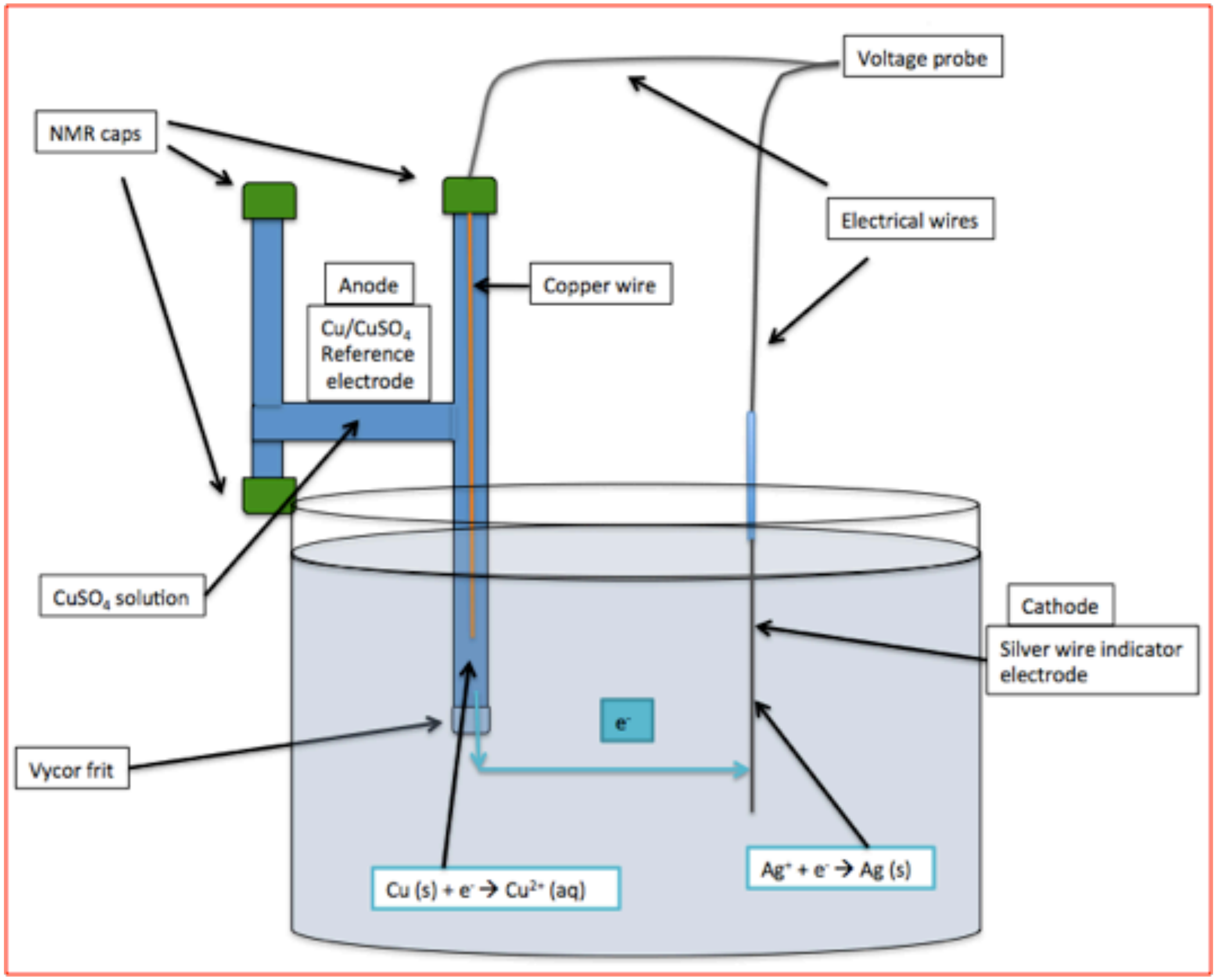
Potentiometric Titration of Chloride



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Chem M3LC
Fall 2013

Potentiometric Titration of Chloride

In this experiment, silver ions will be added to a chloride solution. As Ag^+ is added to the Cl^-, AgCl will form as follows:

$$Ag^+ (aq) + Cl^- (aq) \rightleftharpoons AgCl\ (s)$$

This equation illustrates the solubility equilibrium of silver chloride. Solubility equilibrium exists when a solid compound is in equilibrium with the dissolved ions of that compound. The corresponding solubility constant of AgCl is:

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \text{ x } 10^{-10}$$

The equilibrium constant, K_T, of the titration is:

$$K_T = \frac{1}{[Ag^+][Cl^-]} = \frac{1}{K_{sp}} = \frac{1}{1.8 \text{ x } 10^{-10}} \gg 1$$

As the titration proceeds, the number of moles of chloride decreases.

At the equivalence point, the number of moles of Ag^+ *added* is equal to the number of moles of Cl^- present *initially*.

We will use Electrochemistry to determine the equivalence point.

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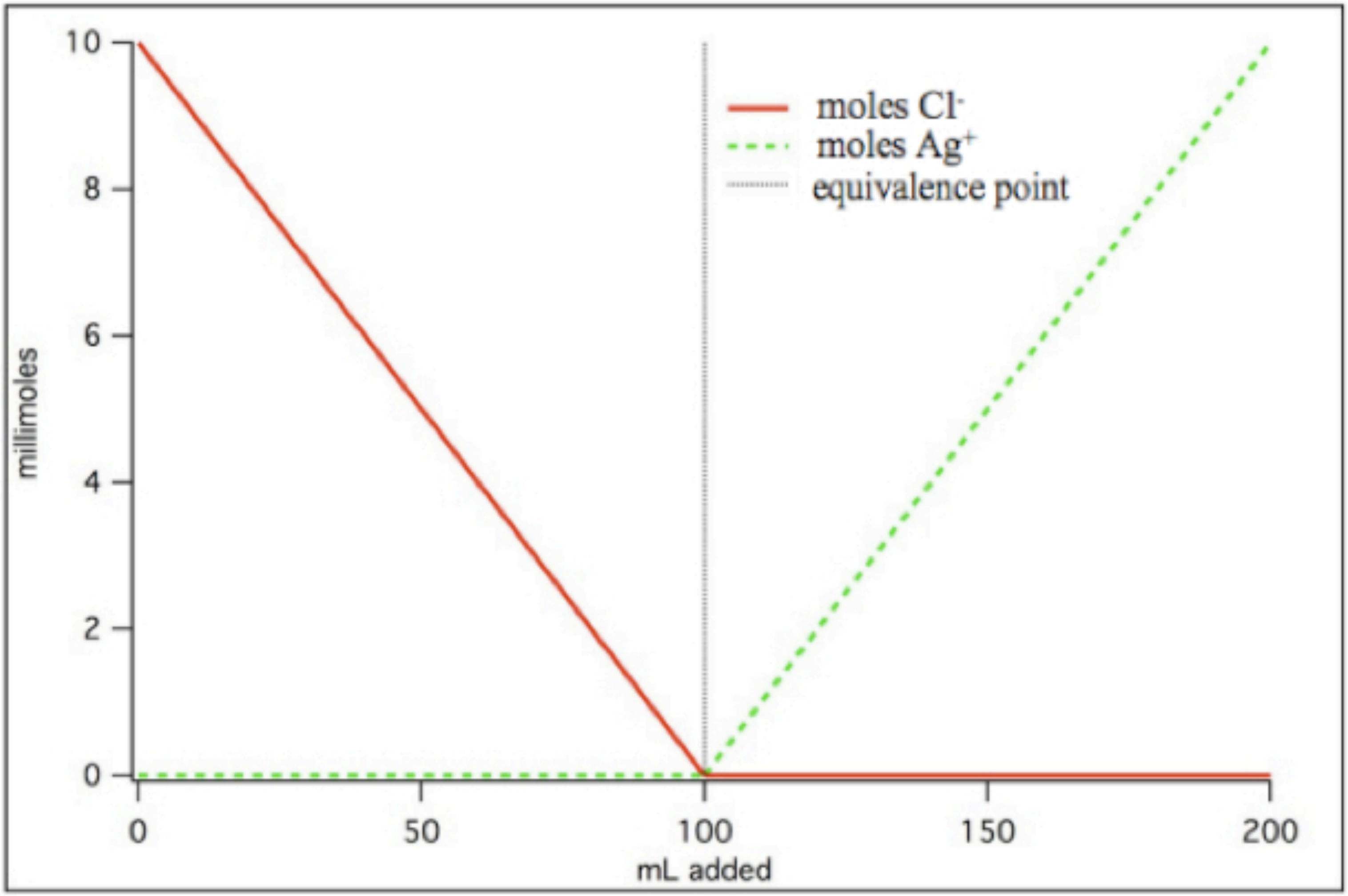

Ag^+ solution is added to react with Cl^-

We will use Electrochemistry to determine the equivalence point.

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Electrochemical cell

In this experiment, a Cu/$CuSO_4$ **reference electrode** will be used in conjunction with a silver wire **indicator electrode**. The oxidation of copper takes place at the anode while the reduction of silver takes place at the cathode. See the Figure for an illustration of the electrochemical cell.

The balanced electrochemical reaction is as follows:

$$Cu^{o}(s) + 2Ag^{+}(aq) \rightarrow 2Ag^{o}(s) + Cu^{2+}(aq)$$

The line notation for the cell is:

$$Cu^{o}|Cu^{2+}(0.100\ M)||Ag^{+} \qquad\qquad ||Ag^{o}$$

The overall standard electrochemical potential, E^{o}_{cell} is:

$$E^{o}_{\mathrm{cell}} = E^{o}_{\mathrm{red(Ag^{+}/Ag)}} - E^{o}_{\mathrm{red(Cu^{2+}/Cu)}}$$

We use the Nernst Equation to calculate the standard cell potential.

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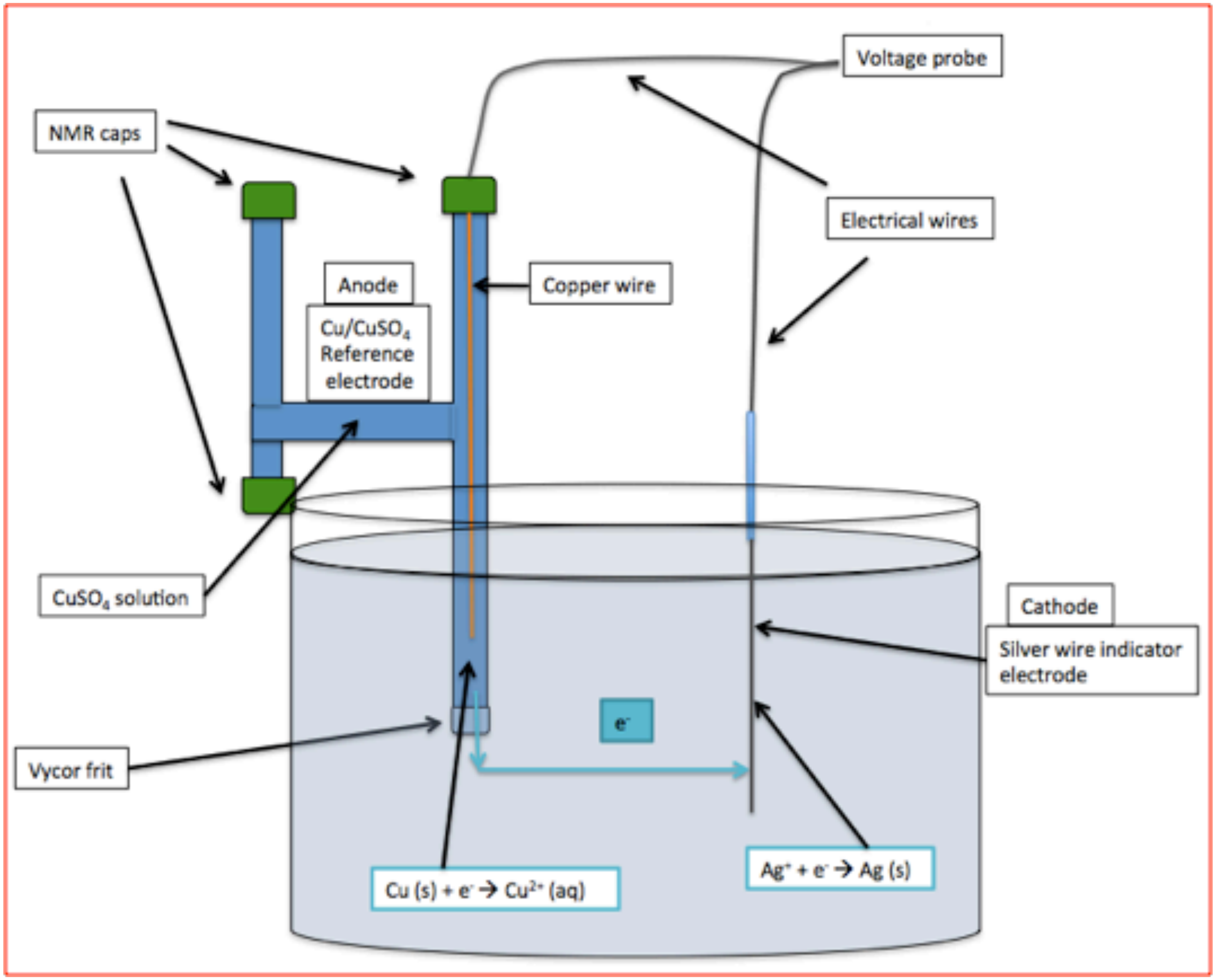

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$$E_{cell} = E_{red} - E_{ox}$$

Silver is being reduced: $E_{red} = E_{Ag}$

$$Ag^{+} + e \rightarrow Ag_{(s)}$$

$$E_{Ag} = E_{Ag}^{0} - \frac{RT}{F} ln \frac{1}{[Ag^{+}]}$$

Copper is being oxidized: $E_{ox} = E_{Cu}$

$$E_{\mathrm{Cu}} = E_{\mathrm{Cu}}^{\mathrm{o}} - \frac{0.0592}{2} \log\left[\frac{1}{[\mathrm{Cu}^{2+}]}\right]$$

E_{Cu} is constant during the titration

Potentiometric Titration of Chloride

We measure pAg during the titration with potentiometry:

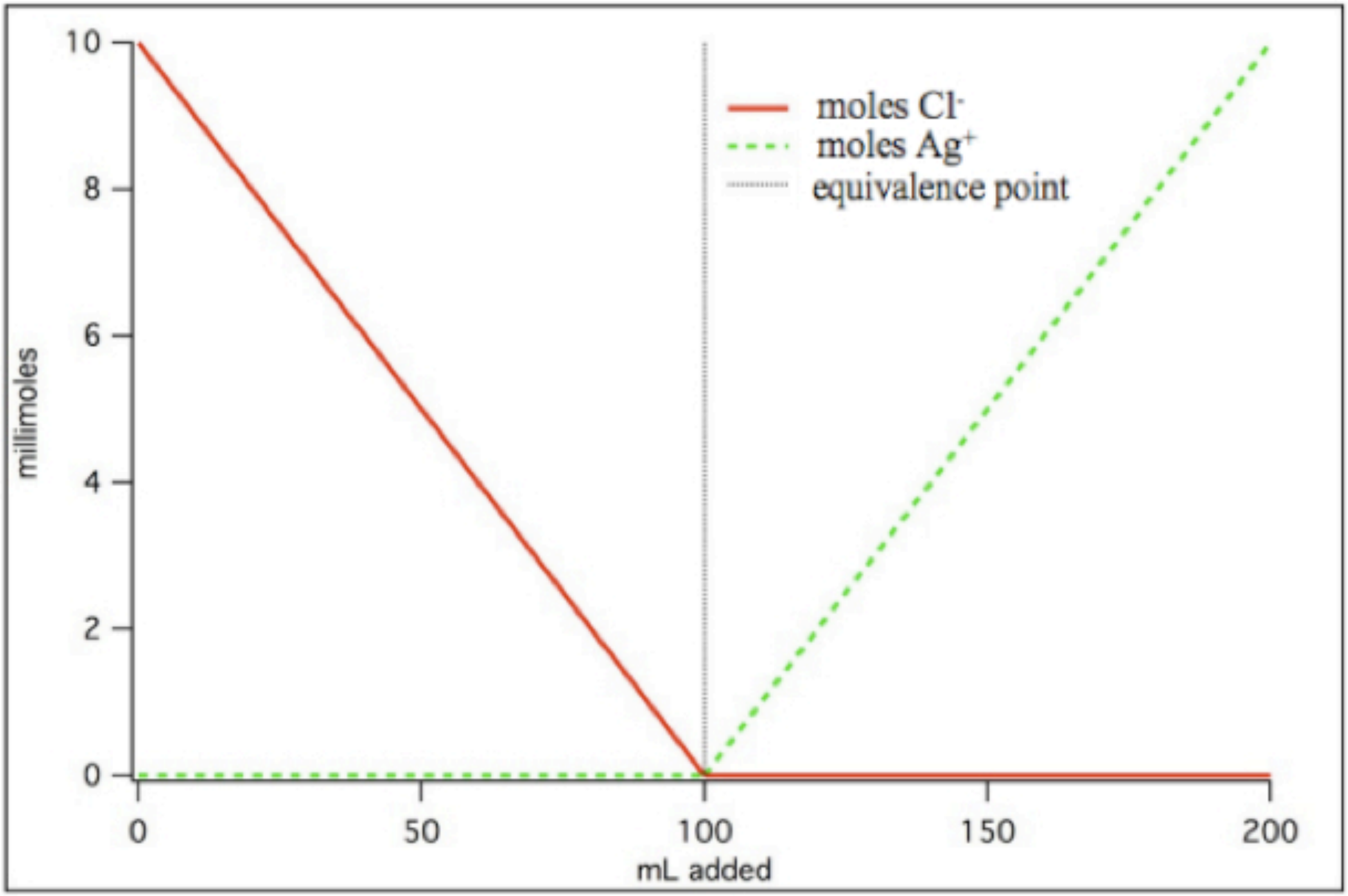
$$E_{cell} = E_{Ag} - E_{Cu}$$

$$E_{cell} = A + B \times pAg$$

A and B are constants

($pAg = -\log [Ag^+]$)

Potentiometric Titration of Chloride



Ag^+ solution is added to react with Cl^-

Potentiometric Titration of Chloride

At the equivalence point, $[Ag^+]$ and $[Cl^-]$ are almost zero, but not quite!

At the eq. pt:

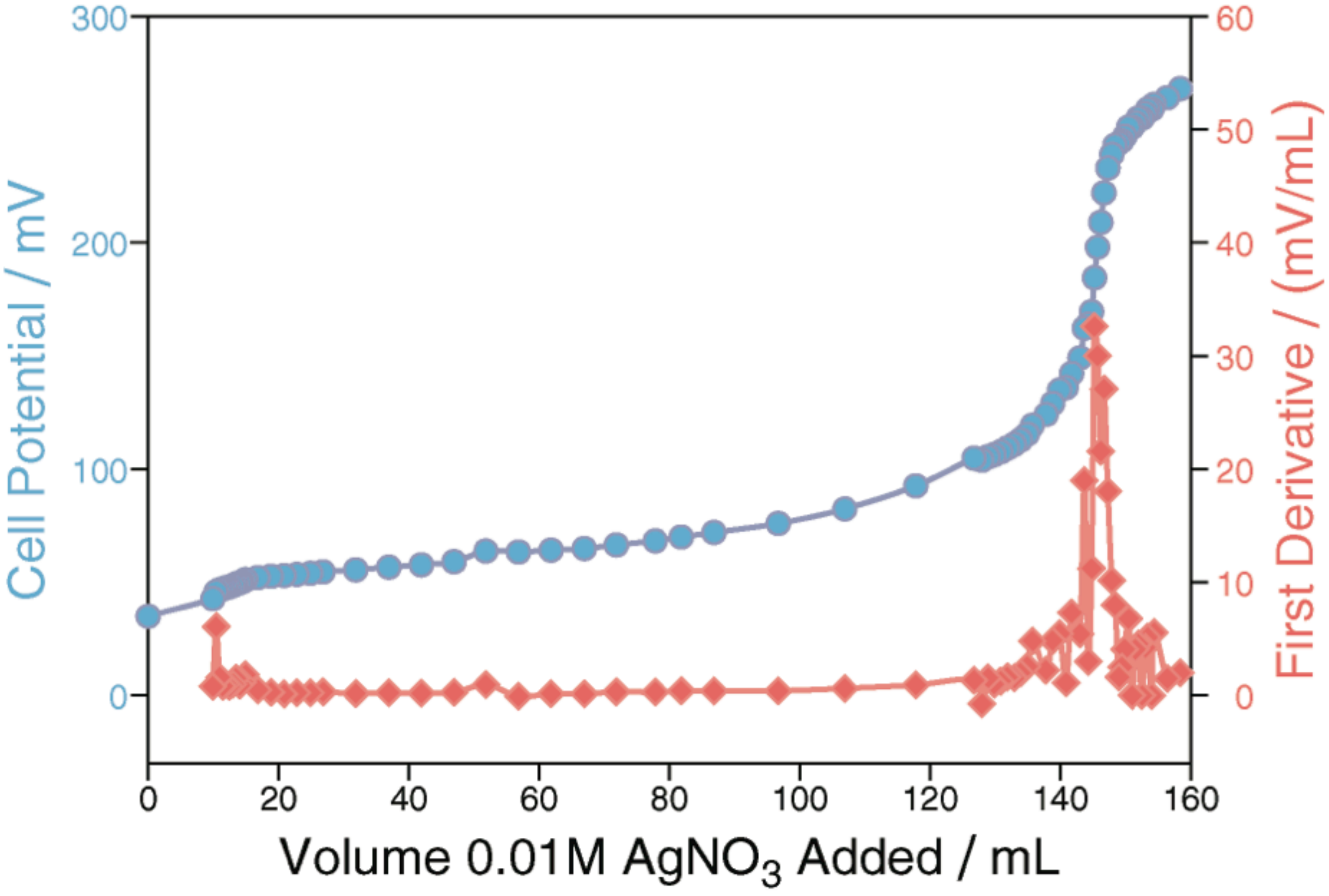
$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+] = [Cl^-]$$

$$[Ag^+] = (K_{sp})^{-1/2}$$

pAg = ??

Potentiometric Titration of Chloride



Example of Potentiometric Titration Data