

# STATISTICAL MOLECULAR THERMODYNAMICS

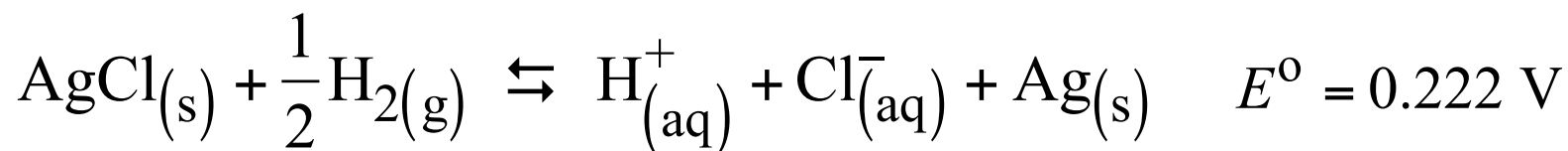
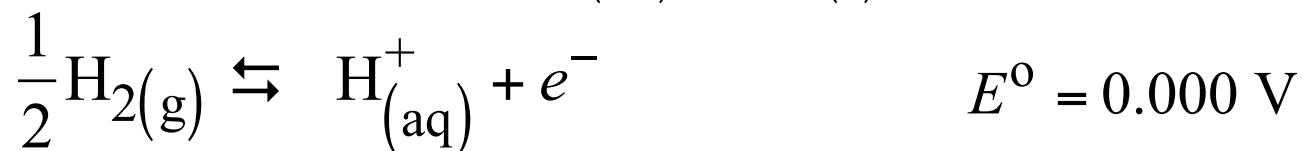
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Video 13.4

Activities and Other Thermodynamic Quantities

# PREDICTING CELL POTENTIALS

Now, consider a full cell as below *but* with pH held at 7.0 and [Cl<sup>-</sup>] buffered to 10<sup>-3</sup> M (for simplicity, taking activities equal to molarities):



$$E = E^{\circ} - \frac{RT}{1 \cdot F} \ln \frac{a_{\text{Ag}} a_{\text{H}^{+}} a_{\text{Cl}^{-}}}{a_{\text{AgCl}} \sqrt{a_{\text{H}_2}}}$$

*The Nernst equation again*

*Much stronger (positive) driving force than E° because two products are at much lower than unit activity.*

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

## DETERMINING ACTIVITY COEFFICIENTS

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

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

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

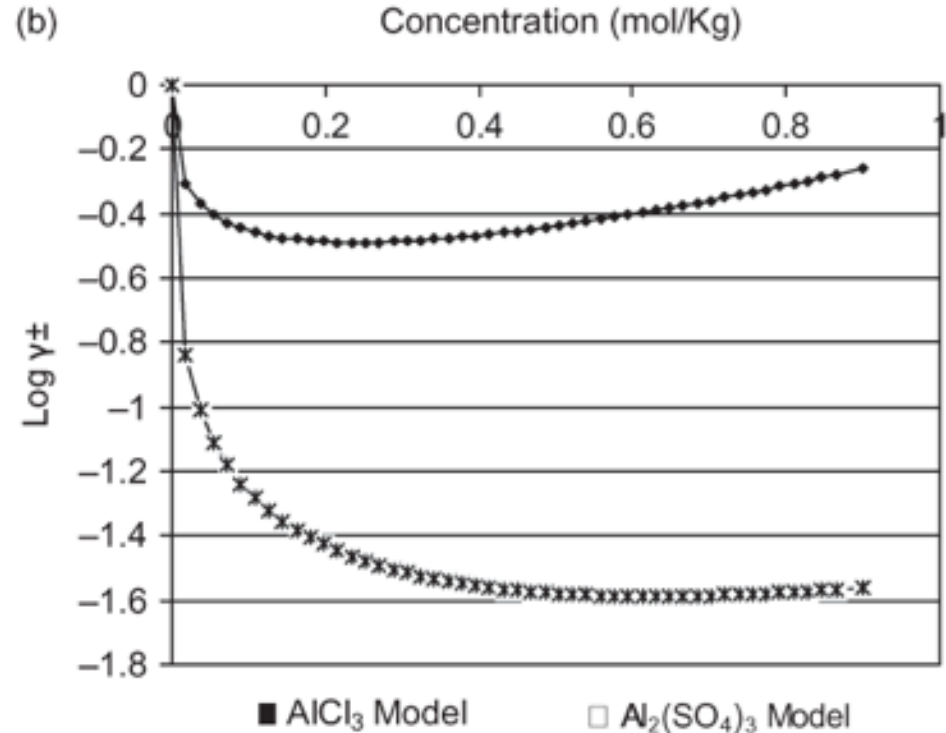
$$\ln \gamma_{\pm} = \frac{F}{2RT} \left( E - E^{\circ} \right) - \ln m$$

# DETERMINING ACTIVITY COEFFICIENTS

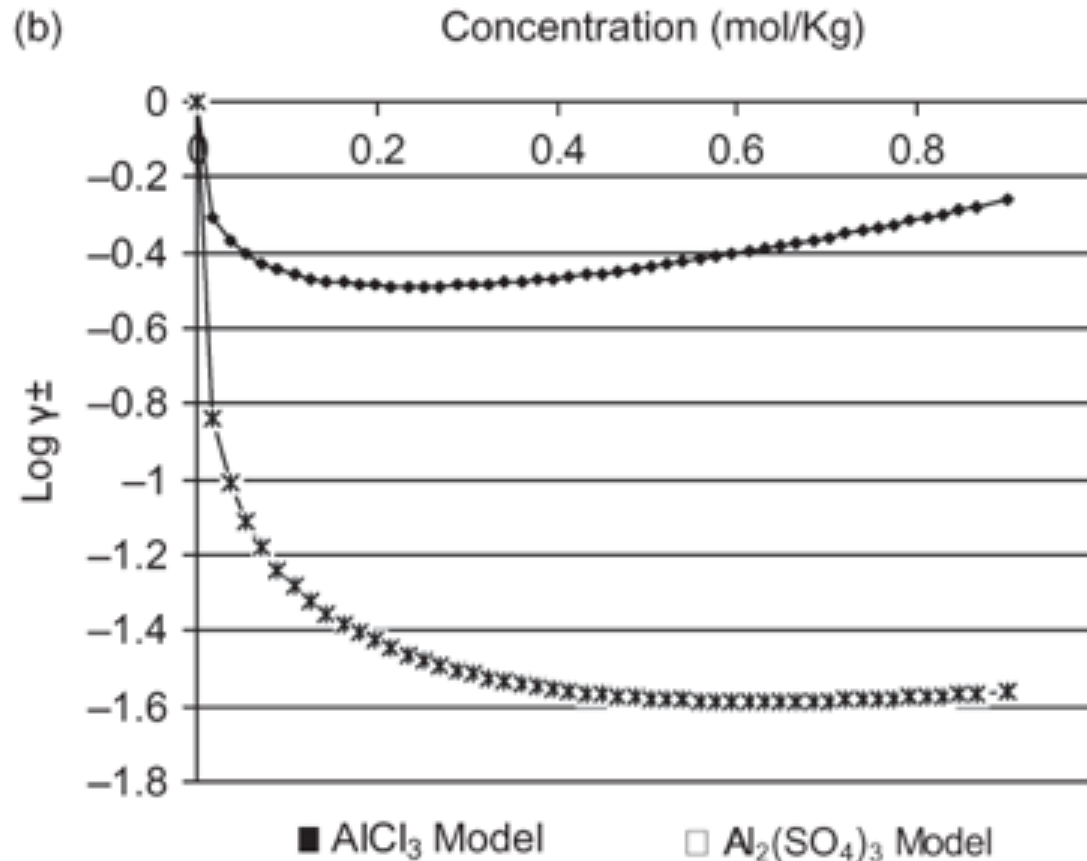
$$\ln \gamma_{\pm} = \frac{F}{2RT} (E - E^{\circ}) - \ln m$$

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?

# Self-assessment Explained

$$\ln \gamma_{\pm} = -|q_{X^{x+}} q_{Y^{y-}}| \left( \frac{\kappa}{8\pi\epsilon_0\epsilon k_B T} \right) \quad \kappa^2 = \frac{2N_A e^2}{\epsilon_0\epsilon k_B T} \left( \frac{1}{2} \sum_{j=1}^k c_j z_j^2 \right)$$

Recall from Debye-Hückel theory that  $\ln \gamma_{\pm}$  goes as minus the square root of ionic strength near infinite dilution.

Thus, we compute

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

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

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  $\text{Al}_2(\text{SO}_4)_3$  should be greater than that for  $\text{AlCl}_3$ , as observed.

  
*the ionic  
strength I*

# 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.,

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

*implies*

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

*much more straightforward than calorimetry...*

# DETERMINING SOLUBILITY PRODUCTS

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

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

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

$$E^{\circ} = \frac{RT}{nF} \ln K_a \quad \text{or, rearranged} \quad K_a = e^{nFE^{\circ} / RT}$$

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



# DETERMINING SOLUBILITY PRODUCTS

Example:  $K_a = e^{nFE^\circ / RT}$

	$E^\circ / \text{V}$
$\text{AgCl}_{(s)} + e^- \rightleftharpoons \text{Cl}^-_{(aq)} + \text{Ag}_{(s)}$	0.222
$\text{Ag}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + e^-$	-0.799
$\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$	-0.577

*a lot easier than trying  
to measure a  
microgram of solid  
isolated from a liter of  
solution!*

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

$$= 1.77 \times 10^{-10}$$

$$dU = \delta q + \delta w$$



*Next: Ionic Free Energies of Formation*