

Chapter 3

Diffusion in Dilute Alloys

Our discussion of the atomistic mechanisms for diffusion has been confined to the situations where the diffusing species is chemically identical to the host atom. We now relax this assumption, and consider the effects of chemical differences on the diffusivities of the impurity and host atom. We begin this treatment by considering dilute alloys of impurity atoms in a host matrix, ignoring the effect of large chemical composition gradients on the intermixing. We examine the diffusivity of each species by considering the effect on the processes of the atomic jumps. In particular, we consider the vacancy mechanism, where the interaction between the impurity and vacancy can have a large affect on the diffusivity of both species.

3.1 Impurity-Vacancy Interactions

An impurity is different from the host atom in either size or electronic structure or both, which can cause the impurity atom to have an interaction with atomic vacancies. The compressive stress fields surrounding a large impurity atom are relieved somewhat by the tensile stress fields surrounding a vacancy. This stress field interaction can result in a net reduction of energy, and hence an attraction between the vacancy and impurity. More important is the electrostatic attraction between a charged impurity and a vacancy. To understand the origin of this attraction, we consider the interaction between a vacancy and a divalent impurity in a monovalent metal. An example of this situation is Zn in Cu, where the Cu atoms each give an electron to the electron sea, while the Zn impurity donates two electrons and resides as a

doubly charged ion in a host of singly charged Cu ions. A vacancy is a hole in this ion charge array, and thus has a unity negative charge. The electron cloud will rearrange to reduce these charge asperities, but there will still be a net electrostatic attraction between the positively charged impurity ion and the negatively charged vacancy. This is shown schematically in Fig. 3.1.

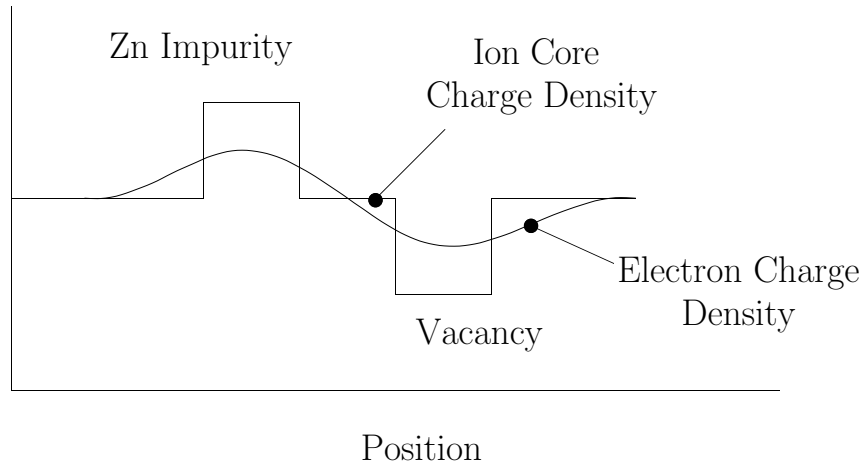


Figure 3.1: Schematic showing the charge density in the region of a vacancy and a doubly charged impurity in a monovalent metal. Also shown is the electron charge density which will reduce the magnitude of the charge for impurity and vacancy.

The magnitude of this interaction is approximated by:

$$\Delta H_B = -\frac{\alpha e^2}{r_c}$$

$$\Delta H_B(\text{eV}) = -\frac{14.4\alpha}{r_c(\text{\AA})}$$

where e is the unit charge, α is the reduction of the charge of the impurity and vacancy due to electron shielding, and r_c is the distance of closest approach between the impurity and vacancy.

One of the consequences of this interaction is to increase the number of vacancies in the neighborhood of an impurity. To see this, we calculate the number of vacancies which join with impurities to form impurity-vacancy pairs.

3.2 Concentration of Vacancy-Impurity Pairs

For a system with N_L total lattice sites, N_I free impurity atoms, N_V free vacancies, and N_{IV} vacancy-impurity pairs, we seek to find the equilibrium concentration of vacancy-impurity pairs. Just as in the calculation of the equilibrium concentration of vacancies, our first task is to calculate the configurational entropy of the system. We can write the number of ways to arrange the impurities, Ω_I , as:

$$\Omega_I = \frac{N_L!}{(N_L - N_I)!N_I!}$$

Similarly for the number of ways to arrange to vacancies, Ω_V :

$$\Omega_V = \frac{N_L!}{(N_L - N_V)!N_V!}$$

For the vacancy-impurity pairs, the total number of sites to place a pair is $zN_L/2$, and the vacancy and impurity of each pair can be swapped, resulting in a different configuration. Thus we have for the number of ways to arrange the vacancy-impurity pairs, Ω_{IV}

$$\Omega_{IV} = \frac{\left(\frac{z}{2}N_L\right)!2^{N_{IV}}}{\left(\frac{z}{2}N_L - N_{IV}\right)!N_{IV}!}$$

The total number of ways to arrange the system is just the product of these three:

$$\begin{aligned} \Omega &= \Omega_I \Omega_V \Omega_{IV} \\ &= \frac{N_L!}{(N_L - N_I)!N_I!} \frac{N_L!}{(N_L - N_V)!N_V!} \frac{\left(\frac{z}{2}N_L\right)!2^{N_{IV}}}{\left(\frac{z}{2}N_L - N_{IV}\right)!N_{IV}!} \end{aligned} \quad (3.1)$$

The entropy of mixing, or configuration entropy, ΔS_{mix} can now be found by:

$$\Delta S_{mix} = k_B \ln \Omega$$

The change in free energy of the system due to the introduction of the vacancies, impurities and impurity-vacancy pairs is just:

$$\Delta G = N_I \Delta G'_I + N_V \Delta G'_V + N_{IV} \Delta G'_{IV} - T \Delta S_{mix}$$

where for $\Delta G'_V$ is the free energy associated with the formation of a vacancy less the mixing entropy contribution and is given by:

$$\Delta G'_V = \Delta H_V - T\Delta S_\nu$$

where ΔS_ν is the excess entropy associated with the change in lattice vibrations due to the presence of the vacancy. Similar expressions can be found for $\Delta G'_I$ and $\Delta G'_{IV}$.

The partial of the system free energy, ΔG , with respect to the number of each constituent, gives that constituent's chemical potential, μ . For example:

$$\begin{aligned} \frac{\partial \Delta G}{\partial N_I} &= \mu_I \\ &= \Delta G'_I - T \frac{\partial \Delta S_{mix}}{\partial N_I} \\ &= \Delta G'_I - k_B T \frac{\partial \ln \Omega_I}{\partial N_I} \\ &\approx \Delta G'_I + k_B T \ln x_I \end{aligned} \quad (3.2)$$

where $x_I = N_I/N_L$. Similarly:

$$\begin{aligned} \mu_V &= \Delta G'_V + k_B T \ln x_V \\ \mu_{IV} &= \Delta G'_{IV} + k_B T \ln \left(\frac{x_{IV}}{z} \right) \end{aligned} \quad (3.3)$$

where $x_V = N_V/N_L$ and $x_{IV} = N_{IV}/N_L$.

At equilibrium, where $x_I = x_I^\circ$, $x_{IV} = x_{IV}^\circ$ and $x_V = x_V^\circ$, we have that:

$$\mu_I^\circ + \mu_V^\circ - \mu_{IV}^\circ = 0$$

so that:

$$\Delta G'_{IV} - \Delta G'_I - \Delta G'_V = -k_B T \left[\ln \left(\frac{x_{IV}^\circ}{z} \right) - \ln x_I^\circ - \ln x_V^\circ \right]$$

It is natural to define ΔG_B as the binding energy of a vacancy-impurity pair as:

$$\Delta G_B = \Delta G'_{IV} - \Delta G'_I - \Delta G'_V$$

so that with $\Delta G_B < 0$ the bound impurity-vacancy complex is stable relative to the free species. We then have:

$$\frac{x_{IV}^\circ}{z x_I^\circ x_V^\circ} = e^{-\Delta G_B / k_B T}$$

If the system is free to arrange itself so as to have the equilibrium concentration of free vacancies, we have:

$$x_V^\circ = e^{-\Delta G'_V/k_B T}$$

Also, since the total number of impurity atoms must be conserved, the concentration of free impurity atoms is just:

$$x_I^\circ = x_{It} - x_{IV}^\circ$$

where x_{It} is the total atomic fraction of impurity atoms. Thus we can write:

$$x_{IV}^\circ = z(x_{It} - x_{IV}^\circ) \exp[-(\Delta G_B + \Delta G'_V)/k_B T]$$

Solving for x_{IV}° we find:

$$x_{IV}^\circ = \frac{zx_{It} \exp[-(\Delta G_B + \Delta G'_V)/k_B T]}{1 + z \exp[-(\Delta G_B + \Delta G'_V)/k_B T]}$$

From the definition of ΔG_B , we can write:

$$\Delta G_B + \Delta G'_V = \Delta G'_{IV} - \Delta G'_V - \Delta G'_I + \Delta G'_V = \Delta G'_{IV} - \Delta G'_I$$

If $\Delta G'_I > \Delta G'_{IV}$, that is, the presence of the vacancy reduces the energy of the impurity (which can occur even if both $\Delta G'_{IV}, \Delta G'_I > 0$), then we can have:

$$\exp[-(\Delta G'_{IV} - \Delta G'_I)/k_B T] \gg 1$$

so that:

$$x_{IV}^\circ \approx x_{It}$$

Every impurity atom will have a vacancy associated with it! So as impurities are introduced into the system, vacancies bind to them forming vacancy-impurity pairs. New vacancies are created to maintain the equilibrium concentration of free vacancies.

3.3 Jump Frequency

We have seen that a strong impurity-vacancy interaction can drastically affect the concentration of vacancies in the neighborhood of an impurity, as each impurity can be involved in a vacancy-impurity pair. Since one of its z

nearest neighbors is vacant, the probability that a given nearest neighbor site is vacant is $p = 1/z$.¹ In considering the effect that this has on the diffusion of the vacancy, it is helpful to look at the atomic hopping rate given by $\Gamma = p\nu z$ where, as in the expression for diffusivity, ν is the vacancy-atom exchange rate. For an impurity bound to a vacancy, the hopping rate becomes:

$$\Gamma_I = \frac{\nu z}{z} = \nu$$

which is much greater than that for the host atoms in a pure solid.

The diffusivity of the host atoms also can be affected by this increase in vacancy concentration, since the host atoms in the neighborhood of the impurity see a higher concentration of vacancies. The effect of this depends on the structure and how many nearest neighbors are shared by a pair of neighboring impurity-host atoms. However, it is clear that the increase in diffusivity of the host atom should be proportional to the impurity concentration for dilute alloys. The size difference between host and impurity can also affect the diffusion rate of the host. If the impurity is larger than the host, the presence of the impurity will cause the lattice to swell proportional to the impurity concentration (Vegard's Law). This larger lattice will reduce the distortion necessary for a jump of the smaller host atoms.

3.4 Correlation Effects

Correlation effects also play an important role in the case of impurity diffusion. This is especially true since the impurity-vacancy exchange rate ν_I might be different from the host-vacancy exchange rate ν_h . This difference can be due to impurity-vacancy attraction which can result in smaller activation energy barriers for the jump process. Another possible cause for the difference in exchange rates is size. If, for example, the impurity is much larger than the host, the lattice distortion associated with an impurity jump might be greater than that for a host atom jump.

We consider the case where the impurity is bound to a vacancy and has just exchanged with the vacancy. The next vacancy jump will be either with

¹There is possible confusion with the variable p here. Without a subscript, p means the occupational probability, which for vacancy diffusion mechanism is the probability that a given nearest neighbor is a vacancy. With a subscript, p_k means the probability that the vacancy will jump to the diffusing atom from its k^{th} nearest neighbor.

the impurity or with one of the host atoms which is a nearest neighbor for both the vacancy and impurity. These jumps occur with probability

$$\frac{\nu_I}{b\nu_h + \nu_I}$$

and

$$\frac{\nu_h}{b\nu_h + \nu_I}$$

respectively, where b is the number of nearest neighbors in common with both the vacancy and impurity. We wish to examine the correlation factor for the impurity, and if we consider only one vacancy jump, we find:

$$\langle \cos \theta \rangle = \sum_{k=1}^z p_k \cos \theta_k = (-1) \frac{\nu_I}{b\nu_h + \nu_I}$$

We can then find the correlation coefficient f for the impurity diffusion:

$$f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} = \frac{b\nu_h}{b\nu_h + 2\nu_I}$$

We then have for diffusivity for the impurity:

$$D_I = f a_0^2 \nu_I p = \frac{b a_0^2 \nu_I \nu_h}{z(b\nu_h + 2\nu_I)} \quad (3.4)$$

It is interesting to examine limiting cases for the impurity diffusivity predicted by Eqn. 3.4.

- $\nu_I \gg \nu_h$ (Fast impurity-vacancy exchange rate.) The correlation coefficient and diffusivity become:

$$f \approx \frac{b\nu_h}{2\nu_I} \quad \text{and} \quad D_I \approx \frac{b a_0^2 \nu_h}{2z}$$

In this case the impurity jumps are fast, and the impurity spends its time jumping back and forth between the same two sites. These jumps are not effective in mass transport, and the diffusivity of the impurity is governed by the slower host-vacancy jump rate ν_h .

- $\nu_I \ll \nu_h$ (Fast host-vacancy exchange rate.) The correlation coefficient and impurity diffusivity become:

$$f \approx 1 \quad \text{and} \quad D_I = \frac{a_0^2 \nu_I}{z}$$

In this case, the vacancy zips around the impurity, exchanging rapidly with its host nearest neighbors, until finally it exchanges with the impurity from some random nearest neighbor. Thus there is no correlation between directions of successive jumps, $\langle \cos \theta \rangle = 0$ and $f = 1$. Again the diffusivity of the impurity is governed by the slower of the two jump frequencies.

- $\nu_I = \nu_h$ (Equal host-vacancy and impurity-vacancy exchange rates.) In this case, the correlation coefficient and diffusivity become:

$$f \approx \frac{b}{b+2} \quad \text{and} \quad D_I = \frac{ba_0^2 \nu_I}{z(2+b)}$$

In this case, it still takes several host-vacancy jumps to move the impurity forward.

3.5 Closing Remarks

We have seen in the preceding sections that the presence of impurities can give rise to an increase in vacancy concentration in the neighborhood of the impurity, and to differences between the impurity-vacancy and host-vacancy exchange rate. We see that in general the diffusivity of the host and impurity can be quite different, and that both can be a function of composition. We next examine the effect of a chemical concentration gradient, which can provide a driving force for diffusion beyond just the random rearrangement of atoms.

Chapter 4

Diffusion with a Chemical Concentration Gradient

Up to this point, we have studied diffusion in mixtures of chemically identical species and in dilute alloys. We have seen that impurity and host atoms can have greatly different diffusivities which can depend on the concentration of the impurity. We have not yet considered the effect of large chemical concentration gradients. We now consider the general situation, allowing for the presence of large concentration gradients of chemically dissimilar species. We see that for ideal or dilute solutions, the diffusive flux is driven by the entropy increase associated with mixing of the species, while for non-ideal solutions, the diffusive flux is driven by the enthalpy of mixing as well. We find that we are able to describe the intermixing of two species using Fick's laws with a single diffusion coefficient \tilde{D} , which depends on concentration and the chemical nature of the two species. In order to do so, we examine the intermixing in a diffusion couple formed by joining two rods of different composition of two mutually soluble elements. There are two effects which are important in this situation. The first, known as the Kirkendall effect, is motion of the atomic planes due to the difference in diffusivities of the two constituents. The second is the effect of the chemical driving force on the diffusion.

4.1 Kirkendall Effect

For the general case of a diffusion couple of two mutually soluble but chemically different elements, the difference in diffusivities of the two species can give rise to motion of atomic planes in the interface region where diffusion is occurring. For example, if in a A - B diffusion couple, the diffusivity of A is greater than that of B , the flux of A across a given lattice plane will be greater than the flux of B in the opposite direction. Thus there will be an accumulation of atoms on one side of the reference plane, resulting in its motion. In order to examine this phenomena, we define a position coordinate z' which is measured from a region in the sample where no diffusion is occurring. There will be two contributions to the atomic flux relative to this fixed coordinate system.

- Flux due to diffusive motion of atoms relative to the moving atomic planes.
- Flux due to the motion of the atomic planes.

The total flux of component A relative to a stationary observer is:

$$J_A = -\tilde{D}_A \frac{\partial c_A}{\partial z'} + v c_A \quad (4.1)$$

where v is the velocity of the atomic planes relative to the fixed reference frame z' , and \tilde{D}_A is the diffusivity of A in the presence of the concentration gradient¹. This situation is analogous to the flux of ink in a moving stream. If we travel in a canoe moving with the water in the stream, then we will observe a drop of ink spreading in response to a diffusive flux:

$$-\tilde{D}_A \frac{\partial c_A}{\partial z}$$

where the coordinate z is measured relative to the boat. But since z and z' are related by $z' = z + vt$ and the composition gradient is independent of the origin of the coordinate system, the diffusive flux is also given by:

$$-\tilde{D}_A \frac{\partial c_A}{\partial z'}$$

¹This diffusivity is sometimes called the intrinsic or chemical diffusion coefficient. We will see that \tilde{D}_A reflects the chemical nature of the intermixing of the constituents.

An observer sitting on the bank will see this flux as well. However, he will also see the ink moving by with the velocity of the water. This is an additional flux vc_A due to motion of the water.²

We now wish to find the velocity and see how the diffusion equation is affected by this extra flux in Eqn. 4.1. We assume that the molar volume is independent of composition so that:

$$c = c_B + c_A = \text{constant} \quad (4.2)$$

therefore:

$$\frac{\partial c}{\partial t} = \frac{\partial c_A}{\partial t} + \frac{\partial c_B}{\partial t} = 0$$

To find how the compositions c_A and c_B change with time, we apply the conservation equation to both species:

$$\begin{aligned} \frac{\partial c_B}{\partial t} &= -\frac{\partial J_B}{\partial z'} \\ \frac{\partial c_A}{\partial t} &= -\frac{\partial J_A}{\partial z'} \end{aligned} \quad (4.3)$$

and insert the flux from Eqn. 4.1:

$$\begin{aligned} \frac{\partial c}{\partial t} &= \frac{\partial}{\partial z'} \left(\tilde{D}_A \frac{\partial c_A}{\partial z'} - vc_A + \tilde{D}_B \frac{\partial c_B}{\partial z'} - vc_B \right) \\ &= \frac{\partial}{\partial z'} \left(\tilde{D}_A \frac{\partial c_A}{\partial z'} + \tilde{D}_B \frac{\partial c_B}{\partial z'} - cv \right) = 0 \end{aligned}$$

Therefore we have that:

$$\tilde{D}_A \frac{\partial c_A}{\partial z'} + \tilde{D}_B \frac{\partial c_B}{\partial z'} - vc = \text{constant} \quad (4.4)$$

To find the value of this constant, we recognize that in a region far away from the interface, where no diffusion occurs, we know that:

$$\frac{\partial c_A}{\partial z'} = \frac{\partial c_B}{\partial z'} = 0$$

And, since there is no diffusion in this region, $v = 0$ also. Therefore the constant in Eqn. 4.4 is zero. Solving Eqn: 4.4 for v , we find:

$$v = \frac{1}{c} \left(\tilde{D}_A \frac{\partial c_A}{\partial z'} + \tilde{D}_B \frac{\partial c_B}{\partial z'} \right)$$

²In fact, we have already seen this type of flux in the moving interface problem.

Furthermore, from Eqn. 4.2 $c_A = c - c_B$ so that:

$$\frac{\partial c_A}{\partial z'} = -\frac{\partial c_B}{\partial z'}$$

and the velocity is just:

$$v = (\tilde{D}_A - \tilde{D}_B) \frac{1}{c} \frac{\partial c_A}{\partial z'} \quad (4.5)$$

Thus we see that a difference in diffusivities of the two constituents will result in a motion of atomic planes in the region where diffusion is occurring.

We can find the diffusion equation for this case by applying the conservation equation to the flux equation, just as we did in deriving Fick's second law. We insert the velocity from Eqn. 4.5 into the flux equation (Eqn. 4.1) and apply the conservation equation (Eqn. 4.3) to find:

$$\begin{aligned} \frac{\partial c_A}{\partial t} &= -\frac{\partial}{\partial z'} \left(-\tilde{D}_A \frac{\partial c_A}{\partial z'} + v c_A \right) \\ &= -\frac{\partial}{\partial z'} \left[-\tilde{D}_A \frac{\partial c_A}{\partial z'} + (\tilde{D}_A - \tilde{D}_B) \frac{c_A}{c} \frac{\partial c_A}{\partial z'} \right] \\ &= -\frac{\partial}{\partial z'} \left[\left(\frac{-c_A \tilde{D}_A - c_B \tilde{D}_A + c_A \tilde{D}_A - c_A \tilde{D}_B}{c} \right) \frac{\partial c_A}{\partial z'} \right] \\ &= \frac{\partial}{\partial z'} \left[\left(\frac{c_B \tilde{D}_A + c_A \tilde{D}_B}{c} \right) \frac{\partial c_A}{\partial z'} \right] \end{aligned}$$

This is just Fick's Second Law:

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial z'} \left(\tilde{D} \frac{\partial c_A}{\partial z'} \right)$$

with:

$$\begin{aligned} \tilde{D} &= \frac{c_B \tilde{D}_A + c_A \tilde{D}_B}{c} \\ &= x_A \tilde{D}_B + x_B \tilde{D}_A \end{aligned}$$

where $x_i = c_i/c$ is the atomic fraction i .