Study Guide for Electrochemistry

How to find cell potentials at non-standard conditions:

1. Things to remember:
- From thermodynamics:

$$\Delta G = \Delta G° + RT\ln Q$$

- Where:
    - ΔG is the Gibbs free energy (in units of $J{*}mol^{-1}$)
    - $\Delta G°$ is the Gibbs free energy at standard conditions (in units of $J{*}mol^{-1}$)
    - R is the thermodynamic form of the gas constant ($R = 8.3145\ J{*}mol^{-1}{*}K^{-1}$)
    - T is the temperature (in units of K)
    - Q is the reaction quotient (unitless)
- From previous electrochemistry discussions:

$$\Delta G° = -nFE°_{cell}$$

- Similarly:

$$\Delta G = -nFE_{cell}$$

- Where:
    - n is the number of moles of electrons transferred in the redox reaction
    - F is Faraday's constant ($F = 96385\ C{*}mol^{-1}$)
    - $E°_{cell}$ is the cell potential at standard conditions
    - E_{cell} is the cell potential at non-standard conditions (what we want)

2. The derivation:
- Putting things together:

$$-nFE_{cell} = -nFE°_{cell} + RT\ln Q$$

$$-nFE_{cell}/-nF = -nFE°_{cell}/-nF + RT\ln Q/-nF$$

$$E_{cell} = E°_{cell} - RT/nF * \ln Q$$

- Since reactions usually take place at 25°C (298 K), this can usually be reduced to:

$$E_{cell} = E°_{cell} - 0.025693/n * \ln Q$$

- You might also see this equation as the Nernst equation:

$$E_{cell} = E°_{cell} - 0.0592/n * \log Q$$

3. Example:

Determine the value of E_{cell} for the following cell at room temperature:

$$Pt|Fe^{2+}_{(aq)}\ (0.10\ M),\ Fe^{3+}_{(aq)}\ (0.20\ M)||\ Ag^{+}_{(aq)}\ (1.0\ M)|Ag_{(s)}$$

1. Rewrite the cell as a set of redox half-reactions:

$$\text{Cathode (Red.): } Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$$

$$\text{Anode (Ox.): } Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^{-}$$

2. Find the standard reduction potential for each half-reaction (from a table):

$$\text{Cathode (Red.): } Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)} \qquad E°_{cathode} = 0.800 \text{ V}$$

$$\text{Anode (Ox.): } Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^{-} \qquad E°_{anode} = 0.771 \text{ V}$$

3. Find $E°_{cell}$:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = 0.800 \text{ V} – 0.771 \text{ V}$$

$$E°_{cell} = 0.029 \text{ V}$$

4. Find n: Because in this reaction 1 electron is gained for every 1 electron that is lost, the total electrons transferred is 1 mole.
5. Find Q:

- Overall reaction:

$$Ag^{+}_{(aq)} + Fe^{2+}_{(aq)} \rightarrow Ag_{(s)} + Fe^{3+}_{(aq)}$$

- General Q equation:

$$Q = [Fe^{3+}]/[Ag^{+}][Fe^{2+}]$$

- Plugging in concentrations:

$$Q = (0.20)/((1.0)(0.10)$$

$$Q = 2$$

6. Find E_{cell}:

$$E_{cell} = E°_{cell} - 0.0592/n * \log Q$$

$$E_{cell} = E°_{cell} - 0.0592/1 * \log(2)$$

$$E_{cell} = 0.029 - 0.0592 * 0.30103$$

$$E_{cell} = 0.011 \text{ V}$$