**Topic 3030**

**Volumes; Solutions; Neutral Solutes**

A given solution is prepared using $n_i$ moles of water and $n_j$ moles of solute $j$ at defined temperature and pressure. The solution is at equilibrium where the affinity for spontaneous change is zero and at a minimum in Gibbs energy. [In the following analysis the equilibrium condition is implicit.] The Gibbs energy $G(aq)$ is given by equation (a).

$$G(aq) = n_i \cdot \mu_i(aq) + n_j \cdot \mu_j(aq) \quad (a)$$

**Ideal Solutions**

We assume initially that the thermodynamic properties of the solution are ideal. Therefore the chemical potential of the solvent (water) is given by equation (b).

$$\mu_i(aq;id;T;p) = \mu_i^*(\ell;T;p^0) - R \cdot T \cdot M_i \cdot m_j + \int_{p^0}^p V_i^*(\ell;T;p) \cdot dp \quad (b)$$

But at fixed temperature, $V_i(aq) = \left(\frac{\partial \mu_i(aq)}{\partial p}\right)_T$. \hspace{1cm} (c)

Hence the partial molar volume of the solvent in the (ideal) solution equals the molar volume of the pure liquid solvent at the same $T$ and $p$, $V_i^*(\ell)$.

The chemical potential of solute $j$ is related to the molality $m_j$ in an ideal solution using equation (d).

$$\mu_j(aq;id;T;p) = \mu_j^0(aq;T;p^0) + R \cdot T \cdot \ln(m_j/m_j^0) + \int_{p^0}^p V_j^*(aq;T;p) \cdot dp \quad (d)$$

But at fixed temperature $V_j(aq) = \left(\frac{\partial \mu_j(aq)}{\partial p}\right)_T$. \hspace{1cm} (e)

Then $V_j(aq;T;p) = V_j^*(aq;T;p)$. \hspace{1cm} (f)

Hence the volume of the ideal solution is given by equation (g).

$$V(aq;id;T;p) = n_i \cdot V_i^*(\ell;T;p) + n_j \cdot V_j^*(aq;T;p) \quad (g)$$
With reference to equation (g), we know $n_j$ and $n_1 \cdot V_1^*(\ell; T; p)$.

Moreover the density of the solution $\rho(aq)$ can be measured. Hence we obtain $V_j^\infty(aq; T; p)$ [1,2]. This is utopia. The thermodynamic properties of a real solution are not ideal. In practice if the solution is dilute, we might assume that the properties of a given solution are ‘close to ideal’. Hence we would obtain an estimate of $V_j^\infty(aq; T; p)$ but this approach is not satisfactory.

**Real Solutions**

We take up the story using equations for the chemical potentials of both solvent and solute but recognising that their properties are not ideal. Then for the solvent,

$$\mu_1(aq; T; p) = \mu_1^*(\ell; T; p^0) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j + \int_{p^0}^{p} V_1^*(\ell; T; p) \cdot dp \quad (h)$$

At all $T$ and $p$, limit $(m_j \to 0)\phi = 1 \quad (i)$

Then $V_1(aq; T; p) = V_1^*(\ell; T; p) - R \cdot T \cdot M_1 \cdot m_j \left( \frac{\partial \phi}{\partial p} \right)_T \quad (j)$

Here limit $(m_j \to 0)\gamma_j = 1 \quad (k)$

In other words we have established a link between the volumetric properties of the solvent in real and ideal solutions.

The chemical potential of solute $j$ is related to the molality $m_j$ in a real solution using equation (l).

$$\mu_j(aq; T; p) = \mu_j^0(aq; T; p^0) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) + \int_{p^0}^{p} V_j^\infty(aq; T; p) \cdot dp \quad (l)$$

At all $T$ and $p$, limit $(m_j \to 0)\gamma_j = 1 \quad (m)$

Then, $V_j(aq; T; p) = V_j^\infty(aq; T; p) + R \cdot T \left( \frac{\partial \ln(\gamma_j)}{\partial p} \right)_T \quad (n)$

At all $T$ and $p$, limit $(m_j \to 0)V_j(aq; T; p) = V_j^\infty(aq; T; p) \quad (o)$
In other words, the partial molar volume \( V_j(aq) \) in the limit of infinite dilution \( V_j^\infty(aq;T;p) \) equals the partial molar volume of solute \( j \) in an ideal solution [1,2].

**Footnotes**
