**Topic 1740**

**Gibbs Energies; Solutions**

**Parameters $\phi$ and $\ln(\gamma_j)$**

The practical osmotic coefficient can be calculated knowing the dependence of $\gamma_j$ on molality of solute $j$. Of course at this stage we do not know the form of the dependence of $\gamma_j$ on $m_j$. In fact $\gamma_j$ also depends on the solute, temperature and pressure. But for a given system (at fixed $T$ and $p$) we might express $\phi$ as a series expansion of the molality $m_j$.

Thus,  
\[ \phi = 1 + a_1 \cdot m_j + a_2 \cdot m_j^2 + a_3 \cdot m_j^3 + \ldots \]  

(a)

Interestingly this assumed dependence is equivalent to a series expansion in mole fraction of solute $x_j$ for $\ln f_1$, where $f_1$ is the (rational) activity coefficient for the solvent [1,2].

\[ \ln f_1 = b_1 \cdot x_j^2 + b_1 \cdot x_j^3 + b_3 \cdot x_j^4 + \ldots \]  

(b)

Here $b_1, b_2, b_3 \ldots$ depend on the solute (for given $T$ and $p$). The link between the two equations can be expressed as follows.

\[ b_1 = -[(1/2) + M_1^{-1} \cdot a_1] \]  

(c)

\[ b_2 = -[(2/3) + 2 \cdot M_1^{-1} \cdot a_1 + M_1^{-2} \cdot a_2] \]  

(d)

\[ b_3 = -[(3/4) + 3 \cdot M_1^{-1} \cdot a_1 + 3 \cdot M_1^{-2} \cdot a_2 + a_3 \cdot M_1^{-3}] \]  

(e)

**Footnotes**


[2] By definition, for a solution $j$ in solvent, chemical substance 1,

\[ x_j = m_j / (M_1^{-1} + m_j) \]  

(a)

where $M_1$ is the molar mass of solvent expressed in kg mol$^{-1}$. Hence molality of solute $j$,  

\[ m_j = x_j \cdot M_1^{-1} \cdot (1 - x_j)^{-1} \]  

(b)

We expand $(1-x_j)^{-1}$ based on the premise that $0 < x_j << 1.0$ for dilute solutions.

Then,  
\[ m_j = x_j M_1^{-1} \cdot [1 + x_j + x_j^2 + x_j^3 + \ldots] \]  

(c)

or,  
\[ m_j = M_1^{-1} \cdot [x_j + x_j^2 + x_j^3 + x_j^4 + \ldots] \]  

(d)
Here we carry all terms up to and including the fourth power of \( x_j \). But from the two methods for relating \( \mu_1(\text{aq}) \) to the composition of a solution,

\[
\ln(x_1 \cdot f_1) = -\phi \cdot M_1 \cdot m_j \quad \text{(e)}
\]

Then,

\[
\ln(x_1 \cdot f_1) = -M_1 \cdot m_j \cdot [1 + a_1 \cdot m_j + a_2 \cdot m_j^2 + a_3 \cdot m_j^3 + \ldots] \quad \text{(f)}
\]

or,

\[
\ln f_1 = -\ln(1 - x_j) - M_1 \cdot [m_j + a_1 \cdot m_j^2 + a_2 \cdot m_j^3 + a_3 \cdot m_j^4 + \ldots] \quad \text{(g)}
\]

But for dilute solutions,

\[
-ln(1-x_j) = x_j + \left(\frac{x_j^2}{2}\right) + \left(\frac{x_j^3}{3}\right) + \left(\frac{x_j^4}{4}\right) \quad \text{(h)}
\]

Using equation (c) for \( m_j \) as a function of \( x_j \) in the context of equation (f), we obtain an equation for \( \ln(f_1) \).

\[
\ln(f_1) = x_j + \left(\frac{x_j^2}{2}\right) + \left(\frac{x_j^3}{3}\right) + \left(\frac{x_j^4}{4}\right) -x_j -x_j^2 -x_j^3 -x_j^4 -M_1^{-1} \cdot x_j \cdot a_1 -2 \cdot M_1^{-1} \cdot x_j^3 \cdot a_1 -3 \cdot M_1^{-1} \cdot x_j^4 \cdot a_1 -M_1^{-2} \cdot x_j^3 \cdot a_2 -3 \cdot M_1^{-2} \cdot x_j^4 \cdot a_2 -M_1^{-3} \cdot x_j^4 \cdot a_3 \quad \text{(i)}
\]

Hence, \( \ln(f_1) = \)

\[
\{-[(1/2) + (a_1 \cdot M_1^{-1})] \cdot x_j^2\} + \{-[(2/3) + (2 \cdot a_1 \cdot M_1^{-1}) + (a_2 \cdot M_1^{-2})] \cdot x_j^3\} + \{-[(3/4) + (3 \cdot a_1 \cdot M_1^{-1}) + (3 \cdot a_2 \cdot M_1^{-2}) + (a_3 \cdot M_1^{-3})] \cdot x_j^4\} \quad \text{(j)}
\]