Triathlon – Electrochemistry

Balancing Redox Reactions
1. Balance the following in acidic solution:

\[
\begin{align*}
2\text{H}^+ + \text{P} & \rightarrow \text{H}_2\text{P}_4^- + 3\text{e}^- \\
2\text{H}^+ & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{P} + \text{Cu}^{2+} & \rightarrow \text{Cu} + \text{H}_2\text{PO}_4^- \\
2\text{e}^- + \text{Cu}^{2+} & \rightarrow \text{Cu}
\end{align*}
\]

\[
\begin{align*}
4\text{H}^+ + 2\text{P} + 3\text{Cu}^{2+} & \rightarrow 3\text{Cu} + 2\text{H}_2\text{PO}_4^-
\end{align*}
\]

2. Balance the following in acidic solution:

\[
\begin{align*}
\text{H}_2\text{O} + \text{NO}_2 & \rightarrow \text{NO}_3^- + \text{NO} \\
2\text{e}^- + 2\text{H}^+ + \text{NO}_2 & \rightarrow \text{NO} + \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} + \text{NO}_2 + \text{NO}_2 & \rightarrow 2\text{NO}_3^- + 2\text{H}^+ + \text{NO}
\end{align*}
\]

3. Balance the following in basic solution:

\[
\begin{align*}
\text{Fe}^{2+} + 4\text{H}^+ + \text{MnO}_4^- & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \\
2\text{e}^- + 2\text{H}^+ + \text{MnO}_4^- & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{C}_2\text{O}_4^{2-} & \rightarrow 2\text{CO}_2 + 2\text{e}^-
\end{align*}
\]

\[
\begin{align*}
\text{CO}_3^- + \text{H}^+ + 2\text{MnO}_4^- + 3\text{C}_2\text{O}_4^{2-} & \rightarrow 6\text{CO}_2 + 2\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{OH}^-
\end{align*}
\]

4. Balance the following in basic solution:

\[
\begin{align*}
\text{Cu(NH}_3)_4^{2+} + \text{S}_2\text{O}_7^{2-} & \rightarrow \text{SO}_3^{2-} + \text{Cu} + \text{NH}_3 \\
2\text{H}_2\text{O} + \text{S}_2\text{O}_7^{2-} & \rightarrow 2\text{SO}_3^{2-} + 4\text{H}^+ + 4\text{e}^-
\end{align*}
\]

\[
\begin{align*}
2\text{Cu(NH}_3)_4^{2+} + 2\text{H}_2\text{O} + \text{S}_2\text{O}_7^{2-} & \rightarrow \text{Cu} + 4\text{NH}_3 + 2\text{SO}_3^{2-} + 4\text{H}^+
\end{align*}
\]

\[
\begin{align*}
4\text{H}^+ + 2\text{Cu(NH}_3)_4^{2+} + 2\text{S}_2\text{O}_7^{2-} & \rightarrow \text{Cu} + 4\text{NH}_3 + 2\text{SO}_3^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

Voltaic Cells and $E^0$

5. 1. You create a voltaic cell with the following reaction:

\[
\text{Fe (s)} + 2\text{Ag}^{+} (\text{aq}) \rightarrow \text{Fe}^{2+} (\text{aq}) + 2 \text{Ag (s)}
\]
Create a diagram of the two half cells. Label the cathode, anode, movement of electrons, salt bridge, and write in cell notation.

6. Calculate the standard reduction potential for the reaction:

\[ \text{Cl}_2 + 2 \text{I}^- (\text{aq}) \rightarrow 2 \text{Cl}^- (\text{aq}) + \text{I}_2 (s) \]

\[ E^0 = E^0_{\text{cathode}} - E^0_{\text{anode}} = 1.36 \text{V} - 0.54 \text{V} = 0.82 \text{V} \]

7. Calculate the standard reduction potential for the reaction:

\[ \text{Ni} (s) + 2 \text{Ce}^{4+} (\text{aq}) \rightarrow \text{Ni}^{2+} (\text{aq}) + 2 \text{Ce}^{3+} \]

\[ E^0 = 1.63 \text{V} - 0.28 \text{V} = 1.35 \text{V} \]

8. Which of the following is a stronger oxidizing agent: Fe (s) or Mg (s)

Fe is a stronger oxidizing agent

**Nernst Equation**

9. Find the emf for the following cell reaction at 298 K:

\[ \text{Zn}(s) + \text{Ni}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Ni}(s) \]

\[ [\text{Ni}^{2+}] = 3.00 \text{ M}, [\text{Zn}^{2+}] = 0.100 \text{ M} \]

\[ E = E^0 - \frac{0.0257}{2} \ln \left( \frac{0.1}{3} \right) \]

\[ E = 0.48 - 0.01285 \ln \left( \frac{0.1}{3} \right) = 0.48 - 0.0437 = 0.52 \text{V} \]

10. Find the emf for the following cell reaction at 298 K:

\[ \text{Zn}(s) | \text{Zn}^{2+} (0.5 \text{ M}) || \text{Cu}^{2+} (0.891 \text{ M}) | \text{Ag}(s) \]

\[ E^0 = 1.1 \text{V} \]

\[ E = 1.1 - \frac{0.0257}{2} \ln \left( \frac{0.5}{0.891} \right) \]

\[ E = 1.1 - 0.0074 = 1.09 \text{V} \]

11. [Diagram of the two half cells with labels for cathode and anode]
An electrochemical cell is constructed with an open switch, as shown in the diagram above. A strip of Sn and a strip of unknown metal, X are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The half-reactions are shown below. 

\[ \text{Sn}^{2+} (aq) + 2 \text{e}^- \rightarrow \text{Sn} (s) \quad E^\circ = -0.14 \text{ V} \]

\[ \text{X}^{3+} (aq) + 3 \text{e}^- \rightarrow \text{X} (s) \quad E^\circ = ? \]

(a) In the diagram above, label the electrode that is the cathode. Justify your answer.

(b) In the diagram above, draw an arrow indicating the direction of electron flow in the external circuit when the switch is closed.

(c) If the standard cell potential \( E^\circ_{\text{cell}} \) is +0.60 V, what is the standard potential, in volts for the \( \text{X}^{3+} / \text{X} \) electrode?

\[
\begin{align*}
0.60 &= 0.14 - E_M \\
-0.74 \text{ V} &= E_M
\end{align*}
\]

(d) Identify metal X.

\[ \text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr} (s) \]

(e) Write balanced net-ionic equation for the overall chemical reaction occurring in the cell.

\[ 3\text{Sn} (s) + 2\text{Cr}^{3+} \rightarrow 2\text{Cr} + 3\text{Sn}^{2+} \]

(f) In the cell, the concentration of \( \text{Sn}^{2+} \) is changed from 1.0 \( M \) to 0.50 \( M \), and the concentration of \( \text{X}^{3+} \) is changed from 1.0 \( M \) to 0.10 \( M \).

(i) Substitute all appropriate values for determining the cell potential, \( E_{\text{cell}} \), into the Nernst equation. (Do not do any calculations.)

\[
E = 0.60 - \frac{0.0257}{6} \ln \left( \frac{(0.50)^3}{(0.1)^2} \right)
\]

(ii) On the basis of your response in (f) (i), will the cell potential be greater than, less than, or equal to \( E^\circ_{\text{cell}} \)? Justify your answer.

The cell potential will be less than \( E^\circ_{\text{cell}} \). This is due to the fact \( \ln (Q) \) would be greater than 1, so \( \ln Q \) is positive and the overall term is negative.
Concentration Cells
12. A voltaic cell is constructed with 2 Zn\textsuperscript{2+} - Zn electrodes. The two half cells have [Zn\textsuperscript{2+}] = 1.8 M and [Zn\textsuperscript{2+}] = 1.00 x 10\textsuperscript{-2} M, respectively.
   a. Which electrode is the anode of the cell?
   \[ [\text{Zn}^{2+}] = 1 \times 10^{-2} \text{ M} \]
   b. What is the standard emf of the cell?
   \[ \mathcal{E}^0 = 0 \text{ V} \]
   c. What is the cell emf for the concentrations given?
   \[ \mathcal{E} = 0 - \frac{0.025}{2} \ln\left( \frac{1 \times 10^{-2}}{1.8} \right) \approx 0.067 \text{ V} \]
   d. For each electrode, predict whether [Zn\textsuperscript{2+}] will increase, decrease, or remain the same as the cell operates.
   Cathode \Rightarrow [\text{Zn}^{2+}] \downarrow \text{ w/ time}
   Anode \Rightarrow [\text{Zn}^{2+}] \uparrow \text{ w/ time}

13. A voltaic cell is constructed with two silver-silver chloride electrodes, each of which is based on the following half-reactions:
   \[ \text{AgCl (s) + e}^{-} \rightarrow \text{Ag (s) + Cl}^{-} (aq) \]
   The two half cells have [Cl\textsuperscript{-}] = 0.0150 M and [Cl\textsuperscript{-}] = 2.55, respectively.
   a. Which electrode is the cathode of the cell?
   \[ [\text{Cl}^{-}] = 2.55 \text{ M} \]
   b. What is the standard emf of the cell?
   \[ \mathcal{E}^0 = 0 \text{ V} \]
   c. What is the cell emf for the concentrations given?
   \[ \mathcal{E} = 0 \text{ V} - \frac{0.025}{1} \ln\left( \frac{0.015}{2.55} \right) = \sqrt{0.132} \text{ V} \]
   d. For each electrode, predict whether [Cl\textsuperscript{-}] will increase, decrease, or remain the same.
   Cathode \Rightarrow [\text{Cl}^{-}] \downarrow \text{ w/ time}
   Anode \Rightarrow [\text{Cl}^{-}] \uparrow \text{ w/ time}

\( \Delta G, K_{eq}, \text{ and } E^0 \)
14. The following galvanic electrochemical cell was constructed:
   \[ \text{Pt (s) | H}_2 (g, 1.00 \text{ atm}) | \text{H}^+ (aq, \text{ concentration unknown}) \parallel \text{Ag}^+ (aq, 0.10 \text{ M}) | \text{Ag (s)} \]
a. Write the balanced chemical equation and calculate \( E^0_{\text{cell}} \) for this galvanic electrochemical cell. Recall that \( E^0 = 0.800 \text{ V} \) for \( \text{Ag}^+ + e^- \rightarrow \text{Ag (s)} \) and \( \text{H}_2/\text{H}^+ = 0.00 \text{ V} \)
   \[
   \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad \text{Ag}^+ + 1e^- \rightarrow \text{Ag} \\
   \text{H}_2 + 2\text{Ag}^+ \rightarrow 2\text{H}^+ + 2\text{Ag}
   \]
   \[ \mathcal{E}^0 = 0.800 \text{ V} \]
b. The source of protons in the hydrogen half-cell is a buffer composed of 0.10 M C₆H₅COOH and 0.050 M C₆H₅COO⁻. The measured cell potential is 0.971 V. Given this fact, determine the pH of the solution and the value of $K_a$ for benzoic acid (C₆H₅COOH).

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15. A galvanic cell is based constructed based on the following half-reactions:

- $\text{Ag}^+ (\text{aq}) + e^- \rightarrow \text{Ag (s)} \quad E^\circ = 0.799 \, \text{V}$
- $\text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu (s)} \quad E^\circ = 0.345 \, \text{V}$

In this cell, the $\text{Ag}^+/\text{Ag}$ half-cell contains a silver electrode and a saturated solution of AgCl ($K_{sp} = 1.6 \times 10^{-10}$), the Cu/Cu²⁺ half-cell contains 1.0 L of a 2.0 M solution of Cu(NO₃)₂ and a copper electrode.

a. Calculate the cell potential for this electrochemical cell.

$$E = 0.454 - 0.0257 \ln \left( \frac{2}{[\text{Ag}^+]^2} \right)$$

Find $u = 1/K_{sp}$

$$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

$$K_{sp} = 1.6 \times 10^{-10} = \frac{x^2}{1.20 \times 10^{-5} M} = x$$

$$E = 0.454 - 0.01285 \ln \left( \frac{2}{(1.20 \times 10^{-5})^2} \right) = 0.155 \, \text{V}$$

b. Calculate the moles of NH₃ (assume no volume change) that would need to be added to the Cu/Cu²⁺ half-cell to give a cell potential of 0.52 V. To answer this question, consider the following reaction:

$$\text{Cu}^{2+} (\text{aq}) + 4 \text{NH}_3 (\text{aq}) \rightarrow \text{Cu(NH}_3)_4^{2+} (\text{aq}) \quad K = 4.0 \times 10^{18}$$