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Darken Plot Slope and the Interaction Coefficient

The Interaction Coefficient the Interaction Parameter are defined as follows:

$$\text{Interaction Coefficient: } e_i^i \equiv \frac{\partial log f_i}{\partial wt\%i} \tag{1}$$

$$\text{Interaction Parameter: } \varepsilon_i^i \equiv \frac{\partial ln f_i}{\partial x_i} \tag{2}$$

The straight line portion of the Darken Plot at the infinite dilution end of the plot may be described as

$$\ln \gamma_i = a + b(1 - x_i)^2 \tag{3}$$

The 1 wt% ss activity coefficient, f_i, is related to the pure ss activity coefficient in the following way:

$$f_i \equiv \frac{h_i}{h_i^{IDEAL}} = \frac{h_i}{wt\%i} = \frac{a_i}{a_i^{1wt\%IDEAL}} = \frac{x_i \gamma_i}{x_i \gamma_i^o} = \frac{\gamma_i}{\gamma_i^o} \tag{4}$$

The equating of f_i to activities a_i is most easily accomplished by simply thinking of the activity a_i vs x_i plot that is also labeled with an activity h_i scale. The ratio of activities is the same on either scale.

Combining Eqs [1-3] gives

$$\varepsilon_i^i \equiv \frac{\partial \ln\left(\gamma_i / \gamma_i^o\right)}{\partial x_i} = \frac{\partial\left[\ln \gamma_i - \ln \gamma_i^o\right]}{\partial x_i} = \frac{\partial\left[a + b(1 - x_i)^2\right] - [a]}{\partial x_i} = \frac{b\partial(1 - x_i)^2}{\partial x_i} = -2b(1 - x_i) \tag{5}$$

Since the mole fraction of i is small compared to unity, the interaction parameter is said to be related to the Darken Plot slope at infinite dilution as follows:

$$\varepsilon_i^i = -2b \tag{6}$$

Converting x_i to wt %i and log to ln in the definitions in Eqs [1] and [2] gives

$$\varepsilon_i^i = \frac{\partial \ln f_i}{\partial x_i} = \frac{2.303\partial \log f_i}{\partial\left[\frac{wt\%i / MWi}{100\% / MWFe}\right]} = \frac{2.303}{\left[\frac{MWFe}{100\% MWi}\right]} \frac{\partial \log f_i}{\partial wt\%i} \tag{7}$$

$$\varepsilon_i^i = \frac{2.303 * 100\% MWi}{MWFe} e_i^i \tag{8}$$

Therefore the interaction coefficient is

$$e_i^i = -2b \frac{MWFe}{2.303 * 100\% MWi} \tag{9}$$