Last Time

Generalized Coupling for the Near-Equilibrium Case

Onsager's Symmetry Relation

Seebeck and Peltier Effects

Diffusion of an Independent Species

3.21 Spring 2002: Lecture 4

One Independent Mobile Species: Highlights

The gradient in chemical potential is the only driving force and the motion of that species is the only flux:

$$J_1 = -L_{11}\nabla\mu_1 \tag{4-1}$$

The chemical potential can be related to local concentration through the activity coefficient γ_1:

$$\mu_1 = \mu_1^o + kT\ln\gamma_1 c_1 \tag{4-2}$$

Therefore, $\nabla\mu$ can be related to ∇c:

$$J_1 = -L_{11}\frac{kT}{c_1}\left(\frac{\partial\ln\gamma_1}{\partial\ln c_1}+1\right)\nabla c_1 \tag{4-3}$$

If this is compared to the most simple version of Fick's first law,

$$D_1 = L_{11}\frac{kT}{c_1}\left(\frac{\partial\ln\gamma_1}{\partial\ln c_1}+1\right) \tag{4-4}$$

The atomic mobility be defined by the the Einstien relation between the average drift velocity and the driving force,

$$\langle v\rangle = -M_1\nabla\mu_1 \tag{4-5}$$

The flux is related to the average velocity by:

$$J_1 = \langle v\rangle c_1 \tag{4-6}$$

Therefore

$$L_{11} = c_1 M_1 \tag{4-7}$$

and the relation between intrinsic diffusivity and mobility is

$$D_1 = kT\left(\frac{\partial \ln \gamma_1}{\partial \ln c_1} + 1\right) M_1 \tag{4-8}$$

If the solution is ideal—as in the case of mixture of radioisotopes of an otherwise identical atomic species—then the diffusivity is called the self-diffusivity D_1^* and since the activity coefficient is constant:

$$D_1^* = kTM_1 \tag{4-9}$$

Diffusion in a Crystal

When substitutional diffusion takes place inside a crystal, the number of sites is conserved. The site conservation provides an additional constraint. The additional constraint, as will be shown below, leads to the consideration of the chemical potential of the vacancy that is switching places with a diffusing substitutional atom. In other words, change in energy associated with a site after one diffusive step has occured is $\mu_A - \mu_{vac}$—the chemical energy associated with the site after the jump minus the chemical energy before the jump.

Consider a system consisting of two mobile species A and B on a lattice with N_V vacancies:

$$\begin{aligned} N_A + N_B + N_V &= N_{sites} \\ c_A &= \frac{N_A}{V_{xtal}} \\ c_B &= \frac{N_B}{V_{xtal}} \end{aligned} \tag{4-10}$$

The site fractions are given by

$$\begin{aligned} X_A &= \frac{N_A}{N_{sites}} \\ X_B &= \frac{N_B}{N_{sites}} \\ X_V &= \frac{N_V}{N_{sites}} \end{aligned} \tag{4-11}$$

The volumes associated with each atom are

$$\begin{aligned} \Omega_A &= \frac{V_A}{N_A} \\ \Omega_B &= \frac{V_B}{N_B} \\ \Omega_V &= \frac{V_V}{N_V} \end{aligned} \tag{4-12}$$

Where $V_{xtal} = V_A + V_B + V_V$ which will be considered constant and therefore:

$$\Omega_{site} \equiv X_A\Omega_A + X_B\Omega_B + X_V\Omega_V = \frac{V_{xtal}}{N_{sites}} \tag{4-13}$$

is constant as well.

The relation between the change in entropy per site with the internal energy and work terms when the only additional work term is the chemical work per site is:

$$\frac{T}{N_{sites}}dS = \frac{1}{N_{sites}}dU - \mu_A dX_A - \mu_B dX_B - \mu_V dX_V \tag{4-14}$$

or in terms of densities of extensive quantities:

$$\begin{aligned} \Omega_{site}Tds &= \Omega_{site}du - \mu_A dX_A - \mu_B dX_B - \mu_V dX_V \\ Tds &= du - \frac{\mu_A dX_A + \mu_B dX_B + \mu_V dX_V}{\Omega_{site}} \end{aligned} \tag{4-15}$$

Because the sites are conserved (Eq. 4-11), $dX_V = -(dX_A + dX_B)$:

$$Tds = du - \frac{(\mu_A - \mu_V)dX_A + (\mu_B - \mu_V)dX_B}{\Omega_{site}}$$

or

$$Tds = du - (\mu_A - \mu_V)dc_A - (\mu_B - \mu_V)dc_B \tag{4-16}$$

The expression for the entropy production is, for example including the heat flow term as well is:

$$T\dot{\sigma} = -\frac{\vec{J}_Q}{T} \cdot \nabla T - \vec{J}_A^{lattice} \cdot \nabla(\mu_A - \mu_V) - \vec{J}_B^{lattice} \cdot \nabla(\mu_B - \mu_V) \tag{4-17}$$

where $\vec{J}_A^{lattice}$ is the flux of A-occupied sites on a lattice.

Self Diffusion of an Isotope in a Crystal

The above analysis can be applied to isotopic diffusion which is traditionally used to obtain measurements of the self-difussion coefficient.

Let the isotope of A be desginated by A^* and while A and A^* may be assumed to be chemically identical, intrinsic mobilities may differ due to their mass differences.

Writing out the linearized flux relationships for this case:

$$\begin{aligned} \vec{J}_A^{lattice} &= -L_{AA}\nabla(\mu_A - \mu_V) - L_{AA^*}\nabla(\mu_{A^*} - \mu_V) \\ \vec{J}_{A^*}^{lattice} &= -L_{A^*A}\nabla(\mu_A - \mu_V) - L_{A^*A^*}\nabla(\mu_{A^*} - \mu_V) \end{aligned} \tag{4-18}$$

where the constant term Ω_{site} has been absorbed into the Onsager coefficients.

If is can be *assumed* that the vacancies are everywhere in equilibrium,[8] then $\nabla\mu_V = 0$; if, futhermore, the vacancy concentration gradient is constant (which is consistent with the assumption of equilibrium), so that the concentration gradients $\nabla c_A = -\nabla c_{A^*}$

$$\vec{J}_{A^*}^{lattice} = -kT\left(\frac{L_{A^*A^*}}{c_A} - \frac{L_{A^*A}}{c_{A^*}}\right)\nabla c_{A^*} \tag{4-19}$$

or using the relation between Onsager coeffients and mobilities,

$$\begin{aligned} \vec{J}_{A^*}^{lattice} &= -kT\left(M_{A^*A^*} - M_{A^*A}\right)\nabla c_{A^*} \\ \vec{J}_{A^*}^{lattice} &= -D^*{}_A\nabla c_{A^*} \end{aligned} \tag{4-20}$$

which defines the self diffusivity on a lattice in terms of the mobilities of each isotope.

[8] i.e. there is a large density of sources and sinks for vacancies such as dislocations.

If the solution is not ideal, then by direct extension, the intrinsic diffusivity is:

$$D_A = \left(\frac{\partial \ln \gamma_A}{\partial \ln c_A} + 1 \right) D^*{}_A \tag{4-21}$$