Enthalpy: Solutions: Partial Molar Enthalpies

The enthalpy of a solution containing \( n_1 \) moles of water and \( n_j \) moles of solute, chemical substance \( j \), is defined by the independent variables, \( T, p, n_1 \) and \( n_j \).

\[
H = H[T, p, n_1, n_j]
\]  

where \( H = n_1 \cdot H_1(aq) + n_j \cdot H_j(aq) \)  

Here \( H_1(aq) \) and \( H_j(aq) \) are the partial molar enthalpies of water and solute \( j \) in the solution.

\[
\frac{\partial H}{\partial n_1} = H_1(aq)
\]  

\[
\frac{\partial H}{\partial n_j} = H_j(aq)
\]

For a solution prepared using 1 kg of solvent, water and \( m_j \) moles of solute \( j \) [2],

\[
H(aq; w_1 = 1 \text{ kg}) = \left( \frac{1}{M_1} \right) \cdot H_1(aq) + m_j \cdot H_j(aq)
\]

The chemical potential of the solvent in an aqueous solution is related to the molality of solute \( j \), \( m_j \) using equation (f) where \( \phi \) is the practical osmotic coefficient, a property of the solvent.

\[
\mu_1(aq) = \mu_1^*(\lambda) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j
\]

The chemical potential and partial molar enthalpy are linked using the Gibbs-Helmholtz equation such that at fixed pressure,

\[
d\left( \frac{\mu_1(aq)}{T} \right)/dT = - \frac{H_1(aq)}{T^2}.
\]

Hence [3] \( H_1(aq) = H_1^*(\lambda) + R \cdot T^2 \cdot M_1 \cdot m_j \cdot \left( d\phi/dT \right)_p \)  

By definition the practical osmotic coefficient is unity for ideal solutions at all \( T \) and \( p \). Then the partial molar enthalpy of the solvent in an ideal solution,

\[
H_1(aq, id) = H_1^*(\lambda)
\]

The definition of \( \phi \) requires that \( \lim_{m_1 \to 0} H_1(aq) = H_1^*(\lambda) \). We express the difference between the partial molar enthalpies of the solvent
in real and ideal solutions using a relative (partial) molar enthalpy, 
\[ \Lambda_i(aq) \].

\[ \Lambda_i(aq) = H_i(aq) - H_i^\infty(\lambda) \] (i)

In equation (i), we encounter another difference in order to take account of
the fact that we cannot measure absolute enthalpies of solutions and
solvents.

The chemical potential of the solute \( j \) (at fixed \( T \) and \( p \), which is close to
ambient pressure) is related to the molality \( m_j \) using equation (j).

\[ \mu_j(aq) = \mu_j^0(aq) + R \cdot T \cdot \ln\left( m_j \cdot \gamma_j / m^0 \right) \] (j)

From the Gibbs-Helmholtz Equation,

\[ H_j(aq) = H_j^0(aq) - R \cdot T^2 \cdot \left( d \ln \gamma_j / dT \right)_p \] (k)

But activity coefficient \( \gamma_j \) is defined such that
limit\( (m_j \to 0) \gamma_j = 1.0 \) at
all \( T \) and \( p \). Moreover for an ideal solution, \( \gamma_j = 1.0 \).

Hence, limit\( (m_j \to 0) H_j(aq) = H_j^0(aq) = H_j^\infty(aq) \) (\( \lambda \))

In other words, with increasing dilution \( H_j(aq) \) approaches a limiting
partial molar enthalpy \( H_j^\infty(aq) \) which equals the partial molar enthalpy of
the solute in an ideal solution. We identify a relative (partial) molar
enthalpy of solute \( j \), \( \Lambda_j(aq) \).

\[ \Lambda_j(aq) = H_j(aq) - H_j^\infty(aq) \] (m)

Hence, at fixed \( T \) and \( p \) limit\( (m_j \to 0) \Lambda_j(aq) = 0 \) (n)

Therefore for simple solutes in solution in the limit of infinite dilution the
relative partial molar enthalpy of solute \( j \) is zero [4].

Footnotes

[1] \( [J] = [\text{mol}] \cdot [\text{J mol}^{-1}] + [\text{mol}] \cdot [\text{J mol}^{-1}] \)

[2] \( [\text{J kg}^{-1}] = [\text{kg mol}^{-1}] \cdot [\text{J mol}^{-1}] + [\text{mol kg}^{-1}] \cdot [\text{J mol}^{-1}] \)

[3] Note the advantage of expressing the composition in terms of
molalities rather than in concentrations for which we would have to take
account of the dependence of volume on temperature.
An interesting comparison is the molar enthalpy of water ($\lambda$) and the limiting molar enthalpy of solute water in a solvent such as methanol. We define a transfer quantity, $\Delta_{tr} \Delta H^0 = H^\infty (H_2O \text{ as solute in a defined solvent}) - H^\infty (\lambda \cdot H_2O)$, characterising the difference in molar enthalpy of liquid water and the limiting partial molar enthalpy of solute water at ambient pressure and 298.15 K. $\Delta_{tr} \Delta H^0$ is 0.85, 4.05 and 10.11 kJ mol$^{-1}$ in CH$_3$OH ($\lambda$), C$_7$H$_{15}$OH ($\lambda$) and C$_2$H$_4$(O.CO.C$_3$H$_7$)$_2$ ($\lambda$) respectively [5].