

Change in Standard State from Pure Component to the 1 wt% in Solution

The one weight percent standard state is designed for convenience when computing the amount of a component present in a molten solution. For example, when using the normal pure component as the standard state, the computation of the amount of Si in molten steel would proceed as follows:



$$\Delta G_1^o = -RT \ln \left[\frac{P_{\text{CO}}^2 a_{\text{Si}}}{a_{\text{C}}^2 a_{\text{SiO}_2}} \right] = -RT \ln [K_1] \quad (2)$$

$$x_{\text{Si}} = \frac{a_{\text{Si}}}{\gamma_{\text{Si}}} \quad (3)$$

$$(\text{wt}\% \text{Si}) = a_{\text{Si}} \frac{100\% \text{MWSi}}{\gamma_{\text{Si}} \text{MWF}_{\text{Fe}}} \quad (4)$$

When the 1 wt % ss is used, the standard state of Si is changed from the pure liquid to the 1 wt % ss so that the computed activity of Si is essentially in wt %. The activity is given the symbol h_{Si} . The computation proceeds as follows where the under score denotes the 1 wt % standard state:



$$\Delta G_3^o = -RT \ln [K_3] = RT \ln \left[\frac{P_{\text{CO}}^2 h_{\text{Si}}}{a_{\text{C}}^2 a_{\text{SiO}_2}} \right] \quad (8)$$

$$h_{\text{Si}} = f_{\text{Si}} (\text{wt}\% \text{Si}) \quad (9)$$

where $f_{\text{Si}} \approx 1$.

Clearly, this is a more convenient method of performing computations when weight percents are needed. The need, then, is how to determine the standard Gibbs energy for the change in standard state for the reaction [5]. That is now shown.

For the reaction

$$Si_{(l)} = \underline{Si} \quad (10)$$

Starting with the identity for chemical potential and substituting the standard Gibb's energies and the definitions of activities for the two different standard states, gives for the standard Gibb's energy change for reaction (2)

$$\mu_i = \mu_i \quad (11)$$

$$\mu_i^o + RT \ln a_i = \mu_i^* + RT \ln h_i \quad (12)$$

$$\Delta G_2^o = \mu_i^* - \mu_i^o = RT \ln \frac{a_i}{h_i} \quad (13)$$

Now the value of this Gibb's Energy can be computed from any pair of a_i and h_i that correspond to an equilibrium condition as required by equating their two chemical potentials. There are infinite such pairs since the equilibrium condition is satisfied by using the same composition when computing the two activities. Therefore, one should choose a pair that is easy to compute. One such pair is when $h_i = 1$. In this case

$$a_i = x_i \Big|_{at\ 1wt\%i} \gamma_i^o \quad (14)$$

The activity coefficient at infinite dilution is used here rather than the value at 1 weight percent for convenience. That means that the 1 wt percent standard state is really

The hypothetical 1 wt% i solution behaving as the infinitely dilute solution

Some minor adjustment for real solution behavior will be needed and is shown later. However, the adjustment will be small since there is very little difference in the infinitely dilute solution and the 1 wt% solution.

The mole fraction is fairly precisely approximated as

$$x_i \Big|_{at\ 1wt\%i} \approx \frac{1}{100} \frac{MWF_e}{MW_i} \quad (15)$$

Therefore

$$\Delta G_2^o = RT \ln \frac{\gamma_i^o}{100} \frac{MWF_e}{MW_i} \quad (16)$$

The adjustment in from the ideal solution, which behaves as the infinitely dilute solution and the real solution is handled using an activity coefficient f_i .

$$f_i \equiv \frac{h_i}{wt\%i} = \frac{h_i}{h_i^{ID}} \quad (17)$$

This is not unlike the definition of the activity coefficient when the pure component is the standard state:

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{a_i}{a_i^{ID}} \quad (18)$$

Furthermore, since the activity scales for both standard states have the same origin and are linear, the ratio in Eq. [17] is also equal to ratio of the pure standard state activities making

$$f_i \equiv \frac{h_i}{wt\%i} = \frac{h_i}{h_i^{ID}} = \frac{a_i}{a_i^{1wt\%ID}} = \frac{\gamma_i x_i}{\gamma_i^\circ x} = \frac{\gamma_i}{\gamma_i^\circ} \quad (19)$$

The value of f_i is always close to unity since dilute solutions depart little from infinite dilution behavior. It is recommended not to exceed a percent or two.

The value of f_i is computed from interaction coefficients which is

$$e_i^j = \frac{\partial \text{Log}(f_i)}{\partial (wt\%i)} \quad (20)$$

Since $f_i = 1$ when $(wt\% i) = 0$, integrating gives

$$\text{Log}(f_i) = e_i^j (wt\%i) \quad (21)$$

To determine $(wt\% i)$ from a value of h_i , one performs an iteration as follows:

Step 1 - Assume $f_i = 1$

Step 2 - Calculate $(wt\%i) = \frac{h_i}{f_i}$

Step 3 - Update the assumed value of $\text{Log}(f_i) = e_i^j (wt\%i)$

Step 4 - Repeat the process from Step 2 using the current value of f_i .

This algorithm will converge on a value of $(wt\% i)$ in two or three iterations.

For a solutions with multiple components that affect the component of interest, i , one may use the following adjustment in the value of f_i :

$$\text{Log}(f_i) = e_i^j (wt\%i) + \sum_{j=1}^n e_i^j (wt\%j) \quad (22)$$

where e_i^j is the interaction coefficient of j on i . Again the weight percent's of j must be less than a percent, or two.

Note that the interaction coefficient comes from the interaction parameter defined as follows:

$$\varepsilon_i^i \equiv \frac{\partial \ln(a_i)}{\partial(x_i)} \quad (23)$$

The relationship between the interaction parameter and the interaction coefficient is for low wt percent in Fe is

$$e_i^i = \varepsilon_i^i \frac{MW_{Fe}}{2.303 * 100 * MW_i} \quad (24)$$

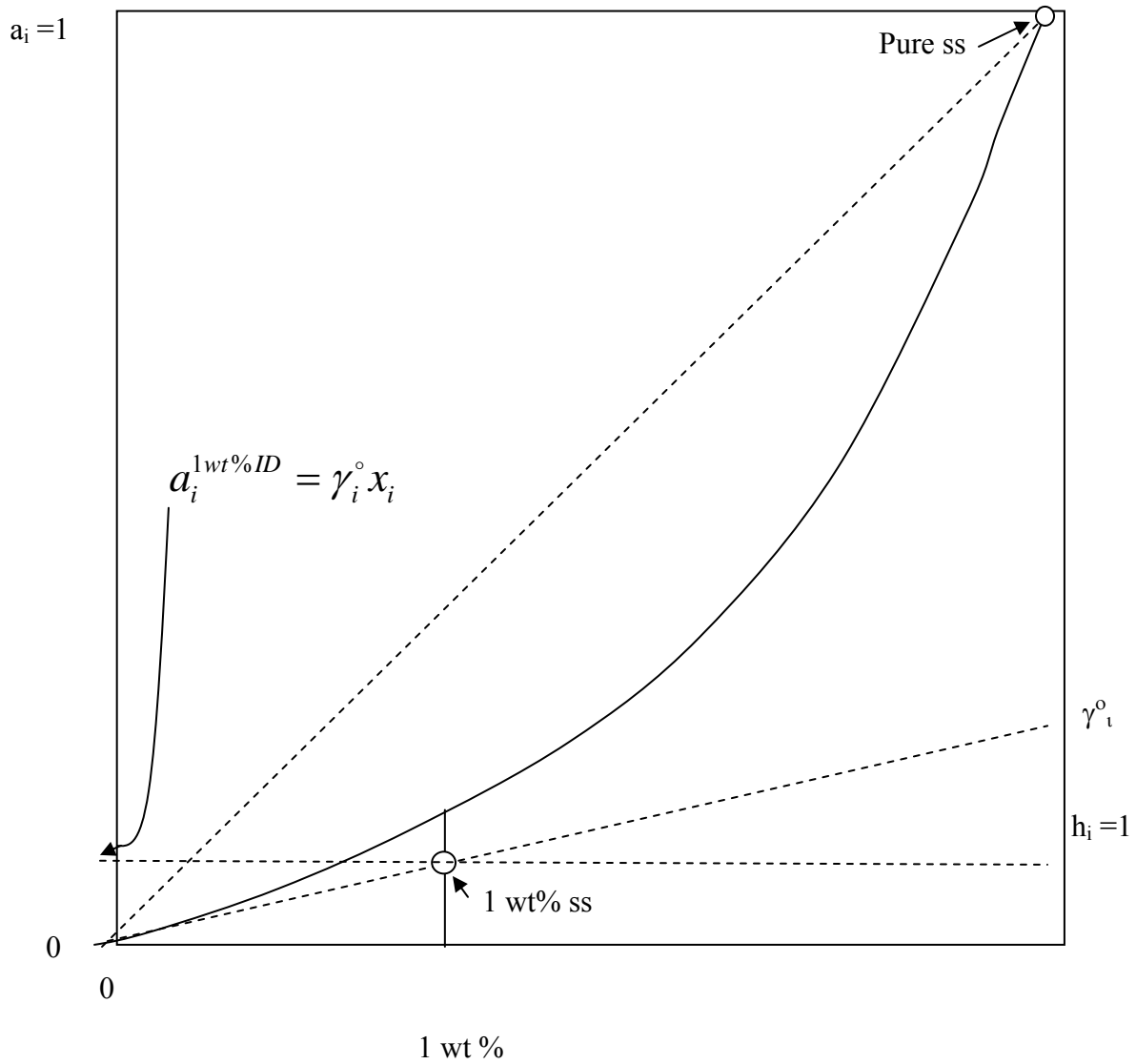


Figure 1 Relative positions and values of pure and 1 wt% Standard States