Appendix: "Darken's Equation" - Relation between self-diffusion & mutual diffusion coefficients.

Mutual Diffusion (definition): $J_A^* = c\, D_{AB} \nabla x_A$ (1)

mutual diffusivity

self diffusivity

Self Diffusion (definition): $J_A^* = \frac{c_A D_A}{RT} \nabla \mu_A$ (2)

$\mu_A = \mu_A^o + RT \ln(\gamma x_A)$ non-ideal solution chemical potential

* Re-write (2) in terms of ∇x_A:

$$\nabla \mu_A = \frac{d\mu_A}{dx_A} \nabla x_A$$

$$\frac{d\mu_A}{dx_A} = \frac{d}{dx_A}\left[\underbrace{\mu_A^o}_{\text{const}} + RT \ln(\gamma_A x_A)\right]$$

$$= RT \frac{d}{dx_A} \ln(\gamma_A x_A) = \frac{RT}{\gamma x_A} \frac{d(\gamma_A x_A)}{dx_A} = \frac{RT}{\gamma x_A}\left(\gamma_A + x_A \frac{d\gamma}{dx_A}\right)$$

$$= \frac{RT}{x_A}\left(1 + \frac{x_A}{\gamma_A}\frac{d\gamma_A}{dx_A}\right) = \frac{RT}{x_A}\left(1 + \frac{d\ln\gamma_A}{d\ln x_A}\right)$$

* substitute into (2)

$$J_A^* = \frac{c_A D_A}{\cancel{RT}} \frac{\cancel{RT}}{x_A}\left(1 + \frac{d\ln\gamma_A}{d\ln x_A}\right) \nabla x_A$$

$$x_A = \frac{c_A}{c_A + c_B} = \frac{c_A}{c}$$

$$J_A^* = c\, D_A \left(1 + \frac{d\ln\gamma_A}{d\ln x_A}\right) \nabla x_A$$

Comparing this to (1), we can identify D_{AB}

$$\boxed{D_{AB} = D_A \left(1 + \frac{d \ln \gamma_A}{d \ln x_A}\right)}$$ Darken's Equation

mutual diffusion coeff. — self diffusion coeff. — non-ideality

Example: Regular solution w/ binary interaction

$$\Delta \tilde{G}_{mix} = RT(x_A \ln x_A + x_B \ln x_B) + \tilde{G}^E$$

$$\ln \gamma_i = \left(\frac{\partial \tilde{G}^E/RT}{\partial n_i}\right)_{P,T,n_j}$$

$$\frac{\tilde{G}^E}{RT} = A x_A x_B = A x_A (1-x_A)$$

$$x_A = \frac{n_A}{n_A+n_B} \longrightarrow = A \frac{n_A n_B}{(n_A+n_B)^2}$$

$$\ln \gamma_A = \frac{\partial \tilde{G}^E/RT}{\partial n_A} = \frac{A n_B}{(n_A+n_B)^2} - 2\frac{A n_A n_B}{(n_A+n_B)^3}$$

$$= \frac{A(n_A+n_B)n_B}{(n_A+n_B)^3} - \frac{2A n_A n_B}{(n_A+n_B)^3}$$

$$= \frac{A\, n_B(n_B - n_A)}{(n_A+n_B)^3}$$

$$= \frac{A\, x_B(x_B - x_A)}{n_A+n_B}$$

$$\frac{d \ln \gamma_A}{d \ln x_A} = x_A \frac{d \ln \gamma_A}{d x_A}$$

$$= A x_A \frac{d}{dx_A}\left(\frac{x_B(x_B - x_A)}{n_A+n_B}\right)$$

$$= \frac{A x_A}{n_A+n_B} \frac{d}{dx_A}\left(\underbrace{(1-x_A)(1-2x_A)}_{(1-2x_A^2-3x_A)}\right)$$

$$= \frac{A x_A}{n_A+n_B}(-4x_A - 3)$$

$$= \frac{A}{n_A+n_B}(-4x_A^2 - 3x_A)$$

Not sure this is very helpful. I was just looking for some intuition here.