Worksheet – Nernst Equation

Under standard conditions, the cell potential, $\xi_\text{cell}$, is calculated from the standard potentials of the two half-reactions:

$\xi_\text{cell} = \xi_\text{reduction} - \xi_\text{oxidation}$

For a voltaic (spontaneous) cell, the cell potential must be positive.

1. Given the following half-reactions, decide which will remain as a reduction reaction and which will be reversed to become an oxidation reaction.

\[
\begin{align*}
2 \left( \text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn} (s) \right) & \quad \xi^\circ = -0.76 \text{ V} \\
2 \left( \text{Al}^{3+} (aq) + 3e^- \rightarrow \text{Al} (s) \right) & \quad \xi^\circ = -1.66 \text{ V} 
\end{align*}
\]

2. Write out the overall reaction and calculate $\xi_\text{cell}$.

\[
3 \text{Fe}^{2+} + 2\text{Al} \rightarrow 3\text{Zn} + 2\text{Al}^{3+} \\
\xi^\circ = -0.76 + 1.66 = 0.90 \text{ V}
\]

3. Which reaction will occur at the anode?

$$\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$$

Which reaction will occur at the cathode?

$$3\text{Zn}^{2+} + 2e^- \rightarrow 3\text{Zn}$$

a) label the solutions and electrodes in the diagram below.

   (put the oxidation half-reaction on the left)

There is a standard notation for electrochemical cells.

- the anode is drawn on the left and the cathode on the right.
- phase changes are shown as vertical lines between components |
- the salt bridge is shown as ||
- The outermost components must be solids

Fill in the components for this pair of half-reactions.

\[
\text{Al}(s) \ | \ \text{Al}^{3+}(1 \text{ M}) \ || \ \text{Zn}^{2+}(1 \text{ M}) \ | \ \text{Zn}(s)
\]

Anode                      Cathode

If there are no solids in a half-reaction, an inert electrode, such as Pt or even C(graphite) can be used.
If the [Zn^{2+}] = 2.0 M and [Al^{3+}] = 0.50 M, this would be a non-standard cell. Using the relationships $\Delta G = -nF\varepsilon$ and $\Delta G^0 = -nF\varepsilon^0$ we can come up with an equation to calculate non-standard cell potentials, the Nernst equation.

$$\varepsilon = \varepsilon^0 - \frac{RT}{nF} \ln Q$$

where

- $n$ = # moles of electrons in the balanced half-reactions
- $F$ = faradays constant $\approx 96,000$ C/mol e$^-$
- $Q$ = reaction quotient, $[\text{products}]^p / [\text{reactants}]^r$

4. Calculate non-standard cell potential ($\varepsilon$) at 298 K when the [Zn^{2+}] = 2.0 M and [Al^{3+}] = 0.50 M.

   a) $Q = \frac{[\text{prod}]}{[\text{react}]} = \frac{[\text{Al}^{3+}]}{[\text{Zn}^{2+}]}^3 = \frac{(0.50)^3}{(2.0)^3} = 0.03125$

   b) $\varepsilon^0 = -0.90$ V

   c) $n = 6$

   d) $\varepsilon = \frac{-0.90 \times 8.314 \times 298}{6 \times 96500} \ln 0.03125 = 0.815$ V

5. Calculate $\Delta G$ and $\Delta G^0$ and discuss the difference in the work being done, in terms of [products] and [reactants].

   a) $\Delta G^0 = -nF\varepsilon^0 = -6(96500)(-0.90) = 521$ kJ

   b) $\Delta G = -nF\varepsilon = -6(96500)(0.915) = -530$ kJ

   The higher potential has a larger [reactant] and a smaller [product].

6. What is the effect on $\varepsilon$ of doubling the size of the aluminum electrode?

   **no effect** $\varepsilon$ is intensive

7. What is the effect on $\varepsilon$ of adding 500 mL of water to the cathode, assuming there was 1 L of the solution to begin with?

   The molar concentration will change [Zn^{2+}] from 2.0 M to 1.0 M

   $$Q = \frac{(0.50)^3}{(1.0)^3} = 0.25$$

   $$\varepsilon = \frac{-0.90 \times 8.314 \times 298}{6 \times 96500} \ln 0.25 = 0.906$ V

   Lower potential [lower reactant]
There is a special kind of non-standard cell, called a **concentration cell**. It is different because the two half-reactions involve exactly the same species. All that drives it is a difference in the concentration of the components. An example is diagramed below.

\[
\text{Ag}^+ (aq) + e^- \rightarrow \text{Ag} (s) \quad \xi^c = 0.800 \text{ V}
\]

\[
\text{Ag} (s) \mid \text{Ag}^+ (1.0 \text{ M}) \parallel \text{Ag}^+ (2.0 \text{ M}) \mid \text{Ag} (s)
\]

\[
\text{Ag} \rightarrow \text{Ag}^+ + e^- \quad \text{Ag}^+ + e^- \rightarrow \text{Ag}
\]

8. Under the anode and cathode, write the half-reactions taking place.
   
   a) What is the product at the anode? \[\text{Ag}^+\]
   
   b) What is the product at the cathode? \[\text{Ag}\]
   
   c) What is the reactant at the anode? \[\text{Ag}\]
   
   d) What is the reactant at the cathode? \[\text{Ag}^+\]
   
   e) What is the value of Q? \[
   \frac{[\text{prod}]}{[\text{react}]} = \frac{[1.0]}{[2.0]} = .5
   \]
   
   f) What is the value of \(n\)? \[= 1\]
   
   g) What is the value of \(\xi^c\) at 298 K? \[E^c = 0 \text{ (0.800 - 0.800)}\]
   
   h) What is the value of \(\xi\) at 298 K? \[
   \xi = 0 - \frac{(8.314 \times 298)}{(1)(96500)} \ln .5 = .018 \text{ V}
   \]