

The relationship between f_i , the 1 wt % SS activity coefficient and the pure component standard state activity coefficient γ_i

Figure 1 shows a plot of the activity of component i. The left vertical coordinate is labeled the activity relative to the pure component i, which corresponds to the lower axis label of mole fraction of component i. The right coordinate is labeled the activity relative to the hypothetical 1 wt% component behaving as the infinitely dilute component; thus, it falls on the extension of the tangent to the infinitely dilute solution. The upper axis of wt % i corresponds to the 1 wt % standard state activity values labeled h_i .

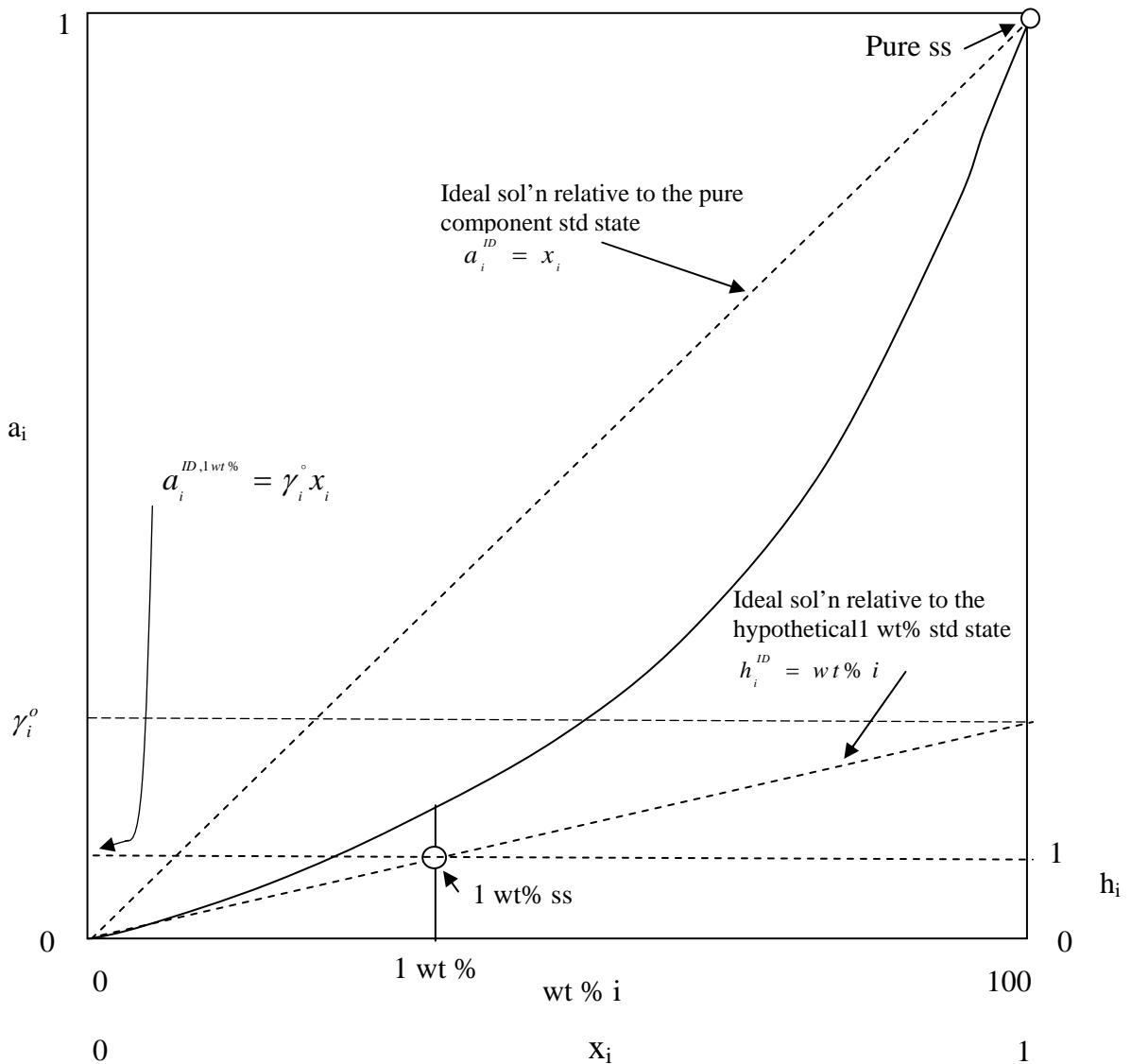


Figure 1 The activity of component i as a function of 1) mole fraction relative to the pure component of component i and 2) the wt % relative to the one weight % std state of component i. (The location of 1 wt % is greatly exaggerated for graphical clarity.)

The one wt % standard state is denoted at 1 wt % i on the line that exhibits infinitely dilute solution behavior: i.e. tangent to the infinitely dilute solution.

The activity coefficient for any standard state is defined as the activity divided by the corresponding measure of “concentration” (mole fraction or wt %). For the pure component standard state,

$$\gamma_i \equiv \frac{a_i}{x_i} \quad (1)$$

Since the ideal solution line pass through (0,0) and (1,1), the mole fraction is equal to the ideal activity. Therefore,

$$\gamma_i = \frac{a_i}{a_i^{ID}} \quad (2)$$

For the 1 wt % standard state

$$f_i \equiv \frac{h_i}{wt\% i} = \frac{h_i}{h_i^{ID}} \quad (3)$$

since the 1 wt% ideal solution line also passes through (0,0) and (1,1).

Since both activity scales have the same zero, the ratio of h_i to h_i^{ID} is the same by either the a_i or the h_i scale. Therefore,

$$f_i = \frac{h_i}{h_i^{ID}} = \frac{a_i}{a_i^{ID, 1wt\%}} = \frac{x_i \gamma_{Si}}{x_i \gamma_{Si}^o} \quad (4)$$

$$f_i = \frac{\gamma_{Si}}{\gamma_{Si}^o} \quad (5)$$

The value of f_i is always close to unity since dilute solutions depart little from infinite dilution behavior. The 1 wt % standard state should not be used much beyond 1 wt%, because the approximation

$$x_i|_{1wt\%} \approx \frac{MW_j}{100 * MW_i} \quad (6)$$

becomes increasing poor. Also, the use of the first order approximation employed for interaction coefficients is inaccurate at higher wt %.