CHAPTER V *DIFFUSION*

5.1 Fundamental equations of diffusion

Diffusion phenomena, i.e., the migration of atoms in the lattice, regulate the kinetics for many material processes, such as phase transformations, thin film deposition, recrystallization, and plastic deformations. Diffusion processes can be described using expressions of Fick's first and second laws.

5.1.1 Phenomenological equations

a) Fick's First Law

$$\overrightarrow{J_A} = -D_A \overrightarrow{grad} C_A \tag{5.1}$$

where $[J_A] =$ # atoms $A / cm^2 s^{-1} =$ flux of atoms A
$[C_A] =$ # atoms $A / cm^3 =$ concentration per unit volume of A
$[D_A] = cm^2 s^{-1} =$ diffusion coefficient of A

$$\frac{\partial C_A}{\partial t} = -div \overrightarrow{J_A} \tag{5.2}$$

b) Fick's Second Law (conservation equation)

Eliminating J_A between (5.1) and (5.2) and supposing that D_A is constant,

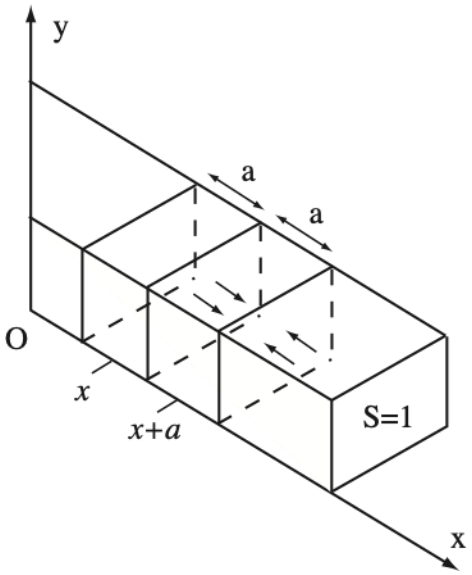
$$\frac{\partial C_A}{\partial t} = D_A \Delta C_A \tag{5.3}$$

which is called **Fick's Second Law** and has the same mathematical form as the heat equation.
This partial differential equation has been solved for many boundary conditions, though its use in metallurgy is relatively limited, as demonstrated in later sections of this chapter.

Proof for the one-dimensional case

a) Fick's First Law

$$J_{A,x} = -D_A \frac{\partial C_A}{\partial x}$$



$J_{A,x} =$ flux of atoms *A* going through a unit surface perpendicular to the axis Ox per unit time.

Let *a* and Γ be the distance and frequency of the atomic jumps, respectively.

Then:

$$J_{A,x} = \frac{1}{2}\Gamma C_A(x)a - \frac{1}{2}\Gamma C_A(x+a)a$$

$$J_{A,x} = \frac{1}{2}\Gamma a[C_A(x) - C_A(x+a)] = -\frac{1}{2}\Gamma a^2 \frac{\partial C_A}{\partial x}$$

From which we derive: $D_A = \frac{1}{2}\Gamma a^2$

Figure 5-1: *One-dimensional flux*

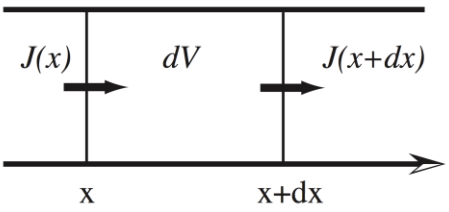


Figure 5-2: *Flux through a volume element dV*

c) *Conservation equation*

$$dV = Sdx$$

Let *n* the number of atoms A in *dV*

$$\frac{dn}{dt} = (J(x) - J(x+dx))S = -S\frac{\partial J}{\partial x}dx = -\frac{\partial J}{\partial x}dV$$

$$\frac{dC}{dt} = -\frac{dJ}{dx}$$

where $\frac{dC}{dt} = -div\vec{J} + \sigma$, σ is a source term.

5.1.2 Solutions to Fick's Second Law

We want to obtain a solution of form C(x,t) with specific boundaries and initial conditions.

a) Thin layer of an element B completely soluble in A

For example, *B=A** can be a radioactive isotope of *A*. We have a Gaussian symmetric distribution.

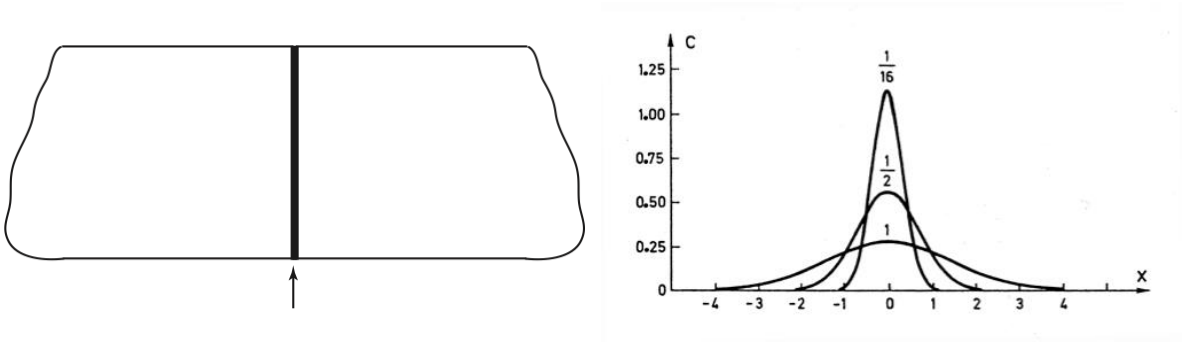


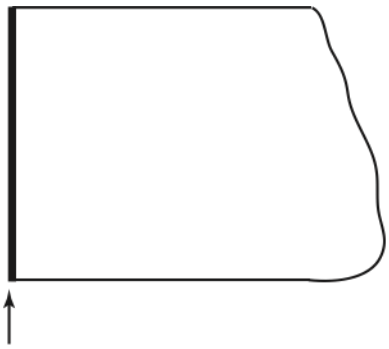
Figure 5-3 : *Symmetric distribution*

In *t=0, C=0* except in *x=0* where we have *M* atoms.

Therefore: $$C(x,t)=\frac{M}{2\sqrt{\pi Dt}}e^{-\frac{x^2}{4Dt}} \qquad (5.4)$$

with $$M=\int_{-\infty}^{\infty}C(x,t)\,dx$$

b) Surface coating

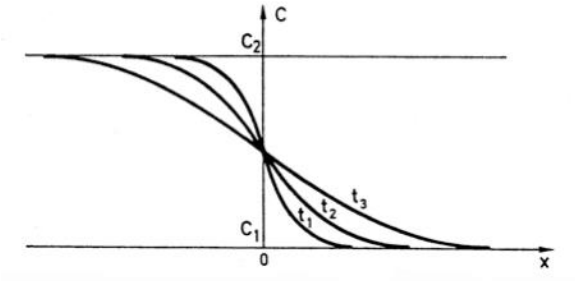


The solution is identical to the one for a thin layer, as seen in *a)*.

$$C(x,t)=\frac{M}{2\sqrt{\pi Dt}}e^{-\frac{x^2}{4Dt}} \qquad (5.5)$$

Figure 5-4: *Surface coating*

c) Interdiffusion

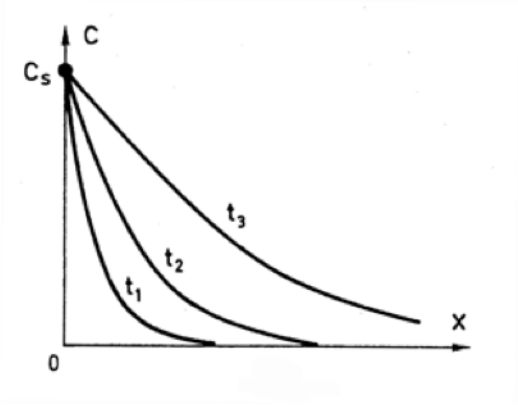


$$t=0 \qquad C=C_0 \text{ for } -\infty<x<0$$
$$C=0 \text{ for } 0<x<\infty$$
$$C(x,t)=\frac{C_0}{2}\left(1-\theta\left(\frac{x}{2\sqrt{Dt}}\right)\right) \qquad (5.6)$$

where $\theta(y)=\frac{2}{\sqrt{\pi}}\int_0^y e^{-z^2}\,dz$ is the error function.

Figure 5-5: *Concentration distribution during interdiffusion*

d) Diffusion from a surface



$$\frac{C(x)-C_0}{C_S-C_0}=\left(1-\theta\left(\frac{x}{2\sqrt{Dt}}\right)\right) \tag{5.7}$$

C_0 is the initial concentration per unit volume of the species that diffuses, and C_S is the surface concentration, e.g., in carburization.

Figure 5-6: *Distribution in the case of diffusion from a surface.*

5.2 Diffusion coefficient and random motion

This section describes how the diffusion coefficient can be derived from statistics laws. First, we suppose that the atoms are located in a lattice. Then, the migration directions are defined by vectors $\vec{\delta l}$ corresponding to the close-packed directions.

For instance, in the BCC structure: $\vec{\delta l}=\frac{1}{2}(1,1,1) \quad \left|\vec{\delta l}\right|=\frac{a\sqrt{3}}{2}$

and in the FCC structure: $\vec{\delta l}=\frac{1}{2}(1,1,0) \quad \left|\vec{\delta l}\right|=\frac{a}{\sqrt{2}}$

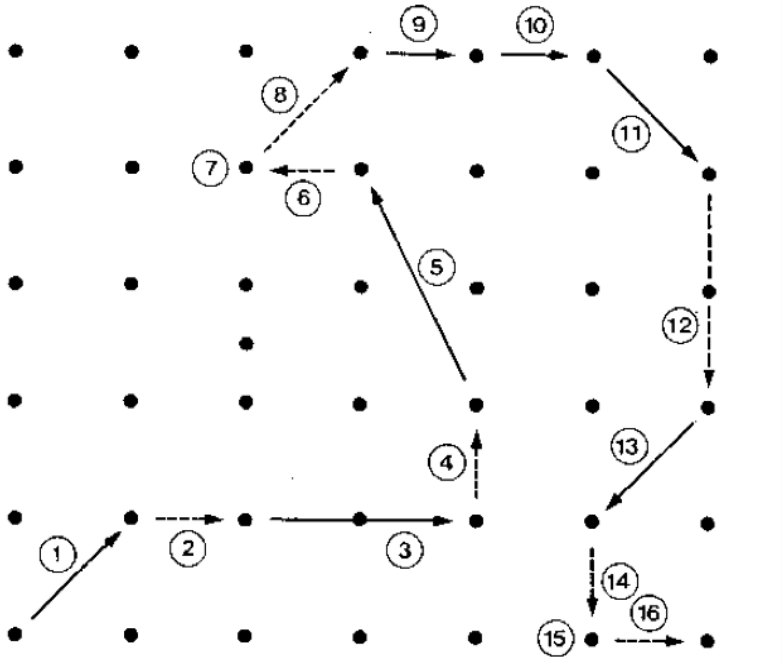


Figure 5-7: *Random path of an atom.*

$$\vec{L} = \sum_i \overrightarrow{\delta l_i} \tag{5.8}$$

We have: $< \vec{L} > = 0$

$$\left\langle \vec{L}^2 \right\rangle = \left\langle \sum_i \overrightarrow{\delta l_i}^2 \right\rangle + \left\langle \sum_{ij} \overrightarrow{\delta l_i} \overrightarrow{\delta l_j} \right\rangle$$

but the mean free path $\sqrt{\left\langle \vec{L}^2 \right\rangle} \neq 0$

The second term in equation (5.9) is zero since it is always possible for any step $\overrightarrow{\delta l_i}$ to find two opposite steps $\overrightarrow{\delta l_j}$

$$\left\langle \vec{L}^2 \right\rangle = \left\langle \sum_{i=1}^{n} \overrightarrow{\delta l_i}^2 \right\rangle = n\overrightarrow{\delta l}^2 = \Gamma t \delta l^2$$

with δl = length of a jump
n = number of jumps in time t
Γ = jump frequency

but: $\vec{L}^2 = x^2 + y^2 + z^2$ and in a cubic crystal: $\left\langle x^2 \right\rangle = \left\langle y^2 \right\rangle = \left\langle z^2 \right\rangle$

from which $\left\langle x^2 \right\rangle = \frac{1}{3}\left\langle \vec{L}^2 \right\rangle$

and thus $\left\langle x^2 \right\rangle = \frac{1}{3}\Gamma t \delta l^2$ (5.10)

Let us consider the particles that have traveled a path of $\pm \Delta$(with $\Delta^2 = \left\langle x^2 \right\rangle$) in the time *t* and calculate the flux of these particles through a surface *S*.

$$= Jt = \frac{1}{2}C(x)\Delta - \frac{1}{2}C(x+\Delta)\Delta = -\frac{1}{2}\Delta^2 \frac{\partial C}{\partial x}$$

$$J = -\frac{1}{2}\frac{\Delta^2}{t}\frac{\partial C}{\partial x} = -\frac{1}{2}\frac{\left\langle x^2 \right\rangle}{t}\frac{\partial C}{\partial x} \qquad \text{so that}$$

$$D = \frac{1}{2}\frac{\left\langle x^2 \right\rangle}{t} \tag{5.11}$$

Einstein obtained this result in 1905, $\left\langle x^2 \right\rangle = 2Dt$ with the quadratic path equaling 2 *Dt.*

Finally: $D = \frac{1}{6}\Gamma \delta l^2$ (5.12)

This result is valid for a simple cubic crystal.

For a BCC crystal: $D = \frac{1}{8}\Gamma a^2$

For an FCC crystal: $D = \frac{1}{12}\Gamma a^2$

Diffusion depends on the temperature: $D = D(T)$ since $\Gamma = \Gamma(T)$. (5.13)

where ν_D is the frequency of vibration of the $\Gamma = \nu_D P$ Debye atoms $\sim 10^{13}\ Hz$

P is the probability that the atom has sufficient energy to jump from one site $P \sim e^{-\frac{\Delta G_a}{kT}}$ to the other.

5.3 Self-diffusion

5.3.1 The mechanisms of diffusion

How do atoms migrate within a crystal? Figure 5-8 schematically shows the principal diffusion mechanisms in a monoatomic crystal. We can list the following mechanisms:

1) Simple switch: the least probable (for example $E_a \sim 10\ eV$ in Cu).

2) Cyclic switch: requires the simultaneous motion of several atoms.

3) Vacancy mechanism: the most probable. The atoms diffusing take the position of a vacant site.

4) Interstitial mechanism: This requires forming a valid self-interstitial for the interstitial impurities O, C, and N, which is a probable mechanism in BCC metals.

5) Interstitials exchange: the mechanism relies on low probability correlated motion.

6) Crowdion: low probability correlated motion.

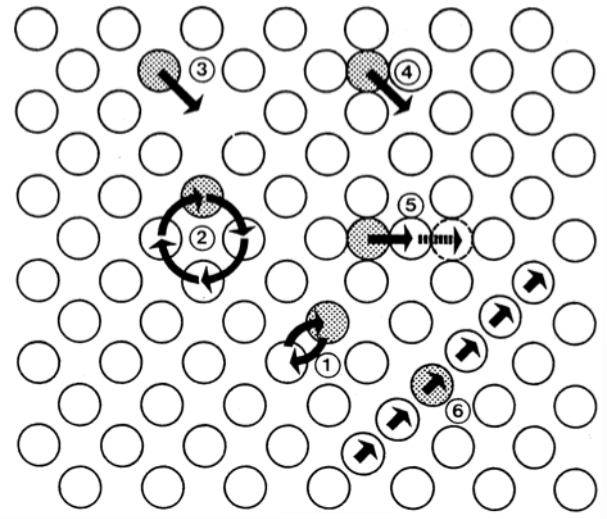


Figure 5-8: *Diffusion mechanisms*

5.3.2 Vacancy mechanism

The relation (5.12) is valid for interstitial diffusion but not quite for the diffusion of substitutional atoms. This type of diffusion needs a free site to happen; in other words, it requires the presence of a vacancy. Nevertheless, once the jump has occurred, it is highly probable that the atom diffuses back to the site it has just left. To calculate the effective displacement of an atom throughout the crystal, we have to consider the probability of multiple jumps. Thus, an atom can jump to a nearby vacancy site if it overcomes the potential threshold for migration. The probability of the jump is given by $\exp(-\Delta G_V^m / kT)$. The probability of finding a vacancy in an adjacent site is given by zC_V where C_V is the concentration of vacancies, and *z* is the number of close neighbors. Thus, considering the density of vacancies at equilibrium:

$$\Gamma = \nu_D z C_V \exp(-\Delta G_V^m / kT) = \nu_D z \exp(-\Delta G_V^m + \Delta G_V^F / kT)$$

and then
$$D = \frac{1}{6} a^2 \nu_D z \exp(-\Delta G_V^m + \Delta G_V^F / kT) \tag{5.14}$$

Considering that $\Delta G = \Delta H - T\Delta S$

$$D = \frac{1}{6} a^2 \nu_D z exp((\Delta S_V^m + \Delta S_V^F)/k) \exp(-(\Delta H_V^m + \Delta \mathrm{H}_V^F)/kT) = D_0 \exp(-Q_{SD}/kT) \tag{5.15}$$

with $D_0 = \frac{1}{6} a^2 \nu_D z \exp((\Delta S_V^m + \Delta S_V^F)/k)$ (5.16)

Q_{SD} is called self-diffusion energy. This quantity can be measured in diffusion experiments (for example, using radioactive trackers), which characterize diffusion's temperature sensitivity in a monoatomic crystal.

5.4 Applied force to the diffusing particle: Einstein's equation

Consider first the random motion of a particle in a potential field characterized by jumps thermally activated (figure 5-9 a). The average speed of atoms is given by:

$$V = \frac{1}{2} a(\Gamma^+ - \Gamma^-) \tag{5.17}$$

where $\Gamma^+ = \Gamma^- = \nu_0 e^{-\frac{\Delta G_a}{kT}}$

with $\nu_0 = cte \cdot \nu_D \sim 10^{13} s^{-1} \cdot \nu_D$ being the frequency of vibration of the atom in its potential well (Debye frequency).

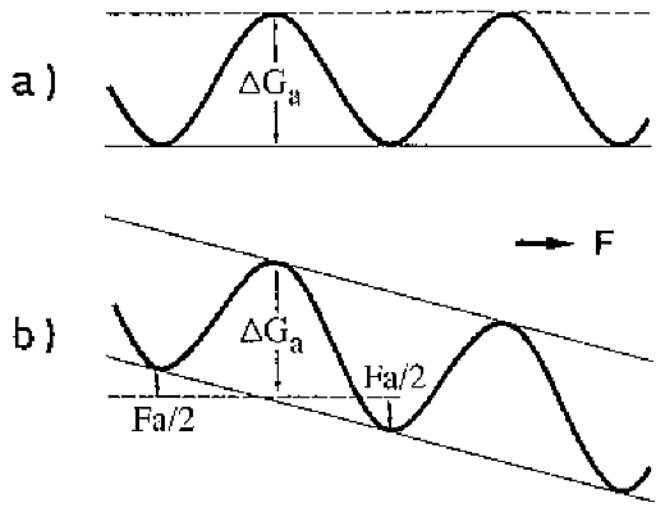


Figure 5-9: *a) Diffusion is performed by jumps in a periodic potential. b) Effect of the application of a force*

The factor of 1/2 comes from the fact that an atom cannot simultaneously perform a positive and negative jump. In these conditions, $\bar{V} = 0$. On the other hand, if a force is applied to the atom, this force is at work during the displacement and determines an inclination of the potential curve (figure 5-9 b) so that the following expressions can be written:

$$\Gamma^- = \nu_0 e^{-\frac{\Delta G_a + F\frac{a}{2}}{kT}} \qquad \Gamma^+ = \nu_0 e^{-\frac{\Delta G_a - F\frac{a}{2}}{kT}}$$

and the potential ΔG_a is modified of $\pm\frac{Fa}{2}$

We conclude:

$$\bar{V} = \frac{1}{2} a \nu_0 e^{-\frac{\Delta G_a}{kT}} \left(e^{\frac{Fa}{2kT}} - e^{-\frac{Fa}{2kT}} \right) \qquad \bar{V} \cong \frac{1}{2} a^2 \nu_0 e^{-\frac{\Delta G_a}{kT}} \frac{F}{kT}$$

and letting $D_A = \frac{1}{2} \nu_0 a^2 e^{-\frac{\Delta G_a}{kT}}$

$$\overline{V_A} = \frac{D_A F_A}{kT} \tag{5.18}$$

Expression (5.18) is equivalent to expressing the force *F* arising from a potential. Consider the combined effect of a concentration gradient and a force leading to a steady state condition. The flux of particles due to the force *F* is given by:

$$J_1 = \langle V \rangle C$$

The concentration gradient leads to an opposite flux.

$$J_2 = -D\frac{dC}{dx}$$

$$J = 0 \Rightarrow D\frac{dC}{dx} = \langle V \rangle C \tag{5.19}$$

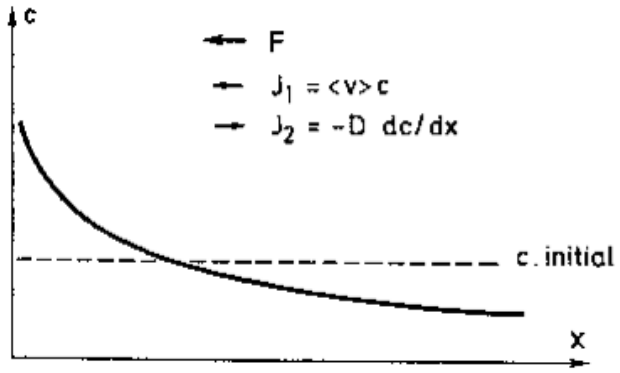


Figure 5-10: *Concentration gradient due to an external force*

If *F* derives from a potential: $F = -\frac{d\Phi}{dx}$

We suppose that the distribution of concentration at equilibrium follows a Boltzmann distribution adjusting to the variation of local potential determined by the introduction of the external force *F*:

$$C(x) = C_0 \exp(-\Phi(x)/kT) \tag{5.20}$$

Thus:
$$\frac{dC}{dx} = -\frac{C}{kT}\frac{d\Phi}{dx} = \frac{CF}{kT} \tag{5.21}$$

Using this expression for the concentration in (5.19), we obtain the following:
$\langle V \rangle = \frac{FD}{kT}$

which is the expression (5.18) derived previously.

As an example, we can show (in exercises, Nerst law) that an electric field E introduces an electric current: $i = \frac{Cq^2D}{kT}E$

From which we can extract the electric ionic conductivity: $\sigma = \frac{Cq^2D}{kT}$

In the case that *F* is due to chemical forces, we let: $\vec{F} = -\overrightarrow{grad}\mu_A$
where μ_A is the chemical potential of A.

For an ideal solution, for instance, we show that (see Chapter XI):

$$\mu_A = kT \ln X_A$$

where X_A is the relative concentration of species A.

Let us consider two atomic species, A and B, of concentration C_A and C_B and where X_A is the relative concentration of species A. We show the development of species A here.

$$\vec{J}_A = C_A \vec{V}_A = -\frac{C_A D_A}{kT} \overrightarrow{grad}\mu_A = -\frac{C_A D_A \partial \mu_A}{kT\, \partial C_A} \overrightarrow{grad} C_A = -(D^\star{}_A \cdot \overrightarrow{grad} C_A) \tag{5.22}$$

with $D^\star{}_A = \frac{C_A D_A}{kT} \frac{\partial \mu_A}{\partial C_A}$

$D^\star{}_A$ is the intrinsic diffusion coefficient, sometimes called the Dehlinger-Darken diffusion coefficient. Therefore, the diffusion equation becomes:

$$\frac{\partial C_A}{\partial t} = div(D^\star{}_A \overrightarrow{grad} C_A) \tag{5.23}$$

In the general case, the driving force of diffusion is not the concentration gradient but the gradient of the **chemical potential**.

5.5 Diffusion couple: the Boltzmann-Matano method

Review of scaling laws. Example: gravitational law.

$$\ddot{\vec{x}}_1(t) = -\frac{GM}{|x_1(t)|^3} \vec{x}_1(t)$$

Consider planet 1 of mass *m* orbiting around the Sun (mass *M*), given $\vec{x}_1(t=0)$

Consider now the scaling law: $t' = \tau t \quad x'_1 = \lambda x_1$

We then have:

$$\ddot{\vec{x}}'_1(t') = -\frac{G' M \vec{x}'_1(t')}{|\vec{x}'_1|^3}$$

$$\vec{x}'_1(t=0) = \lambda \vec{x}_1(t=0)$$

$$\ddot{\vec{x}}_1(t) = \frac{\tau^2}{\lambda^3} G' \frac{M \vec{x}_1(t)}{|\vec{x}_1|^3} \Rightarrow \frac{\tau^2}{\lambda^3} G' = G$$

Consider another planet 2.

$$\ddot{\vec{x}}_2(t) = -\frac{G' M \vec{x}_2(t)}{|\vec{x}_2(t)|^3}$$

$$\vec{x}_2(t=0) = \lambda \vec{x}_1(t=0)$$

Then, if $G=G'$, i.e., $\tau^2 / \lambda^3 = 1$, $\vec{x}'_1(t')$ and $\vec{x}_2(t')$, is described by the same equations, the two planets have similar trajectories. In particular:

$$\left(\frac{t'}{t}\right)^2 = \left(\frac{x'_1}{x_1}\right)^3 = \left(\frac{x_2}{x_1}\right)^3$$

This is Kepler's third law.

Similarly, we find a similar criterion in fluid mechanics with Reynold's number.

$$R = \frac{\rho v L}{\eta}$$

We apply the method described above to the problem of interdiffusion between two materials, A and B, joined together in a diffusion couple. First, we determine the diffusion coefficient $D^{\star}{}_{A}$, which characterizes the diffusion from A to B or vice versa.

$$\frac{\partial}{\partial t} c'(x,t) = \frac{\partial}{\partial x}\left(D \frac{\partial}{\partial x} c_1(x,t) \right)$$

$$c_1(t=0) = c(x,0)$$

Changing the variable in $x' = \lambda x \qquad t' = \tau t$

$$\frac{\partial}{\partial t'} c'_1(x',t') = \frac{\partial}{\partial x'}\left(D' \frac{\partial}{\partial x'} c'(x',t') \right) \qquad c'_1(x,t) = c_1(x,t)$$

$$\frac{\partial}{\partial t} c'_1(\lambda x,\tau t) = \frac{\partial}{\partial x}\left(\frac{\tau D'}{\lambda^2} \frac{\partial}{\partial x} c'_1(\lambda x,\tau t) \right) \qquad c'_1(t=0) = c(\lambda x,0) \tag{5.24}$$

Consider a new concentration distribution that obeys the same diffusion equation but with initial conditions.

$$c(\lambda x,0) = c_2(t=0)$$

$$\frac{\partial}{\partial t_2} c_2(x_2,t_2) = \frac{\partial}{\partial x_2}\left(D \frac{\partial}{\partial x_2} c_2(x_2,t_2) \right)$$

From (5.24), we have that:

$$\frac{\tau D'}{\lambda^2} = D \tag{5.25}$$

This similarity can also be deduced from the expression (5.11) for the mean free path:

$$2D' = \frac{\bar{x}'^2}{t'} = \frac{\lambda^2}{\tau}\frac{\bar{x}^2}{t} = 2D\frac{\lambda^2}{\tau} \Rightarrow D' = \frac{D\lambda^2}{\tau} \tag{5.26}$$

This cannot be derived in any other way, given that we derive the mean free path from the Gaussian probability distribution, a diffusion equation solution.

As for gravitation, if $D=D'$ then $\lambda^2/\tau = 1$. The diffusion processes are determined by initial conditions $c'_1(t=0)$ and $c_2(t=0)$ give the same results on different scales.

We have: $\frac{x}{\sqrt{t}} = \frac{x'}{\sqrt{t'}}$

This brings us to solve equation (5.23) with the reduced variable $\eta = \frac{x}{\sqrt{t}}$

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D^{\star}_{A} \frac{\partial}{\partial x} C_A \right)$$

$$\frac{\partial}{\partial t} = \frac{\partial \eta}{\partial t}\frac{\partial}{\partial \eta} = -\frac{x}{2t^{3/2}}\frac{\partial}{\partial \eta}$$

$$\frac{\partial}{\partial x} = \frac{\partial \eta}{\partial x}\frac{\partial}{\partial \eta} = \frac{1}{\sqrt{t}}\frac{\partial}{\partial \eta}$$

We obtain:

$$-\frac{\eta}{2}\frac{dC_A}{d\eta} = \frac{d}{d\eta}\left(D^{\star}_{A} \frac{dCA}{d\eta} \right)$$

$$D^{\star}_{A}(C) = -\frac{1}{2}\frac{\int_{C_A^1} \eta\, dC}{\left.\frac{dC_A}{d\eta}\right|_C} \qquad (5.27)$$

Writing this expression again in *x* and *t* variables:

$$D^{\star}_{A}(C) = -\frac{1}{2t}\frac{\int_{C_A^1}^{C} x\, dC}{\left.\frac{dC}{dx}\right|_C} \qquad (5.28)$$

which can be easily measured experimentally.

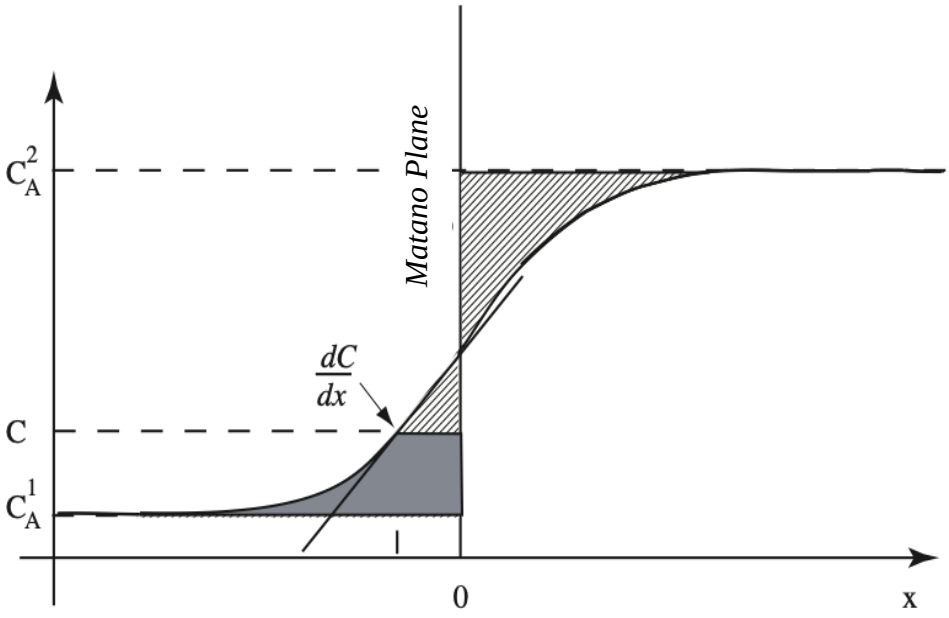


Figure 5-11: *Graphical method to determine the diffusion coefficient from the concentration profile of a diffusion couple.*

If we integrate from C_A^1 to C_A^2 so as:

$$\int_{C_A^1}^{C_A^2} \lambda\, dc = \int_{C_A^1}^{C_A^2} x\, dc = 0$$

This condition sets the origin on the λ or x-axis. Moreover, it determines the position of the so-called "Matano plane," which separates the two equal areas (shaded area in Figure 5-11).

To determine the diffusion coefficient $D_A^*(C)$ from a concentration profile, as shown in Figure 5-11, we need to determine the position of the Matano plane graphically and then apply equation (5.28). In this expression, the numerator represents the area delimited by the curve $C_A = C_A(x)$, the Matano plane, and the lines $C_A = C_A^1$ and $C_A = C$. The denominator represents the slope of the tangent in point P. Here, we give an example of a diffusion couple of Al-Ag. The optical microscopy image in Figure 5-12 shows this diffusion couple's interfaces in a cross-sectional sample.

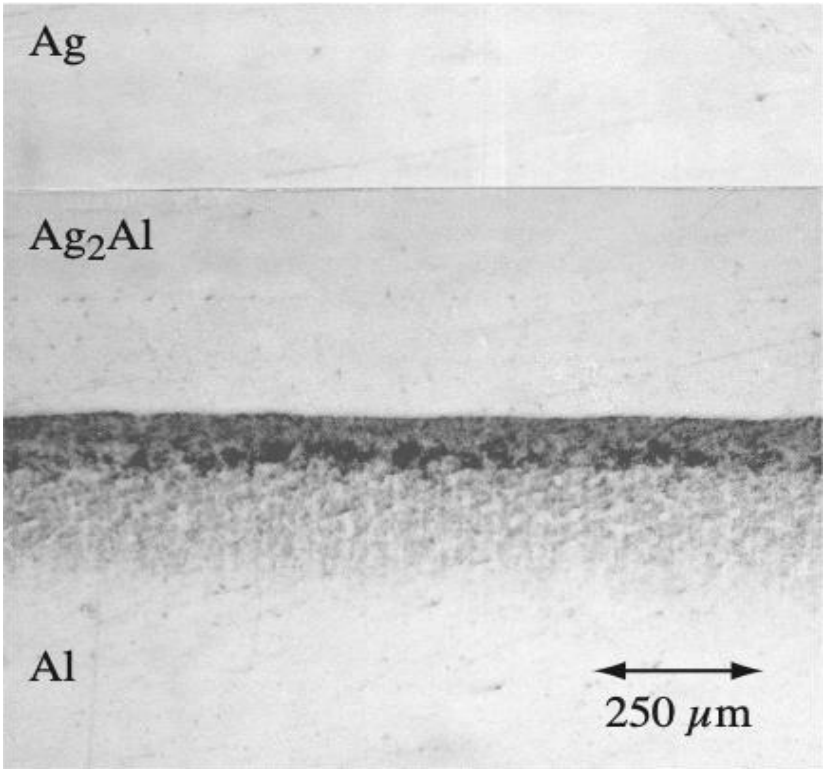


Figure 5-12: *Metallographic image of a diffusion couple Ag-Al annealed for 196 hours at 500˚C. Aluminum diffuses more rapidly than silver. An out equilibrium condition for the vacancy defects concentration thus arises. We note the porosity formed at the interface with aluminum due to the coalescence of vacancies.*

Figure 5-13 shows the variation of concentration in Ag as a function of the position within a diffusion couple of Al-Ag prepared by an 86-hour long annealing process at 500˚C. The concentration has been measured using a microprobe. We note the presence of a plateau at around $C_{Ag} / C_{Al} = 2$. This plateau corresponds to the formation of the intermetallic phase Ag_2Al. The position of the Matano plane, determined graphically (or by computer calculations), is found inside this phase.

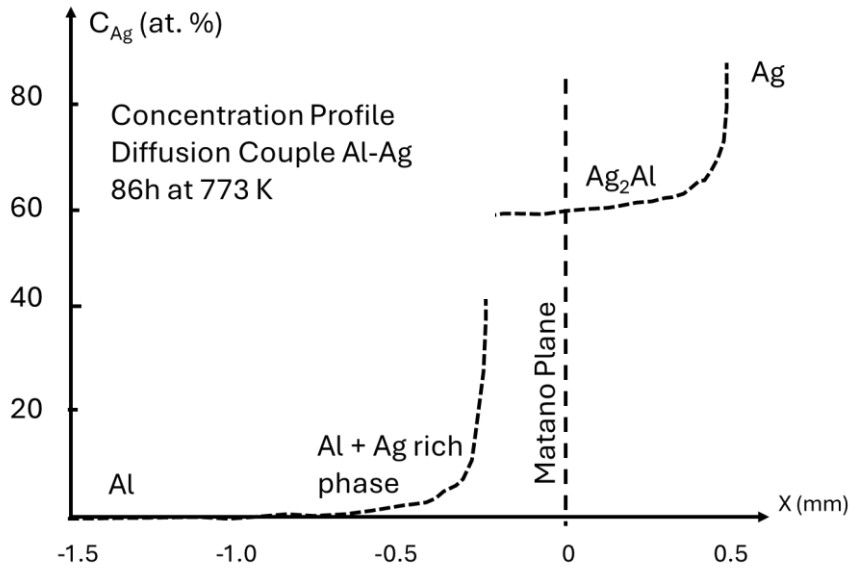


Figure 5-13: *Measured Ag concentration in Al-Ag diffusion couple and the Matano plane.*

Remark: we must note that the solution of (5.4) is not a function of the reduced variable $\eta = x/\sqrt{t}$. The problem is different because of the initial conditions. In the case of Einstein's solution, we are looking at a problem where a thin layer of substance B diffuses in a medium A. The initial condition is then $C_B(x, t=0) = \delta(x)$.

In the case of the Boltzmann-Matano solution, the diffusion problem is one where two species - A and B - interdiffusion from an initial state where they are separate. The initial condition is then $C_A(x, t=0) = \theta(x)$, and $C_B(x, t=0) = \theta(-x)$ where $\theta(x)$ is a step function. We then have:

$$\lim_{t\to 0} \left.\frac{\partial C_A}{\partial x}\right|_t = \delta(x)$$

Solving equation (5.23) with $D^*_A = const$

$$\frac{\partial C_A}{\partial t} = D^*_A \frac{\partial^2}{\partial x^2} C_A$$

$$-\frac{\eta}{2}\frac{dC_A}{d\eta} = D^*_A \frac{d^2}{d\eta^2} C_A$$

$$\frac{d}{d\eta}(C_A(\eta)) = k e^{-\eta^2/4 D^*_A}$$

$$\lim_{t\to 0} \left.\frac{\partial C_A}{\partial x}\right|_t = \delta(x)$$

$$\left.\frac{\partial c}{\partial x}\right|_t = \frac{\partial c}{\partial \eta}\frac{\partial \eta}{\partial x} = \frac{1}{\sqrt{t}}\frac{\partial c}{\partial \eta}$$

$$\lim_{t\to 0}\left(\frac{k}{\sqrt{t}}e^{-\eta^2/4D_A^\star}\right)=\delta(x)\Rightarrow k=\frac{1}{\sqrt{4D_A^\star\pi}}$$

$$\frac{d}{d\eta}C_A=\frac{1}{\sqrt{4\pi D_A^\star}}\exp[-\eta^2/4D_A^\star]$$

From this result, we can write: $(\eta = x/\sqrt{t})$

$$\frac{\partial C_A}{\partial x}=\frac{1}{\sqrt{4\pi D_A^\star t}}\exp[-x^2/4D_A^\star t] \text{ and thus}$$

$$C_A(x)=C_0 erf(e/2\sqrt{D_A^\star t})$$

$$\text{with } erf(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-z^2}dz$$

This solution is described in section 5.1.2, for example, c on interdiffusion.

5.6 The Kirkendall Effect

Frequently, in a diffusion couple, the diffusion coefficients of a species in another are different. This results in a physical displacement of the sample, which must be considered when determining the diffusion coefficients. The process can be described schematically in Figures 5-14 below. We suppose that $D_A >> D_B$. Then, the diffusion of A (substitutional) into B can only happen due to vacancies. If the number of vacancy sites in the lattice is constant, vacancies must be equally created and annihilated.

From a fixed reference system, we would observe a flux of vacancies, which compensates for the flux of A (and of B):

$$J_v + J_A + J_B = 0 \tag{5.29}$$

In other words, the flux of vacancies on the one hand and the excess of the flux of atoms on the other cause a displacement of the sample with respect to a fixed reference, which can be visualized by markers that do not diffuse. If the vacancies do not have the time to annihilate, they coalesce and form "Kirkendall porosity" (figure 5-12).

The fluxes J_A and J_B are defined (5.22) by these equations:

$$J_A=-D_A^\star\frac{\partial C_A}{\partial x} \tag{5.30}$$

$$J_B=-D_B^\star\frac{\partial C_B}{\partial x} \tag{5.31}$$

where $D_{A,B}^\star$ are the intrinsic coefficients of diffusion or the more general Dehlinger-Darken coefficients (see eq. 5.23), and they are measured with respect to a *plane of the crystal lattice*.

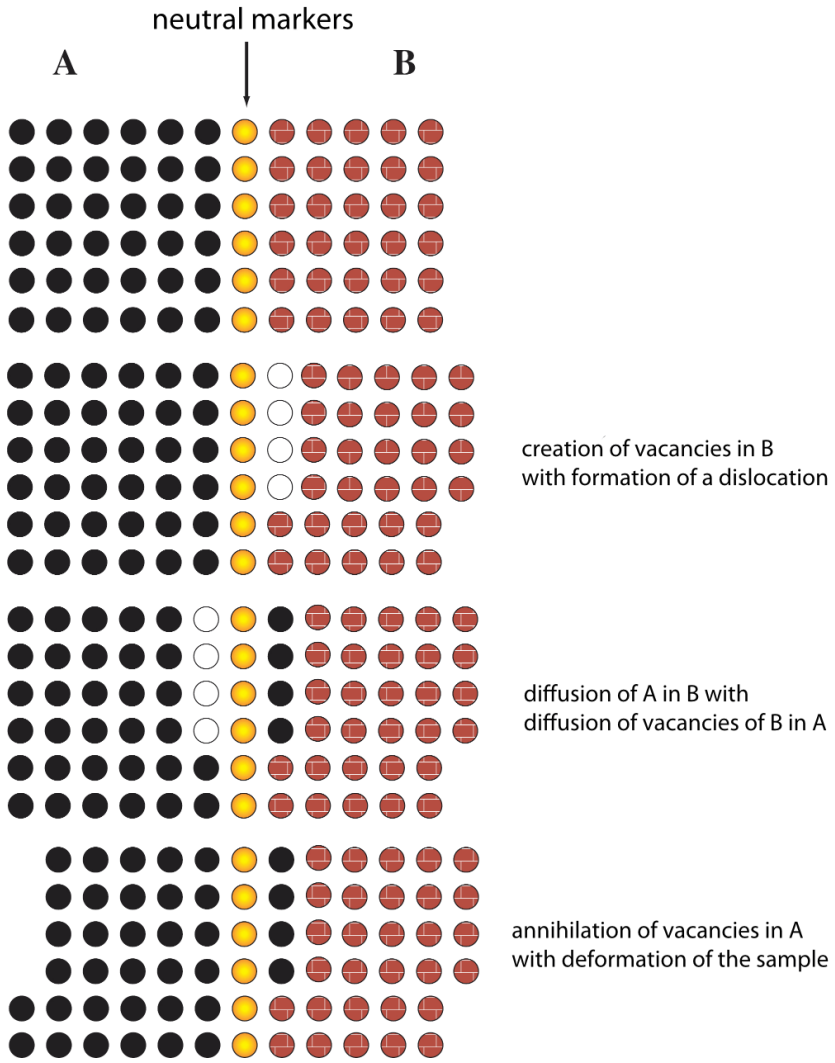


Figure 5-14: *Consecutive images of diffusion with the creation and annihilation of vacancy defects*

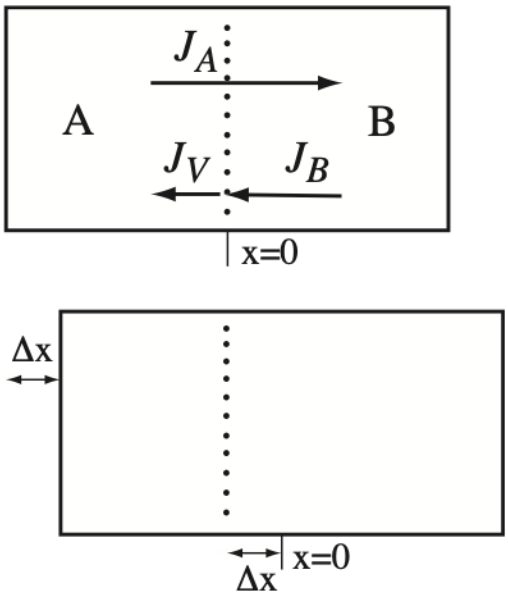


Figure 5-15: *Kirkendall effect: the motion of vacancies and atoms causes the translation of the sample by* ***Δx****. The makers moved in the direction of the flux of vacancies of the same distance Δx with respect to the sample.*

The experimental measures cannot be taken to the sample coordinate system S_0. We note that in this reference system, the vacancy process is only transient, and the total observed flux is zero since:

$$C_A + C_B = const \tag{5.32}$$

and thus:

$$J_A^0 + J_B^0 = 0 \tag{5.33}$$

The sample displacement relative to the crystal lattice is determined by the velocity of the vacancies (Kirkendall velocity).

$V = J_v \Omega$ with $\Omega =$ atomic volume

Since $D_A^\star \neq D^\star{}_B$, then $J_A \neq J_B$ and

$$V = -(J_A + J_B)\Omega \tag{5.34}$$

On the other hand, equation (5.32) implies that $\frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$ and thus:

$$V = (D_A^\star - D_B^\star)\frac{\partial X_A}{\partial x} \qquad (\text{as } X_A = C_A \cdot \Omega \ )$$

If $D_A^\star > D_B^\star$ then V < 0.

We can measure the Kirkendall effect experimentally, as described in Figure 5-16:

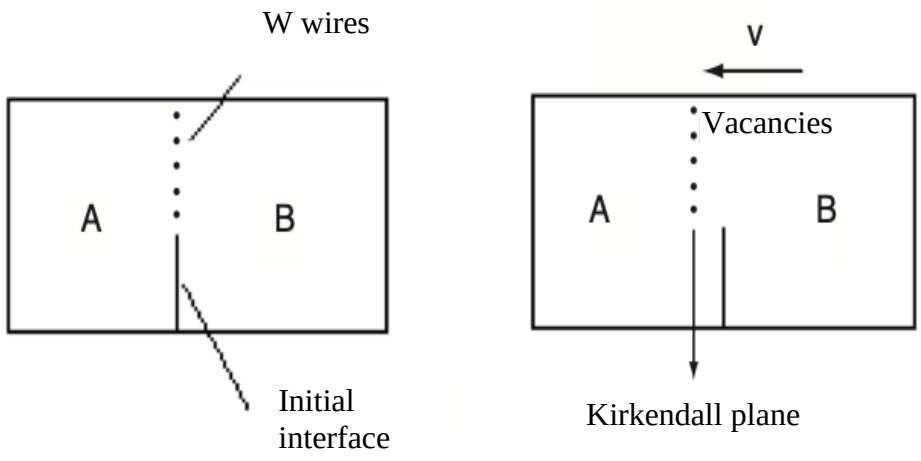


Figure 5-16: *Kirkendall experiment showing the displacement of the reference attached to the initial interface. After diffusion, the wires have moved. This allows for measuring the velocity (V)*

Consider the reference of the sample S_0. The Matano plane is linked to this system of coordinates. We know (5.33) that $J_A^0 + J_B^0 = 0$. J_A^0 and J_B^0 are defined by the diffusion equations with a new diffusion coefficient /, which has to be the same for A and B by symmetry. This change of coordinates implies:

$$J_A^0 = -\tilde{D}\frac{\partial C_A}{\partial x} \quad J_B^0 = -\tilde{D}\frac{\partial C_B}{\partial x} \tag{5.35}$$

$$J_A^0 = J_A + VC_A = -D_A^\star \frac{\partial C_A}{\partial x} + VC_A$$
$$J_B^0 = J_B + VC_B = -D_B^\star \frac{\partial C_B}{\partial x} + VC_B \tag{5.36}$$

$$J_A^0 = -D_A^\star \frac{\partial C_A}{\partial x} + (D_A^\star - D_B^\star)\frac{\partial C_A}{\partial x} X_A = -(D_A^\star - X_A D_A^\star + X_A D_B^\star)\frac{\partial C_A}{\partial x}$$

As $1 - X_A = X_B$:

$$\tilde{D} = X_A D_A^\star + X_A D_B^\star \tag{5.37}$$

This is the coefficient of interdiffusion.

The concentration of each species is measured in the reference system of the sample and thus:

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J_A^0}{\partial x}$$

As a consequence, the new diffusion equation is given by:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial C_A}{\partial x}\right) \tag{5.38}$$

Experimental method

1) Measure $\tilde{D}$ with the Boltzmann-Matano method

2) Obtain $D_A^\star$ and $D_B^\star$ by measuring the speed of the Kirkendall plane:

$$V = (D_A^\star - D_B^\star)\frac{\partial X_A}{\partial x}$$

In Figure 5-17, we graphically show (in an ideal case of perfect reciprocal solubility) the displacement of the Kirkendall plane relative to the Matano plane, which remains practically fixed. We can show that:

$D^\star{}_B / D_A^\star = B/A$

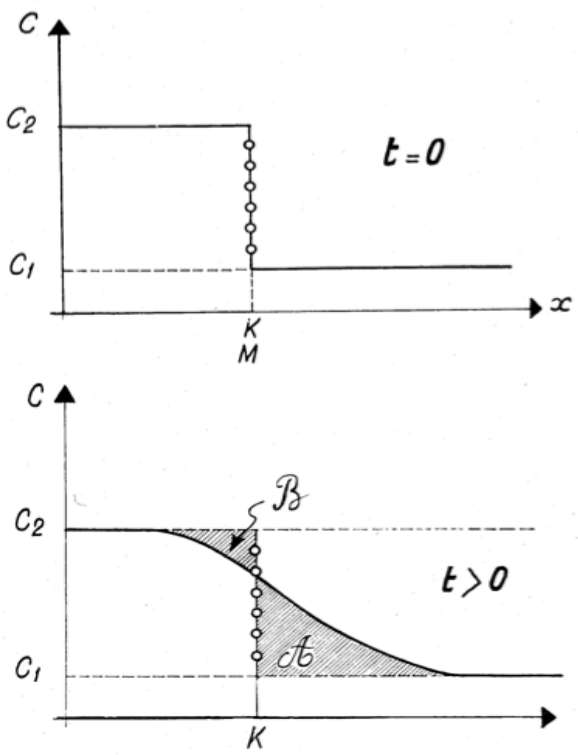


Figure 5-17: *At the beginning of diffusion, the Kirkendall plane and the Matano plane coincide; after that, the Kirkendall plane moves with the lattice, whereas the equality of the surfaces defines the Matano plane.*

5.7 Real solutions

The solutions above do not apply to cases where the concentration varies over a long range and the solubility of the diffusing element is limited.
The results showed a very different outcome (figure 5-19). This result can be understood if we compare it to the phase diagram of the Al-Ag alloy.

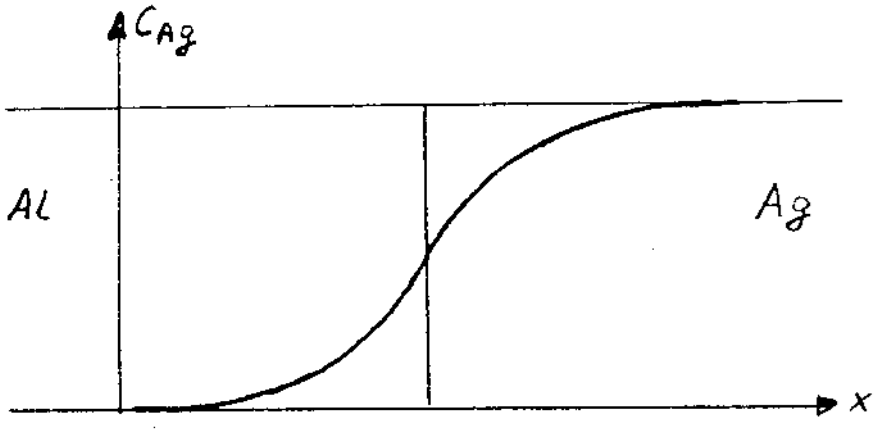


Figure 5-18: *Theoretical concentration profile of the alloy Ag-Al*

Consider a diffusion couple formed by the assembly of an aluminum and a silver cube. At a temperature of ≈ 500˚C, Al diffuses in Ag and Ag in Al. From equation 5.5, we can predict a concentration-distance curve in Figure 5-18.

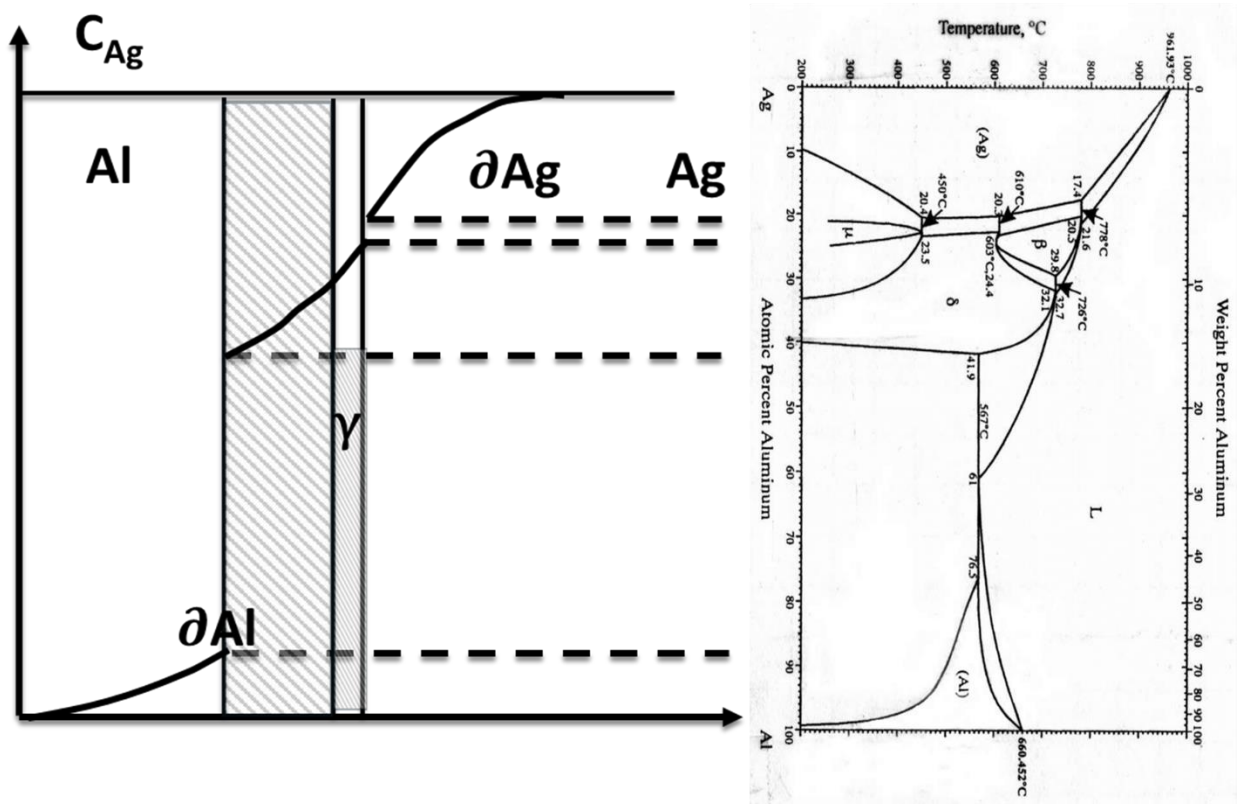


Figure 5-19: *Concentration in the couple Ag-Al and binary phase diagram of the alloy*

Consequently, the preceding analysis regarding the thermodynamic equilibrium between phases must be reconsidered. We address this subject in Chapter XI.