Debye-Hückel

Notes on Chemical Potential

Recall $\Delta G = \Delta G^o + RT \ln K$

Chemical potential of i, μ_i, = $(\partial G / \partial n_i)_{T,P}$, is related to activity of i, a_i, by

$\mu_i = \mu_i^o + RT \ln a_i$

For the reaction aA + bB = cC + dD,

$(c\mu_C + d\mu_D - a\mu_A - b\mu_B) = (c\mu_C^o + d\mu_D^o - a\mu_A^o - b\mu_B^o) + RT \ln (a_A^a a_B^b / a_C^c a_D^d)$

So, $\Delta G = (c\mu_C + d\mu_D - a\mu_A - b\mu_B)$ and $\Delta G^o = (c\mu_C^o + d\mu_D^o - a\mu_A^o - b\mu_B^o)$.

At equilibrium,

$\Delta G = \Sigma v_i \mu_i$, that is, using the above reaction,

$c\mu_C + d\mu_D = a\mu_A + b\mu_B$

Development of Single-Ion Activity Coefficient

Write chemical potential in terms of concentration and activity coefficient, $a = m\gamma$, and consider that deviation from ideal behavior ($\gamma < 1$) is due to electrostatic interactions among ions, i.e.,

$\mu_{EL} = RT \ln \gamma$

Take the single, central ion as a point charge for which the radial electric potential is

$(1 / r^2)\, d\,(r^2\, (d\varphi / dr)) / dr = - 4\pi\rho / D$

where ρ is charge density and D is dielectric constant. The equation can be solved if ρ is expressed in terms of φ. Since $\rho = \Sigma z_i e n_i$, where z_i is valance, e is single electronic charge and n_i is concentration, n_i can be related to potential by

$n_i = n_i^o \exp(-z_i e\varphi / kT)$

where n_i^o is average, bulk concentration (ions per mL) , k is the Boltzmann constant (R / N_A) and T is absolute temperature. Thus,

$(1 / r^2)\, d\,(r^2\, (d\varphi / dr)) / dr = -(4\pi / D)\, \Sigma z_i e n_i^o \exp(-z_i e\varphi / kT)$

If the exponential is expressed as a series and truncated at the first two terms, $1 - z_i e\varphi / kT$,

$(1 / r^2)\, d\,(r^2\, (d\varphi / dr)) / dr = -(4\pi / D)\, \Sigma z_i e n_i^o + (4\pi / D)\, \Sigma z i^2 e^2 n_i^o \varphi / kT$

Electrical neutrality results in the first term on the right hand side being zero, leaving

$(1 / r^2)\ d\ (r^2\ (d\varphi / dr)) / dr = (4\pi / D)\ \Sigma z_i^2 e^2 n_i^o \varphi / kT$

for which $(4\pi / D)\ \Sigma z_i^2 e^2 n_i^o \varphi / kT$ is written as $\kappa^2 \varphi$, i.e., $\kappa^2 = (4\pi / D)\ \Sigma z_i^2 e^2 n_i^o / kT$

A solution to $(1 / r^2)\ d\ (r^2\ (d\varphi / dr)) / dr = \kappa^2 \varphi$ is

$(A / r)\ \exp(-\kappa r) + (B / r)\ \exp(\kappa r)$

But since φ goes to 0 as r increases, B = 0, so that $\varphi = (A / r)\ \exp(-\kappa r)$. As for the constant, A, consider that if the solution is very dilute, n_i^o approaches zero and κ approaches zero, so that

$\varphi = A / r$

In this case, the potential would be that due to a point charge,

$\varphi = z_i e / Dr$

so that $A = z_i e / D$ and $\varphi = (z_i e / Dr)\ \exp(-\kappa r)$.

If $\exp(-\kappa r)$ were approximated as $1 - \kappa r$,

$\varphi = (z_i e / Dr) - (z_i e \kappa / D)$ for which the first term corresponds to potential due to the central ion

and the second term corresponds to the ion atmosphere, which has been assumed responsible for deviations from ideality, i.e., is related to γ.

The final matter is to relate potential, $\varphi^* = - (z_i e \kappa / D)$, to chemical potential, μ_{EL} (= RT ln γ). The approach taken is to charge a mole of central ions, each within the potential of its ion atmosphere, from zero to its actual charge,

$\mu_{EL} = N_A \int \varphi^*\ d(z_i e) = N_A \int -(z_i e \kappa / D)\ d(z_i e) = -N_A\ z_i^2 e^2 \kappa / 2D$

If $\kappa = [(4\pi / D)\ \Sigma z_i^2 e^2 n_i^o / kT]^{1/2}$ is substituted,

$\mu_{EL} = -N_A\ z_i^2 e^2\ [(4\pi / D)\ \Sigma z_i^2 e^2 n_i^o / kT]^{1/2}\ / 2D$

and from μ_{EL} = RT ln γ

$\log \gamma_i = -N_A\ z_i^2 e^2\ [(4\pi / D)\ \Sigma z_i^2 e^2 n_i^o / kT]^{1/2}\ / (2.303\ 2DRT)$

Since the concentrations, n_i^o, are in ions per mL and the final form of this model for single ion activity coefficient is written in terms of ionic strength ($I = \frac{1}{2}\ \Sigma z_i^2 m_i$, m is moles / kg),

$\log \gamma_i = - z_i^2\ [N_A^2 e^3 / (2.303\ (DRT)^{3/2})][2\pi\rho / 1000]^{1/2}\ I^{1/2}$

where ρ is solution density. For water at 25 ^{o}C, the two bracketed factors multiply to 0.511, and

$\log \gamma_i = -0.511\ z_i^2\ I^{1/2}$