4.2 Chemical Driving Force

A second effect of a chemical concentration gradient on diffusion is to change the nature of the driving force. This is because diffusion changes the bonding in a solid. If, for example, two constituents in a diffusion couple have a preference for bonding with unlike neighbors, that is, they have a negative heat of mixing, then the decrease in free energy associated with diffusional mixing will have an enthalpy contribution as well as the mixing entropy contribution characteristic of ideal or dilute solutions. This added enthalpy contribution will act as a driving force to increase intermixing. Conversely, if the mixing enthalpy is positive, then the diffusional rate will be lower than that for an ideal or dilute solution. In order to examine this effect we must generalize Fick's first law, the flux equation, by realizing that flux occurs as a result of a system's drive to approach thermodynamic equilibrium. With this treatment, generally attributed to Darken, we can describe the mixing of chemically dissimilar materials with a diffusion coefficient which is a function of the chemical nature of the solution.

4.2.1 Generalized Flux Equations

Thermodynamic equilibrium is characterized by the absence of spatial or temporal variations in temperature T, pressure P, external potentials ϕ , and chemical potentials of the components μ_i . This condition does not always mean the absence of concentration gradients. Hence it is more reasonable to assert that the rate of return to equilibrium, that is, the flux of atoms, energy, and defects, is proportional the deviation from equilibrium. Hence, to first order, the flux will be proportional to gradients in temperature, pressure, potential, and chemical potential, rather than just to composition gradients. The flux of the i^{th} component is given by:

$$J_i = -\sum_k M_{ik} \nabla \mu_k - M_{iT} \nabla T - M_{iP} \nabla P - M_{i\phi} \nabla \phi$$
(4.6)

where the M_{ij} 's are the coupling coefficients between fluxes in *i* and gradients in *k*. These coefficients reflect the strength driving the flux and the mobility of the species in responding with movement.

In the case of a one-dimensional, isothermal, isobaric diffusion with no external potential gradients of an alloy of two components with a vacancy mechanism we can write for the flux of the components:

$$J_{A} = -M_{AA} \frac{\partial \mu_{A}}{\partial z} - M_{AB} \frac{\partial \mu_{B}}{\partial z} - M_{AV} \frac{\partial \mu_{V}}{\partial z}$$

$$J_{B} = -M_{BA} \frac{\partial \mu_{A}}{\partial z} - M_{BB} \frac{\partial \mu_{B}}{\partial z} - M_{BV} \frac{\partial \mu_{V}}{\partial z}$$

$$J_{V} = -M_{VA} \frac{\partial \mu_{A}}{\partial z} - M_{VB} \frac{\partial \mu_{B}}{\partial z} - M_{VV} \frac{\partial \mu_{V}}{\partial z}$$
(4.7)

Vacancies can only be created or destroyed at sources or sinks such as surfaces or defects. Hence, throughout most of the crystal, the number of lattice sites is conserved, so that the fluxes of the three species which can reside on a lattice site are related by:

$$J_A + J_B + J_V = 0$$

If this is to be true for arbitrary gradients, the sum of the coefficients must be zero, i.e.:

$$M_{AA} + M_{BA} + M_{VA} = 0$$

$$M_{AB} + M_{BB} + M_{VB} = 0$$

$$M_{AV} + M_{BV} + M_{VV} = 0$$

In addition there is a set of reciprocity relations, known as the Onsager relations, which state that $M_{ij} = M_{ji}$. Combining these with Eqn. 4.7 we find:

$$J_{A} = -M_{AA} \frac{\partial}{\partial z} (\mu_{A} - \mu_{V}) - M_{AB} \frac{\partial}{\partial z} (\mu_{B} - \mu_{V})$$
$$J_{B} = -M_{BA} \frac{\partial}{\partial z} (\mu_{A} - \mu_{V}) - M_{BB} \frac{\partial}{\partial z} (\mu_{B} - \mu_{V})$$

4.2.2 Darken's Flux Equation

To arrive at Darken's flux equation, we must make the further assumptions that the vacancies are in thermal equilibrium everywhere, so that $\mu_V = 0$, and that the off diagonal terms are negligible. The flux for a given component then reduces to:

$$J_i = -M_{ii} \frac{\partial \mu_i}{\partial z}$$

The chemical potential for a given component can be written:

$$\mu_i = \mu_0(T, P) + k_B T \ln a_i$$

= $\mu_0 + k_B T (\ln x_i + \ln \gamma_i)$ (4.8)

where a_i is the activity of component *i*, and γ_i is the activity coefficient of *i*, defined as:

$$\gamma_i = \frac{a_i}{x_i}$$

where x_i is the atomic fraction of the i^{th} component $(x_i = c_i/c)$. The term $k_B T \ln x_1$ represents the ideal mixing entropy contribution, while the term $k_B T \ln \gamma_i$ deals with the non-ideality of the solution. For example, in considering the chemical potential of a system of vacancies, impurities, and vacancy-impurity pairs, we only considered the ideal mixing entropy term and found:

$$\mu_i^{ideal} = \mu_0 + k_B T \ln x_i$$

In this treatment, we are interested in deviations from ideality, and so must use the more general expression for chemical potential Eqn. 4.8.

Our expression for the flux is then:

$$J_{i} = -M_{ii}\frac{\partial\mu_{i}}{\partial z}$$

$$= -M_{ii}k_{B}T\left(\frac{\partial\ln x_{i}}{\partial z} + \frac{\partial\ln\gamma_{i}}{\partial z}\right)$$

$$= -M_{ii}k_{B}T\left(\frac{\partial\ln x_{i}}{\partial z} + \frac{\partial\ln\gamma_{i}}{\partial\ln x_{i}}\frac{\partial\ln x_{i}}{\partial z}\right)$$

$$= \frac{-M_{ii}k_{B}T}{c_{i}}\left(1 + \frac{\partial\ln\gamma_{i}}{\partial\ln x_{i}}\right)\frac{\partial c_{i}}{\partial z}$$
(4.10)

Equation 4.10 relates the flux of a component to its concentration gradient, and as such is a generalization of Fick's first law. In order to examine the relationship between Eqn. 4.10 and Fick's first law, we consider the case of an ideal solution where $a_i = x_i$, or the case of a dilute solution where the activity follows Henry's Law, that is $a_i = \gamma_i^0 x_i$ where $\gamma_i^0 = \text{constant}$. In either case, $\partial \ln \gamma_i / \partial \ln x_i = 0$ so that flux will be given by:

$$J_i = -D_i \frac{\partial c_i}{\partial z} = -\frac{M_{ii}k_BT}{c_i} \frac{\partial c_i}{\partial z}$$

where D_i is the tracer diffusivity of component *i*, and $D_i dc_i/dz$ is just the Fick's Law flux. The tracer diffusivity D_i is the diffusion coefficient for the constituent *i* which would be measured in a homogeneous alloy where the only concentration gradients were in the relative concentration of *i* and a chemically identical but distinguishable tracer *i*^{*}. Hence, although D_i is affected by the alloying effects discussed in chapter 3, and as such can be a function of composition, it does not reflect the presence of concentration gradients of chemically dissimilar materials. In a pure material, the tracer and self diffusivities are only different by the correlation factor. We see that the tracer diffusivity is related to the mobility by:

$$D_i = \frac{k_B T M_{ii}}{c_i}$$

We also note that Fick's first law with the tracer diffusivity results from considering only the ideal mixing entropy term in the chemical potential.

4.2.3 Relationship Between Tracer and Intrinsic Diffusivities

If we now return to the more general case of a nonideal, nondilute solution, we can write:

$$J_i = -\tilde{D}_i \frac{\partial c_i}{\partial z} = -\frac{M_{ii}k_BT}{c_i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x_i}\right) \frac{\partial c_i}{\partial z}$$

From this we can find that:

$$\tilde{D}_{i} = \frac{M_{ii}k_{B}T}{c_{i}} \left(1 + \frac{\partial \ln \gamma_{i}}{\partial \ln x_{i}}\right)
= D_{i} \left(1 + \frac{\partial \ln \gamma_{i}}{\partial \ln x_{i}}\right)$$
(4.11)

This gives us a relationship between the tracer diffusivity, D_i which is measured in dilute solution or by tracer diffusion in a otherwise homogeneous alloy, and the intrinsic diffusivity, \tilde{D}_i , which takes into account the effects of a concentration gradient and nonideality of the solution.

If we write our expression for the flux in terms of the tracer diffusivities:

$$J_i = -D_i \frac{\partial c_i}{\partial z} - D_i \frac{\partial \ln \gamma_i}{\partial \ln x_i} \frac{\partial c_i}{\partial z}$$

we see that the first term in this expression comes from the concentration driving force arising from the ideal entropy of mixing, and the second term arises from the non-ideality of the solution.

4.2.4 Chemical Diffusion Coefficient

By combining the effect of the thermodynamic biasing with the results we found by examining the Kirkendall effect of the moving atomic planes we can find the chemical interdiffusion coefficient \tilde{D} with which we can describe the intermixing of two constituents which form a nonideal solution. Recall our expression for \tilde{D} :

$$\tilde{D} = x_A \tilde{D}_B + x_B \tilde{D}_A$$

where \tilde{D}_A and \tilde{D}_B are the intrinsic diffusivities of the two components. We can find a relationship between the thermodynamic biasing of these diffusivities by using the Gibbs-Duhem relation:

$$x_A d\mu_A + x_B d\mu_B = 0 \tag{4.12}$$

Looking at our expression for μ :

$$\mu_A = \mu_0 + k_B T \ln a_A = \mu_0 + k_B T \left(\ln x_A + \ln \gamma_A \right)$$

we find:

$$x_A d\mu_A = k_B T \left(dx_A + x_A d \ln \gamma_A \right)$$
$$= k_B T \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right) dx_A$$

Plugging this into the Gibbs-Duhem relation (Eqn 4.12) we find:

$$k_B T \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right) dx_A + k_B T \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln x_B} \right) dx_B = 0$$

And since $dx_A = -dx_B$ we can find that:

$$\frac{\partial \ln \gamma_A}{\partial \ln x_A} = \frac{\partial \ln \gamma_B}{\partial \ln x_B}$$

Plugging Eqn. 4.11 into our expression for the chemical diffusivity, \tilde{D} , and using the above relation, we find:

$$\tilde{D} = \tilde{D}_A x_B + \tilde{D}_B x_A
= D_A x_B \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right) + D_B x_A \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln x_B} \right)
= (D_A x_B + D_B x_A) \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right)$$

This is our final expression relating the chemical diffusivity, \tilde{D} , which is a measure of how a diffusion couple intermixes and is defined by Fick's laws, and the tracer diffusivities, D_i , which measure the interdiffusion of dilute or ideal solutions, and the non-ideality of the solution represented by the activity coefficient, γ_i .

4.2.5 Regular Solution Example

As an example of the thermodynamic driving force for diffusion, we consider a regular solution of N atoms, where the entropy of mixing is given by the ideal solution mixing entropy:

$$\Delta S_{mix} = -k_B N \left(x_A \ln x_A + x_B \ln x_B \right)$$

and the non-ideality of the solution is represented by the enthalpy of mixing, which in the quasichemical approximation is given by:

$$\Delta H_{mix} = x_A x_B n \Omega^{\rm RS}$$

where Ω^{RS} is a measure of the strength of unlike bonds, and is given by:

$$\Omega^{\rm RS} = z \left[H_{AB} - \frac{1}{2} \left(H_{AA} + H_{BB} \right) \right]$$

where z is the number of nearest neighbors, n is the total number of moles of atoms, and H_{ij} is the bond enthalpy per mole for i - j bonds. Here the bonding enthalpy is negative for a stable bond, so the enthalpy of mixing ΔH_{mix} is negative for systems where the A-B bond is stable relative to A-A and B-B bonds. we see that the first term in this expression comes from the concentration driving force arising from the ideal entropy of mixing, and the second term arises from the non-ideality of the solution.