\frac{4\pi nr^2 M}{C_0 - C_\alpha} \cdot \frac{D(C_t - C_\alpha)}{D + rM} = \frac{dx}{dt} \qquad \textbf{(viii)}$$

From Eq. (iv), we have

$$r^3 = \frac{3(C_0 - C_t)}{4\pi nC_\beta}$$

then with Eq. (iii), we have

$$r^3 = \frac{3(C_0 - C_t)}{4\pi nC_\beta} = \frac{3(C_0 - C_\alpha)}{4\pi nC_\beta} \cdot x(t)$$

or

$$r = (\frac{3}{4\pi nC_\beta})^{1/3}(C_0 - C_\alpha)^{1/3} x^{1/3} \qquad \textbf{(ix)}$$

Also with Eq. (iii), we have,

$$\frac{C_t - C_\alpha}{C_0 - C_\alpha} = 1 - \frac{C_0 - C_t}{C_0 - C_\alpha} = 1 - x \qquad \textbf{(x)}$$

Now, with Eq. (x), we can re-write Eq. (viii) as

$$dt = \frac{(C_0 - C_\alpha)}{4\pi nMDr^2} \cdot \frac{(D + rM)}{(C_t - C_\alpha)} \cdot dx \;=\; \frac{1}{4\pi nMD}\frac{1}{r^2} \cdot (D + rM)\frac{dx}{1 - x}$$

$$= \frac{1}{4\pi n}\{\frac{dx}{Mr^2(1 - x)} + \frac{dx}{Dr(1 - x)}\}$$

Substituting “r” with Eq. (ix), we have

$$dt = \frac{1}{4\pi n}\left\{\frac{dx}{M(\frac{3}{4\pi nC_\beta})^{2/3}(C_0 - C_\alpha)^{2/3}x^{2/3}(1-x)} + \frac{dx}{D(\frac{3}{4\pi nC_\beta})^{1/3}(C_0 - C_\alpha)^{1/3}x^{1/3}(1-x)}\right\}$$

Now let's set 2 new parameters

$$K_1 = [\frac{36\pi n(C_0 - C_\alpha)^2}{C_\beta{}^2}]^{1/3} \quad \text{and} \quad K_2 = [\frac{48\pi^2 n^2(C_0 - C_\alpha)}{C_\beta}]^{1/3}$$

Then we have

$$dt = \frac{dx}{MK_1 x^{2/3}(1-x)} + \frac{dx}{DK_2 x^{1/3}(1-x)} \qquad \textbf{(xi)}$$

From this equation, it is not possible to express x as an explicit function of 't'. Rather, we can show that 't' is an explicit function of 'x'. That is, we can determine the time required for the transformation to progress to a given extent, in term of fraction transformed, x(t), as defined at the very beginning above.

Set $y^3 = x$, then Eq. (xi) can be re-written as

$$dt = \frac{3dy}{MK_1(1-y^3)} + \frac{3ydy}{DK_2(1-y^3)}$$

The "t" can be expressed as

$$t = \frac{1}{2}(\frac{1}{MK_1} + \frac{1}{DK_2})\ln[\frac{1+y+y^2}{(1-y)^2}] + \sqrt{3}(\frac{1}{MK_1} - \frac{1}{DK_2})\tan^{-1}(\frac{2y+1}{\sqrt{3}}) + A$$

Where A is a constant

Submitting back with $y = x^{1/3}$, we have

$$t = \frac{1}{2}(\frac{1}{MK_1} + \frac{1}{DK_2})\ln[\frac{1+x^{1/3}+x^{2/3}}{(1-x^{1/3})^2}] + \sqrt{3}(\frac{1}{MK_1} - \frac{1}{DK_2})\tan^{-1}[\frac{2x^{1/3}+1}{\sqrt{3}}] + A$$

Now, considering the fact: when t=0, x=0, then we can deduce the value of the constant "A"

$$A = -\sqrt{3}(\frac{1}{MK_1} - \frac{1}{DK_2})\tan^{-1}(\frac{1}{\sqrt{3}}) = -\sqrt{3}(\frac{1}{MK_1} - \frac{1}{DK_2})\frac{\pi}{6}$$

Submitting back "A" into the equation, we have

$$t = \frac{1}{2}(\frac{1}{MK_1} + \frac{1}{DK_2})\ln[\frac{1+x^{1/3}+x^{2/3}}{(1-x^{1/3})^2}] + \sqrt{3}(\frac{1}{MK_1} - \frac{1}{DK_2})[\tan^{-1}(\frac{2x^{1/3}+1}{\sqrt{3}}) - \frac{\pi}{6}] \qquad \textbf{(xii)}$$

Eq. (xii) can be re-written as

$$\frac{t}{\tan^{-1}(\frac{2x^{1/3}+1}{\sqrt{3}})-\frac{\pi}{6}} = \frac{1}{2}(\frac{1}{MK_1}+\frac{1}{DK_2})\frac{\ln[\frac{1+x^{1/3}+x^{2/3}}{(1-x^{1/3})^2}]}{\tan^{-1}(\frac{2x^{1/3}+1}{\sqrt{3}})-\frac{\pi}{6}} + \sqrt{3}(\frac{1}{MK_1}-\frac{1}{DK_2})$$

Then, a plot of $\frac{t}{\tan^{-1}(\frac{2x^{1/3}+1}{\sqrt{3}})-\frac{\pi}{6}}$ vs. $\frac{\ln[\frac{1+x^{1/3}+x^{2/3}}{(1-x^{1/3})^2}]}{\tan^{-1}(\frac{2x^{1/3}+1}{\sqrt{3}})-\frac{\pi}{6}}$ gives a straight line

with slope $\frac{1}{2}(\frac{1}{MK_1}+\frac{1}{DK_2})$ and intercept $\sqrt{3}(\frac{1}{MK_1}-\frac{1}{DK_2})$

Now consider 2 situations:

If $MK_1 << DK_2$, ***interface transfer much slower than diffusion***: slop is $\approx \frac{1}{2MK_1}$, intercept $\approx \frac{\sqrt{3}}{MK_1}$

If $MK_1 >> DK_2$, ***diffusion much slower than interface transfer***: slope is $\approx \frac{1}{2DK_2}$, intercept $\approx -\frac{\sqrt{3}}{DK_2}$

So, from real experiments:

A negative intercept ($-\frac{\sqrt{3}}{DK_2}$) indicates ***diffusion limited*** growth, and ratio $= \frac{intercept}{slope} = -2\sqrt{3}$;

A positive intercept ($\frac{\sqrt{3}}{MK_1}$) indicates ***interface limited*** growth, and ratio $= \frac{intercept}{slope} = 2\sqrt{3}$