An Example and Explanation of the Gibbs-Duhem Equation

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Written: December 13, 2008
Last edit: January 19, 2009

The Gibbs-Duhem equation allows one to find the activity of a component of a binary solution, if the other activity is known as a function of composition. As a consequence of this equation, if we can show that either component behaves ideally, the other component must behave ideally also. The relevance of this equation in practice is that one can measure the activity of either component for a variety of different compositions, and in turn obtain information about the other component.

Derivation:

We start with the Gibbs energy of mixing, and then differentiate it.

$$\underline{G} = x_A\overline{G}_A + x_B\overline{G}_B \tag{1}$$

$$d\underline{G} = \overline{G}_A dx_A + \overline{G}_B dx_B + x_A d\overline{G}_A + x_B d\overline{G}_B \tag{2}$$

However, it is given that the following must also be true.

$$d\underline{G} = \overline{G}_A dx_A + \overline{G}_B dx_B \tag{3}$$

This implies that the last two terms must cancel exactly.

$$x_A d\overline{G}_A + x_B d\overline{G}_B = 0 \tag{4}$$

This equation is the Gibbs-Duhem Equation, however it is often reorganized into the following more useful forms.

$$x_A d(RT \ln a_A) + x_B(RT \ln a_B) = 0 \tag{5}$$

$$d(\ln a_A) = -\frac{x_B}{x_A}(\ln a_B) \tag{6}$$

$$d(\ln \gamma_A) = -\frac{x_B}{x_A} d(\ln \gamma_B) \tag{7}$$

Example 1

Suppose we know that the activity of zinc in brass (Cu and Zn alloy) obeys the following relation:

$$RTln(\gamma_{Zn}) = -38,300x_{Cu}^2$$

Find an expression for the activity coefficient of copper (γ_{Cu}).

$$d(\ln\gamma_{Cu}) = -\frac{x_{Zn}}{x_{Cu}}d(\ln\gamma_{Zn}) \tag{1}$$

$$d(\ln\gamma_{Zn}) = \frac{-38,300x_{Cu}^2}{RT} \tag{2}$$

$$d(\ln\gamma_{Cu}) = -\frac{x_{Zn}}{x_{Cu}}d(\frac{-38,300x_{Cu}^2}{RT}) \tag{3}$$

$$d(\ln\gamma_{Cu}) = \frac{x_{Zn}(2*38,300)}{RT}dx_{Cu} \tag{4}$$

We know that the total mole fraction is always one, therefore, in a binary mixture, the change in one must be the negative change of the other. This allows a substitution on the left side.

$$dx_{Cu} = -dx_{Zn} \tag{5}$$

$$d(\ln\gamma_{Cu}) = -\frac{x_{Zn}(2*38,300)}{RT}dx_{Zn} \tag{6}$$

Now we can integrate.

$$\int_0^{ln\gamma_{Cu}} d(\ln\gamma_{Cu}) = \int_0^{ln\gamma_{Zn}} \frac{x_{Zn}(2*38,300)}{RT}dx_{Cu} \tag{7}$$

$$ln\gamma_{Cu} = \frac{x_{Zn}^2(38,300)}{RT} \tag{8}$$

Now to find the activity coefficient for copper, we exponentiate.

$$\gamma_{Cu} = e^{\frac{x_{Zn}^2(38,300)}{RT}} \tag{9}$$