**Infinite Dilution**

The term ‘infinite dilution’ is often encountered in reviewing the properties of solutions. However, some caution has to be exercised when this term is used [1]. There is merit in distinguishing between the properties of aqueous solutions containing simple neutral solutes and those containing salts because the impact of solute-solute interactions plays an important role in the analysis. Further, we need to distinguish the properties of solutes and solvents.

**Neutral Solutes: The Solute**

The chemical potential of solute \( j \), \( \mu_j(aq) \) is related to the composition of the solution, molality \( m_j \), at temperature \( T \) and pressure \( p \) which is assumed to be close to the standard pressure.

\[
\mu_j(aq; T; p) = \mu_j^0(aq; T; p) + R \cdot T \cdot \ln(m_j / m^0) + R \cdot T \cdot \ln(\gamma_j) \tag{a}
\]

Or

\[
\mu_j(aq; T; p) = \mu_j^0(aq; T; p) + R \cdot T \cdot \ln(m_j / m^0) + R \cdot T \cdot \ln(\gamma_j) \tag{b}
\]

For simple solutes in aqueous solutions, \( \ln(\gamma_j) \) is a linear function of the molality \( m_j \).

\[
\ln(\gamma_j) = \chi \cdot (m_j / m^0) \tag{c}
\]

Here \( \chi \) is a function of temperature and pressure.

\[
\mu_j(aq; T; p) = \mu_j^0(aq; T; p) + R \cdot T \cdot \ln(m_j / m^0) + R \cdot T \cdot \chi \cdot (m_j / m^0) \tag{d}
\]

We note therefore that \( \lim (m_j \to 0) \mu_j(aq; T; p) = -\infty \) \( \tag{e} \)

Hence, with increasing dilution of the solution, solute \( j \) is increasingly stabilised, \( \mu_j(aq; T; p) \) decreasing to ‘\(-\infty\)’ in an infinite amount of solvent.

Using the Gibbs-Helmholtz Equation, equation (a) yields equation (f).

\[
-H_j(aq; T; p)/T^2 = -H_j^0(aq; T; p)/T^2 + R \cdot (\partial \ln(\gamma_j)/\partial T)_p \tag{f}
\]

\( H_j(aq; T; p) \) is the partial molar enthalpy of solute \( j \).

\[
H_j(aq; T; p) = H_j^0(aq; T; p) - R \cdot T^2 \cdot (\partial \ln(\gamma_j)/\partial T)_p \tag{g}
\]

Using equation (c),

\[
H_j(aq; T; p) = H_j^0(aq; T; p) - R \cdot T^2 \cdot (m_j / m^0) \cdot (\partial \gamma / \partial T)_p \tag{h}
\]

Hence, limit \( (m_j \to 0)H_j(aq; T; p) = H_j^\infty(aq; T; p) = H_j^0(aq; T; p) \tag{i} \)

As the solution becomes more dilute and approaches infinite dilution so \( H_j(aq; T; p) \) in the limit of infinite dilution approaches the partial molar enthalpy of solute \( j \) in the
The partial molar enthalpy is identified as \( H^0_{\text{aq}}(p;T) \) granted the latter conclusion based on equation (h), this equation offers information concerning the form of the plot of \( H_j(\text{aq};T;p) \) against \( m_j \).

\[
[\frac{\partial H_j(\text{aq};T;p)}{\partial m_j}] = -R \cdot T^2 \cdot (m^0_j)^{-1} \cdot \left( \frac{\partial \chi}{\partial T} \right)_p
\]

In other words the gradient of the plot of \( H_j(\text{aq};T;p) \) against \( m_j \) is finite, the gradient being determined by the sign of \( \left( \frac{\partial \chi}{\partial T} \right)_p \).

The partial molar isobaric heat capacity of the solute \( j \) is given by the differential of equation (h) with respect to temperature.

\[
C^0_p(\text{aq};T;p) = C^0_p(\text{aq};T;p) - R \cdot (m_j / m^0_j) \cdot \left[ \frac{\partial}{\partial T} \left( T^2 \cdot \left( \frac{\partial \chi}{\partial T} \right)_p \right) \right]
\]

Limit \((m_j \to 0)C^0_p(\text{aq};T;p)\) is a finite quantity, \( C^0_p(\text{aq};T;p) \). In other words the limiting partial molar isobaric heat capacity of the solute \( C^\infty_p(\text{aq};T;p) \) equals the standard partial molar isobaric heat capacity, \( C^0_p(\text{aq};T;p) \).

\[
\lim_{m_j \to 0} C^\infty_p(\text{aq};T;p) = C^\infty_p(\text{aq};T;p) = C^0_p(\text{aq};T;p)
\]

A similar conclusion is reached when we turn our attention to partial molar volumes recognising that for solute \( j \), \( V_j(\text{aq};T;p) = (\partial \mu_j / \partial p)_T \).

\[
V_j(\text{aq};T;p) = V^0_j(\text{aq};T;p) + R \cdot T \cdot (m_j / m^0_j) \cdot (\partial \chi / \partial p)_T
\]

Therefore, \( \lim_{m_j \to 0} V_j(\text{aq};T;p) = V^0_j(\text{aq};T;p) \) (n)

The limiting value of \( V_j(\text{aq};T;p) \) is a finite quantity such that the limiting (i.e. infinite dilution) value of \( V_j(\text{aq};T;p) \), namely \( V^\infty_j(\text{aq};T;p) \) equals the standard partial molar volume, \( V^0_j(\text{aq};T;p) \).

The interesting question arises as to why the limiting values of partial molar enthalpies, volumes and isobaric heat capacities are real (and important) properties but limiting chemical potentials are not. We start again with equation (b) recalling that partial molar entropy \( S_j = -(\partial \mu_j / \partial T)_p \).

\[
S^0_j(\text{aq};T;p) - R \cdot \ln(m_j / m^0_j) - R \cdot \ln(\gamma_j) - R \cdot T \cdot (\partial \ln(\gamma_j) / \partial T)_p
\]

But \( \lim_{m_j \to 0} \ln(m_j / m^0_j) = \text{minus infinity} \) (p)

Then \( \lim_{m_j \to 0} S_j = \text{plus infinity} \) (q)
With increase in dilution $S_j(aq; T; p)$ tends to the asymptotic limit, plus infinity.

For a solution at fixed $T$ and $p$ prepared using 1 kg of water, the Gibbs energy is given by equation (r).

$$G(T; p; aq; w_i = 1 \text{ kg}) = (1/M_i) \cdot \mu_j(aq) + m_j \cdot \mu_j(aq) \quad (r)$$

Or,

$$G(T; p; aq; w_i = 1 \text{ kg}) = (1/M_i) \cdot [\mu_j(\ell) - \phi \cdot R \cdot T \cdot M_i \cdot m_j] + m_j \cdot [\mu_j(0) + R \cdot T \cdot \ln(m_j / m^0) + R \cdot T \cdot \ln(\gamma_j)] \quad (s)$$

$$\text{limit}(m_j \to 0) G(T; p; aq; w_i = 1 \text{ kg}) = \mu_j(\ell) / M_i \quad (t)$$

Salt Solutions; The Salt

We consider a dilute 1:1 salt solution, confining the analysis to a consideration of the impact of the Debye - Huckel Limiting Law (DHLL). For a salt solution, molality $m_j$,

$$\mu_j(aq; T; p) = \mu_j(0)(aq; T; p) + 2 \cdot R \cdot T \cdot \ln(m_j / m^0) + 2 \cdot R \cdot T \cdot \ln(\gamma_j) \quad (u)$$

Or, using the DHLL

$$\mu_j(aq; T; p) = \mu_j(0)(aq; T; p) + 2 \cdot R \cdot T \cdot \ln(m_j / m^0) - 2 \cdot R \cdot T \cdot \gamma^j \cdot (m_j / m^0)^{1/2} \quad (v)$$

From equation (u),

$$\left[ \frac{\partial \mu_j(aq; T; p)}{\partial m_j} \right] = \frac{2 \cdot R \cdot T}{m_j} + R \cdot T \cdot \left[ \frac{\partial \ln(\gamma^j)}{\partial m_j} \right] \quad (w)$$

As for a non-ionic solute, \( \text{limit}(m_j \to 0) \left[ \frac{\partial \mu_j(aq; T; p)}{\partial m_j} \right] = \infty \quad (x) \)

From the Gibbs - Helmholtz equation and equation (v),

$$H_j(aq; T; p) = H_j(0)(aq; T; p) + 2 \cdot R \cdot T \cdot S_H \cdot (m_j / m^0)^{1/2} \quad (y)$$

where \( S_H = (\partial S_j / \partial T) \quad (z) \)

$$[\partial H_j(aq; T; p) / \partial m_j] = R \cdot T \cdot S_H \cdot (m_j / m^0)^{1/2} \quad (aa)$$

Further,

$$[\partial H_j(aq; T; p) / \partial m_j] = R \cdot T \cdot (m_j / m^0)^{1/2} \cdot (\partial S_H / \partial m_j)$$

Thus the gradient of a plot of $H_j(aq)$ against $m_j$ has infinite slope in the limit ($m_j \to 0$). A similar pattern emerges in the case of partial molar volumes of the salt [2].

A similar analysis can be undertaken with respect to the partial molar properties of the solvent and apparent molar thermodynamic properties of salts and neutral solutes.

Footnote