**Chemical Potentials: Solute: Molality and Mole Fraction Scales**

The chemical potential of solute \( j \) in aqueous solution at temperature \( T \) and at close to ambient pressure is related to the molality \( m_j \) and mole fraction \( x_j \) [1].

\[
\mu_j^0(\text{aq}; T; p) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0_j) = \mu_j^0(\text{aq}; T; p; x \text{- scale}) + R \cdot T \cdot \ln(x_j \cdot f_j^*) \quad (a)
\]

Therefore,

\[
\ln(f_j^*) = \ln \gamma_j + \ln(m_j / x_j \cdot m^0_j)
+ (1/R \cdot T) [\mu_j^0(\text{aq}; T; p) - \mu_j^0(\text{aq}; T; p; x \text{- scale})] \quad (b)
\]

For dilute solutions [1], \( 1/M_1 > m_j \). Hence \( (m_j / m^0_j \cdot x_j) \) equals \( (m^0_j \cdot M_1)^{-1} \), a dimension-less quantity. Therefore,

\[
\ln(f_j^*) = \ln \gamma_j - \ln(m^0_j \cdot M_1)
+ (1/R \cdot T) [\mu_j^0(\text{aq}; T; p) - \mu_j^0(\text{aq}; T; p; x \text{- scale})] \quad (c)
\]

It is unrealistic to expect that \( \mu_j^0(\text{aq}; T; p) \) equals \( \mu_j^0(\text{aq}; T; p; x \text{- scale}) \) because the two reference states for solute-\( j \) are quite different. In general terms, \( f_j^* \) does not equal \( \gamma_j \) for the same solution. Nevertheless, both \( f_j^* \) and \( \gamma_j \) tend to the same limit, unity, as the solution approaches infinite dilution.

Hence as \( n_j \) tends to zero,

\[
\mu_j^0(\text{aq}; T; p) - \mu_j^0(\text{aq}; T; p; x \text{- scale}) = R \cdot T \cdot \ln(m^0_j \cdot M_1) \quad (d)
\]

For example, in the case of aqueous solutions at 298.15 K, \( R \cdot T \cdot \ln(m^0_j \cdot M_1) \) equals \( (-9.96 \text{ kJ mol}^{-1}) \) meaning that, with respect to the reference states for the two solutions, the chemical potential of solute \( j \) is higher on the mole fraction scale than on the molality scale.

Combination of equations (b) and (d) yields an equation relating the two
activity coefficients with the two terms describing the composition of the solution.

\[ \ln(f^*_j) = \ln \gamma_j + \ln(m_j \cdot M_j / x_j) \quad (e) \]

The term ‘unitary’ is sometimes used to describe reference chemical potentials on the mole fraction scale, \( \mu_j^0(aq;T;p;x_j = 1) \). The term \( R \cdot T \cdot \ln(m^0 \cdot M_1) \) in equation (d) is called cratic [2] because it refers to different amounts of solute and solvent which are mixed to form reference states for the solute on molality, mole fraction and concentration scales. The impression is sometimes given that standard states for solutes based on the mole fraction scale (sometimes identified as the unitary scale) are more fundamental but there is little experimental evidence to support this view.

**Footnotes**

[1] For a solution prepared using \( w_1 \) kg of water and

\[ n_j \text{ moles of solute } j, \]

\[ x_j = n_j / [(w_1 / M_j) + n_j] \text{ and } m_j = n_j / w_1. \]

\[ m_j / m^0 \cdot x_j = n_j \cdot [(w_1 / M_1) + n_j] / w_1 \cdot m^0 \cdot n_j \]

\[ m_j / m^0 \cdot x_j = [(1 / M_j) + m_j] / m^0 \]