Electrochemistry

05/03/2013

Electrochemistry basics

Helpful pneumonic devices:

OIL RIG

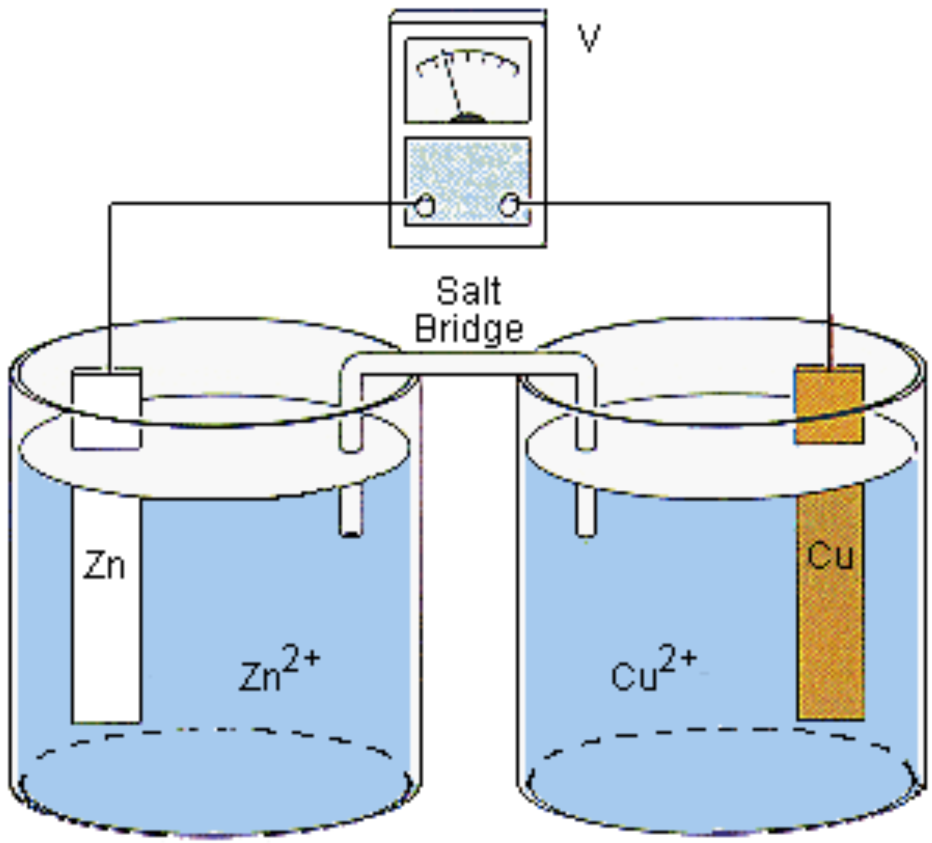
Oxidation is losing electrons, reduction is gaining electrons

AnOx RedCat

Anode oxidation, cathode reduction

Electrons flow from anode to cathode

What are the half cell reactions?



http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#voltaic

What are the half cell reactions?

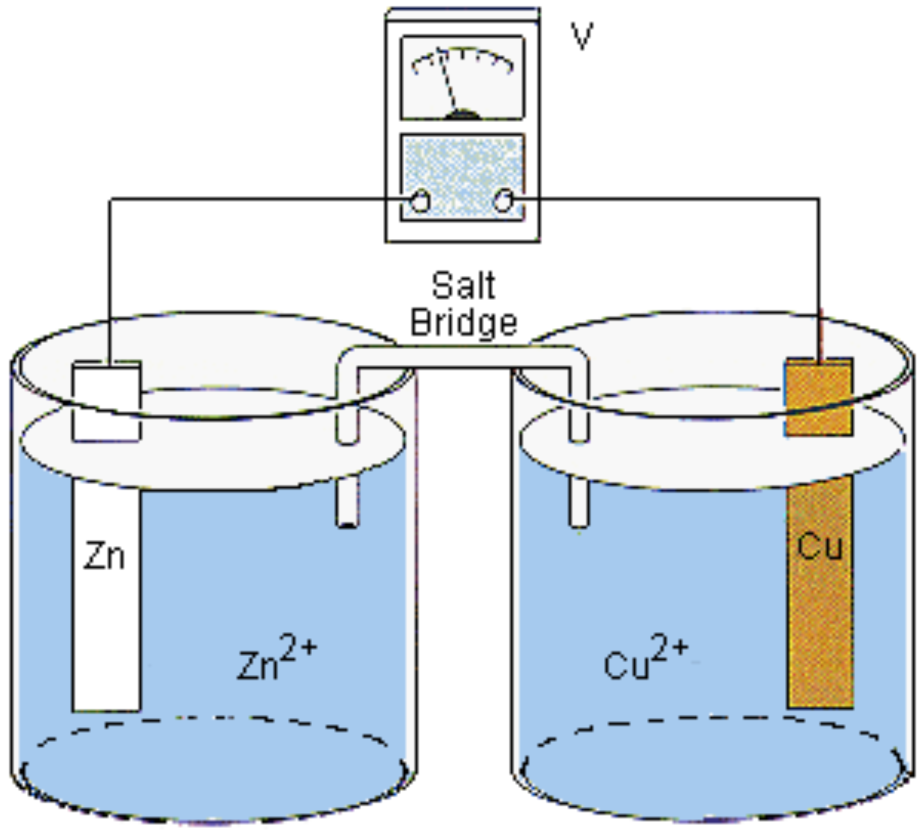
$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^o_{red} = -0.76$

$Cu^{2+} + e^- \rightleftharpoons Cu \quad E^o_{red} = 0.34$

Positive potential = spontaneous

The reduction of Cu^{2+} is spontaneous → this will be the reduction reaction

Overall Cell potential?



http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#voltaic

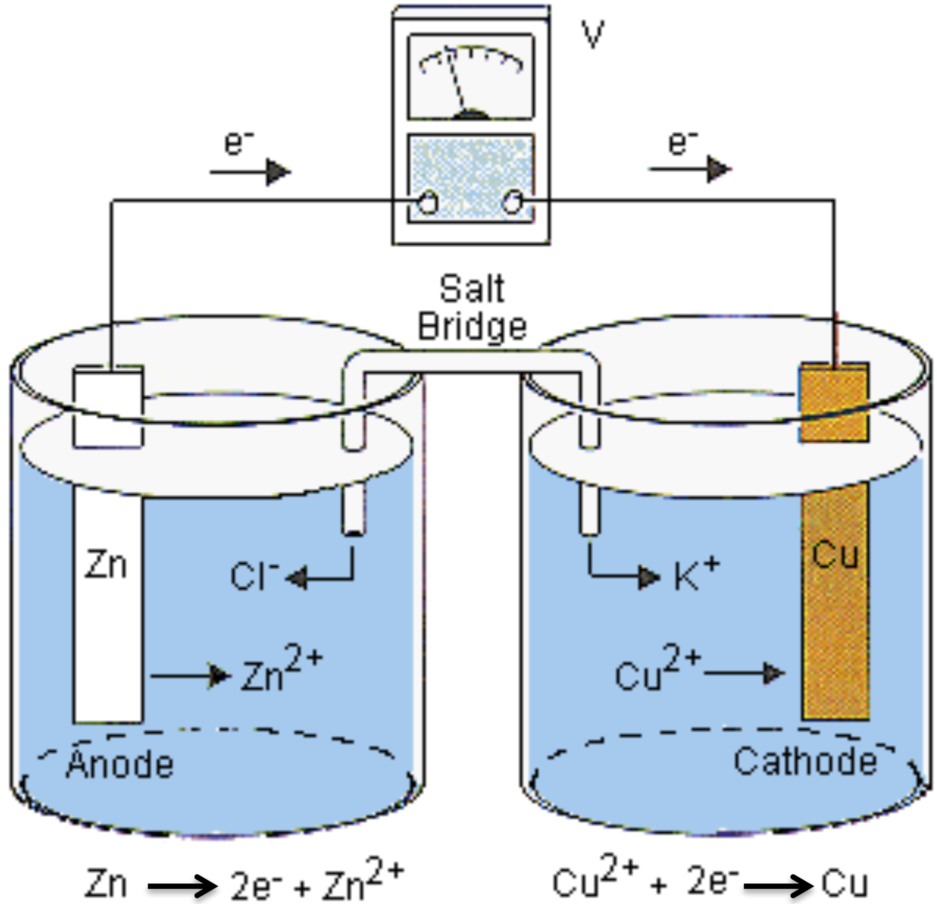
Overall Cell potential

$E^o_{cell} = E^o_{Cu} - E^o_{Zn}$

$E^o_{cell} = 0.34 - (-\ 0.76)$

$E^o_{cell} = 1.10\ V$

Anode and Cathode

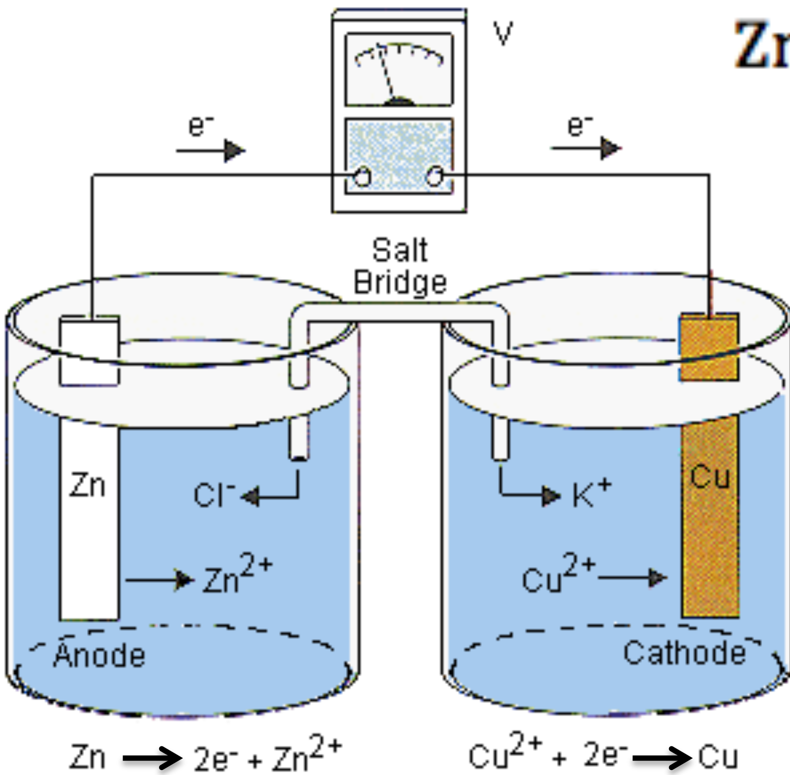


http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#voltaic

Line notation

Anode Cathode

$$Zn|Zn^{2+}(1.00\ M)||Cu^{2+}(0.10\ M)|Cu$$



1.00 M Zn^{2+} 0.10 M Cu^{2+}

Single line = phase boundary

Double line = two phase boundaries (one
at each end of the salt bridge)

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#voltaic

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

If $Zn^{2+} = 1.0\ M = Cu^{2+}$, $E_{cell} = ?$

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{1.0}{1.0}\right]$$

If $Zn^{2+} = 1.0\ M = Cu^{2+}$, $E_{cell} = 1.1\ V$

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

If $Zn^{2+} = 1.0$ M, $Cu^{2+} = 0.10$ M, $E_{cell} = ?$

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{1.0}{0.10}\right]$$

If Zn^{2+} = 1.0 M, Cu^{2+} = 0.10 M, E_{cell} = 1.07 V

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

If Zn^{2+} = 1.0 M, Cu^{2+} = 0.0001 M, E_{cell} = ?

The Nernst Equation

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

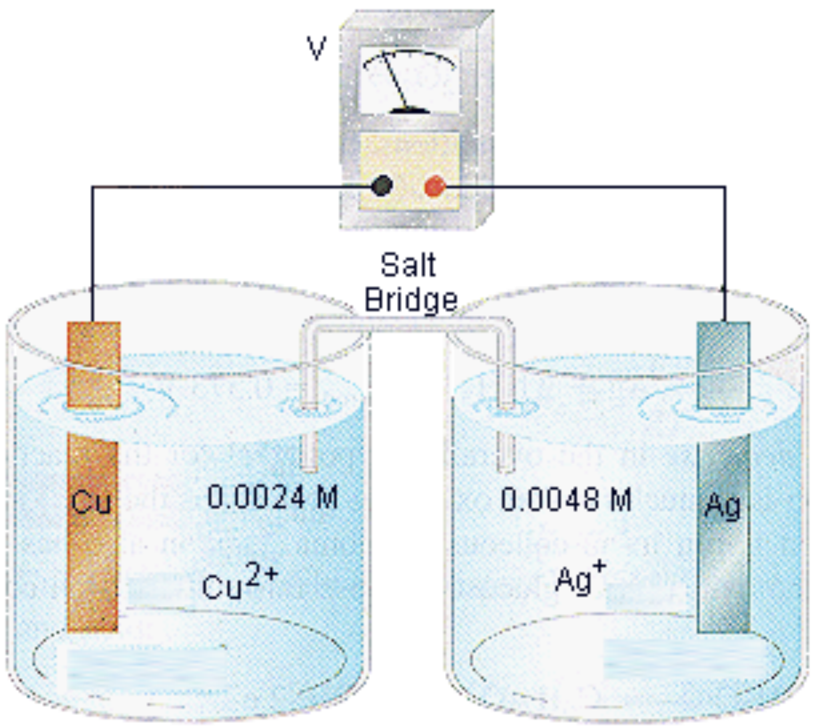
$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right]$$

$$E_{cell} = 1.1\ V - \frac{0.0592}{2}\log\left[\frac{1.0}{0.0001}\right]$$

If Zn^{2+} = 1.0 M, Cu^{2+} = 0.0001 M, E_{cell} = 0.98 V

Example 2



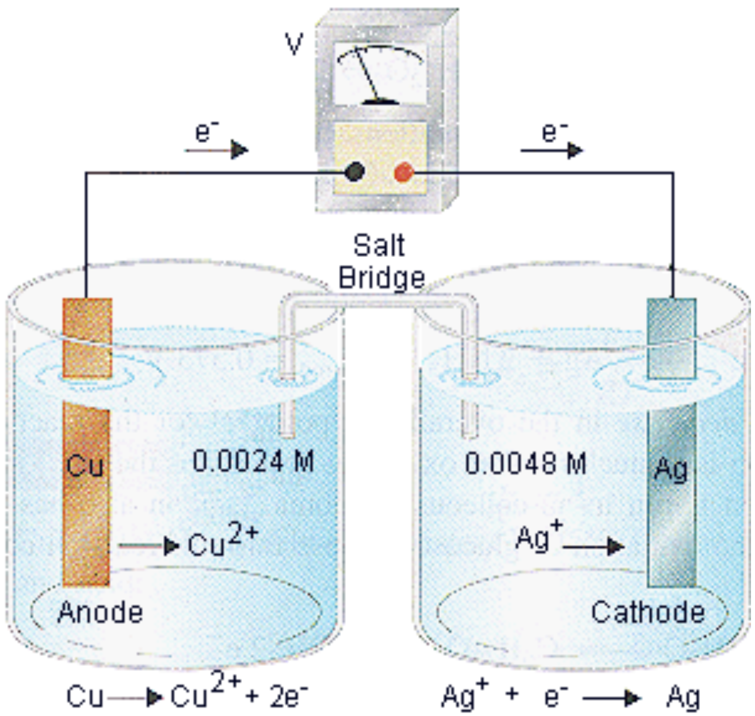
http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#voltaic

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^o = 0.337$ V

$Ag^+ + e^- \rightleftharpoons Ag$ $E^o = 0.799$ V

1. Calculate E^o_{cell}.
2. Write the overall reaction.
3. Determine which is the anode and which is the cathode.
4. Write the line notation
5. Calculate E_{cell} using the concentrations shown.

Example 2: Answers

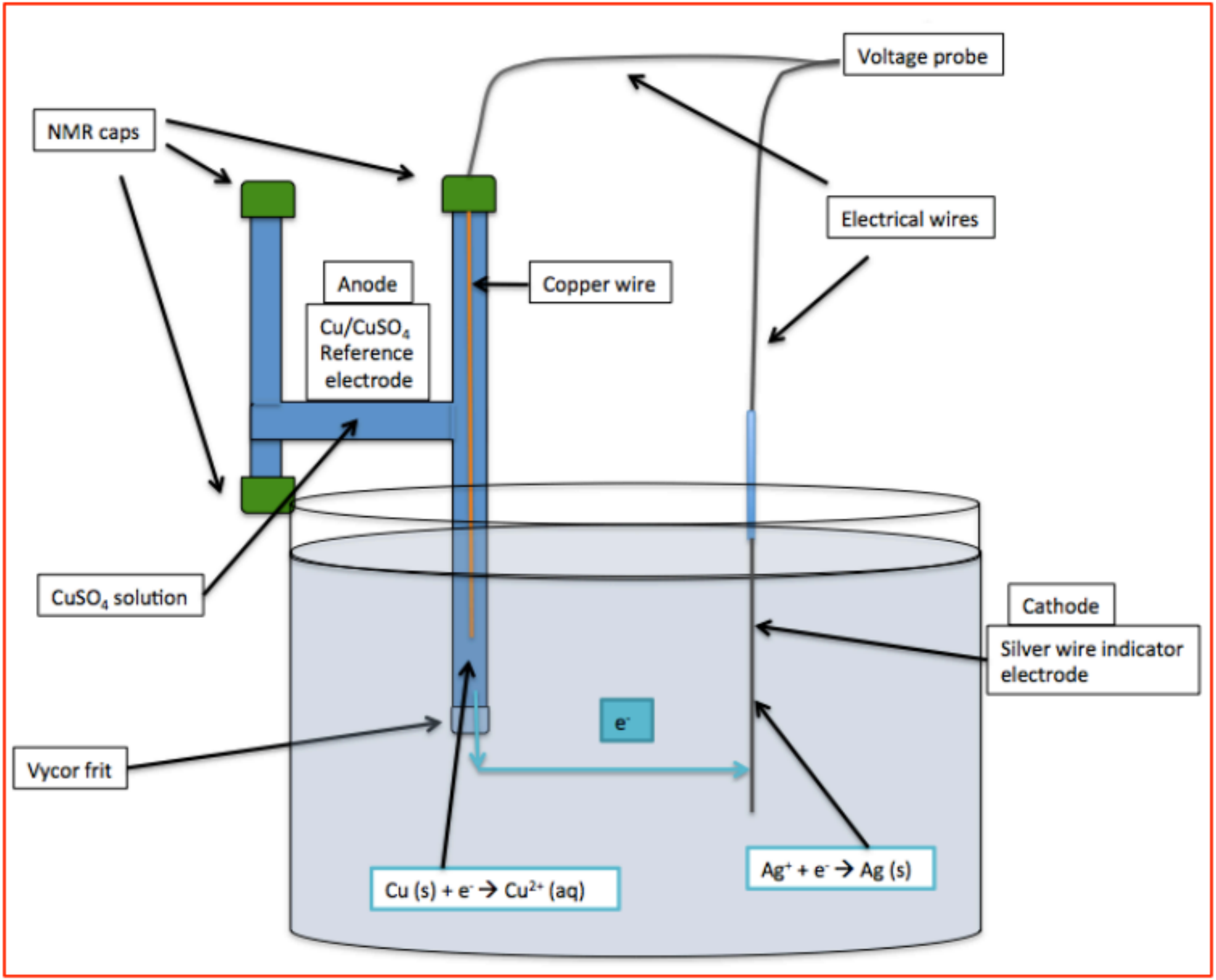


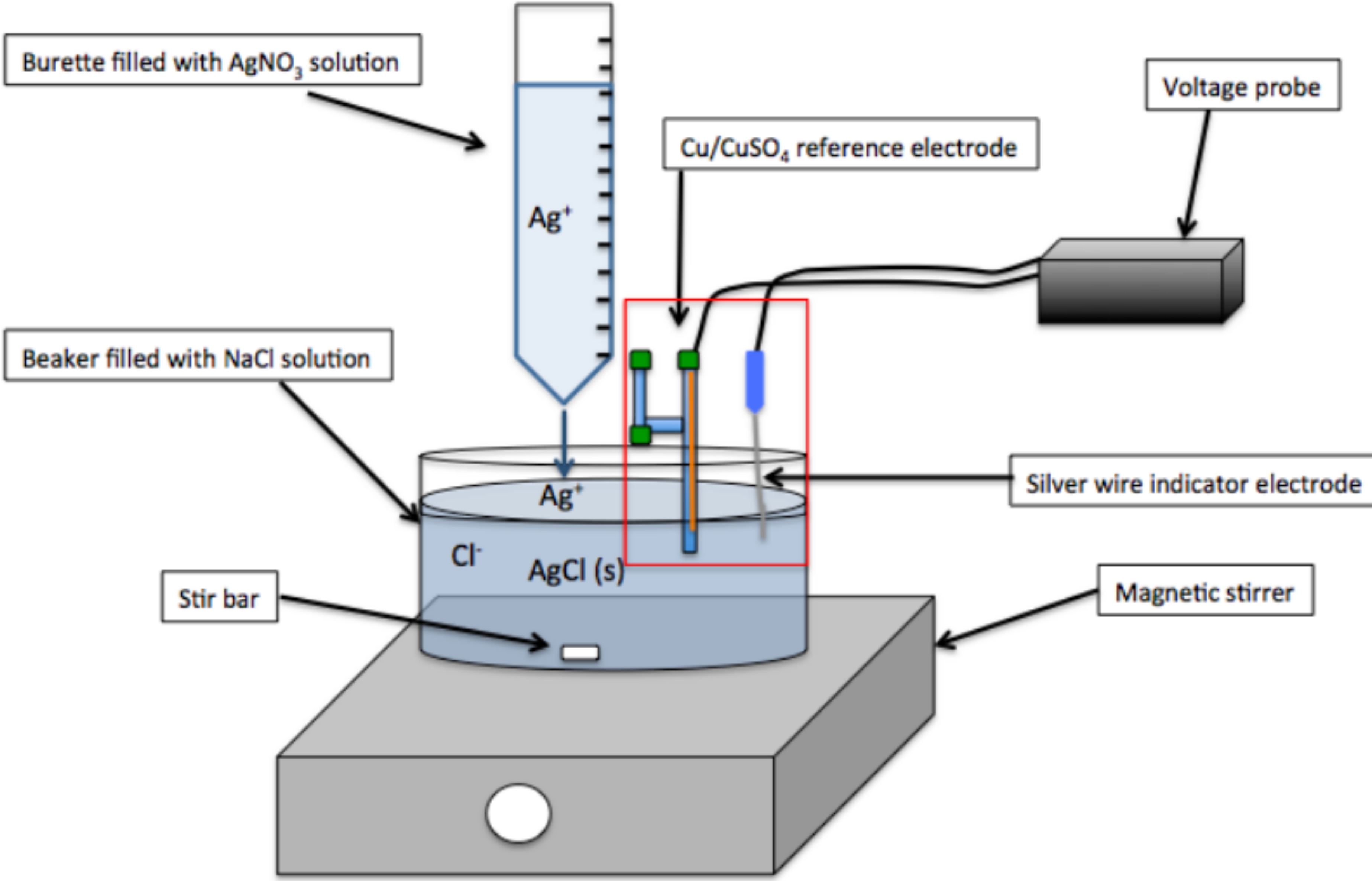
$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^o = 0.337\ V$

$Ag^+ + e^- \rightleftharpoons Ag \quad E^o = 0.799\ V$

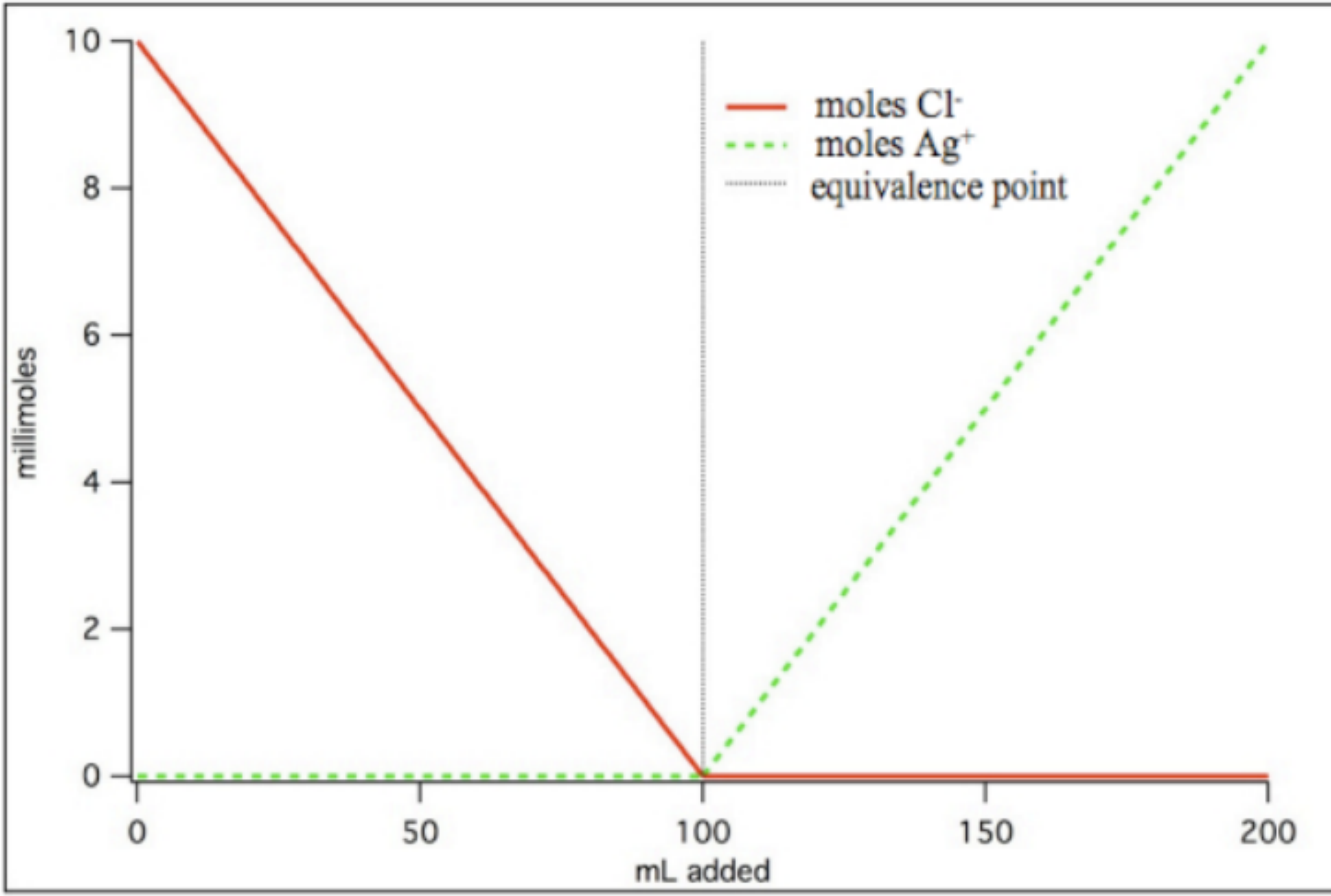
1. $E^o_{cell} = 0.462\ V$
2. $Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$
3. Determine which is the anode and which is the cathode.
4. $Cu|Cu^{2+}(0.0024\ M)||Ag^+(0.0048\ M)|Ag$
5. $$E_{cell} = 0.462 - \frac{0.0592}{2}\log\left[\frac{[Cu^{2+}]}{[Ag^+]^2}\right]$$

$E_{cell} = 0.402\ V$


Voltage probe
NMR caps
Electrical wires
Anode
Cu/CuSO$_4$ Reference electrode
Copper wire
CuSO$_4$ solution
Cathode
Silver wire indicator electrode
e$^-$
Vycor frit
Cu (s) + e$^-$ → Cu^{2+} (aq)
Ag$^+$ + e$^-$ → Ag (s)



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



$$Ag^{+}\,(aq) + Cl^{-}(aq) \rightleftharpoons AgCl\,(s) \quad K_{sp} = [Ag^{+}][Cl^{-}] = 1.8 \times 10^{-10}$$

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

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

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

$$E_{cell} = E^o_{cell} - \frac{0.0592}{2} \log\left[\frac{[Cu^{2+}]}{[Ag^+]^2}\right]$$