Statistical Molecular Thermodynamics

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Video 13.4

Activities and Other Thermodynamic Quantities
Predicting Cell Potentials

Now, consider a full cell as below but with pH held at 7.0 and [Cl\textsuperscript{−}] buffered to 10\textsuperscript{−3} M (for simplicity, taking activities equal to molarities):

\[
\text{AgCl(s)} + e^- \rightleftharpoons \text{Cl}^{−}(aq) + \text{Ag(s)} \quad E^0 = 0.222 \text{ V}
\]

\[
\frac{1}{2} \text{H}_2(g) \rightleftharpoons \text{H}^+(aq) + e^- \quad E^0 = 0.000 \text{ V}
\]

\[
\text{AgCl(s)} + \frac{1}{2} \text{H}_2(g) \rightleftharpoons \text{H}^+(aq) + \text{Cl}^{−}(aq) + \text{Ag(s)} \quad E^0 = 0.222 \text{ V}
\]

The Nernst equation again

\[
E = E^0 - \frac{RT}{1 \cdot F} \ln \frac{a_{\text{Ag}} a_{\text{H}^+} a_{\text{Cl}^{−}}}{a_{\text{AgCl}} \sqrt{a_{\text{H}_2}}}
\]

\[
= 0.222 \text{ V} - \left( \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}{96,485 \text{ C mol}^{-1}} \right) (300 \text{ K}) \ln \left( \frac{1 \cdot 10^{-7} \cdot 10^{-3}}{1 \cdot \sqrt{1}} \right) = 0.817 \text{ V}
\]

Much stronger (positive) driving force than \(E^0\) because two products are at much lower than unit activity.
We’ve discussed vapor pressure measurements to get activities (cf. videos 11.3 and 11.6), but measuring cell potentials is still more convenient. Thus, for example, recalling the Nernst equation for a 1-1 electrolyte solution may be expressed as

$$E = E^o - \frac{2RT}{F} \left( \ln m + \ln \gamma_\pm \right)$$

we may rearrange and solve for the log of the mean ionic activity coefficient as

$$\ln \gamma_\pm = \frac{F}{2RT} \left( E - E^o \right) - \ln m$$
Determining Activity Coefficients

\[
\ln \gamma_{\pm} = \frac{F}{2RT} (E - E^o) - \ln m
\]

Thus, variations in the cell voltage as a function of the molality of the electrolyte provide activity coefficients directly, which is quite simple to measure, in practice.

Note much larger non-ideality of \( \text{Al}_2(\text{SO}_4)_3 \) compared to \( \text{AlCl}_3 \), as expected given the larger charge of the sulfate ion compared to chloride.
Self-assessment

As the concentration approaches zero, what should the relation between the slopes of the two activity coefficient curves be?
Recall from Debye-Hückel theory that $\ln \gamma_{\pm}$ goes as minus the square root of ionic strength near infinite dilution. Thus, we compute

$$\ln \gamma_{\pm}(\text{AlCl}_3) \propto -\sqrt{\frac{1}{2} \left( c \cdot 3^2 + 3c \cdot 1^2 \right)} = -\sqrt{6c}$$

$$\ln \gamma_{\pm}(\text{Al}_2(\text{SO}_4)_3) \propto -\sqrt{\frac{1}{2} \left( 2c \cdot 3^2 + 3c \cdot 2^2 \right)} = -\sqrt{15c}$$

The graph on the prior slide should not have $\ln \gamma_{\pm}$ linear in $c$ near infinite dilution, but rather in $c^{(1/2)}$, but the above equations make clear that the slope for Al$_2$(SO$_4$)$_3$ should be greater than that for AlCl$_3$, as observed.
Determining Enthalpy and Entropy

The relationship between standard free energy of reaction and standard cell potential permits measurement of standard enthalpies and entropies of reaction from variations in cell potentials as a function of $T$, i.e.,

$$\Delta S_r^o = - \left( \frac{\partial \Delta G_r^o}{\partial T} \right)_P \quad \text{and} \quad \Delta H_r^o = \Delta G_r^o - T \left( \frac{\partial \Delta G_r^o}{\partial T} \right)_P$$

implies

$$\Delta S_r^o = nF \left( \frac{\partial E^o}{\partial T} \right)_P \quad \text{and} \quad \Delta H_r^o = -nFE^o + nFT \left( \frac{\partial E^o}{\partial T} \right)_P$$

much more straightforward than calorimetry…
Determining Solubility Products

Recalling for the cell reaction \( wW + xX \rightleftharpoons yY + zZ \)

\[
E = E^o - \frac{RT}{nF} \ln \frac{a_Y^y a_Z^z}{a_W^w a_X^x}
\]

We may note that since at equilibrium \( E = 0 \), then it must also be true (generically) that

\[
E^o = \frac{RT}{nF} \ln K_a \quad \text{or, rearranged} \quad K_a = e^{nFE^o / RT}
\]

could be used to measure/predict solubility products of sparingly soluble salts, acid dissociation constants of weak acids, etc.
Determining Solubility Products

Example: \( K_a = e^{nF E^o / RT} \)

\[
\begin{align*}
\text{AgCl (s)} + e^- & \iff \text{Cl}^- (aq) + \text{Ag} (s) & & 0.222 \\
\text{Ag} (s) & \iff \text{Ag}^+ (aq) + e^- & & -0.799 \\
\text{AgCl} (s) & \iff \text{Ag}^+ (aq) + \text{Cl}^- (aq) & & -0.577
\end{align*}
\]

\[
K_{sp} = \exp \left[ \frac{(1)(96,485 \text{ C mol}^{-1})(-0.577 \text{ V})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \right] = 1.77 \times 10^{-10}
\]

a lot easier than trying to measure a microgram of solid isolated from a liter of solution!
\[ dU = \delta q + \delta w \]