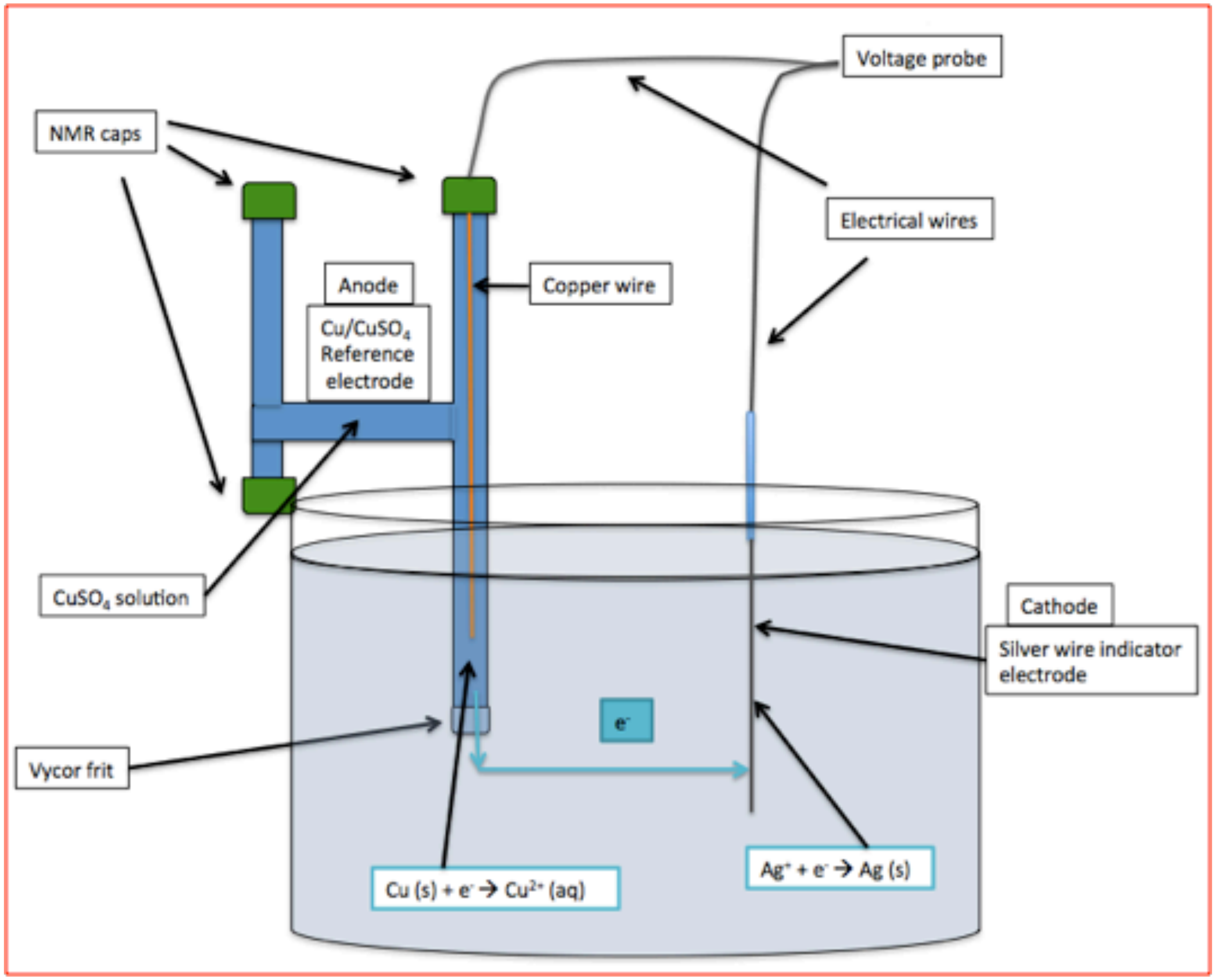
Potentiometric Chloride Precipitation Titration



Silver Ion Potentiometry

R. Corn - Chem M3LC

Potentiometric Chloride Precipitation Titration

In this titration, Ag^+ will be added to a Chloride solution:

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)} \qquad K_T = K_{sp}^{-1} = 10^{+9.74} \gg 1$$

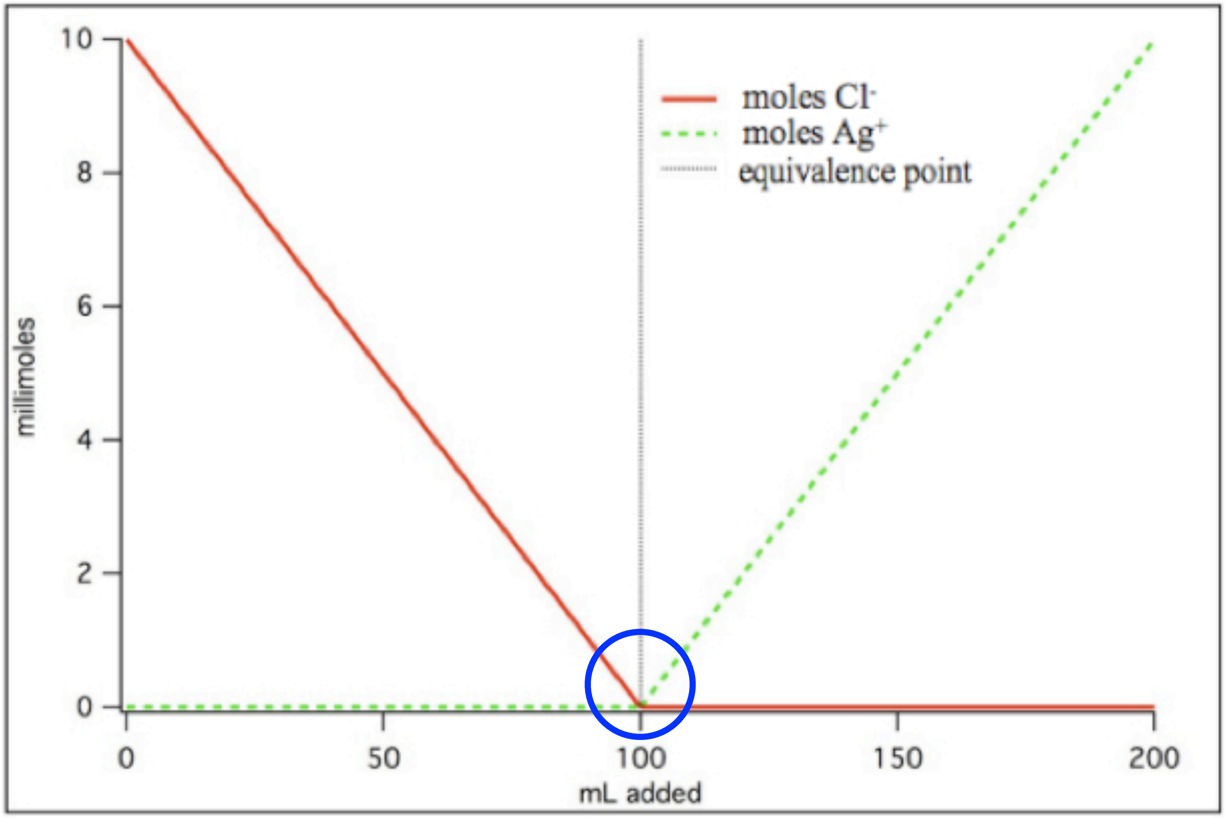
$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$\log K_{sp} = -9.74$$

The equilibrium constant for this titration is very large, so we assume that the Ag^+ reacts quantitatively with the Cl^- in solution.

We can use a graphic representation of this process similar to what we made for acid-base titrations.

A Standard Ag$^+$ solution is added and reacts quantitatively with Cl$^-$



At the equivalence point:

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

$$\boxed{[Ag^+] = \sqrt{K_{sp}}}$$

@ Eq. pt: $[Ag^+] \approx [Cl^-]$

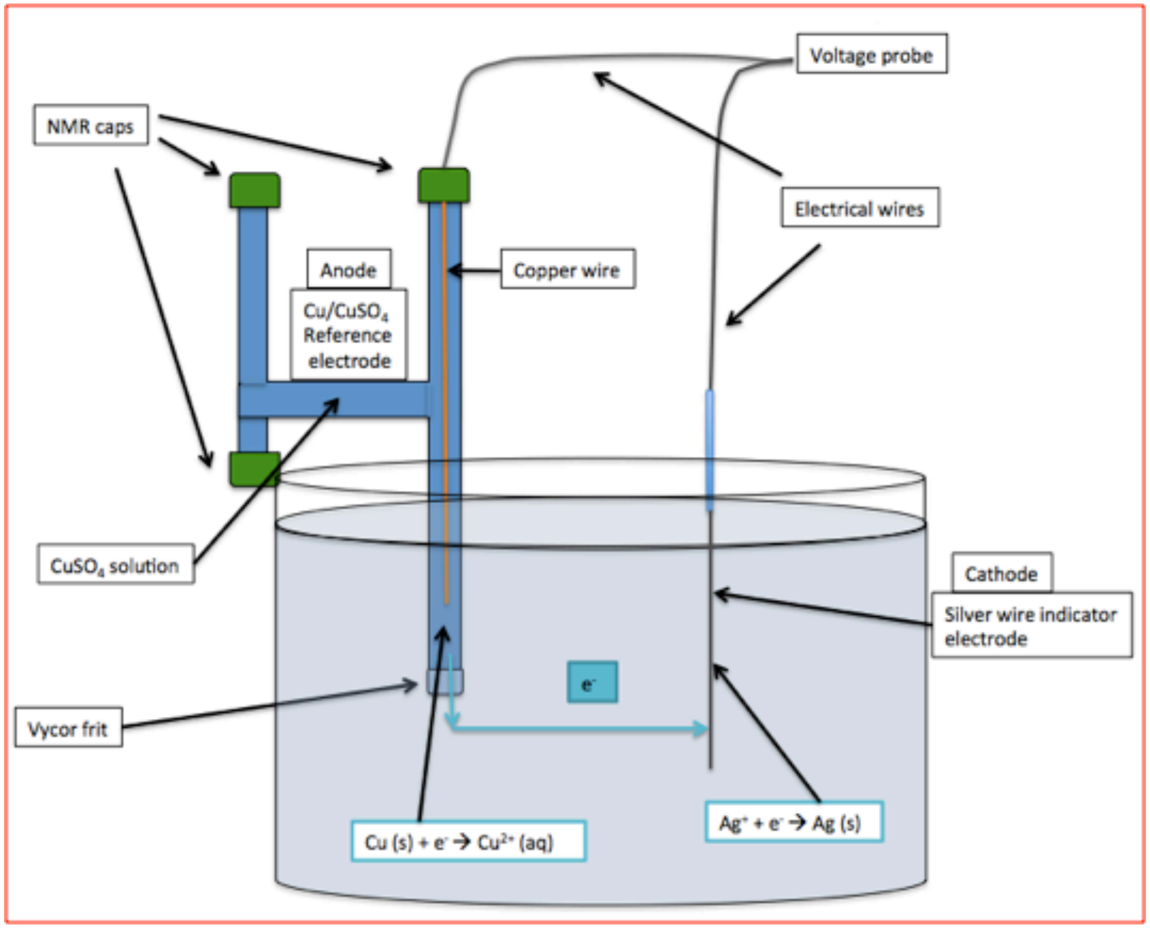
$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2$$

We will use Potentiometry to measure [Ag$^+$] during the titration.

Potentiometric Titration of Chloride

Electrochemical Cell: a silver wire indicator electrode will be used in conjunction with a Cu/$CuSO_4$ reference electrode:

$$Cu_{(s)} \,|\, Cu^{2+}(0.100M) \,||\, Ag^{+}(xM) \,|\, Ag_{(s)}$$



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

We will monitor E_{cell} during the titration.

Potentiometric Titration of Chloride

$$Cu_{(s)}\,|\,Cu^{2+}(0.100M)\,||\,Ag^{+}(xM)\,|\,Ag_{(s)}$$

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

The copper half cell potential is constant:

$$Cu^{2+} + 2e \rightleftharpoons Cu_{(s)} \qquad E^{0}_{Cu} = +0.337V$$

$$E_{Cu} = E^{0}_{Cu} - \frac{0.0592}{2}\log\frac{1}{[Cu^{2+}]}$$

$$\boxed{E_{Cu} = +.307V}$$

$$E_{Cu} = +0.337V - \frac{0.0592}{2}\log\frac{1}{0.100}$$

E_{Cu} is our reference electrode.

Potentiometric Titration of Chloride

$$E_{cell} = E_{Ag} - E_{Cu} = E_{Ag} - 0.307V$$

The silver half cell potential varies with log[Ag$^+$]:

$$Ag^+ + e \rightleftharpoons Ag_{(s)} \qquad E^0_{Ag} = +0.799V$$

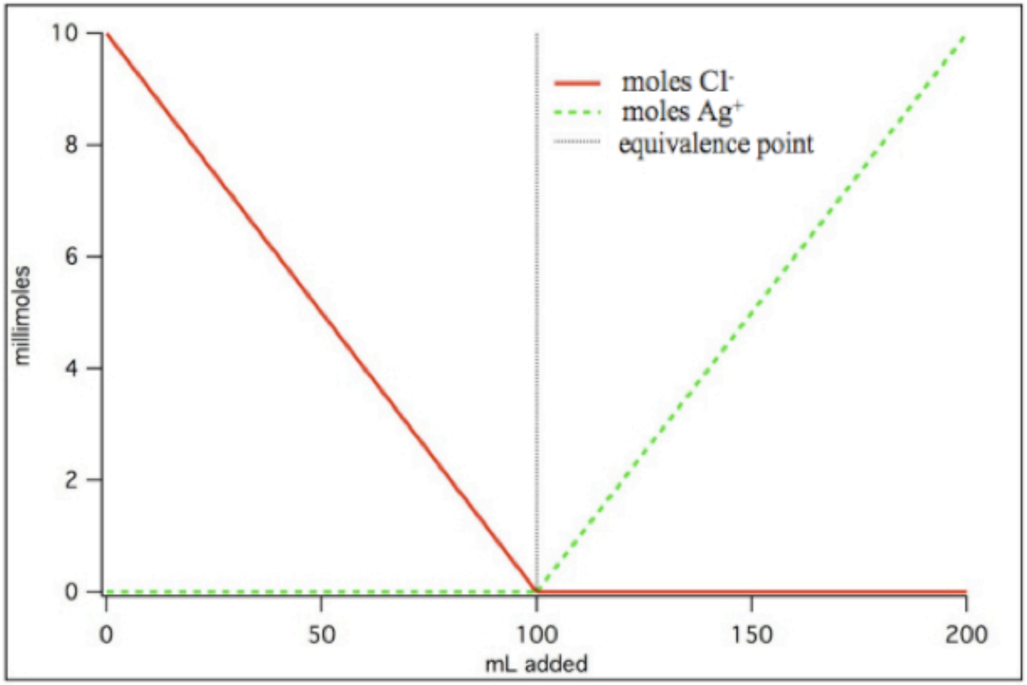
$$E_{Ag} = E^0_{Ag} - \frac{0.0592}{1}\log\frac{1}{[Ag^+]}$$

$$E_{Ag} = 0.799 + 0.0592\log[Ag^+]$$

$$\boxed{E_{cell} = 0.492 + 0.0592\log[Ag^+]}$$

What is E_{cell} at the equivalence point?

Equivalence Point Potential



@ Eq. pt: $[Ag^+] \approx [Cl^-]$

$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2$$

$$[Ag^+] = \sqrt{K_{sp}}$$

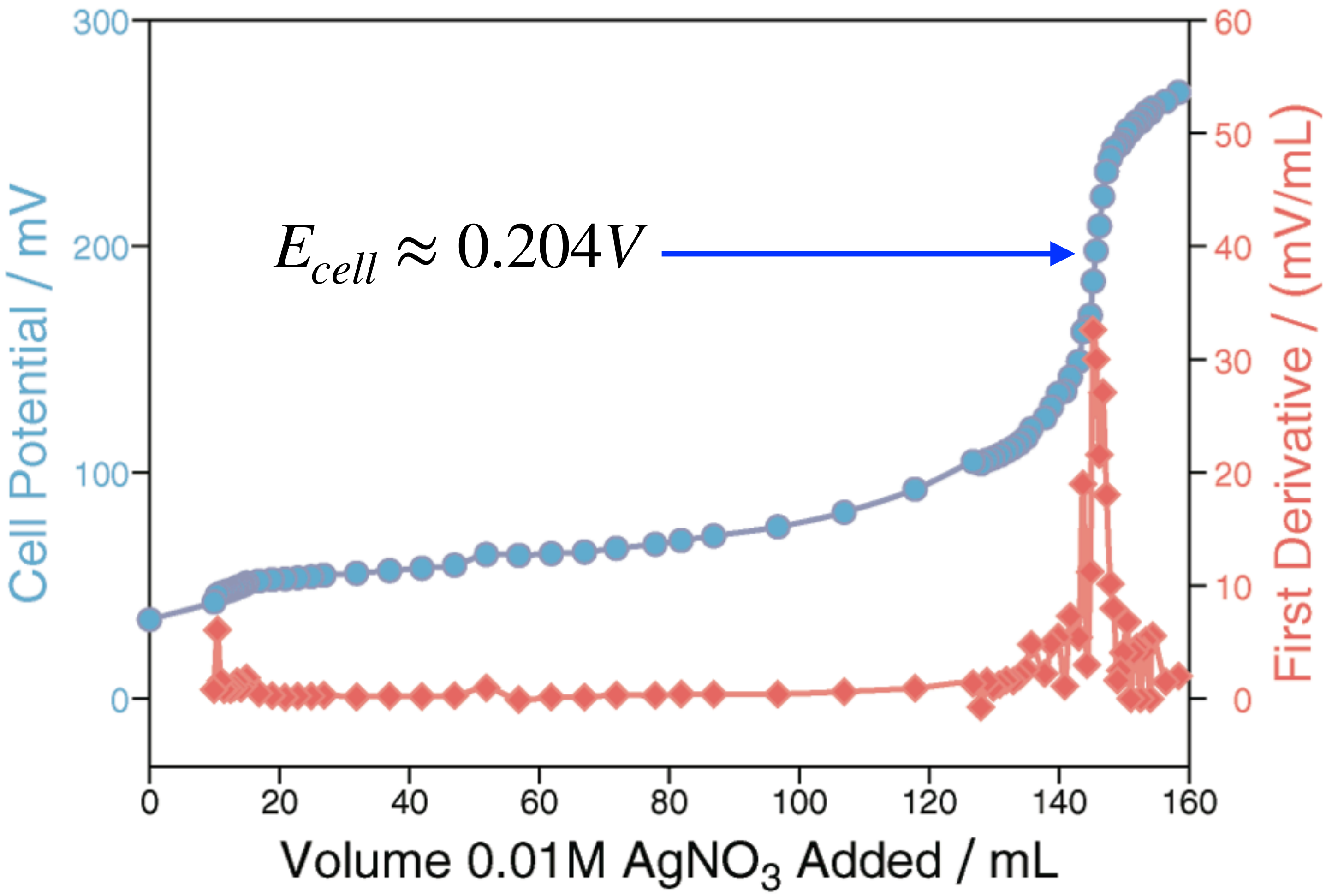
At the equivalence point:

$$[Ag^+] = \sqrt{K_{sp}} = 10^{-4.87} M$$

$$E_{cell} = 0.492 + 0.0592 \log[Ag^+]$$

$$\boxed{E_{cell} = 0.204V}$$

Example of Potentiometric Titration Data


$E_{cell} \approx 0.204V$

For more details, see the J. Chem. Ed. paper in the Handouts:

M. Berger, "Potentiometric Determination of Chloride in Natural Waters: An Extended Analysis", *J. Chem. Educ.* **89**, 812−81 (2012).