Statistical Molecular Thermodynamics

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Video 11.8

Debye-Hückel Theory 2

Total Electrostatic Energy

Our ultimate goal in Debye-Hückel theory is to understand how chemical potential (free energy) changes with concentration. So, we can ask first what is the total electrostatic energy. For any *one* ion i, we can compute that as:

$$U_i = \frac{q_i}{4\pi\varepsilon_0\varepsilon}\int_0^{\infty}\rho_i(r)\,4\pi r\,dr$$

Given our derivation of $\rho_i(r)$ in Video 11.7, one can show that for each ion i the electrostatic energy is:

$$U_i = -\frac{q_i^2\kappa}{4\pi\varepsilon_0\varepsilon}$$

then for all ions

in a volume V

$$U^{\mathrm{el}} = -\frac{Vk_{\mathrm{B}}T\kappa^3}{8\pi}$$

Total Electrostatic Free Energy

We may then use the Gibbs-Helmholtz equation to connect the internal energy to the Helmoltz free energy

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2}$$

$$U^{\text{el}} = -\frac{Vk_B T\kappa^3}{8\pi}$$

$$d(A/T) = \frac{Vk_B\kappa^3}{T8\pi}dT$$

$$\int_0^{A'/T'=A/T} d(A'/T') = -\int_\infty^{T'=T} \frac{Vk_B\kappa^3}{T8\pi}dT$$

$$\frac{A}{T} = -\int_\infty^{T'=T} \frac{Vk_B\left(\sum_{j=+,-} q_j^2 C_j\right)^{3/2}}{T^{5/2}8\pi(\varepsilon_0\varepsilon k_B)^{3/2}}dT = \frac{2}{3}\frac{Vk_B\left(\sum_{j=+,-} q_j^2 C_j\right)^{3/2}}{8\pi(\varepsilon_0\varepsilon k_B)^{3/2}}\left.\frac{1}{T^{3/2}}\right|_\infty^{T'=T}$$

$$\frac{A}{T} = \frac{Vk_B\kappa^3}{12\pi} \Rightarrow A^{\text{el}} = -\frac{Vk_B T\kappa^3}{12\pi}$$

One Ionic Activity Coefficient

If electrostatic interactions are sole reason for non-ideality:

i = cation or anion ⟶ $$\left(\frac{\partial A^{\mathrm{el}}}{\partial N_i}\right)_{T,V,N_j} = k_{\mathrm{B}}T\ln\gamma_i^{\mathrm{el}}$$

$$A^{\mathrm{el}} = -\frac{Vk_{\mathrm{B}}T\kappa^3}{12\pi}$$

Then

$$\ln\gamma_j^{\mathrm{el}} = -\frac{V}{12\pi}\bullet\frac{\partial}{\partial N_j}\left[\frac{\left(\sum_{j=+,-} q_j^2\frac{N_j}{V}\right)^{3/2}}{\left(\varepsilon_0\varepsilon k_{\mathrm{B}}T\right)^{3/2}}\right]$$

$$= -\frac{V}{12\pi\varepsilon_0\varepsilon k_{\mathrm{B}}T}\bullet\frac{3}{2}\left(\frac{\sum_{j=+,-} q_j^2 C_j}{\varepsilon_0\varepsilon k_{\mathrm{B}}T}\right)^{1/2}\frac{q_j^2}{V} = -\frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon k_{\mathrm{B}}T}$$

Mean Ionic Activity Coefficient

$$\ln \gamma_i^{\text{el}} = -\frac{\kappa q_i^2}{8\pi\varepsilon_0 \varepsilon k_{\text{B}} T}$$

Recalling:

$$\gamma_{\text{X}^{x+}}^{r_+} \gamma_{\text{Y}^{y-}}^{s_-} = \gamma_{\pm}^{(r_+ + s_-)}$$

implies

$$\ln \gamma_{\pm} = \frac{r_+ \ln \gamma_{\text{X}^{x+}} + s_- \ln \gamma_{\text{Y}^{y-}}}{r_+ + s_-}$$

so

$$\ln \gamma_{\pm} = -\left(\frac{\kappa}{8\pi\varepsilon_0 \varepsilon k_{\text{B}} T}\right)\left(\frac{r_+ q_{\text{X}^{x+}}^2 + s_- q_{\text{Y}^{y-}}^2}{r_+ + s_-}\right)$$

$$= -\left|q_{\text{X}^{x+}} q_{\text{Y}^{y-}}\right|\left(\frac{\kappa}{8\pi\varepsilon_0 \varepsilon k_{\text{B}} T}\right)$$

Self-assessment

Prove what we used in the last step a moment ago, namely:

$$\left(\frac{r_+ q^2_{X^{x+}} + s_- q^2_{Y^{y-}}}{r_+ + s_-} \right) = \left| q_{X^{x+}} q_{Y^{y-}} \right|$$

Self-assessment Explained

$$\left(\frac{r_+ q_{X^{x+}}^2 + s_- q_{Y^{y-}}^2}{r_+ + s_-}\right) = \left[\frac{q_{X^{x+}}\left(r_+ q_{X^{x+}}\right) + s_- q_{Y^{y-}}^2}{r_+ + s_-}\right]$$

$$= \left[\frac{q_{X^{x+}}\left(s_- \left|q_{Y^{y-}}\right|\right) + s_- q_{Y^{y-}}^2}{r_+ + s_-}\right]$$

$$= \left|q_{X^{x+}} q_{Y^{y-}}\right| \left[\frac{s_- + s_- \dfrac{\left|q_{Y^{y-}}\right|}{q_{X^{x+}}}}{r_+ + s_-}\right]$$

$$= \left|q_{X^{x+}} q_{Y^{y-}}\right|$$

by electroneutrality, twice using:

$$r_+ q_{X^{x+}} = s_- \left|q_{Y^{y-}}\right|$$

Behavior Near Infinite Dilution

$$\ln\gamma_{\pm} = -\left|q_{X^{x+}}q_{Y^{y-}}\right|\left(\frac{\kappa}{8\pi\varepsilon_0\varepsilon k_B T}\right)$$

$$\kappa^2 = \frac{2N_A e_-^2}{\varepsilon_0\varepsilon k_B T}\left(\frac{1}{2}\sum_{j=1}^{k} c_j z_j^2\right)$$

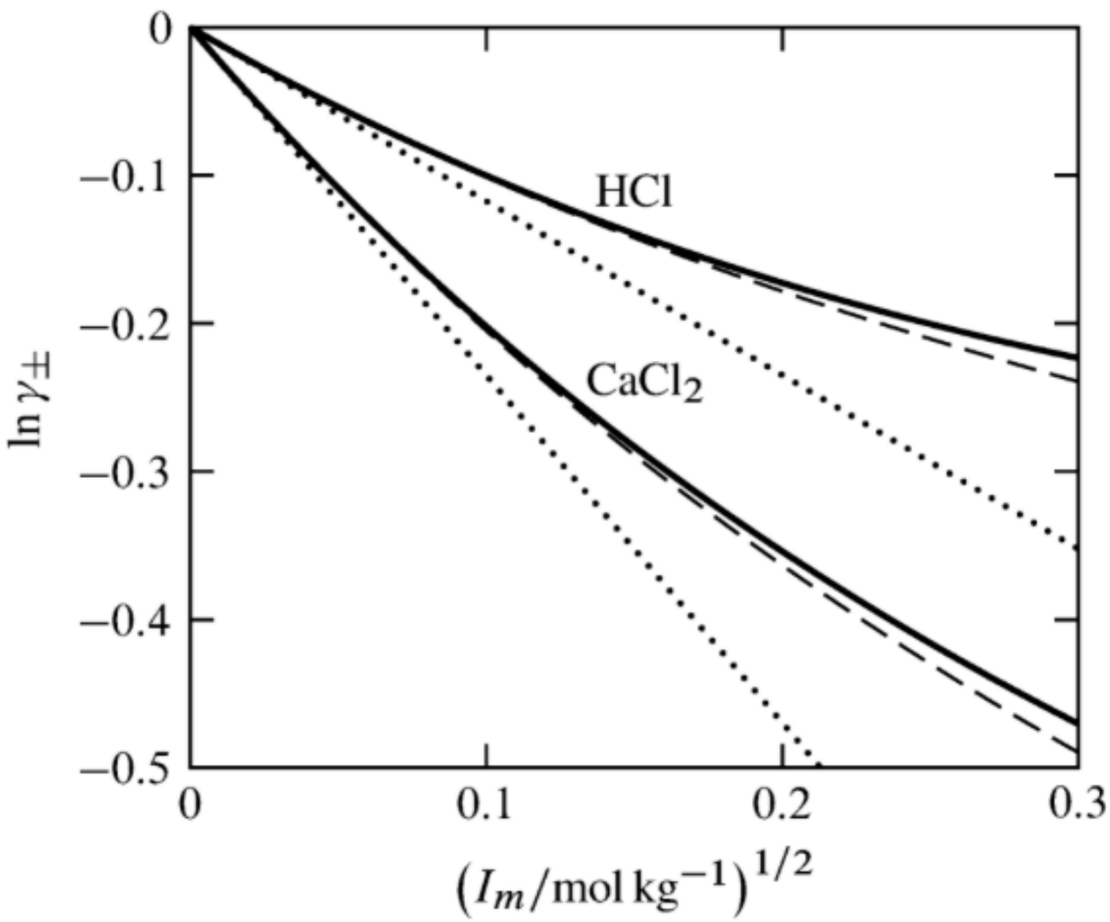
the ionic strength I

In the specific case of aqueous solution at $T = 298$ K:

$$\ln\gamma_{\pm} = -0.509\left|x \bullet y\right|\sqrt{I}$$

At low concentrations, $\ln\gamma_{\pm}$ should decrease linearly as the square root of the ionic strength (or, for a n:n electrolyte, as the square root of the molality) with slope $-A|x \bullet y|$ (alternatively written as $-A|z_+z_-|$).

Experimental Consistency



Solid lines derive from experiment; dotted lines represent Debye-Hückel theory; dashed lines are from an empirically improved expression for limiting behavior, namely:

$$\ln \gamma_{\pm} = -\frac{A\left|x \bullet y\right|\sqrt{I}}{1 + B\sqrt{I}}$$

where A derives from the usual constants and B is a fitting parameter.

Knowledge of limiting behavior will prove useful when we arrive at electrochemistry

Next: Review of Module 11