## Topic1040

## 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 $n_j$.

$$H = H[T, p, n_1, n_j] \qquad (a)$$

where [1], $H = n_1 \cdot H_1(aq) + n_j \cdot H_j(aq)$ (b)

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

$$H_1(aq) = (\partial H/\partial n_1)_{T,p,n(j)} \qquad (c)$$

$$H_j(aq) = (\partial H/\partial n_j)_{T,p,n(1)} \qquad (d)$$

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

$$H(aq; w_1 = 1\,kg) = (1/M_1) \cdot H_1(aq) + m_j \cdot H_j(aq) \qquad (e)$$

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.

$$\mu_1(aq) = \mu_1^*(\lambda) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j \qquad (f)$$

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

$d(\mu_1(aq)/T)/dT = -H_1(aq)/T^2$ .

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

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,

$$H_1(aq, id) = H_1^*(\lambda) \qquad (h)$$

The definition of $\phi$ requires that $\text{limit}(m_j \to 0)\ H_1(aq)$ equals $H_1^*(\lambda)$. We express the difference between the partial molar enthalpies of the solvent in real and ideal solutions using a relative (partial) molar enthalpy, $L_1(\mathrm{aq})$.

$$L_1(\mathrm{aq}) = H_1(\mathrm{aq}) - H_1^*(\lambda) \qquad \text{(i)}$$

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).

$$\mu_j(\mathrm{aq}) = \mu_j^0(\mathrm{aq}) + R \cdot T \cdot \ln\left(m_j \cdot \gamma_j / m^0\right) \qquad \text{(j)}$$

From the Gibbs-Helmholtz Equation,

$$H_j(\mathrm{aq}) = H_j^0(\mathrm{aq}) - R \cdot T^2 \cdot \left(d \ln \gamma_j / dT\right)_p \qquad \text{(k)}$$

But activity coefficient $\gamma_j$ is defined such that $\mathrm{limit}\left(m_j \rightarrow 0\right) \gamma_j = 1.0$ at all T and p. Moreover for an ideal solution, $\gamma_j = 1.0$.

Hence, $\mathrm{limit}\left(m_j \rightarrow 0\right) \ H_j(\mathrm{aq}) \ = \ H_j^0(\mathrm{aq}) \ = \ H_j^\infty(\mathrm{aq}) \qquad (\lambda)$

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

$$L_j(\mathrm{aq}) \ = \ H_j(\mathrm{aq}) \ - \ H_j^\infty(\mathrm{aq}) \qquad \text{(m)}$$

Hence, at fixed T and p $\mathrm{limit}\left(m_j \rightarrow 0\right) L_j(\mathrm{aq}) \ = \ 0 \qquad$ (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] $[\mathrm{J}] \ = \ [\mathrm{mol}] \cdot [\mathrm{J\ mol}^{-1}] \ + \ [\mathrm{mol}] \cdot [\mathrm{J\ mol}^{-1}]$

[2] $[\mathrm{J\ kg}^{-1}] \ = \ [\mathrm{kg\ mol}^{-1}]^{-1} \cdot [\mathrm{J\ mol}^{-1}] \ + \ [\mathrm{mol\ kg}^{-1}] \cdot [\mathrm{J\ mol}^{-1}]$

[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.

[4] 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, $\Delta_{tr}H^0$ $\left[= H^\infty\right.$ ($H_2O$ as solute in a defined solvent) $\left. -H_1^*(\lambda; H_2O)\right]$, 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. $\Delta_{tr}H^0$ is 0.85, 4.05 and 10.11 kJ $mol^{-1}$ in $CH_3OH\,(\lambda)$, $C_7H_{15}OH\,(\lambda)$ and $C_2H_4(O.CO.C_3H_7)_2$ $(\lambda)$ respectively [5].

[5] S.-O. Nilsson, J. Chem. Thermodyn., 1986, **18**, 1115.