APPENDIX A

CONTINUUM DIFFUSION

The molar concentrations, x_i, are fundamentally intensive properties of a single phase mixture. In equilibrium these potentials are uniform. If a gradient exists in one of them, it will result in diffusion of that species.[24] The carrier particles for diffusion are the particles of the diffusing species. In that respect, diffusion is unlike momentum and heat transport which occur even when the carrier particle flux is isotropic. Diffusion is more like charge transport in that it requires a drift, or net unbalanced movement, of the carrier particles.

Diffusion in a Continuum. The mass rate of diffusion of species i in a single direction is the product of particle mass and the difference between the positive and negative fluxes of that species $\dot{j}''_i = m^*_i(\dot{n}''_{i,+} - \dot{n}''_{i,-})$. The magnitudes of these two interpenetrating particle fluxes are governed by the positive-direction flux leaving position $z - \lambda_{z,i}$ and the negative-direction flux leaving $z + \lambda_{z,i}$. Our development concerns diffusion in a continuum. Thus both fluxes can be expanded in a Taylor series about the position z.[25]

$$\dot{j}''_i = m^*_i\left(\dot{n}''_{i,+} - \dot{n}''_{i,-}\right) = m^*_i\left\{\left[\dot{n}''_i(z) - \lambda_{z,i}\frac{\partial \dot{n}''_i(z)}{\partial z}\right] - \left[\dot{n}''_i(z) + \lambda_{z,i}\frac{\partial \dot{n}''_i(z)}{\partial z}\right]\right\} = -2m^*_i\lambda_{z,i}\frac{\partial \dot{n}''_i(z)}{\partial z}$$

Now the species flux can be expressed in terms of eqn. IIIE-11, $\dot{n}''_i(z) = \dot{n}_{v,i}(z)\hat{V}_i/4 = n_v V_i x_i(z)/4$, where only the mole fraction is a function of position. ($\hat{V}_i$ varies with temperature and n_v with temperature or pressure. Such gradients have been considered separately and are ignored in our discussion of diffusion.) In addition, the directional mean free path component can be replaced by the mean free path, $\lambda_{z,i} = (2/3)\lambda_{c,i}$. This gives $\dot{j}''_i = -(m^*_i n_v \hat{V}_i \lambda_{c,i})/3 \cdot [\partial x_i(z)/\partial z]$. The standard form is obtained by introducing the mass fraction, $y_i = M_i x_i/M_m$ (where $m^*_i N_A = M_i$ and $n_v = N_A \rho/M$).

$$\dot{j}''_i = -\rho\left(\frac{\hat{V}_i \lambda_{c,i}}{3}\right)\frac{\partial y_i(z)}{\partial z} \qquad \text{(IIIE-A1)}$$

This constitutive equation, called *Fick's Law*, is normally introduced as a definition of the diffusion coefficient, $\dot{j}''_i = -\rho D_i \partial y_i/\partial z$. Comparing this to eqn. IIIE-A1, we obtain

$$D_i = \frac{\hat{V}_i \lambda_{c,i}}{3} \qquad \text{(IIIE-A2a)}$$

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[24] More correctly, equilibrium implies uniformity of the chemical potential. In single phase mixtures this is equivalent to uniform concentrations. Our discussion also ignores imposed fields. In a gravitational field nonuniform, hydrostatically distributed concentrations is the equilibrium state.

[25] We use z as the spatial coordinate to avoid confusion with x_i and y_i.