Study Guide for Electrochemistry

How to find K from $E°_{cell}$

1. To review:

- Cell potentials are intensive properties, meaning that they don't depend on the amount of material. For example:

$$Pb^{2+} + 2e^- \rightarrow Pb_{(s)} \qquad E° = -0.125$$

$$2Pb^{2+} + 4e^- \rightarrow 2Pb_{(s)} \qquad E° = -0.125$$

- Standard conditions for electrochemical cells:
  - Pure solids and liquids
  - 1 M solutions
  - 1 bar (~ 1 atm) gases
- Le Chatelier's Principle: Changing the conditions of a reaction at equilibrium will cause the reaction to produce more reactant or product until equilibrium is reestablished.

2. Relating $E°_{cell}$ to K

- Standard conditions apply for both $E°_{cell}$ and K
- From thermodynamics:

$$\Delta G° = -RT\ln K$$

- From previous electrochemistry discussions:

$$\Delta G° = -nFE°_{cell}$$

- Putting both together:

$$-RT\ln K = -nFE°_{cell}$$

$$E°_{cell} = (RT/nF)\ln K$$

- Where:
  - $E°_{cell}$ is the standard cell potential (in V)
  - R is the thermodynamic form of the gas constant ($R = 8.\ 3145\ J*mol^{-1}*K^{-1}$)
  - T is the temperature (in K)
  - n is the number of moles of electrons that are transferred in the reaction
  - F is Faraday's constant ($F = 96485\ C*mol^{-1}$)
  - K is the equilibrium constant for the reaction
- Usually, the cell is at room temperature (298 K). This reduces the equation to:

$$E°_{cell} = (0.025693/n)*\ln K$$

3. Example:

Using the following standard reduction potentials:

$$Ag^+ + e^- \leftrightarrow Ag_{(s)}\ E° = 0.799V$$

$$Ag_2Mo4_{(s)} + 2e^- \leftrightarrow 2Ag_{(s)} + MoO_4^{2-} \qquad E° = 0.486\ V$$

Calculate the solubility product constant for $Ag_2MoO_{4(s)}$

Solution:

- We know that the solubility product constant equation has this form:

$$Ag_2MoO_{4(s)} <-> 2Ag^+_{(aq)} + MoO_4^{2+}{}_{(aq)}$$

- To get to this equation, we first have to flip one of the half-reactions (changing it from reduction to oxidation) and multiply it by 2. After that we can add the half-reactions.

$$2Ag_{(s)} <-> 2Ag^+ + 2e^-$$

$$Ag_2MoO_{4(s)} + 2e^- <-> 2Ag_{(s)} + MoO_4^{2-}$$

$$Ag_2MoO_{4(s)} <-> 2Ag^+ + MoO_4^{2-}$$

We now have the 2 half-reactions. The oxidation half-reaction's E° becomes $E°_{anode}$. The reduction half-reaction's E° becomes $E°_{cathode}$. We can then find $E°_{cell}$:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = 0.486 \text{ V} - 0.799 \text{ V}$$

$$E°_{cell} = -0.313 \text{ V}$$

- We can now find K:

$$E°_{cell} = (0.025693/n)*\ln K$$

$$E°_{cell} *(n/0.025693) = \ln K$$

$$e^{E°cell *(n/0.025693)} = K$$

$$e^{-0.313*(2/0.025693)} = K$$

$$K = 2.622*10^{-11}$$

- Conceptually, this makes sense. We should expect a non-spontaneous reaction (one with a negative $E°_{cell}$) to produce very little, if any product at equilibrium (to have a very small K)