Topic 1685

Gibbs-Duhem Equation: Aqueous Salt Solutions; Salt and Solvent;

Debye-Huckel Limiting Law

A given aqueous salt solution at temperature T and pressure p (which is close to the standard pressure) is prepared using water (1 kg) and m_j moles of a 1:1 salt-j. The chemical potential of salt–j is related to m_j and the mean ionic activity coefficient \( \gamma_{\pm} \) using equation (a) where \( \mu_j^0(aq) \) is the chemical potential of salt-j in an aqueous solution where m_j = 1 mol kg^-1 and the thermodynamic properties of the solution are ideal.

\[
\mu_j(aq) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j \cdot \gamma_{\pm} / m^0) \quad (a)
\]

At all T and p, limit \( (m_j \to 0) \gamma_{\pm} = 1 \) \( (b) \)

The chemical potential of solvent, water \( \mu_1(aq) \) is related to salt molality \( m_j \) by equation (c) where \( \mu_1^*(\ell) \) is the chemical potential of water \( \ell \) at the same T and p and \( \phi \) is the molal osmotic coefficient.

\[
\mu_1(aq) = \mu_1^*(\ell) - 2 \cdot \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad (d)
\]

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

For a solution at fixed T and p, the Gibbs-Duhem equation relates \( \mu_1(aq) \) and \( \mu_j(aq) \) using equation (e).

\[
(1/M_1) \cdot d\mu_1(aq) + m_j \cdot d\mu_j(aq) = 0 \quad (e)
\]

Therefore

\[
(1/M_1) \cdot d[\mu_1^*(\ell) - 2 \cdot \phi \cdot R \cdot T \cdot M_1 \cdot m_j] + m_j \cdot d[\mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j \cdot \gamma_{\pm} / m^0)] = 0 \quad (f)
\]

\[
d(-\phi \cdot m_j) + m_j \cdot d \ln(m_j \cdot \gamma_{\pm}) = 0 \quad (g)
\]

At ‘\( m_j =0 \)’, \( \phi \) is unity. Therefore integration [1] of equation (g) yields equation (h)

\[
\phi = 1 + \frac{1}{m_j} \cdot \int_0^{m_j} m_j \cdot d \ln(\gamma_{\pm}) \quad (h)
\]

We have an equation for \( \phi \) in terms of \( m_j \) and \( \gamma_{\pm} \). Equation (h) signals the limit of the thermodynamic analysis. To make progress we need an equation for \( \gamma_{\pm} \) in terms of \( m_j \). The Debye-Huckel Limiting Law provides such an equation having
the form shown in equation (i) where $S_\gamma$ is positive and a function of temperature, pressure and relative permittivity of the solvent.

Thus  \[ \ln(\gamma_z) = -S_\gamma \cdot \left( \frac{m_j}{m_0} \right)^{1/2} \]  (i)

From equation (h), \[ \phi = 1 - \frac{S_\gamma}{(m_0)^{1/2} \cdot m_j} \cdot \frac{m^{(j)}}{0} \cdot m_j \cdot d(m_j)^{1/2} \]  (j)

Hence [2], \[ \phi = 1 - \left( \frac{S_\gamma}{3} \right) \cdot \left( \frac{m_j}{m_0} \right)^{1/2} \]  (k)

We examine the impact of equations (i) and (k) on the chemical potentials of solute and solvent.

From equation (c),

\[ \mu_j(aq) - \mu_j^{**}(\ell) = -2 \cdot R \cdot T \cdot M_1 \cdot m_j \cdot [1 - \left( \frac{S_\gamma}{3} \right) \cdot \left( \frac{m_j}{m_0} \right)^{1/2}] \]  (l)

For a salt solution having thermodynamic properties which are ideal,

\[ \mu_j(aq:id) - \mu_j^{**}(\ell) = -2 \cdot R \cdot T \cdot M_1 \cdot m_j \]  (m)

Then, \[ \mu_j(aq) - \mu_j(aq:id) = 2 \cdot R \cdot T \cdot M_1 \cdot \left( \frac{S_\gamma}{3} \right) \cdot \left( \frac{m_j}{m_0} \right)^{-1/2} \cdot \left( m_j \right)^{3/2} \]  (n)

But $S_\gamma$ is positive. Hence $[\mu_j(aq) - \mu_j(aq:id)]$ is positive so that in terms of the DHLL the chemical potential of water is raised above that in the corresponding solution having ideal thermodynamic properties.

For the solute, equation (a) requires that $\mu_j(aq)$ is given by equation (o).

\[ \mu_j(aq) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j / m_0) + 2 \cdot R \cdot T \cdot \ln(\gamma_z) \]  (o)

Or, \[ \mu_j(aq:id) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j / m_0) \]  (p)

Then using equation (i),

\[ \mu_j(aq) - \mu_j(aq:id) = -2 \cdot R \cdot T \cdot S_\gamma \cdot \left( \frac{m_j}{m_0} \right)^{1/2} \]  (q)

According therefore to the DHLL, salt $j$ in a real solution is stabilised relative to that in an ideal solution. In other words according to the DHLL the salt is stabilised whereas the solvent is destabilised, the impact of ion-ion interactions on the Gibbs energy of a solution is moderated.

Footnotes

[1] \[ -\phi \cdot dm_j - m_j \cdot d\phi + m_j \cdot d[\ln(m_j)] + m_j \cdot d \ln(\gamma_z) = 0 \]

\[ -\phi \cdot dm_j - m_j \cdot d\phi + (m_j / m_j) \cdot dm_j + m_j \cdot d \ln(\gamma_z) = 0 \]

Then, \[ -(\phi - 1) \cdot dm_j - m_j \cdot d\phi + m_j \cdot d \ln(\gamma_z) = 0 \]
Hence, \[\int_0^{m(j)} (-\phi + 1) \cdot dm_j = \int_0^{m(j)} m_j \cdot d\phi = -\int_0^{m(j)} m_j \cdot d\ln(\gamma_z)\]

Or, \[\phi = 1 + \frac{1}{m_j} \cdot \int_0^{m(j)} m_j \cdot d\ln(\gamma_z)\]

[2] Put \((m_j)^{1/2} = x\); \[\int_0^{m(j)} x^2 \cdot dx = \frac{x^3}{3} = (m_j)^{3/2}/3\]