Topic 1800

Gibbs Energies

Solutions

Hydrates in aqueous solution

An explanation of the properties of a given solute j in aqueous solutions is in terms of the formation of a hydrate; j.hH₂O where h is the hydration number independent of temperature and pressure[1]. In summary there are two descriptions of the solutions prepared using n₁ moles of water and n_j moles of solute j. In description A there are n_j moles of solute, chemical substance j, and n₁ moles of solvent. In description B there are n_j moles of solute j.hH₂O and (n₁ − h · n_j) moles of water [2]. At fixed T and p the system is at equilibrium, being therefore at a minimum in Gibbs energy. The Gibbs energy is not dependent on our description of the system [3]; it does not know which description we favour!

We imagine two open dishes in a partially evacuated chamber at constant T. Each dish contains the same amount of a given solution but we label one dish A and the other dish B [4]. Further the Gibbs energies are equal; G(A) = G(B). The vapour pressures are the same so that

$$\mu_{j}^{(aq)}(A) = \mu_{j}^{(aq)}(B)$$

For dish A, G(A) = n₁ · µ₁(aq) + n_j · µ_j(aq)  \hspace{1cm} (a)

For dish B, G(B) = (n₁ − n_j · h) · µ₁(aq) + n_jh · µ_jh(aq) \hspace{1cm} (b)

Here $\mu_{jh}^{(aq)}$ is the chemical potential of hydrate j.hH₂O in solution. We notes that n_j = n_jh. Because G(A) = G(B), and the chemical potentials of the solvent are the same,

$$\mu_{jh}^{(aq)} = \mu_{j}^{(aq)} + h \cdot \mu_{1}^{(aq)}.$$  

The molality of hydrate j.hH₂O,

$$m_{jh} = n_{jh} / [(n₁ − h · n_{jh}) · M_j ]$$  whereas the molality of solute j

$$m_{j} = n_{j} / [n_{1} · M_{j}] .$$

Then at fixed T and p,

$$\mu_{jh}^{(aq)} + R · T · \ln(m_{jh} · \gamma_{jh} / m_{j}^{0}) =$$

$$\mu_{j}^{(aq)} + R · T · \ln(m_{j} · \gamma_{j} / m_{j}^{0}) + h · [\mu_{1}^{(aq)}(f) − \phi · R · T · M_{j} · m_{j}] \hspace{1cm} (c)$$

In the limit(m_j → 0)γ_j = 1.0 at all T and p; in the limit(m_{jh} → 0)γ_{jh} = 1.0 at all T and p. In the same limit, $\phi=1$. 


Hence assuming $h$ is independent of $m_j$. 
\[
\mu_{j\text{h}}^0(aq) = \mu_{j}^0(aq) + h \cdot \mu_1^*(\ell) \quad \text{(d)}
\]

We use equation (d) and reorganise equation (c) as an equation for $\gamma_j$.
\[
\ln(\gamma_j) = \ln(m_{j\text{h}} / m_j) + h \cdot \phi \cdot M_1 \cdot m_j + \ln(\gamma_{j\text{h}}) \quad \text{(e)}
\]

We assert that the formation of hydrate by solute $j$ accounts for the fact that the properties of solute $j$ are not ideal. We also assert that the properties of the hydrate are ideal; $\gamma_{j\text{h}} = 1$. Moreover, $(m_j / m_{j\text{h}}) = 1 - (h \cdot m_j \cdot M_1)$

Then, \[
\ln(\gamma_j) = -\ln[1 - (h \cdot m_j \cdot M_1)] + h \cdot \phi \cdot M_1 \cdot m_j \quad \text{(f)}
\]

If the solution is dilute, $\phi \cong 1$.

Then, \[
\ln(\gamma_j) = 2 \cdot h \cdot m_j \cdot M_1 \quad \text{(g)}
\]

The hydrate model for activity coefficients can be understood in the following fashion. When $\delta n_j$ moles of solute are added to a solution molality $m_j$, $h \cdot \delta n_j$ moles of water are removed from ‘solvent’ and transferred to the solute. In these terms each solute molecule responds to this increased competition for solvent by other solute molecules and therefore ‘knows’ that there are other solute molecules in the solution. Any communication between solute molecules in solution is reflected in the extent to which $\gamma_j$ differs from unity.

**Footnotes**


[2] $h \cdot n_j$ must be $< n_l$
