GALVANIC CELLS:
-spontaneous reaction is utilized. ; voltaic cell. the 2 reactants are not in contact so that electrons must be transferred thru a conductor ie an external circuit.

We can determine the spont rxn by means of the electrochemical potentials. (standard potentials). Convention: std red’n potentials. in relation to the SHE. =0V,

3) Know how to analyze galvanic cells. Review how to write the cell(line) notation for galvanic cells.

Cu$^{2+}$ +2e$^-$ --> Cu .339 V and
Zn$^{2+}$ +2e --> Zn -.762 V
Spont rxn:
Zn + Cu$^{2+}$ → Zn$^{2+}$ + Cu(s) +1.102 V

(Zn is oxidized and Cu is reduced)
draw the cell. anode = oxidation (-), cathode is reduction (+)
Eg: Daniell Cell: Zn$^{2+}$ | Zn‖Cu$^{2+}$ ;

5) do sample calculations
1) In electrogravimetry, analyte deposited as a solid ("plated") onto one of the electrodes.

In contrast to the galvanic cell which is spontaneous, electrolysis occurs by a nonspontaneous reaction.

To drive rxn an external emf must be supplied. 
$E_{cell}$ for an electrolytic cell is negative. e.g. Plating Cu is nonspont.
Can calculate $E^\circ$ for nonspont reaction using Nernst equation. 
We call this $E_{eq}$ (i.e. potential that needs to be supplied such that there is no current flow.) If this is exceeded, then a reversal is expected to occur. I.e the current would flow the opposite direction.

example: Cu$^{2+}$ + 2e --> Cu(s) (a reduction) $E^\circ = 0.339$ V
\[ \text{Pb}^{2+} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{PbO}_2(\text{s}) + \text{H}_2(\text{g}) + 2\text{H}^+ \quad \text{E}^\circ = 1.458 \text{ V} \]

If these 2 represent the redox couple, then \( E^\circ_{\text{cell}} = 1.458 - .339 = 1.119 \text{V} \) and Cu is oxidized to \( \text{Cu}^{2+} \). If instead, we want \( \text{Cu}^{2+} \) reduced then we need to reverse this spont rxn. We apply an external applied \( E \) of \( E_{\text{appl}} = -1.119 \text{V} \). But that's not enough. We need more negative to actually reverse the current. And the resulting current is actually voltage dependent.

Current-voltage behaviour: Both galvanic and electrolytic cells have a typical current voltage behavior:

Why voltage changes as current flows:

3 factors:
   a) ohmic potential given by \( E_{\text{ohmic}} = IR \)
   b) concentration potential:
   c) overpotential

Ohmic potential, \( R = \text{resistance of the cell in ohms (Ω)} \). I current in amperes (A), \( E = \text{potential in volts (V)} \). (note: 1 volt = 1 amp-ohm

If we have a battery cell: It reads 1.5 volts in the voltmeter but as soon as you turn on the flashlight it starts to dim. (it doesn't really deliver a potential of 1.5 volts. That's only true if \( I = 0 \). The reason? ohmic potential.

eg. if the volts of a galvanic cell is 1.5 volts but its internal resistance is 0.5Ω, if the output is .25 amps, then the actual output voltage (taking only ohmic potential into account) is 1.5 V -(0.25A)(0.5 Ω) = 1.5 V -.125 V = 1.375 V.

The same goes for electrolytic cells. Here, the potential applied by an external potential is written as negative. We need to subtract the ohmic potential

**Electrolysis:** \( \#\text{mol} = \text{it/nF} \). Suppose that you want to deposit a metal like copper, say it involves a constant current of 2.0 amps for exactly 1.0 hour at 3.0V. How many grams of Cu are deposited during that 1 hour assuming only \( \text{Cu}^{2+} \) is being reduced?

OK the deposition involves: \( \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)} \)

\[ \#\text{grams Cu} = \text{AW(it/nF)} = (63.546 \text{g/mol})(2.0 \text{C/s})(1.0 \text{h})(60\text{s/h})/(2 \text{e/mol Cu}^{2+})(96500 \text{C/mole e}) \]

\[ = 0.0395 \text{ g Cu} \]

4) Write the Nernst equation. Relate it to free energy.

note that \( \Delta G = \Delta G^\circ + R\text{TlnQ} \Rightarrow -n\text{FE} = -n\text{FE}^\circ + RT(2.303\log \text{Q}) \)

\[ E = E^\circ + (2.303)(\text{RT/nF}) \log \text{Q} = E^\circ + (0.059\text{V/n}) \log \text{Q} = \Rightarrow \text{Nernst Eqn} \]

\[ E = E^\circ + R\text{TlnQ} \text{and} \Delta G = -n\text{FE}; \]

**Concentration cell:**

consider: \( \text{Cu(s)}|\text{CuSO}_4 (1.0 \text{ M})||\text{Cu(NO}_3)_2 (0.0010\text{M})| \text{Cu(s)} \)

note: \( [\text{Cu}^{2+}]_L = 1.0 \text{ M, } [\text{Cu}^{2+}]_R = 0.0010\text{M} \)

and the half reactions:

\( \text{Cu}^{2+}_L + 2\text{e}^- \rightarrow \text{Cu}_L \& \text{Cu}^{2+}_R + 2\text{e}^- \rightarrow \text{Cu}_R \)

but from just considerations of diffusion, we know that the tendency is for Cu to decrease on left side and Cu to increase on the right side to approach
equilibrium: So from electrochemical considerations, on left side, Cu\(^{2+}\) will be reduced (cathode, +) and right side will be oxidized (anode, -).

Usually: 

\[
E = E_\text{Ce} = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{0.059}{2} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \\
E_\text{Fe} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \]

It reminds us that we can use potential to measure concentrations.

Concentration cells:

Consider the potential of the ff:

\[|\text{Cu(s)}|\text{Cu}^{2+}(0.00010\text{M})||\text{Cu}^{2+}(1.00\text{M})|\text{Cu(s)}\]

write the rxn:

write the Nernst Equation:

POTENTIOMETRIC TITRATION:

E.G. Fe\(^{2+}\) titrated with Ce\(^{4+}\)

the potentials:

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{ V} \\
\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+} \quad E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} = 1.44 \text{ V} 
\]

the titration reaction (i.e. the spont. rxn):

\[
\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+} 
\]

\[
E^\circ = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} - E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 1.44 - 0.771 \text{ V} = 0.67 \text{ V} 
\]

\[
K = \frac{[\text{Ce}^{3+}][\text{Fe}^{3+}]}{[\text{Ce}^{4+}][\text{Fe}^{2+}]} = 10^{nE^\circ/0.059} = 10^{1 \times 0.67/0.059} = 10^{11.37} = 2.34 \times 10^{11}. 
\]

Now assume: 50.0 mL of 0.100M Fe\(^{2+}\) titrated with 0.100 M Ce\(^{4+}\) (e.p. @ 50. mL Ce\(^{4+}\))

The cell potential can be expressed in terms of Ce or Fe. Both are valid:

\[
E = E_{\text{Ce}} = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} - \frac{0.059}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \\
E_{\text{Fe}} = E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} - \frac{0.059}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} 
\]

(note that here we are ignoring the \(E_{\text{ref}}\), the reference electrode; later, we’ll include it by just subtracting it from the values we get above).

But before ep, \(E_{\text{Fe}}\) is better since we know the ratio of Fe\(^{2+}/\text{Fe}^{3+}\).

Regions: NOTE: before e.p., \([\text{Fe}^{2+}]/[\text{Fe}^{3+}]\) is known so: we use
a) @ $V_{Ce^{4+}} = 0$; $[Fe^{2+}]/[Fe^{3+}] = \infty$, so, $E = -\infty$ (actually it will be some finite but difficult to predict value since any trace contaminants will affect the potential greatly).

b) @ $V_{Ce^{4+}} = 10.0$ mL: $(10.0\text{mL})(0.100\text{M}) = 1.0 \text{mmol Ce}^{4+}$ added

$$[Fe^{3+}] = 1.0 \text{mmol}/(50+10\text{mL}) = 1/60; \quad [Fe^{2+}] = (5.0-1.0)/60$$

$$E = 0.77 - 0.059/1 \log(1/60 / 4/60) = 0.77 - 0.035 = 0.74 \text{V}$$

(same as: $E = 0.77 - 0.059\log(10/(50-10)) = 0.74\text{V}$)

c) @ $V_{Ce^{4+}} = 25.0$ mL: $(25.0\times1.00 = 2.50\text{mmol})$

$$E = 0.77 - 0.059 \log (2.5/2.5) = 0.77 \text{ (so at half equiv, E = E}_{Fe}^o)$$

what is $[Ce^{4+}] = ?$ $E = E_{Fe} = E_{Ce} = 0.77 = 1.44 - 0.059/1 \log[Ce^{3+}]/[Ce^{4+}]$

$$\log [Ce^{3+}]/[Ce^{4+}] = (1.44 - 0.77)/0.059 = [Ce^{3+}]/[Ce^{4+}] = 10^{11.37}$$

$$[Ce^{4+}] = [Ce^{3+}]/10^{11.37} = (2.5\text{mmol}/75.0\text{mL})/ 10^{11.37} = 1.42 \times 10^{-13} \text{M}$$

d) @ ep: $[Fe^{3+}] = [Ce^{3+}]$ and therefore (unrxted): $[Fe^{2+}] = [Ce^{4+}]$

$$E_{ep} = E_{Ce^{4+}/Ce^{3+}} - 0.059/1 \log \{[Ce^{3+}]/[Ce^{4+}]\}$$

$$E_{ep} = E_{Fe^{3+/Fe^{2+}}} - 0.059/1 \log \{[Fe^{3+}]/[Fe^{2+}]\}$$

adding: $2 E_{ep} = (E_{Ce^{4+/Ce^{3+}} + E_{Fe^{3+/Fe^{2+}}}) - 0.059 \log \{[Ce^{3+}][Fe^{2+}]/[Ce^{4+}][Fe^{3+}]\}$

$2^{nd}$ term = 0: $E_{ep} = (1/2)(E_{Ce^{4+/Ce^{3+}} + E_{Fe^{3+/Fe^{2+}}}) = (1/2)(0.77+1.44) = 1.10 \text{V}$

Past ep, we know ratio of Ce’s so that’s what we use.

Eg $V_{Ce} = 100$ mL:

$$E = E_{ce} = 1.44 \text{V} - 0.059 \log[Ce^{3+}]/[Ce^{4+}] = 1.44 - 0.059\log(50/(100-50)) = 1.44$$

show E vs $V_{Ce^{4+}}$ curve.

More complex example: (i.e. not just a 1:1 titration)

titrates 50.0 mL of 0.0200 M FeSO$_4$ with 0.010 M KMnO$_4$; buffered at pH 4.2 during titration.

$$8H^+ + 5 Fe^{2+} + MnO_4^- \rightarrow Mn^{2+} + 5 Fe^{3+} + 4H_2O$$

at ep: $n_{Fe^{2+}} = 5 \times n_{MnO_4}: M_{Fe}V_{Fe} = 5 M_{MnO_4}V_{MnO_4}$

$=> V_{MnO_4} = (1/5)(M_{Fe}V_{Fe}/M_{MnO_4}) = 20.0 \text{mL}$

Before ep: we know $[Fe^{2+}]/[Fe^{3+}]$:

$$E = E_{Fe} - 0.059\log[Fe^{2+}]/[Fe^{3+}]$$
after ep: we know $[\text{Mn}^{2+}]/[\text{MnO}_4^-]$

$$ E = E_{\text{MnO}_4^-} - (.059/5) \log \left\{ [\text{Mn}^{2+}]/[\text{MnO}_4^-][\text{H}^+] \right\} $$

at ep:

$$ E_{\text{ep}} = (1/6)(E_{\text{Fe}} + 5 E_{\text{MnO}_4^-}) - (.059/6)\log(1/[\text{H}^+]) $$

(note: $E = (1/6)(.77 + 5 \times 1.51) - (.059/6)\log(1/10^{-4.2}) = 1.39-.33 = 1.06\text{V} $)

Use of the reference electrodes has to be included in the potential:

Note that the above $E$’s we were calculating were the “indicator potentials”. It would be the same value if our reference electrode was the standard hydrogen electrode (S.H.E.). But that’s hard to set up. Instead, we often use Ag/AgCl or else standard calomel electrodes (SCE).

To see how that is measured, we use a reference electrode and measure the potential of the cell relative to the reference electrode:

$$ E_{\text{measured}} = E_{\text{indicator}} - E_{\text{reference}} $$

_____ / ______ / \ _______/ \ E(V vs S.H.E.)

| $E_{\text{ind}}$ | 0 (SHE) | 0.197(Ag|AgCl) | 0.241(SCE) |

SHE : Std H electrode: $\text{H}^+(\text{aq}) + e^- \rightarrow (1/2) \text{H}_2(\text{g})$ $E^\circ_{\text{H}^+/\text{H}_2} = 0.0 \text{ V (definition)}$

SCE = Sat’d Calomel Elect: $1/2 \text{Hg}_2\text{Cl}_2(\text{s}) + e^- \rightarrow \text{Hg}(\text{l}) + \text{Cl}^-(\text{aq})$ $E_{\text{Hg}_2\text{Cl}_2/\text{Hg}} = 0.268 \text{V} (=0.241\text{V satd KCl})$

Ag/AgCl:

:Red'n 1/2 rxns: (1) $\text{AgCl}(\text{s}) + e^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-$ & (2) $\text{Fe}^{3+} + \text{Fe}^{2+}$

how to hook it up: $\text{Ag|AgCl(s)|Cl}^- || \text{Fe}^{3+}(\text{aq}),\text{Fe}^{2+}(\text{aq})||\text{Pt(s)}$

Note: $E^\circ_{\text{AgCl}/\text{Ag}} = 0.222 \text{V} ; E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \text{V}$

Draw the picture:

Note:Ecell is if want to know spont rxn: red'n is $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$.

But more useful is the reading which can be (+) or (-): $\Delta E = E^+ - E^-$ where $E^+$ is the cell connected to the + of the voltmeter and $E^-$ is the electrode connected to the - of the voltmeter.

Know to calculate unknowns in Latimer diagrams.

[Diagram]

suppose we have: $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}(\text{s})$

$0.161 \text{v} \quad 0.518 \text{v}$ $\Delta G^\circ = -nF E^\circ$

we write the 2 steps that add up to the step we want:

$e^+ \text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}$ $0.161 \text{V}$ $-0.161 \text{F}$

$e^+ \text{Cu}^+ \rightarrow \text{Cu} \rightarrow \text{Cu}$ $0.518 \text{V}$ $-0.518 \text{F}$

net: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ $0.339 \quad -0.679 \text{F} = -2E^\circ$