

15.5: The Chemical Potential, Fugacity, and Activity of a Pure Solid

The relationship between the standard Gibbs free energy of formation of a substance whose standard state is a solid and the Gibbs free energy of the substance in its hypothetical ideal-gas standard state is essentially the same as described in the previous section for a liquid. In each case, to find the fugacity of the condensed phase in its standard state, it is necessary to find a reversible path that takes the condensed-phase substance to its hypothetical ideal-gas standard state. If the solid substance has a significant vapor (sublimation) pressure, the paths described for a liquid in the previous section are also available for the solid. Otherwise, it may be possible to determine the Gibbs free energy change along some more complicated path.

Of course, whether the Gibbs free energy of formation for the hypothetical ideal-gas standard state can be evaluated or not, the fugacity and activity relationships remain valid. For substance A in another state—in which A need not be pure and the pressure is generally not one bar—we have

$$\mu_A = \mu_A^\circ + RT \ln \left[\frac{f_A(P, T, x_A, x_B, \dots)}{f_A(HIG^\circ)} \right]$$

where $\mu_A^\circ = \Delta_f G^\circ(A, HIG^\circ, T)$, and the fugacity of substance A , $f_A(P, T, x_A, x_B, \dots)$, is simply an alternative expression of the difference between the chemical potential of the substance, as it occurs in the system, and its chemical potential in the hypothetical ideal-gas standard state. We write $f_A(P, T, x_A, x_B, \dots)$ to indicate that the state of the system is specified by its pressure, temperature, and composition.

When the fugacity is difficult to measure, the activity function becomes essential. Choosing the standard state for the activity to be pure solid A in the same standard state that we use for the Gibbs free energy of formation, we have

$$\tilde{\mu}_A^\circ(s) = \Delta_f G^\circ(A, s)$$

and

$$\tilde{\mu}_A^\circ(s) = \mu_A^\circ + RT \ln \left[\frac{f_A^\bullet(s, P^\circ)}{f_A(HIG^\circ)} \right]$$

Then, for substance A in an arbitrary state at the temperature of interest:

$$\begin{aligned} \mu_A &= \mu_A^\circ + RT \ln \left[\frac{f_A(P, T, x_A, x_B, \dots)}{f_A(HIG^\circ)} \right] \\ &= \tilde{\mu}_A^\circ(s) - RT \ln \left[\frac{f_A^\bullet(s, P^\circ)}{f_A(HIG^\circ)} \right] + RT \ln \left[\frac{f_A(P, T, x_A, x_B, \dots)}{f_A(HIG^\circ)} \right] \\ &= \tilde{\mu}_A^\circ(s) + RT \ln \left[\frac{f_A(P, T, x_A, x_B, \dots)}{f_A^\bullet(s, P^\circ)} \right] \\ &= \tilde{\mu}_A^\circ(s) + RT \ln \tilde{a}_A \end{aligned}$$

From one perspective, the activity function is simply a mathematical device that expresses the chemical potential relative to an arbitrarily chosen reference state. If we can measure this difference experimentally, we can find \tilde{a}_A whether we can measure the fugacity of A or not. For clarity, we designate the chemical potential in the reference state as $\tilde{\mu}_A^\circ(s)$. When we let $\tilde{\mu}_A^\circ(s)$ be the Gibbs free energy of formation of the substance in the arbitrarily chosen reference state and let the activity in this reference state be unity, μ_A is the chemical potential difference between the substance in the state of interest and the chemical potential of its constituent elements in their standard states at the same temperature.

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