**Apparent Molar Properties: Solutions: General**

Consider the general apparent molar property $\phi(Q_j)$ and the corresponding extensive property of a solution, $Q$; e.g. $C_p$, $E_p$, $E_S$, $K_T$, and $K_S$. The latter are all extensive properties of a given system. The corresponding volume intensive property $q$ is given by the ratio $Q/V$; c.f. $q = \text{isobaric expansivity } \alpha_p$, $\text{isentropic expansivity } \alpha_S$, $\text{isothermal compressibility } \kappa_T$, $\text{isentropic compressibility } \kappa_S$, and heat capacitance $\sigma$ respectively. The following four general equations [1] show how the volume intensive properties of the solution and solvent, $q$ and $q_1^*$ respectively, form the basis for the calculation of apparent molar property $\phi(Q_j)$ [2].

\[
\begin{align*}
\phi(Q_j) &= (q - q_1^*) \cdot (m_j \cdot \rho_1^*)^{-1} + q \cdot \phi(V_j) \\
\phi(Q_j) &= (q - q_1^*) \cdot (c_j)^{-1} + q_1^* \cdot \phi(V_j) \\
\phi(Q_j) &= (q \cdot \rho_1^* - q_1^* \cdot \rho) \cdot (m_j \cdot \rho \cdot \rho_1^*)^{-1} + q \cdot M_j \cdot \rho^{-1} \\
\phi(Q_j) &= (q \cdot \rho_1^* - q_1^* \cdot \rho) \cdot (c_j \cdot \rho_1^*)^{-1} + q_1^* \cdot M_j \cdot (\rho_1^*)^{-1}
\end{align*}
\]

In these four equations, $\rho$ is the density of the solution; $\rho_1^*$ is the density of the solvent at the same $T$ and $p$. The theme running through these equations is the link between the apparent molar property $\phi(Q_j)$ of a given solute and the measured property $q$. Interestingly apparent molar enthalpies break the pattern in that the enthalpy of a solution cannot be measured. Nevertheless apparent molar enthalpies are used in the analysis of calorimetric results. There are no advantages in defining apparent chemical potentials and apparent molar entropies of solutes.

**Footnotes**


[2] $\phi(Q_j)$ is defined by the following equation with reference to the extensive variable $Q$ in terms of amounts of solvent and solute $n_1$ and $n_j$ respectively where $Q_1^*$ is the molar property of the solvent at the same $T$ and $p$. 
We shift to volume intensive properties \( q \) and \( q^*_1 \).

\[
Q = n_j \cdot Q^*_1 + n_j \cdot \phi(Q_j)
\]  \hspace{1cm} (a)

We express the volume using the following equation incorporating apparent molar volume \( \phi(V_j) \) and molar volume of the solvent \( V^*_1(\lambda) \) at the same \( T \) and \( p \).

\[
V = n_i \cdot V^*_1(\lambda) + n_j \cdot \phi(V_j)
\]  \hspace{1cm} (b)

We solve equation (b) for \( \phi(Q_j) \) using equation (c).

Hence,

\[
\phi(Q_j) = \frac{n_i \cdot V^*_1(\lambda) \cdot q}{n_j} + q \cdot \phi(V_j) - \frac{n_i \cdot V^*_1(\lambda) \cdot q^*_1}{n_j}
\]  \hspace{1cm} (d)

But [3] \( n_i \cdot V^*_1(\lambda)/n_j = (m_j \cdot \rho^*_1)^{-1} \).

Equation (e) follows.

\[
\phi(Q_j) = (q - q^*_1) \cdot (m_j \cdot \rho^*_1)^{-1} + q \cdot \phi(V_j)
\]  \hspace{1cm} (e)

Using the latter equation, molalities are converted to concentrations using equation (f).

\[
(m_j \cdot \rho^*_1)^{-1} = (c_j)^{-1} - \phi(V_j)
\]  \hspace{1cm} (f).

Then \( \phi(Q_j) = (q - q^*_1) \cdot (c_j)^{-1} - \phi(V_j) \cdot (q - q^*_1) + q \cdot \phi(V_j) \) \hspace{1cm} (g)

Or \( \phi(Q_j) = (q - q^*_1) \cdot (c_j)^{-1} + q^*_1 \cdot \phi(V_j) \) \hspace{1cm} (h)

We return to equation (b) and express the volume using the following equation.

\[
V = [n_i \cdot M_1 + n_j \cdot M_j]/\rho
\]  \hspace{1cm} (i)

Then [4] \( \phi(Q_j) = \frac{n_i \cdot M_1 \cdot q}{n_j \cdot \rho} + \frac{M_j \cdot q}{\rho} - \frac{n_i \cdot V^*_1 \cdot q^*_1}{n_j} \) \hspace{1cm} (j)

Then [3,5] \( \phi(Q_j) = \frac{q}{m_j \cdot \rho} + \frac{M_j \cdot q}{\rho} - \frac{q^*_1}{m_j \cdot \rho^*_1} \) \hspace{1cm} (k)

Or,

\[
\phi(Q_j) = (q \cdot \rho^*_1 - q^*_1 \cdot \rho) \cdot (m_j \cdot \rho \cdot \rho^*_1)^{-1} + q \cdot M_j \cdot \rho^{-1}
\]  \hspace{1cm} (l)
To obtain an equation using concentrations, we use the following equation.

\[ \frac{1}{m_j} = \rho / c_j - M_j \]

Thus \[ \phi \] is given by \[ \frac{q \cdot \rho_i^* - q_i^* \cdot \rho}{c_j \cdot \rho_i^*} - \frac{M_j \cdot (q \cdot \rho_i^* - q_i^* \cdot \rho)}{\rho_i^* \cdot \rho} + \frac{q \cdot M_j}{\rho} \quad (m) \]

Or, \[ \phi(Q_j) = (q \cdot \rho_i^* - q_i^* \cdot \rho) \cdot (c_j \cdot \rho_i^*)^{-1} + q_i^* \cdot M_j \cdot (\rho_i^*)^{-1} \quad (n) \]

Because the equations used for converting molalities to concentrations are exact, no approximations are involved. Therefore equations (e), (h), (\( \lambda \)) and m are rigorously equivalent.

\[ \frac{n_1 \cdot V_i^*(\lambda)}{n_j} = \frac{n_1 \cdot V_i^*(\lambda) \cdot \rho_i^*(\lambda)}{n_j \cdot \rho_i^*(\lambda)} = \frac{w_i}{n_j \cdot \rho_i^*(\lambda)} = [m_j \cdot \rho_i^*(\lambda)]^{-1} \quad (3) \]

[4] From equations (b) and (i),

\[ (n_1 \cdot M_i + n_j \cdot M_j) \cdot q / \rho = n_1 \cdot V_i^*(\lambda) \cdot q_i^* + n_j \cdot \phi(Q_j) \]

[5] \( n_1 \cdot M_i / n_j = (m_j)^{-1} \)

[6] From equation (\( \lambda \)),

\[ \phi(Q_j) = \left[\frac{[q \cdot \rho_i^*(\lambda) - q_i^* \cdot \rho]}{\rho \cdot \rho_i^*(\lambda)} \cdot [(\rho / c_j) - M_j] + [q \cdot M_j / \rho]\right] \]