

Study Guide for Electrochemistry

How to find cell potentials at non-standard conditions:

1. Things to remember:

- From thermodynamics:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

• Where:

- ΔG is the Gibbs free energy (in units of $\text{J} \cdot \text{mol}^{-1}$)
- ΔG° is the Gibbs free energy at standard conditions (in units of $\text{J} \cdot \text{mol}^{-1}$)
- R is the thermodynamic form of the gas constant ($R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
- T is the temperature (in units of K)
- Q is the reaction quotient (unitless)

• From previous electrochemistry discussions:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

• Similarly:

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

• Where:

- n is the number of moles of electrons transferred in the redox reaction
- F is Faraday's constant ($F = 96385 \text{ C} \cdot \text{mol}^{-1}$)
- 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:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q$$

$$-nFE_{\text{cell}} / -nF = -nFE^\circ_{\text{cell}} / -nF + RT \ln Q / -nF$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - RT/nF * \ln Q$$

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

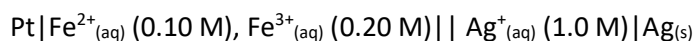
$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.025693/n * \ln Q$$

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

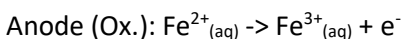
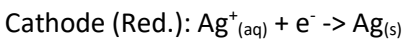
$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/n * \log Q$$

3. Example:

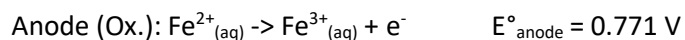
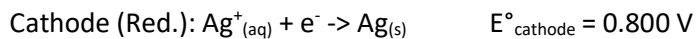
Determine the value of E_{cell} for the following cell at room temperature:



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



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



3. Find E°_{cell} :

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

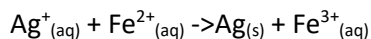
$$E^\circ_{\text{cell}} = 0.800 \text{ V} - 0.771 \text{ V}$$

$$E^\circ_{\text{cell}} = 0.029 \text{ V}$$

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:



- General Q equation:

$$Q = \frac{[\text{Fe}^{3+}]}{[\text{Ag}^+][\text{Fe}^{2+}]}$$

- Plugging in concentrations:

$$Q = \frac{(0.20)}{(1.0)(0.10)}$$

$$Q = 2$$

6. Find E_{cell} :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/n * \log Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/1 * \log(2)$$

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

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