Equilibrium isobaric heat capacities of solutions can be treated for most purposes as extensive variables. Thus for an aqueous solution prepared using \(n_{1}\) moles of solvent (water) and \(n_{j}\) moles of a simple solute \(j\) the isobaric (equilibrium) heat capacity of the solution \(C_{p}(\text{aq})\) can be related to the composition of the solution using equations (a) and (b) [1].

\[
C_{p}(\text{aq}) = n_{1}C_{p1}(\text{aq}) + n_{j}C_{pj}(\text{aq})
\]

where

\[
C_{p1}(\text{aq}) = \left(\frac{\partial C_{p}(\text{aq})}{\partial n_{1}}\right)_{T, p, n(j)} \quad \text{and} \quad C_{pj}(\text{aq}) = \left(\frac{\partial C_{p}(\text{aq})}{\partial n_{j}}\right)_{T, p, n(l)}
\]

Similar equations are encountered in a discussion of the partial molar enthalpies but with reference to these properties we develop a number of strategies because it is not possible to determine the enthalpy of a solution. In the present case the outlook is much more favourable because it is possible to measure isobaric heat capacities of solutions [1-3]. The fact that we can measure the temperature dependence of the equilibrium enthalpy of a solution but not the actual enthalpy is an interesting philosophical point. Nevertheless it is informative to develop the analysis starting from equations relating partial molar enthalpies and compositions of solutions.

A given aqueous solution is prepared using \(n_{1}\) moles of solvent (water) and \(n_{j}\) moles of solute. The partial molar enthalpies are related to the composition of the solution by the following equations. Thus

\[
H_{1}(\text{aq}) = H_{1}^{*}(\ell) + R T^2 M_{1} m_{j} \left(\frac{\partial \phi}{\partial T}\right)_{p}
\]

and

\[
H_{j}(\text{aq}) = H_{j}^{\infty}(\text{aq}) - R T^2 \left(\frac{\partial \ln \gamma_{j}}{\partial T}\right)_{p}
\]

At all \(T\) and \(p\),

\[
\lim_{m_{j} \to 0} \phi = 1 \quad \text{and} \quad \gamma_{j} = 1
\]

By definition,

\[
C_{p1}(\text{aq}) = \left(\frac{\partial C_{p}}{\partial n_{1}}\right)_{T, p, n(j)} = \left(\frac{\partial H_{1}}{\partial T}\right)_{p} = \left(\frac{\partial^{2} H}{\partial n_{1} \partial T}\right)_{p, n(j)}
\]

And,
The latter two equations trace the story from the enthalpy of the solution to partial molar isobaric heat capacities. Using equation (f) in conjunction with equation (c) we obtain an equation for dependence for \( C_{p1}^{\text{aq}} \) on molality \( m_j \).

\[
C_{p1}^{\text{aq}} = C_{p1}^{\infty}(\ell) + 2R T M_1 m_j \left( \frac{\partial \phi}{\partial T} \right)_{p} + R T^2 M_1 m_j \left( \frac{\partial^2 \phi}{\partial T^2} \right)_{p}
\]

Similarly using equations (d) and (g), we obtain an equation relating \( C_{pj}^{\text{aq}} \) and molality \( m_j \); the origin of the two minus signs is the Gibbs - Helmholtz Equation.

\[
C_{pj}^{\text{aq}} = C_{pj}^{\infty}(\text{aq}) - 2R T \left[ \frac{\partial \ln(\gamma_j)}{\partial T} \right]_p - R T^2 \left[ \frac{\partial^2 \ln(\gamma_j)}{\partial T^2} \right]_p
\]

We consider a solution prepared using 1 kg of water and \( m_j \) moles of solute \( j \) [4].

\[
C_{p}(\text{aq} ; w_1 = 1 \text{kg}) = \left( 1/M_1 \right) C_{p1}^{\infty}(\ell) + m_j C_{pj}^{\infty}(\text{aq})
\]

If the thermodynamic properties of the solution are ideal, from the definitions of both practical osmotic coefficient \( \phi \) and activity coefficient \( \gamma_j \), the last two terms in equations (h) and (i) are zero.

\[
C_{p}(\text{aq} ; \text{id} ; w_1 = 1 \text{kg}) = \left( 1/M_1 \right) C_{p1}^{\infty}(\ell) + m_j C_{pj}^{\infty}(\text{aq})
\]

This is an interesting equation because two experiments yield \( C_{p}(\text{aq} ; \text{id}) \) and \( C_{p1}^{\infty}(\ell) \). Hence, granted the ideal conditions, we obtain an estimate of \( C_{pj}^{\infty}(\text{aq}) \), limiting isobaric heat capacity of solute \( j \) in solution. Unfortunately the assumption concerning ideal properties of a solution is often unrealistic. Nevertheless equation (k) offers a reference against which we can examine the properties of real solutions.

Footnotes


\[ \left[ \text{J K}^{-1} \text{kg}^{-1} \right] = \left[ \text{J K}^{-1} \text{mol}^{-1} \right] + \left[ \text{mol}^{-1} \text{kg} \right] \left[ \text{J K}^{-1} \text{mol}^{-1} \right] \]