

## 15.3: The Pressure-dependence of the Fugacity and Activity of a Condensed Phase

So far, we have investigated fugacity and activity only for gases. Let us now consider a system that consists entirely of substance  $A$  present as either a pure liquid or a pure solid. We assume that the temperature is fixed and that the pressure on this condensed phase can be varied. For our present discussion, it does not matter whether the condensed phase is a liquid or a solid. For specificity, let us assume that it is a liquid. We can imagine that the pressure changes are effected with the pure substance contained in a cylinder that is sealed by a frictionless piston. We ask how the fugacity and activity vary when the system pressure changes. Let the molar volume of the pure condensed phase be  $\bar{V}_A$ . Since the coefficient of isothermal compression is small for condensed phases, it is often adequate to assume that  $\bar{V}_A$  is a constant. We do so here.

We have developed several designations for the molar Gibbs free energy of the condensed phase. For pure liquid  $A$  at pressure  $P$ , we can write

$$\bar{G}^\bullet(A, \ell, P) = \bar{G}_A^\bullet(\ell, P) = \mu_A^\bullet(\ell, P)$$

(pure liquid)

For the pure liquid at a pressure of one bar, it is convenient to let the molar Gibbs free energy of the liquid be equal to the molar Gibbs free energy of formation. We let

$$\bar{G}^\bullet(A, \ell, P^\circ) = \bar{G}_A^\bullet(\ell, P^\circ) = \mu_A^\bullet(\ell, P^\circ) = \Delta_f G^\circ(A, \ell, P^\circ)$$

(pure liquid,  $P = 1$  bar)

We also have several designations for the pressure dependence of the Gibbs free energy of this liquid. Since the system consists entirely of the pure liquid, we have

$$\begin{aligned} \left( \partial \bar{G}^\bullet(A, \ell, P) / \partial P \right)_T &= \left( \partial \bar{G}_A^\bullet(\ell, P) / \partial P \right)_T \\ &= \left( \partial \mu_A^\bullet(\ell, P) / \partial P \right)_T \\ &= RT \left( \partial \left\{ \ln [f_A^\bullet(\ell, P)] \right\} / \partial P \right)_T \\ &= RT \left( \partial \left\{ \ln [\tilde{a}_A^\bullet(\ell, P)] \right\} / \partial P \right)_T \\ &= \bar{V}_A^\bullet(\ell, P) dP \end{aligned}$$

We are free to choose any state of any system that contains  $A$  as the standard state for the activity of substance  $A$ . Often, it is convenient to let this standard state be the pure liquid (or the pure solid) at a pressure of one bar. The activity of  $A$  is unity in the standard state. Taking the partial molar volume to be constant,  $\bar{V}_A^\bullet(\ell, P) = \bar{V}_A^\bullet$ , and integrating between one bar and an arbitrary pressure,  $P$ , we can express the pressure dependence of the Gibbs free energy of the pure liquid in several equivalent ways:

$$\begin{aligned} \bar{G}_A^\bullet(\ell, P) &= \bar{G}^\bullet(A, \ell, P) - \bar{G}^\bullet(A, \ell, P^\circ) \\ &= \bar{G}^\bullet(A, \ell, P) - \Delta_f G^\circ(A, \ell) \\ &= \mu_A^\bullet(\ell, P) - \mu_A^\bullet(\ell, P^\circ) \\ &= RT \ln \left[ \frac{f_A^\bullet(\ell, P)}{f_A^\bullet(\ell, P^\circ)} \right] \\ &= RT \ln [\tilde{a}_A^\bullet(\ell, P)] \\ &= \bar{V}_A^\bullet(P - P^\circ) \end{aligned}$$

From the last equations, we see that the activity and fugacity of the pure liquid vary with the system pressure as

$$\tilde{a}_A^*(\ell, P) = \frac{f_A^*(\ell, P)}{f_A^*(\ell, P^o)} = \exp \left[ \frac{\bar{V}_A^*(P - P^o)}{RT} \right]$$

At ordinary temperatures and pressures,  $\bar{V}_A^*(P - P^o) \ll RT$ . In consequence, the system pressure must become much greater than one bar before the exponential term becomes significantly different from one. Thus, the activity of a condensed phase is approximately unity until the system reaches high pressures. At pressures near one bar, the fugacity of a condensed phase is only a weak function of pressure.

This argument provides rigorous justification for treating the activities (or concentrations) of pure solids and liquids as constants when we use equilibrium constant data to calculate the compositions of systems that are at equilibrium. (We address this issue previously in [Section 5.17](#) and [Section 13.8](#).)

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