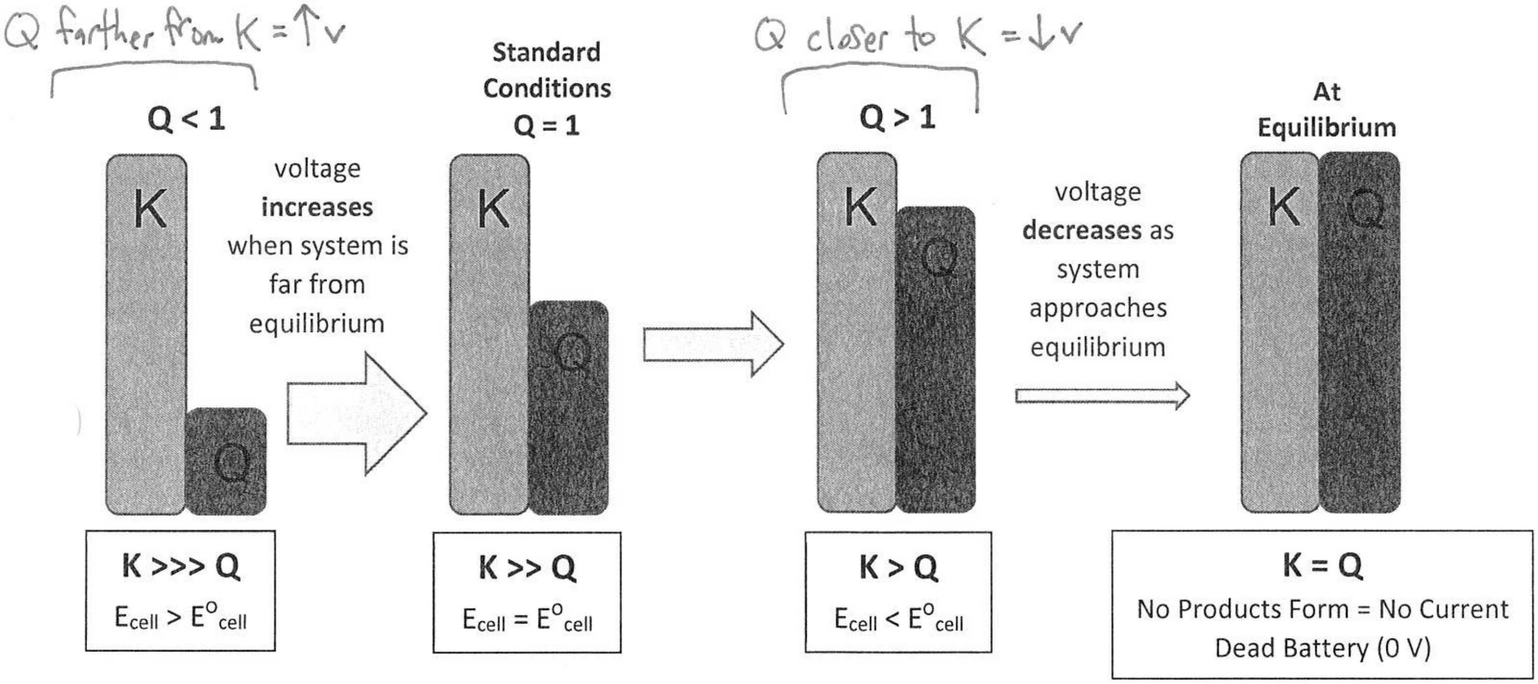
Electrochem Equilibrium: Non-standard Conditions

Standard Cell Potential (E^{o}_{cell}): cell potential measured at standard conditions of **1 atm, 1.0 M solution, and 25°C**.

- As a voltaic cell discharges, reactants are consumed and products are generated. Therefore, as the cell operates, the conditions become non-standard and the voltage decreases !

Non-Standard Cell Potential (E_{cell}): cell potential measured at nonstandard conditions (concentration ≠ 1.0 M)

- In a standard galvanic/voltaic cell: K >> 1 and Q = 1, voltage measured = E^{o}_{cell}
  - If concentrations change to make **Q larger** (closer to K), **voltage decreases**! $E_{cell} < E^{o}_{cell}$
  - If concentrations change to make **Q smaller** (farther from K), **voltage increases**! $E_{cell} > E^{o}_{cell}$



system closer to equilibrium

Conditions that Increase Q, Decrease Voltage ($E_{cell} < E^{o}_{cell}$)] lower measured voltage

- Increase [products]
- Decrease [reactants]

system farther from equilibrium

Conditions that Decrease Q, Increase Voltage ($E_{cell} > E^{o}_{cell}$)] higher measured voltage

- Increase [reactants]
- Decrease [products]

Note about thermodynamic favorability:

- If $E_{cell} > E^{o}_{cell}$, cell voltage increases and the cell is more thermodynamically favorable.
- If $E_{cell} < E^{o}_{cell}$, cell voltage decreases and the cell is less thermodynamically favorable.

Let's Practice!

1. Given the information below, answer the following questions.

$$Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s), \quad E^{o}_{cell} = +0.59\ V$$

   a. A galvanic cell is constructed where $[Cu^{2+}]$ = 0.50 M and $[Ni^{2+}]$ = 1.0 M. Is the voltage of this cell (E_{cell}) higher, lower, or equal to the standard cell potential (E°_{cell})? Why?

$E_{cell} < E^{\circ}_{cell}$, b/c $[Cu^{2+}]$ is less than standard conditions. Decreasing the concentration of a reactant increases Q, bring the rxn closer to equilibrium.

   b. A galvanic cell is constructed where $[Cu^{2+}]$ = 2.0 M and $[Ni^{2+}]$ = 2.0 M. Is the voltage of this cell higher, lower, or equal to the standard cell potential? Explain. What would happen to the time the cell could operate?

$Q = \frac{[Ni^{2+}]}{[Cu^{2+}]} = \frac{2.0}{2.0} = 1$, which is the same value as Q at standard conditions:

Thus, $E_{cell} = E^{\circ}_{cell}$, b/c still standard distance from equilibrium.

Also, this cell could run twice as much time as a standard cell, even though voltage is the same, b/c it has twice as much reactants available (assuming Ni (s) is excess).

   c. A standard galvanic cell is constructed (using the balanced equation provided), and the voltage is measured to be 0.59 V. After two hours, the voltage is re-measured: would you expect the new cell potential to be higher, lower, or equal to the standard cell potential? Justify your answer.

As the cell runs, over time, reactants are used up + products are formed, bringing the cell closer to equilibrium. Therefore, voltage (+ the cell potential) decreases.

In Summary

- Increasing [reactants] or decreasing [products] will cause voltage to **increase**. ($E_{cell} > E^{o}_{cell}$)
- Decreasing [reactants] or increasing [products]will cause voltage to **decrease**. ($E_{cell} < E^{o}_{cell}$)
- Increasing or decreasing **both** [reactants] and [products] **by the same factor** will cause voltage to stay the same **if and only if** they have the same stoichiometric coefficient in the balanced equation.
- Removing **ALL** of one or more reactants will cause voltage to drop to zero.
- Removing the solid product (cathode electrode) has **NO** effect on voltage.

★ ↑ reactants allows the cell to operate for a longer time!

How to Answer FR Questions about Nonstandard Cell Conditions

You do not need to ~~use the Nernst equation~~ do math for non-std conditions on the AP Chem test; you will only be asked to make qualitative predictions about E_{cell} or voltage (does it increase, decrease, or remain the same relative to standard?). ***However***, you WILL need to explain how the nonstandard concentrations affect the value of the reaction quotient, *Q*, and what that means for voltage or the cell potential.

- It can be very helpful, on FR, to calculate the value of the reaction quotient, *Q*, (if you're given sufficient data) and compare that value to when *Q* = 1 (standard conditions).
- If you don't have actual numbers, you can qualitatively compare Q to Q under standard conditions.

Example FR Explanations

Example #1: ↑ [reactants], [reactants] = 1.0 M. *Will cell potential be higher, lower, or the same as standard conditions?*

- Because the concentration of reactants increased, the reaction has a lower value of Q than under standard conditions. Since the reaction is farther from equilibrium, the cell potential will increase: $E_{cell} > E^o_{cell}$.

Example #2: ↑ [products], [reactants] = 1.0 M. *Will cell potential be higher, lower, or the same as standard conditions?*

- Because the concentration of products increased, the reaction has a greater value of Q than under standard conditions. Since the reaction is closer to equilibrium, the cell potential will decrease: $E_{cell} < E^o_{cell}$.

Example #3: ↑ [reactants] and [products] by same factor (with same stoich coefficient)

- Because the ratio of [products] to [reactants] is the same as standard conditions, Q = 1, and therefore the cell voltage is the same as the voltage at standard conditions: $E_{cell} = E^o_{cell}$.

★ ↑ [reactants] ⇒ cell can operate for longer time, even if voltage doesn't change.

Let's Practice!

⇒ E^o_{cell} = +

1. A nonstandard galvanic cell is constructed based on the following half-reactions at 25°C, where $[Cd^{2+}]$ = 0.010 M and $[Pb^{2+}]$ = 0.100 M.

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E^o = -0.40\ V \Rightarrow E^o_{ox} = +0.40V$$
$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E^o = -0.13\ V = E^o_{red}$$

a. Identify and write the equation for the half-reaction which occurs at the anode and the half-reaction that occurs at the cathode.

anode: $Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$

cathode: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

b. Write the balanced reaction occurring in this galvanic cell.

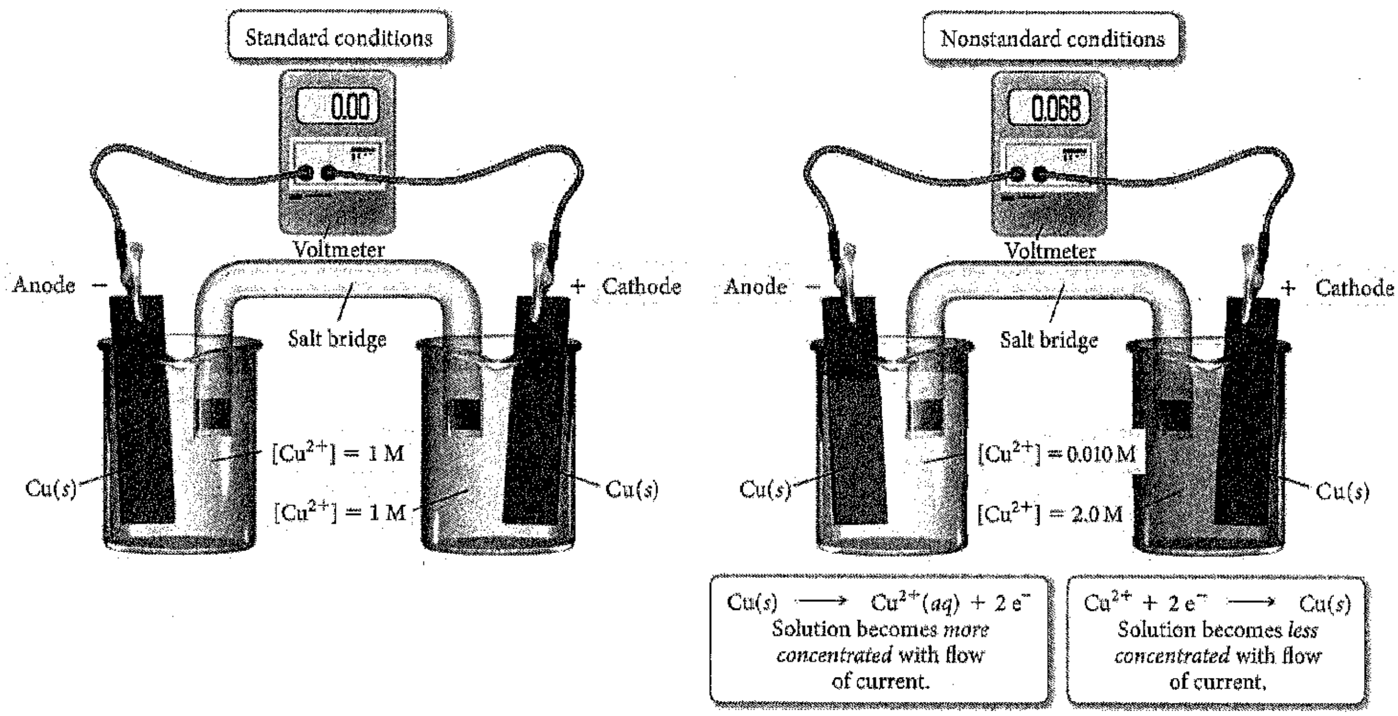
$$Pb^{2+}(aq) + Cd(s) \rightarrow Pb(s) + Cd^{2+}(aq)$$

c. Under these conditions would the cell potential be greater than, less than, or equal to the cell potential under standard conditions? Justify your answer.

$Q = \frac{[Cd^{2+}]}{[Pb^{2+}]} = \frac{0.010}{0.100} < 1$, so the rxn is further from equilibrium than standard conditions, so the cell potential is greater: $E_{cell} > E^o_{cell}$.

Concentration Cells

You can make a concentration cell by using two half cells with the <u>same</u> metal/ion combination, as long as the ion <u>concentrations</u> differ! **Electrons will flow from the lower concentration half-cell to the higher concentration half-cell to achieve equilibrium.**



Let's Practice!

2. A cell has on its left side a 0.20 M Zn^{2+} solution. The right side has a 0.050 M Zn^{2+} solution. The compartments are connected by Zn electrodes and a salt bridge. Draw this galvanic cell and designate the cathode, anode, and direction of current.