Electrochemistry Notes

Vocabulary

- Electrochemistry: the study of the interchange of chemical and electrical energy
- Redox reaction: a transfer of electrons from the reducing agent to the oxidizing agent
- Oxidation: a loss of electrons (an increase in the oxidation number)
- Reduction: a gain of electrons (a decrease in the oxidation number)
- Half-reactions: a redox reaction broken in to two parts, one half with the oxidation and the other half with the reduction
- Salt bridge: the connection between the two solutions
- Galvanic cell: device in which chemical energy is changed to electrical energy
- Anode: the electrode at which oxidation occurs (an-ox)
- Cathode: the electrode at which reduction occurs (red-cat)
- Cell potential, \( E_{\text{cell}} \): potential difference between the oxidation and reduction
- Volt: the unit of electrical potential (J/C)
- Standard hydrogen electrode: a platinum electrodes in contact with 1M H\(^+\) ions bathed by H\(_2\) gas at 1 atm
- Standard reduction potentials, \( E^0 \): likelihood for the reduction to occur with all solutes at 1M or 1 atm
- Concentration cell: cell with both electrodes having identical components but at different concentrations
- Nernst equation: converts cells that are at nonstandard conditions to standard conditions
  \[ E = E^0 - \frac{RT}{nF} \ln(Q) \]
- Glass electrode: contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane
- Lead storage battery: lead serves as the anode and lead coated with lead dioxide serves as the cathode
- Electrolytic cell: an apparatus that uses electrical energy to produce chemical change for nonspontaneous cells
- Electrolysis: forcing a current through a cell to produce a chemical change; used for nonpontaneous cells
- Ampere: measure of current in coulombs per second (C/s). Often used to help convert the number of electrons flowing (current) to the rate of reaction in time
Description of Cells

Galvanic Cells:

An electrochemical cell of the reaction:
\[ \text{Zn(s)} + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu(s)} \]

anode (+) \hspace{1cm} cathode (-) \hspace{1cm} Anode (+) is always written first.

Oxidation at the anode \hspace{1cm} Reduction at the cathode \hspace{1cm} So oxidation is always written first.

Electrons flow from where they are lost (anode) to where they are gained (cathode).

Note that a porous frit or disc may substitute for the salt bridge.

**Electron Flow, Spontaneity and Electrolysis**

1\textsuperscript{st} Electrons flow in the spontaneous direction.

2\textsuperscript{nd} For a spontaneous cell, electrons will flow from the anode to the cathode as illustrated.

3\textsuperscript{rd} For a nonspontaneous cell, a power source [with a voltage greater than the electrochemical potential, $E_{\text{cell}}$]

4\textsuperscript{th} Nonspontaneous cells are electrolytic cells, electrolysis reactions.

The calculations typically involve reducing/oxidizing a mass, g, in a time, s or with a current, Amp (C/s). To do the calculations set up a series of conversions between the given and wanted using the three conversion factors:

\[ \frac{e^-}{\text{mol}} \quad \frac{96485 \text{C}}{\text{mol-e}^-} \quad \frac{F}{s} \]

See p 868 example problem 17.9.
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**Calculating Electrochemical Potential of a Cell**

1) Write two \( \frac{1}{2} \) reactions written as reductions

2) Compare E’s—the reaction with the highest E is reduced, the other is oxidized

3) Flip the oxidized reaction, or change the sign of E

4) Balance/add the reaction

5) \( E_{\text{rxn}} = E_{\text{reduced}} + E_{\text{oxidized}} \)
   * If E > 0, the reaction is spontaneous
   * If E < 0, the reaction is nonspontaneous

This is because \( \Delta G = -nFE_{\text{rxn}} \) where \( n \) is the number of moles of electrons,

\( F = \) Faraday’s constant, 96485 C/mol,

\( E_{\text{rxn}} = \) electrochemical potential

and for a reaction to be ... spontaneous:

- \( \Delta G = < 0, \ so \ E > 0 \)
- \( \Delta G = > 0, \ so \ E < 0 \)

Note: The preceding notes are for nonstandard conditions (E and \( \Delta G \)).
For standard conditions (\( E^\circ \) and \( \Delta G^\circ \)) the same concepts apply.

**The Nernst Equation:**
The Nernst equation is used to relate a cell’s electrochemical potential, \( E \), that is not at standard conditions (1 atm. 25 °C, 1 M solutions) with an electrochemical potential that is at standard conditions, \( E^\circ \).

\[
E = E^\circ - \frac{nF}{n} \ln(Q)
\]

where
- \( E \) = cell potential under nonstandard conditions
- \( E^\circ \) = cell potential under standard conditions
- \( n \) = number of moles of electrons
- \( R = 8.314 \) VC/mol K
- \( F = 96485 \) C/mol
- \( T = \) temperature
- \( K \) = number of moles of electrons
- \( Q \) = the reaction quotient (use initial concentrations and is \( Q = \) [prod] / [react] )

*As the concentration of the products of a redox reaction increases, the potential voltage decreases; and as the concentration of the reactants in a redox reaction increases, the potential voltage increases.

\[
E^\circ = \frac{RT}{nF} \ln K , \ K \text{ is the equilibrium constant}
\]

*If \( E^\circ \) is positive, then K is greater than 1 and the forward reaction is favored. If \( E^\circ \) is negative, then K is less than 1 and the reverse reaction is favored.
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Example Problems

1. Consider the galvanic cell based on the reaction
   \[ \text{Al}^{3+} + \text{Mg} \rightarrow \text{Al} + \text{Mg}^{2+} \]

   The half reactions are
   \[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \quad E^0 = -1.66 \text{V} \]
   \[ \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} \quad E^0 = -2.37 \text{V} \]

   Give the balanced cell reaction and calculate \( E^0 \) for the cell.

   (See work on page 845)

   Solution: \( 0.71 \text{V} \)

2. Using the data in Table 17.1, calculate the \( \Delta G \) for the reaction
   \[ \text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+} \]

   Is this reaction spontaneous?

   (See work on page 850)

   Solution: \( \Delta G = -1.5 \times 10^3 \text{J}, \) spontaneous

3. Describe the cell based on the following half reactions
   \[ \text{VO}_2^+ + 2H^+ + e^- \rightarrow \text{VO}^{2+} + H_2O \quad E^0 = 1.00 \text{V} \]
   \[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad E^0 = -0.76 \text{V} \]

   where \( T = 25^\circ \text{C} \)
   \[ [\text{VO}_2^+] = 2.0M \]
   \[ [H^+] = 0.50M \]
   \[ [\text{VO}^{2+}] = 1.0 \times 10^{-2}M \]
   \[ [\text{Zn}^{2+}] = 1.0 \times 10^{-1}M \]

   (See work on page 855)

   Solution: \( 1.89 \text{V} \)

3. Determine the cell potential for the rxn \( \text{Al}^{3+} (aq) + \text{Mg} (s) \rightarrow \text{Al} (s) + \text{Mg}^{2+} (aq) \)

   Half-Reactions:
   \[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \quad E^0 = -1.66 \text{V} \]
   \[ \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} \quad E^0 = -2.37 \text{V} \]

   work
   \[ 2 (\text{Al}^{3+} + 3e^- \rightarrow \text{Al}) \]
   \[ 3 (\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-) \]

   \[ 2\text{Al}^{3+} (aq) + 3\text{Mg} (s) \rightarrow 2\text{Al} (s) + 3\text{Mg}^{2+} (aq) \quad E^0 = 0.71 \text{V} \]
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4. Write the line notation for the cell, given:

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \]
\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \]

**work** Line Notation:

\[ \text{Pt(s)} \parallel \text{Fe}^{2+} (aq), \text{Fe}^{3+} (aq) \parallel \text{Ag}^+ (aq) \parallel \text{Ag} (s) \]

5. Determine the free energy of the cell that has the rxn:

\[ \text{Cu}^{2+} (aq) + \text{Fe(s)} \rightarrow \text{Cu(s)} + \text{Fe}^{2+} (aq) \]

\[ \begin{align*}
\text{Cu}^{2+} + 2e^- &\rightarrow \text{Cu} & \varepsilon^0 = 0.34 \text{ V} \\
\text{Fe} &\rightarrow \text{Fe}^{2+} + 2e^- & -\varepsilon^0 = 0.44 \text{ V}
\end{align*} \]

\[ \begin{align*}
\text{Cu}^{2+} + \text{Fe} &\rightarrow \text{Fe}^{2+} + \text{Cu} & \varepsilon^0 = 0.78 \text{ V}
\end{align*} \]

\[ \Delta G^0 = -nF \varepsilon^0 \]
\[ \Delta G^0 = -(2 \text{ mol})(96,485 \frac{C}{\text{mol}})(0.78 \frac{J}{C}) \]
\[ \Delta G^0 = -1.5 \times 10^5 \text{ J} \]

6. Determine the cell potential for the galvanic cell with the following half-reactions at 25 °C with the given concentrations: [Ag⁺] = 1.0 M, [H₂O₂] = 2.0 M, [H⁺] = 2.0 M.

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \]
\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \]

**work**

\[ -2 (\text{Ag}^+ + e^- \rightarrow \text{Ag}) \]
\[ \varepsilon^0 = 0.80 \text{ V} \]
\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \]
\[ \varepsilon^0 = 1.78 \text{ V} \]

\[ \begin{align*}
2\text{Ag} + \text{H}_2\text{O}_2 + 2\text{H}^+ &\rightarrow 2\text{Ag}^+ + 2\text{H}_2\text{O} & \varepsilon^0 = 0.98 \text{ V}
\end{align*} \]

\[ \varepsilon_{cell} = \varepsilon^0_{cell} = \frac{RT}{nF} \ln \left( \frac{[\text{Ag}^+]^2}{[\text{H}^+]^2[\text{H}_2\text{O}_2]} \right) \]

\[ \varepsilon_{cell} = 0.98V - \frac{(8.314 \frac{J}{K \cdot \text{mol}})(298K)}{(2 \text{ mol})(96485 \frac{C}{\text{mol}})} \ln \left( \frac{(1.0M)^2}{(2.0M)^2(2.0M)^2} \right) \]
\[ \varepsilon_{cell} = 1.01 \text{ V} \]