From thermodynamics, we know that at equilibrium, $\Delta G = 0$.

Also, $\Delta G = -nFE$.
- Since both $n$ and $F$ are greater than zero, it means that at equilibrium, $E = 0$.

$Q$ = mass action quotient.
- At equilibrium (by definition) $Q = K$.

**Calculation of Equilibrium Constants**

We know $E = E^0 + \frac{0.05916}{n} \log Q$.

$\therefore$ At equilibrium $0 = E^0 + \frac{0.05916}{n} \log K$.

Rearranging: $E^0 = \frac{-0.05916}{n} \log K$.

$\therefore nE^0 = \log K$.

$K = 10^{-nE^0/0.05916}$.

**Calculation of Standard Cell Potentials**

- Standard cell potentials can be calculated for many cells involving slightly soluble metal salts.
  - In these cases, the electrochemical process involved the reduction of the metal ion.
  - If we can calculate the underlying ion concentration, we can calculate the standard $\frac{1}{2}$ cell potential.
  - Must know $K_{sp}$. 
AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)

- ‘Driving’ ½ reaction is the reduction of Ag
  - Ag⁺ + e⁻ → Ag
  - Note that there is no change in the oxidation state of chlorine
  - Under standard conditions, all species are at unit activity.
  - AgCl and Ag are under standard conditions when there is ‘some’ present
  - Cl⁻ is at unit activity when the concentration is such that the activity is 1 (assume γCl = 1)

AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)

- For AgCl ⇌ Ag⁺ + Cl⁻
  - Ksp = 1.8 x 10⁻¹⁰
  - This IS NOT the same as the ½ reaction!!!
    - Ag⁺ rather than Ag as the product
    - NO electron exchange
  - If Ksp = [Ag⁺] * [Cl⁻] and by definition [Cl⁻] = 1
    * Ksp = [Ag⁺]

AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)

- From the Nernst equation for the reduction of silver
  - E = E° - (0.05916/n) log (1/Ksp)
  - E = 0.799 – (0.05916/1) log (1/1.8 x 10⁻¹⁰)
  - E = 0.223
  - But since these conditions came from the standard conditions for the above reaction, E° = 0.223V

Calculation of Ksp values

Consider AgBr(s) ⇌ Ag⁺ + Br⁻

- Not normally considered an electrochemical process
- K is a state function
  - Independent of the path used to derive the value
  - If we can write the reaction as a redox process, we can calculate E°, and from that we can calculate K

Calculation of Ksp values

For AgBr(s) ⇌ Ag⁺ + Br⁻

AgBr(s) + e⁻ → Ag⁺ + Br⁻  E° = 0.073
Ag → Ag⁺ + e⁻  E° = 0.799

E°cell = E°cathode - E°anode
E°cell = 0.073 - 0.799 = -0.726

log K = n E°cell / 0.05916 = (1)(-0.726) / 0.05916
K = 5.3 x 10⁻¹³

Potentiometric Titrations

- For a potentiometric titration curve, we plot volume of titrant (x-axis) vs ½ cell potential (y-axis) vs. the SHE
  - We can measure the ½ cell potential for either the cathode and anode
  - During a titration reaction, the overall cell potential is zero
    - Cathodic ½ cell potential has to equal the anodic ½ cell potential
Potentiometric Titration

- We must also determine the reaction!

Consider the titration of 50.0 mL of 0.050 M Sn⁴⁺ with 0.020 M MnO₄⁻ in 1 M H₂SO₄.

What is the reaction?

Potentiometric Titration

- Two things we MUST remember
  - We have to have an oxidation and a reduction ½ reaction combined for our overall reaction.
  - The REACTANTS are MnO₄⁻ and Sn²⁺
  - One of the reactants MUST be listed as a product in the reduction ½ reactions.
  - When we reverse that reaction, we get redox and the proper reactants.

\[ 2\text{MnO}_4^- + 16\text{H}^+ + 5\text{Sn}^{2+} \rightarrow 5\text{Sn}^{4+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \]

Potentiometric Titration

- At the equivalence point

\[ E_{\text{eq}} = \frac{n_\text{c} E_{\text{c}} + n_\text{a} E_{\text{a}}}{n_\text{c} + n_\text{a}} \]

This equation will work ONLY if
- No pH dependance OR
- pH = 0
- Will not work with non 1:1 stoichiometry between the oxidized and reduced forms in the ½ reaction.
  - \[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

Potentiometric Titration

- For permanganate, the only viable ½ reaction for titration is reduction to Mn²⁺
  - \[ \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]
- For tin, there are a couple of ½ reactions
  - \[ \text{Sn}^{2+} + 2e^- \rightarrow \text{Sn} \]
  - \[ \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \]
- What is the reaction?

Potentiometric Titration

- Consider the titration of 50.0 mL of 0.050 M Sn⁴⁺ with 0.020 M MnO₄⁻ (assume \([\text{H}^+] = 1\text{M}\))
  - Before the equivalence point
    - \(\text{Sn}^{2+}\) is in excess
    - ½ reaction – \(\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}\)
      - Note that the ½ reaction is shown as a reduction for purposes of calculation using the Nernst equation.
  - After the equivalence point
    - \(\text{MnO}_4^-\) is in excess
    - ½ reaction – \(\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \)

At the equivalence point, the analyte is in excess.

After the equivalence point, the titrant is in excess.
50.0 mL of 0.050 M \text{Sn}^{2+} with 0.020 M \text{MnO}_4^- ([\text{H}^+] = 1\text{M})

After 10.00 mL of titrant is added:
\[2\text{MnO}_4^- + 5\text{Sn}^{2+} \rightleftharpoons 5\text{Sn}^{4+} + 2\text{Mn}^{2+}\]

\[
\begin{array}{c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c}
I & 0.20 & 2.50 & 0 & 0 \\
\Delta & -0.20 & -0.50 & +0.50 & +0.20 \\
F & \sim 0 & 2.00 & 0.50 & 0.20 \\
\end{array}
\]

Using \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}

\[E = 0.154 - (0.05916/5) \times \log[[2.00/60]/(0.50/60)]
E = 0.136 \text{ V} \]

50.0 mL of 0.050 M \text{Sn}^{2+} with 0.020 M \text{MnO}_4^- ([\text{H}^+] = 1\text{M})

After 50.00 mL of titrant is added:
\[2\text{MnO}_4^- + 5\text{Sn}^{2+} \rightleftharpoons 5\text{Sn}^{4+} + 2\text{Mn}^{2+}\]

\[
\begin{array}{c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c}
I & 1.00 & 2.50 & 0 & 0 \\
\Delta & -1.00 & -2.50 & +2.50 & +1.00 \\
F & \sim 0 & \sim 0 & 2.50 & 1.00 \\
\end{array}
\]

Equivalence Point

\[E = \left[(5 \times 1.51) + (2 \times 0.154)\right]/(5+2)
E = 1.12 \text{ V} \]

50.0 mL of 0.050 M \text{Sn}^{2+} with 0.020 M \text{MnO}_4^- ([\text{H}^+] = 1\text{M})

After 70.00 mL of titrant is added:
\[2\text{MnO}_4^- + 5\text{Sn}^{2+} \rightleftharpoons 5\text{Sn}^{4+} + 2\text{Mn}^{2+}\]

\[
\begin{array}{c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c}
I & 1.40 & 2.50 & 0 & 0 \\
\Delta & -1.00 & -2.50 & +2.50 & +1.00 \\
F & 0.40 & \sim 0 & 2.50 & 1.00 \\
\end{array}
\]

Using \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}

\[E = 1.51 - (0.05916/5) \times \log[[1.00/120]/(0.40/120)]^{1^\text{st}}
E = 1.14 \text{ V} \]