**Topic 2150**

**Heat Capacities; solutions**

**Solute-solute interaction parameters**

We describe an excess enthalpy $H^E$ for a solution prepared using 1 kg of water and $m_j$ moles of solute $j$ (at fixed $T$ and $p$) in terms of solute-solute enthalpic interaction parameters.

$$H^E(\text{aq}; w_1 = 1 \text{ kg}) = h_{jj} \cdot (m_j / m^0)^2 \quad (a)$$

The corresponding excess isobaric heat capacity is defined by equation (b).

$$C_p^E(\text{aq}; w_1 = 1 \text{ kg}) = c_{pjj} \cdot (m_j / m^0)^2 \quad (b)$$

where $c_{pjj} = \left( \frac{\partial h_{jj}}{\partial T} \right)_p \quad (c)$

Here $c_{pjj}$ is a pairwise solute-solute interaction isobaric heat capacity [1].

From $H_j(aq) = H_j^\ast(\ell) - M_j \cdot h_{jj} \cdot (m_j / m^0)^2 \quad (d)$

then, $C_{p jj}(aq) = C_{p jj}^\ast(\ell) - M_j \cdot c_{pjj} \cdot (m_j / m^0)^2 \quad (e)$

From $H_j(aq) = H_j^\ast(aq) + 2 \cdot h_{jj} \cdot (m^0)^{-2} \cdot m_j \quad (f)$

then, $C_{p jj}(aq) = C_{p jj}^\ast(aq) + 2 \cdot c_{pjj} \cdot (m^0)^{-2} \cdot m_j \quad (g)$

**Footnote**

[1] For a solution prepared using 1 kg of water and $m_j$ moles of solute (at fixed $T$ and $p$)

$$C_p(\text{aq}; w_1 = 1 \text{ kg}) = (1 / M_j) \cdot C_{p jj}(aq) + m_j \cdot C_p(aq)$$

Hence $C_p(\text{aq}; w_1 = 1 \text{ kg}) = (1 / M_j) \cdot [C_{p jj}(\ell) - M_j \cdot c_{pjj} \cdot (m_j / m^0)^2]$

$$+ m_j \cdot [C_{p jj}^\ast(aq) + 2 \cdot c_{pjj} \cdot (m^0)^{-2} \cdot m_j]$$

Then, $C_p(\text{aq}; w_1 = 1 \text{ kg}) = (1/M_j) \cdot C_{p jj}(\ell) + m_j \cdot C_p(aq) + c_{pjj} \cdot (m_j / m^0)^2$

Since, $C_p(\text{aq}; w_1 = 1 \text{ kg}) = (1/M_j) \cdot C_{p jj}^\ast(aq) + m_j \cdot C_{p jj}^\ast(aq)$

$$C_{p jj}(\text{aq}; w_1 = 1 \text{ kg}) = c_{pjj} \cdot (m_j / m^0)^2$$