Vacancy Diffusion

The jumping of atoms into vacant sites can equally be considered as the jumping of vacancies onto atom sites. If excess vacancies are introduced into the lattice, they will diffuse at a rate which depends on the jump frequency.

However, a vacancy is always surrounded by sites to which it can jump and is therefore analogous to an interstitial atom.

$$D_v = \frac{1}{6}\Delta x^2 \Gamma_v$$

remember $D_B = \left[\frac{1}{6}\Delta x^2 z\nu \exp\frac{\Delta S_m}{R}\right]\exp\frac{-\Delta H_m}{RT} \Rightarrow D_v = \frac{1}{6}\Delta x^2 z\nu \exp\frac{\Delta S_m}{R}\exp\frac{-\Delta H_m}{RT}$

ΔH_m and ΔS_m apply for the migration of a vacancy, and are therefore same as for the migration of a substitutional atom.

Comparing 2 equations: $D_A = \frac{1}{6}\Delta x^2 z\nu \exp\frac{\Delta S_m + \Delta S_v}{R}\exp -\left(\frac{\Delta H_m + \Delta H_v}{RT}\right)$ and $D_v = \frac{1}{6}\Delta x^2 z\nu \exp\frac{\Delta S_m}{R}\exp\frac{-\Delta H_m}{RT}$

$\Rightarrow D_v = D_A / X_v^e \Rightarrow$ D_v is many orders of magnitude greater than D_A, the diffusivity of substitutional atoms.

Diffusion in Substitutional Alloys

In self-diffusion, all atoms are identical. Therefore the probability of finding a vacancy adjacent to any atom and the probability that the atom will make a jump into the vacancy is equal for all atoms. This leads to a simple relationship btw jump frequency and diffusion coefficient.

In binary substitutional alloys, the situation is more complex. In general the rate at which solvent A and solute B atoms can move into a vacant site is not equal. Each one has its own intrinsic diffusion coefficients; D_A and D_B.

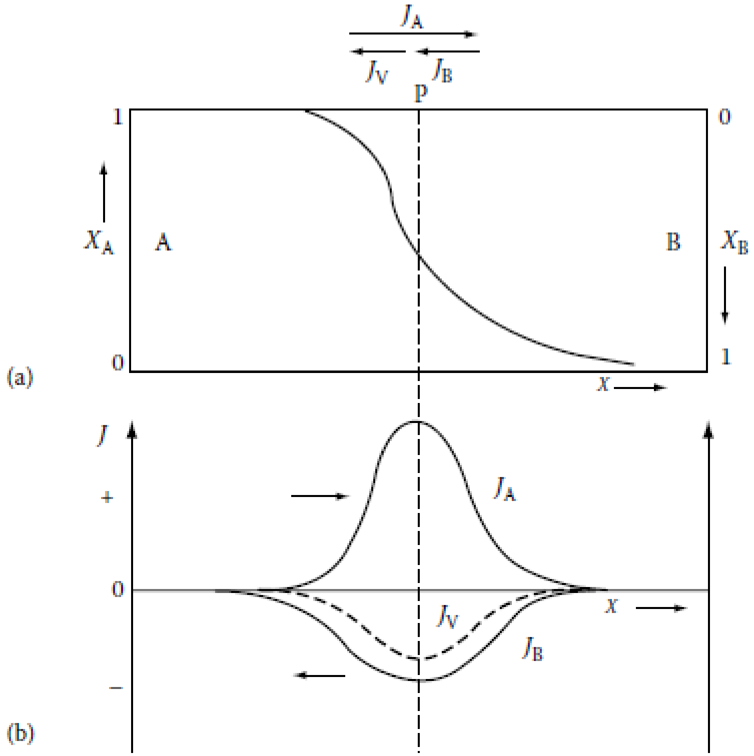
They are defined such that Fick's first law applies relative to the lattice;

$$J_A = -D_A \frac{\partial C_A}{\partial x} \qquad J_B = -D_B \frac{\partial C_B}{\partial x}$$

To simplify, assume that total number of atoms per unit volume is constant, C_0;

$$C_0 = C_A + C_B \quad \text{and} \quad \frac{\partial C_A}{\partial x} = -\frac{\partial C_B}{\partial x}$$

In order do derive Fick's second law let us consiter the interdiffusion of A and B as shown in the figure. A and B atoms in a diffusion couple that is made by welding together blocks of pure A and B.



Interdiffusion and vacancy flow. (a) Composition profile after interdiffusion of A and B. (b) The corresponding fluxes of atoms and vacancies as a function of position x.

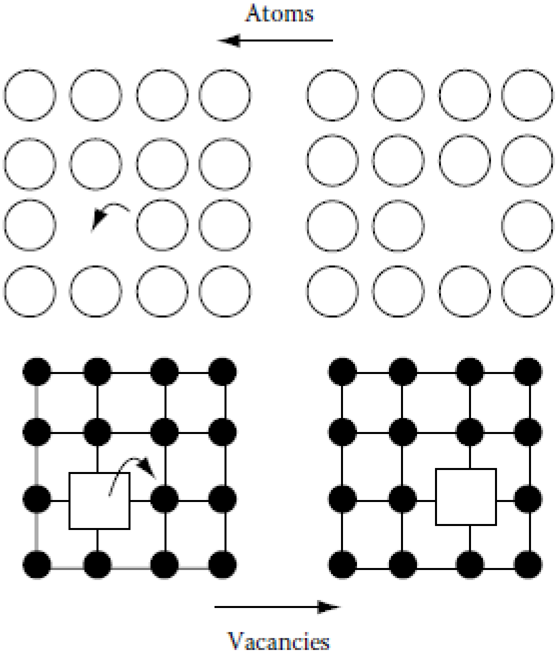
$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad , \quad J_B = D_B \frac{\partial C_A}{\partial x}$$

from the figure, for the case $D_A > D_B$, i.e. $|J_A| > |J_B|$

When atoms migrate by the vacancy process the jumping of an atom into a vacant site can equally well be regarded as the jumping of the vacancy onto the atom.

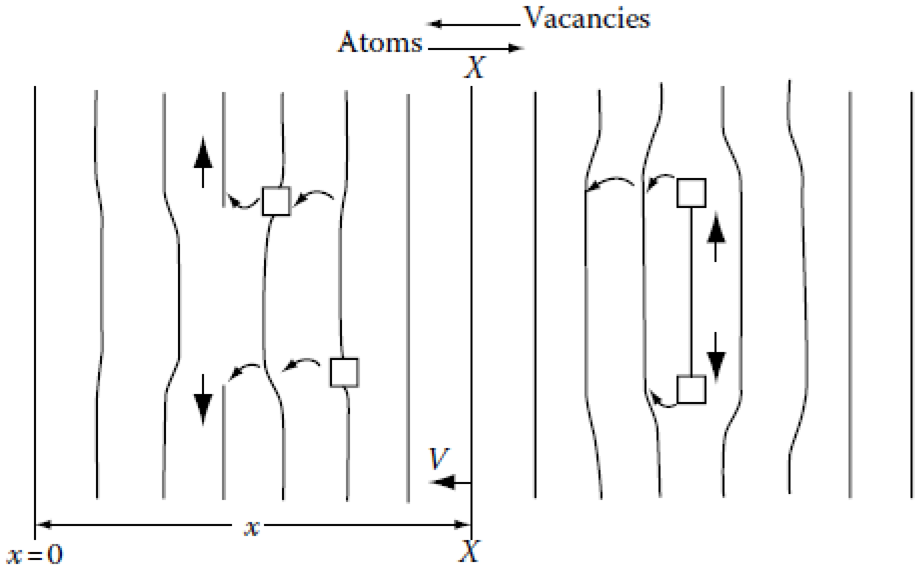
$$\Rightarrow J_v = -J_A - J_B$$

$$\Rightarrow J_v = (D_A - D_B)\frac{\partial C_A}{\partial x}$$



In order to maintain the vacancy concentration everywhere near equilibrium vacancies must be created on the B-rich side and destroyed on the A-rich side.

It is the net flux of vacancies across the middle of the diffusion couple that gives rise to movement of the lattice. Edge dislocations can provide a convenient source or sink for vacancies. Vacancies can be absorbed by the extra half-plane of the edge dislocation shrinking while growth of the plane can occur by the emission of vacancies. If this or a similar mechanism operates on each side of the diffusion couple then the required flux of vacancies can be generated



A flux of vacancies causes the atomic planes to move through the specimen

The velocity at which any given lattice plane moves, v, can be related to the flux of vacancies crossing it. If the plane has an area A, during a small time interval δt, the plane will sweep out a volume of $Avdt$ containing $Av\,dt\,C_0$ atoms.

This number of atoms is removed by the total number of vacancies crossing the plane in the same time interval, i.e. $J_v A \cdot \delta t$, giving

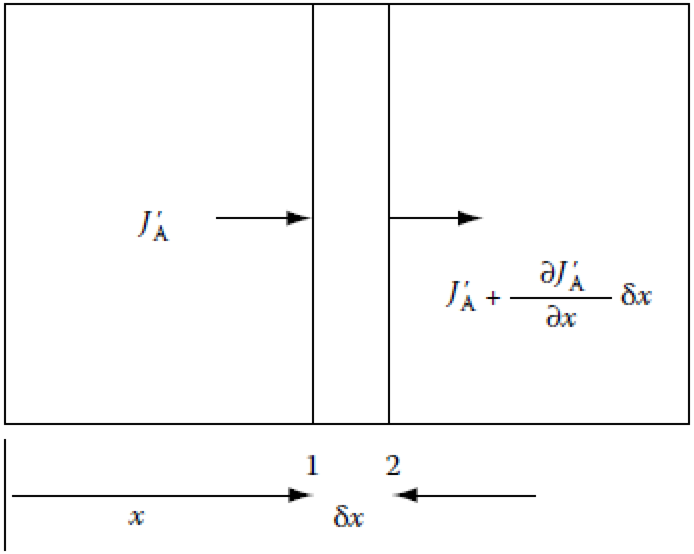
$$J_v = C_0 v$$

Since the mole fraction of A, $X_A = C_A/C_0$

$$v = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

Consider a thin slice of material δx thick at a *fixed distance x from one end of the couple* which is outside the diffusion zone as shown in Figure

$$\frac{\partial C_A}{\partial t} = -\frac{\partial J'_A}{\partial x}$$



The total flux of A atoms across a stationary plane with respect to the *specimen* is the sum of two contributions: (i) a diffusive flux, $J_A = -D_A\, \partial C_A/\partial x$ due to diffusion relative to the *lattice*, and (ii) a flux vC_A due to the velocity of the lattice in which diffusion is occurring. Therefore:

$$J'_A = -D_A \frac{\partial C_A}{\partial x} + vC_A$$

By combining this equation with $v = (D_A - D_B)\dfrac{\partial X_A}{\partial x}$

$$J'_A = -(X_B D_A + X_A D_B)\frac{\partial C_A}{\partial x}$$

where $X_A = C_A/C_0$ and $X_B = C_B/C_0$

This can be simplified by defining an *interdiffusion coefficient* $\tilde{D}$ as

$$\tilde{D} = X_B D_A + X_A D_B$$

so that Fick's first law becomes

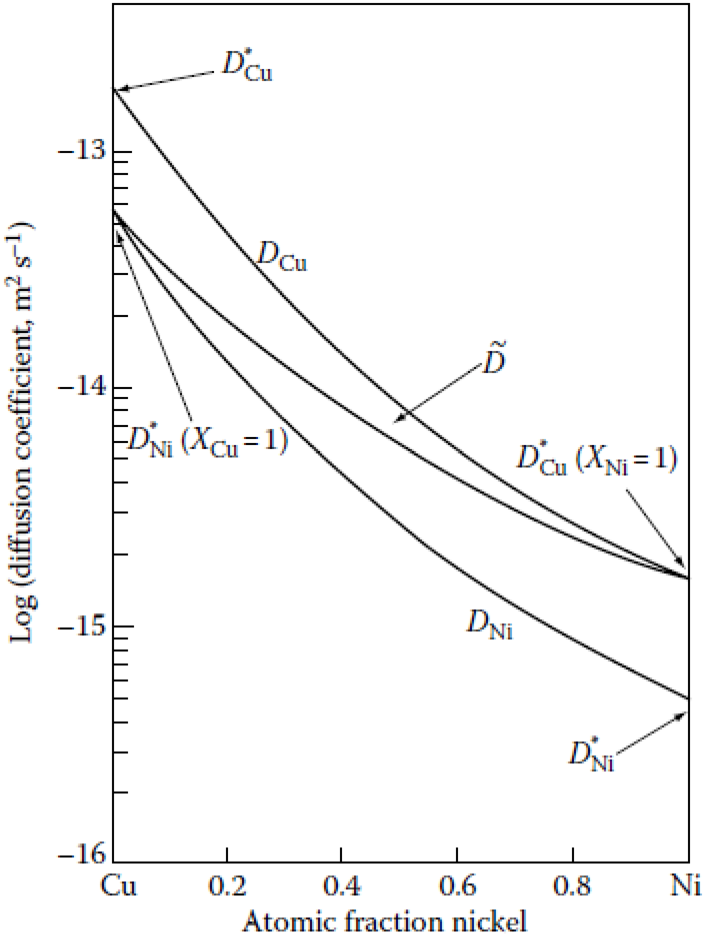
$$J'_A = -\tilde{D}\frac{\partial C_A}{\partial x}$$

Likewise;

$$J'_B = -\tilde{D}\frac{\partial C_B}{\partial x} = \tilde{D}\frac{\partial C_A}{\partial x}$$

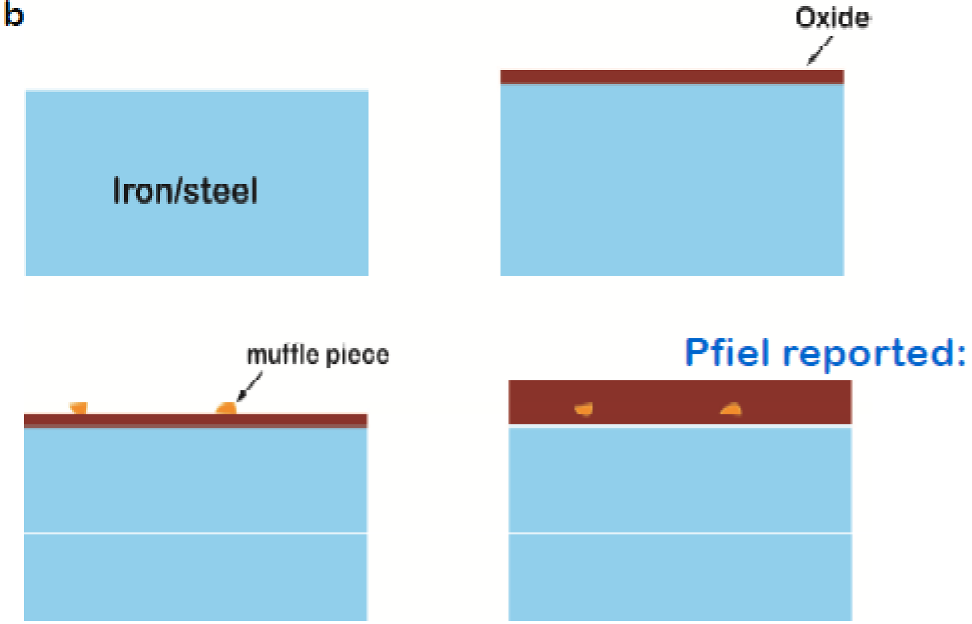
where $J'_B = -J'_A$

the *interdiffusion* coefficient $\widetilde{D}$ for substitutional alloys depends on D_A and D_B whereas in interstitial diffusion D_B alone is needed.



The relationship between the various diffusion coefficients in the Cu-Ni system at 1000°C

- Pfiel's was studying oxidation of steel and noticed one strange behavior as explained b

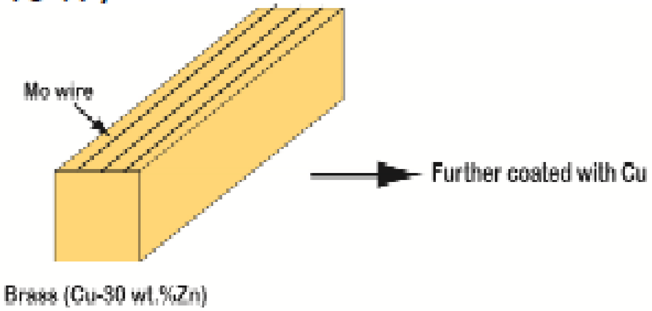


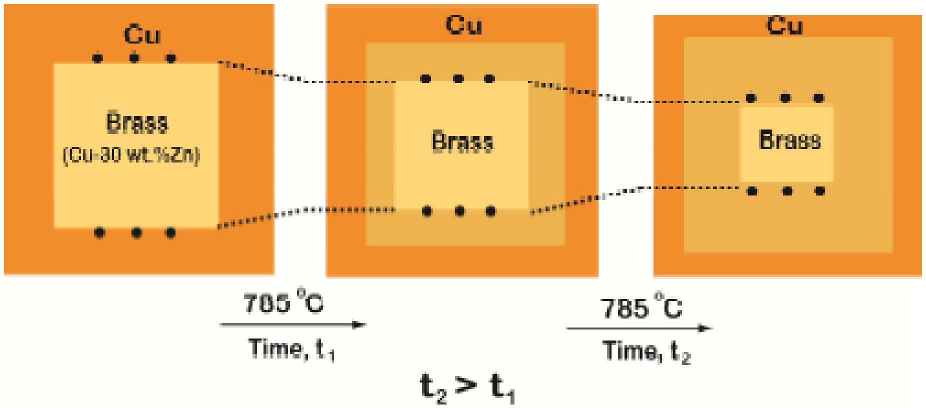
"It had frequently been noticed that small particles of foreign matter (such as pieces of muffle) falling on the surface of oxidising iron were gradually buried. The scale grew up around these particles until they finally disappeared beneath the surface, but they could afterwards be found by breaking up the layer of scale".

- This was rather an indication that the oxide scale was growing from the oxide/air interface. Then only the muffle pieces could get buried.
- This further indicated that the diffusion rate of the species Fe and O were most probably not the same.

L.B. Pfeil, The oxidation of iron and steel at high temperatures, J. Iron Steel **119** (1929) 501-47

- To check this issue Kirkendall with his student Smigelkas designed a special experiment (published in 1947)



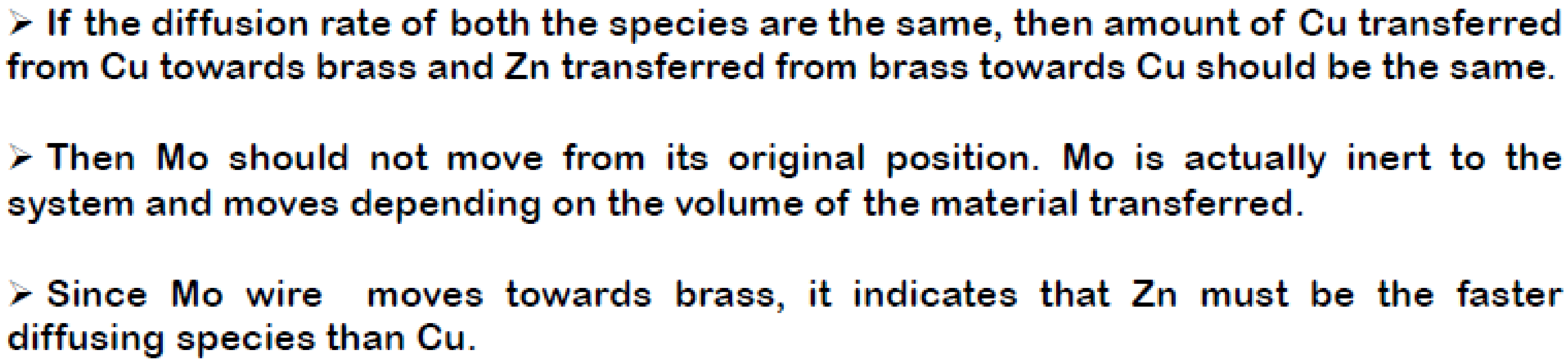


- They took a rectangular block of brass, which is a Cu-Zn alloy and wound with Mo wire

- Following, they electroplated the block with pure Cu

- Then this block was annealed at an elevated temperature for different times.

- To their surprise they found that Mo wires moved inside from its original position. With the increase in annealing time it moved even more.



- If the diffusion rate of both the species are the same, then amount of Cu transferred from Cu towards brass and Zn transferred from brass towards Cu should be the same.
- Then Mo should not move from its original position. Mo is actually inert to the system and moves depending on the volume of the material transferred.
- Since Mo wire moves towards brass, it indicates that Zn must be the faster diffusing species than Cu.

ATOMIC MOBILITY

Fick’s first law is based on the assumption that diffusion eventually stops, that is equilibrium is reached, when the concentration is the same everywhere. However, this situation is never true in practice because real materials always contain lattice defects such as grain boundaries, phase boundaries and dislocations. Some atoms can lower their free energies if they migrate to such defects and at ‘equilibrium’ their concentrations will be higher in the vicinity of the defect than in the matrix. Diffusion in the vicinity of these defects is therefore affected by both the concentration gradient and the gradient of the interaction energy. Fick’s law alone is insufficient to describe how the concentration will vary with distance and time.

As an example consider the case of a solute atom that is too big or too small in comparison to the space available in the solvent lattice. The potential energy of the atom will then be relatively high due to the strain in the surrounding matrix. However, this strain energy can be reduced if the atom is located in a position where it better matches the space available, e.g. near dislocations and in boundaries, where the matrix is already distorted.

Segregation of atoms to grain boundaries, interfaces and dislocations is of great technological importance. For example the diffusion of carbon or nitrogen to dislocations in mild steel is responsible for strain ageing and blue brittleness.

The segregation of impurities such as Sb, Sn, P and As to grain boundaries in low-alloy steels produces temper embrittlement.

Segregation to grain boundaries affects the mobility of the boundary and has pronounced effects on recrystallization, texture and grain growth.

Similarly the rate at which phase transformations occur is sensitive to segregation at dislocations and interfaces.

The problem of atom migration can be solved by considering the thermodynamic condition for equilibrium; namely that the chemical potential of an atom must be the same everywhere. Diffusion continues in fact until this condition is satisfied.

Therefore it seems reasonable to suppose that in general the flux of atoms at any point in the lattice is proportional to the chemical potential gradient.

An alternative way to describe a flux of atoms is to consider a net *drift* velocity (v) superimposed on the random jumping motion of each diffusing atom. The drift velocity is simply related to the diffusive flux via the equation

$$J_B = v_B C_B$$

Since atoms always migrate so as to remove differences in chemical potential it is reasonable to suppose that the drift velocity is proportional to the local chemical potential gradient,

$$v_B = -M_B \frac{\partial \mu_B}{\partial x}$$

where M_B is a constant of proportionality known as the atomic mobility.

Since *chemical potential is* energy and the derivative of *it* with respect to distance is effectively the chemical ‘force’ causing the atom to migrate. By combining last 2 equations;

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

Intuitively it seems that the mobility of an atom and its diffusion coefficient must be closely related. The relationship can be obtained by relating $\partial\mu/\partial x$ to $\partial C/\partial x$ for a stress-free solid solution. Using Equation

$$-X_A \mathrm{d}\mu_A = X_B \mathrm{d}\mu_B = RT\left\{1+\frac{\mathrm{d}\ln\gamma_A}{\mathrm{d}\ln X_A}\right\}\mathrm{d}X_B = RT\left\{1+\frac{\mathrm{d}\ln\gamma_B}{\mathrm{d}\ln X_B}\right\}\mathrm{d}X_B$$

and $C_B = X_B/V_m$, *above flux equation* becomes

$$J_B = -M_B \frac{X_B}{V_m}\cdot\frac{RT}{X_B}\left\{1+\frac{d\ \mathit{In}\ \gamma_B}{d\ \mathit{In}\ X_B}\right\}\frac{\partial X_B}{\partial x}$$

$$J_B = -M_B RT\left\{1+\frac{\mathrm{d}\ \mathrm{In}\ \gamma_B}{\mathrm{d}\ \mathrm{In}\ X_B}\right\}\frac{\partial C_B}{\partial x}$$

Comparison with Fick’s first law gives the required relationship

$$D_B = M_B RT \left\{ 1 + \frac{\mathrm{d} \ln \gamma_B}{\mathrm{d} \ln X_B} \right\}$$

Similarly

$$D_A = M_A RT \left\{ 1 + \frac{\mathrm{d} \ln \gamma_A}{\mathrm{d} \ln X_A} \right\}$$

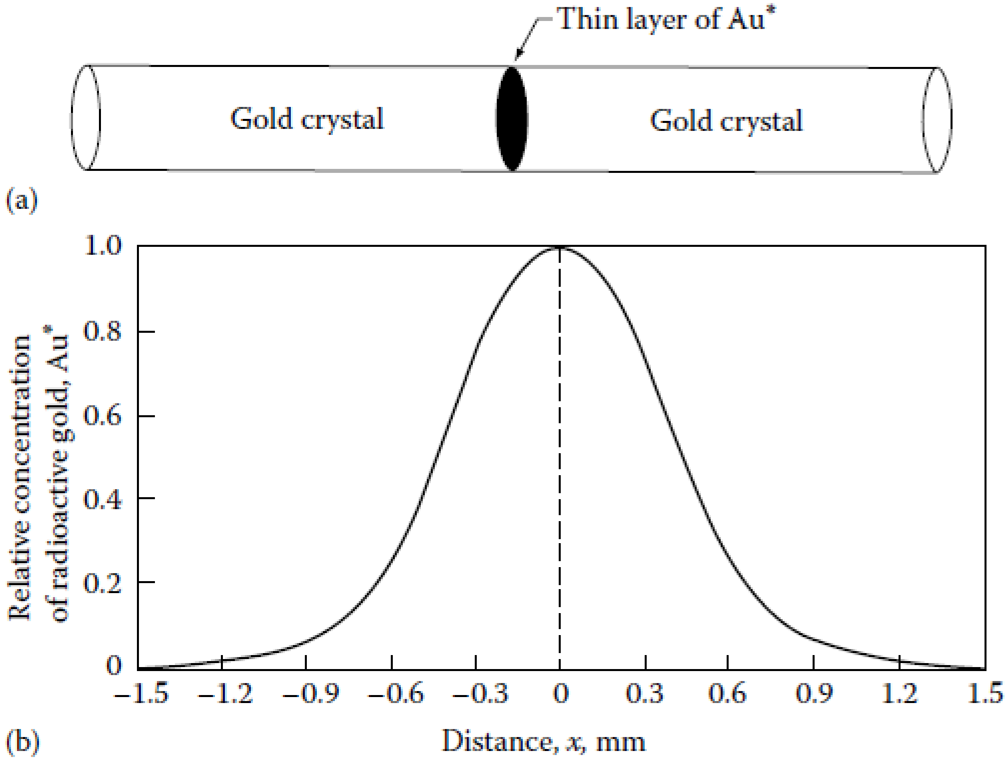
For *ideal* or *dilute* solutions ($X_B \rightarrow 0$), γ_B is a constant and the term in brackets is unity, i.e.

$$D_B = M_B RT$$

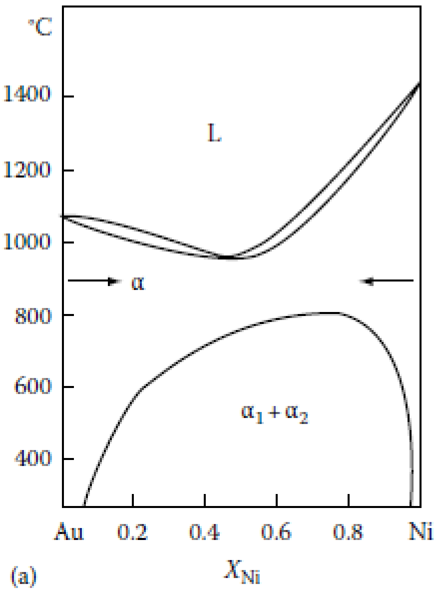
Tracer Diffusion in Binary Alloys

The use of radioactive tracers were described in connection with self-diffusion in pure metals. It is, however, possible to use radioactive tracers to determine the intrinsic diffusion coefficients of the components in an alloy.

The method is similar to that shown in Figure below, except that a small quantity of a suitable radioactive tracer, e.g. B*, is allowed to diffuse into a homogeneous bar of A/B solution. The value obtained for D from is the tracer diffusion coefficient D^*_B



Such experiments have been carried out on a whole series of gold-nickel alloys at 900°C. At this temperature gold and nickel are completely soluble in each other.



Since radioactive isotopes are chemically identical it might appear at first sight that the tracer diffusivities (D^*_{Au} and D^*_{Ni}) should be identical to the intrinsic diffusivities (D_{Au} and D_{Ni}) determined by marker movement in a diffusion couple.

However, it can be demonstrated that this is not the case. D^*_{Au} gives the rate at which Au* (or Au) atoms diffuse in a *chemically homogeneous* alloy, whereas D_{Au} gives the diffusion rate of Au when a concentration gradient is present.

The Au-Ni phase diagram contains a miscibility gap at low temperatures implying that ΔHmix > 0 (the gold and nickel atoms ‘dislike’ each other).

Therefore, whereas the jumps made by Au atoms in a chemically homogeneous alloy will be equally probable in all directions, in a concentration gradient they will be biased away from the Ni-rich regions. (because they dont like eacother)

The rate of homogenization will therefore be slower in the second case, i.e. $D_{Au} < D^*_{\mathrm{Au}}$ and $D_{Ni} < D^*_{\mathrm{Ni}}$. On the other hand since the chemical potential gradient is the driving force for diffusion in both types of experiment it is reasonable to suppose that the atomic mobilities are not affected by the concentration gradient. If this is true the intrinsic chemical diffusivities and tracer diffusivities can be related as follows.

$$D^*_B = M^*_B RT = M_B RT$$

$$D_A = F D^*_A$$

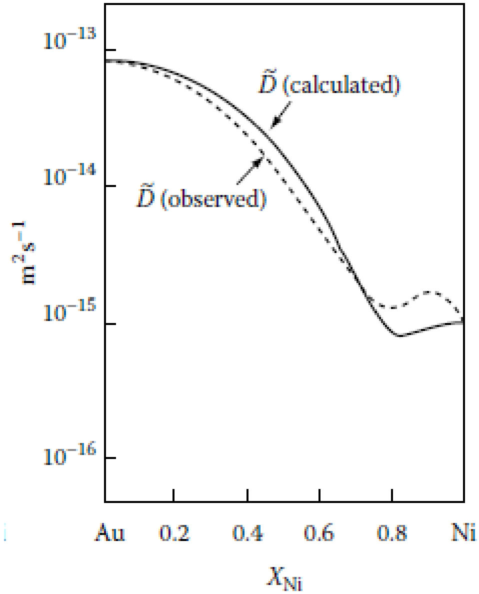
$$D_B = F D^*_B$$

$$\tilde{D} = F(X_B D^*_A + X_A D^*_B)$$

where *F* is the thermodynamic factor, i.e.

$$F = \left\{1 + \frac{d\ \ln \gamma_A}{d\ \ln X_A}\right\} = \left\{1 + \frac{d\ \ln \gamma_B}{d\ \ln X_B}\right\} = \frac{X_A X_B}{RT}\frac{d^2G}{dX^2}$$

In the case of the Au-Ni system, diffusion couple experiments have also been carried out so that data are available for the interdiffusion coefficient $\widetilde{D}$, the full line in Figure



It is interesting to note how the diffusion coefficients are strongly composition dependent. There is a difference of about three orders of magnitude across the composition range. This can be explained by the lower liquidus temperature of the Au-rich compositions. Also, with the lower melting temperature, Au diffuses faster than Ni at all compositions

High-Diffusivity Paths

In Atomic Mobility section, the diffusion of atoms towards or away from dislocations, interfaces, grain boundaries and free surfaces was considered. In this section diffusion *along* these defects will be discussed.

All of these defects are associated with a more open structure and it has been shown experimentally that the jump frequency for atoms migrating along these defects is higher than that for diffusion in the lattice. It will become apparent that under certain circumstances diffusion along these defects can be the dominant diffusion path.

Diffusion along Grain Boundaries and Free Surfaces

It is found experimentally that diffusion along grain boundaries and free surfaces can be described by

$$D_b = D_{b0}\ \exp\frac{-Q_b}{RT} \qquad D_s = D_{s0}\exp\frac{-Q_s}{RT}$$

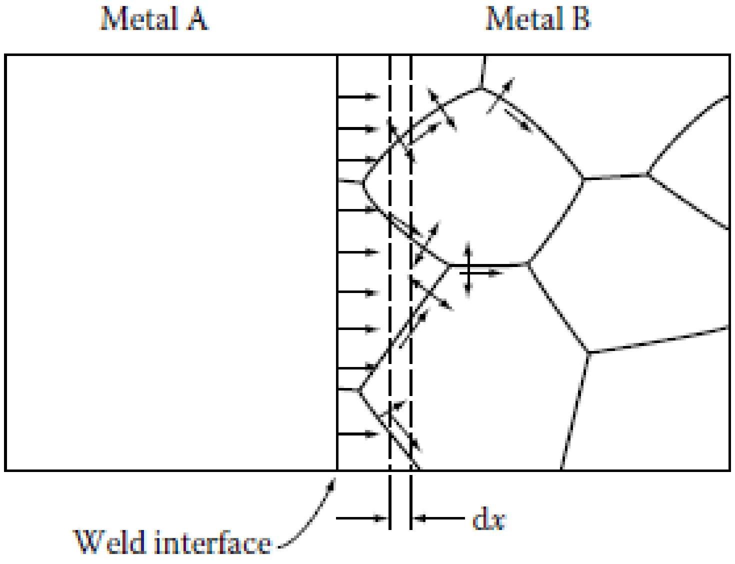
where D_b and D_s are the grain boundary and surface diffusivities and D_{b0} and D_{s0} are the frequency factors. Q_b and Q_s are the experimentally determined values of the activation energies for diffusion.

In general, at any temperature the magnitudes of D_b and D_s relative to the diffusivity through defect-free lattice D_l, are such that

$$D_S > D_b > D_1$$

This means the relative ease with which atoms can migrate along free surfaces, grain boundaries and through the lattice. Surface diffusion can play an important role in many metallurgical phenomena, but in an average metallic specimen the total grain boundary area is much greater than the surface area so that grain boundary diffusion is usually most important.

The effect of grain boundary diffusion can be illustrated by considering a diffusion couple made by welding together two metals, A and B, as shown in Figure

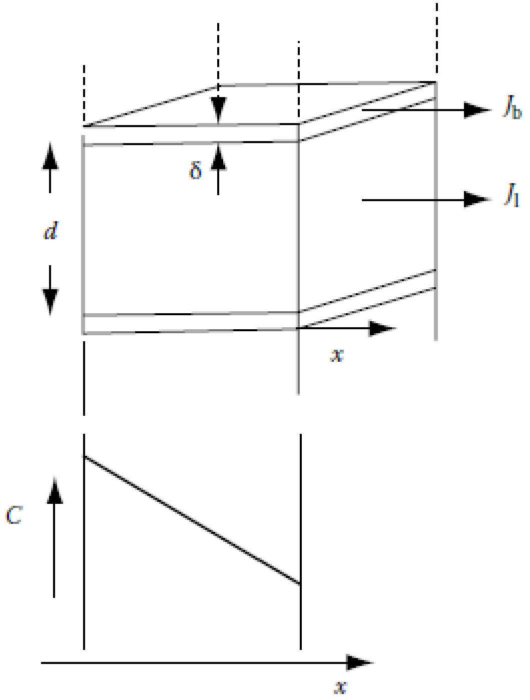


A atoms diffusing along the boundary will be able to penetrate much deeper than atoms which only diffuse through the lattice. In addition, as the concentration of solute builds up in the boundaries atoms will also diffuse from the boundary into the lattice.

Points in the lattice close to grain boundaries can receive solute via the high conductivity path much more rapidly than if the boundaries were absent. Rapid diffusion along the grain boundaries increases the mean concentration in a slice such as d*x* in Figure and thereby produces an increase in the apparent diffusivity in the material as a whole.

Consider now under what conditions grain boundary diffusion is important

For simplicity let us take a case of steady-state diffusion through a sheet of material in which the grain boundaries are perpendicular to the sheet as shown in Figure.



Assuming that the concentration gradients in the lattice and along the boundary are identical, the fluxes of solute through the lattice J_l and along the boundary J_b will be given by

$$J_1 = -D_1 \frac{dC}{dx} \quad J_b = -D_b \frac{dC}{dx}$$

However the contribution of grain boundary diffusion to the total flux through the sheet will depend on the relative cross-sectional areas through which the solute is conducted.
If the grain boundary has an effective thickness δ and the grain size is *d* the total flux will be given by

$$J = (J_b\delta + J_1\mathrm{d})/\mathrm{d} = -\left(\frac{D_b\delta + D_1\mathrm{d}}{\mathrm{d}}\right)\frac{\mathrm{d}C}{\mathrm{d}x}$$

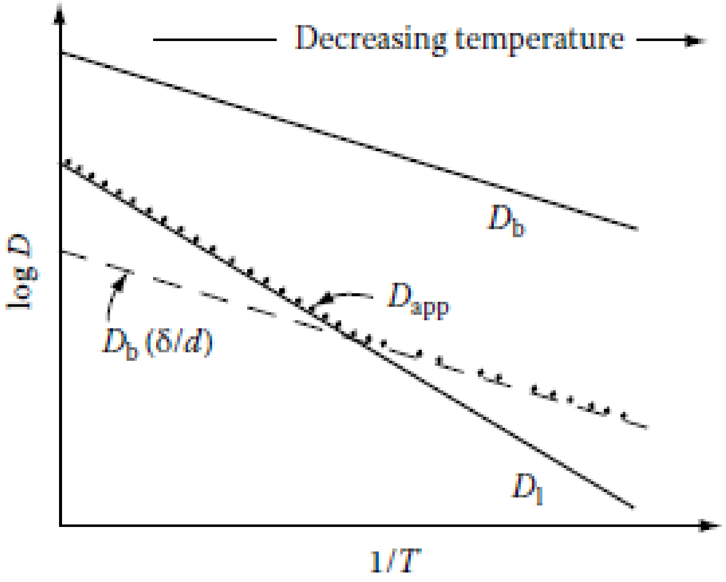
Thus the apparent diffusion coefficient in this case

$$D_{\mathrm{app}} = D_1 + D_b\delta/\mathrm{d}$$

$$\frac{D_{\mathrm{app}}}{D_1} = 1 + \frac{D_b\delta}{D_1\mathrm{d}}$$

It can be seen that the relative importance of lattice and grain boundary diffusion depends on the ratio $D_b\delta/D_l\mathrm{d}$. When $D_b\delta > D_l\mathrm{d}$ diffusion through the lattice can be ignored in comparison to grain boundary diffusion

The effective width of a grain boundary is ~0.5 nm. Grain sizes on the other hand can vary from ~1 to 1000 μm and the effectiveness of the grain boundaries will vary accordingly. The relative magnitudes of D_bd and D_ld are most sensitive to temperature. This is illustrated in Figure which shows the effect of temperature on both D_l, and D_b.



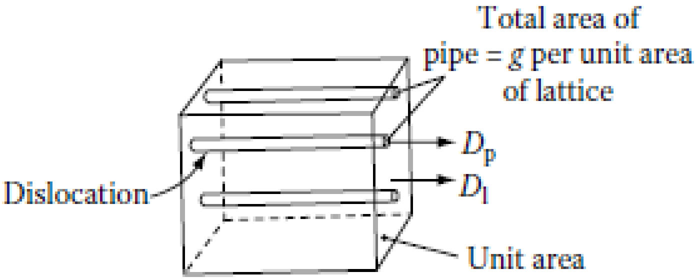
In general it is found that grain boundary diffusion becomes important below about 0.75-0.8 *Tm*, where *Tm* is the equilibrium melting temperature in Kelvin

Diffusion along Dislocations

The dislocations effectively act as pipes along which atoms can diffuse with a diffusion coefficient D_p. The contribution of dislocations to the total diffusive flux through a metal will of course depend on the relative crossectional areas of pipe and matrix. Using the simple model illustrated in Figure, it can easily be shown that the apparent diffusivity through a single crystal containing dislocations, D_{app}, is related to the lattice diffusion coefficient by D

$$\frac{D_{\mathrm{app}}}{D_1} = 1 + g \cdot \frac{D_p}{D_1}$$

where g is the cross-sectional area of 'pipe' per unit area of matrix. In a well annealed material there are roughly 10^5 dislocations mm^{-2}. Assuming that the cross-section of a single pipe accommodates about 10 atoms while the matrix contains about 10^{13} atoms mm^{-2}, makes $g \simeq 10^{-7}$.



At high temperatures diffusion through the lattice is rapid and gD_p/D_l is very small so that the dislocation contribution to the total flux of atoms is negligible.

However, since the activation energy for pipe diffusion is less than for lattice diffusion, D_l decreases much more rapidly than D_p with decreasing temperature, and at low temperatures gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocations.