

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 13.2

Potential and Electromotive Force

POTENTIAL AND ELECTROMOTIVE FORCE

V is the “potential” — a *positive* potential attracts negative electrons. So, the cathode has a more positive potential than the anode.

$$\Delta V = V_{\text{cathode}} - V_{\text{anode}}$$

cell voltage is always positive (or else you've misassigned which is the anode and which is the cathode)

Electromotive force (EMF), E , is defined as ΔV for an open circuit, i.e., one through which no current is flowing ($I = 0$)

But, if electrons spontaneously flow from anode to cathode, how can we apply *equilibrium* thermodynamics to electrochemical cells?

ELECTROMOTIVE FORCE AND FREE ENERGY

$$E = \lim_{\varepsilon \rightarrow 0} \Delta V(I \rightarrow 0 \pm \varepsilon)$$

Insertion of a potentiometer into the circuit permits control of the current. Application of a counter-potential can be used to achieve a current of zero, at which point the system is in equilibrium (no spontaneous flow of electrons).

Recall, *positive E* implies spontaneous anode-to-cathode electron flow, negative *E* implies spontaneous “cathode-to-anode” (reversed) flow, and the infinitesimal change ε implies that we are operating reversibly, so that *E* is related to free energy (e.g., *G*, if operating at constant *T* and *P*). If we write anode to left and cathode to right (by convention), then spontaneous positive *E* is equivalent to spontaneous negative *G*.

Since ΔG is equal to $-w_{\text{non-PV}}$, we need to determine the work associated with a transfer of electrons from one potential to another. That is nFE , where *n* is the # of moles of electrons, *F* is the Faraday constant (96,485 C mol⁻¹), and *E* is the EMF (note: 1 C•V = 1 J).

$$\Delta G = -nFE$$

THE NERNST EQUATION

Consider the generic cell reaction $wW + xX \rightleftharpoons yY + zZ$

$$-nFE = \Delta G = \Delta G^{\circ}(T, P) + RT \ln \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

if $-nFE^{\circ} = \Delta G^{\circ}(T, P)$

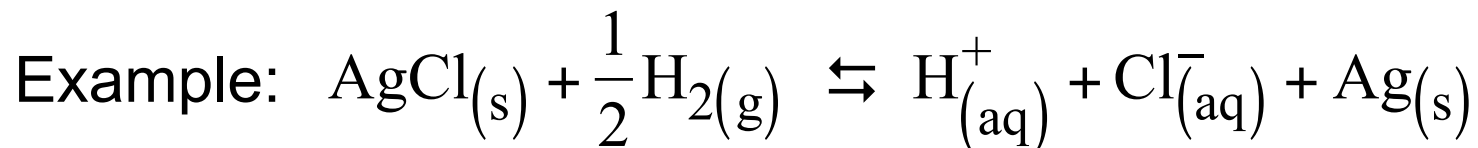
then $E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$

The Nernst equation

E° is $-\Delta G/nF$
when all reaction
participants are
at unit activity

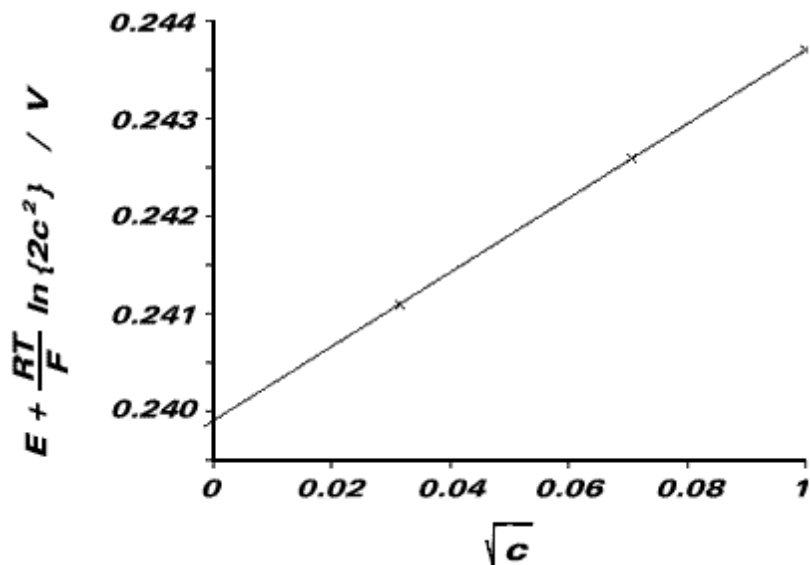
But, how do we create a mixture with all reactants and products at unit activity? Not trivial. At least all pure phases have unit activity at 1 bar (by definition) and gases at 1 bar are sufficiently close to ideal to typically have unit activity. But, what about solutes?

STANDARD EMF



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

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



Debye-Hückel theory!

$$\ln \gamma_{\pm} = -|q_{+}q_{-}| \frac{\kappa}{8\pi\epsilon_0\epsilon_1 k_B T} \propto \sqrt{m}$$

Thus, a plot of $E + (2RT/F) \ln(m)$ vs. $m^{1/2}$ will have an intercept of E° . Without a theory to relate electrolyte activity coefficients to concentrations, we'd be in trouble...

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



Next: Standard Potentials