Chapter 14 Notes
Fundamentals of Electrochemistry

Redox Reactions – Reactions involving the transfer of electrons from one species to another.

LEO says GER
  Oxidation – Loss of electrons
  Reduction – Gain of electrons

A given species is said to be “reduced” when it gains electrons and “oxidized” when it loss electrons.

Example

\[
2\text{Fe}^{3+} + \text{Cu(s)} \leftrightarrow 2\text{Fe}^{2+} + \text{Cu}^{2+}
\]

oxidizing agent  reducing agent
reduced species  oxidized species

Electrochemistry - The study of redox chemistry

Electrochemical cells: The reactants are separated from one another, and the reaction is forced to occur via the flow of electrons through an electrical circuit.

But for what purpose:
1) produce electricity (batteries; chemical energy from spontaneous redox reactions are converted to electrical work).
2) To force non-spontaneous reactions to occur by supplying an external energy source.
3) Quantitative analysis of redox active analytes
4) To study the energetics and kinetics of redox processes

Types of electrochemical experiments
1) Construction of a battery (ch 14)
2) Potentiometry (measurement of cell voltages to extract chemical information, ex. pH meter) ch 15
3) Redox titrations (ch 16)
4) Electrogravimetric analysis (depositing analyte on an electrode) – ch 17
5) Coulometry (measuring the number of electrons being transferred at constant cell voltage)- ch 17
6) Voltammetry (measuring current as a function of cell voltage, quantitative and qualitative info) – ch 17
Remind the students that they need to review the material presented in section 14.1

Electrochemical Cells

Cell voltage – A measure of the spontaneity of the redox reaction

\[ \Delta G = -nFE, \]

where \( E \) is the cell voltage, \( n \) is the number of electrons being transferred (2e-/mol Cu in the example above), and \( F \) is Faraday's constant \(-9.649 \times 10^4 \text{ C/mol}\)

Note: when the cell voltage is positive the reaction is spontaneous. The redox reaction is at equilibrium when the cell voltage is zero.

Galvanic cells: A cell that uses a spontaneous chemical reaction to generate electricity.

Ex. Fig 14.3

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(s) ↔ Cd^{2+} + 2e-</td>
<td></td>
<td>Oxidation</td>
</tr>
<tr>
<td>2AgCl(s) + 2e- ↔ 2Ag(s) + 2Cl^-</td>
<td></td>
<td>Reduction</td>
</tr>
</tbody>
</table>

Cd(s) + AgCl(s) ↔ Cd^{2+} + Ag(s) + 2Cl^-  

\( E = 0.77 \text{ V}, \) spontaneous reaction

Cathode – Electrode where reduction occurs

Anode - Electrode where oxidation occurs
Note: The two solids are separated and that the transfer of electrons must flow through the external circuit.

Example 2 of a galvactic cell

\[
\begin{align*}
\text{Cd(s)} & \leftrightarrow \text{Cd}^{2+} + 2\text{e}^- & \text{Oxidation} \\
2\text{Ag}^+ + 2\text{e}^- & \leftrightarrow 2\text{Ag(s)} & \text{Reduction} \\
\text{Cd(s)} + 2\text{Ag}^+ & \leftrightarrow \text{Cd}^{2+} + 2\text{Ag(s)}
\end{align*}
\]

If we set up this redox reaction in the same manner as the other one, no current flows through the circuit even though the energetics of the reaction is the same. Why? The reactants are no longer physically separated. The Ag\(^+\) ions can migrate to the Cd electrode and reaction between the reactants can occur directly. Electrons are not forced to flow through circuit.

We must physically separate the Ag\(^+\) from the Cd electrode!!

Still no e- flow! Why? If electrons were to flow we would have a build up of negative charge in the half-cell containing the anode and a build up of positive charge on the half-cell containing the cathode. This is energetically unfavorable!!!!!!

We need a salt bridge – a gel typically containing KCl
Describe how a salt bridge works to maintain electroneutrality
Nernst Equation

For the balance redox reaction: \( aA + bB \leftrightarrow cC + dD \)

The cell voltage is a function of the activities of the reactants and products (in an analogous manner in which \( \Delta G \) is related to \( Q \).)

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \frac{\mathcal{A}_C^{\mathcal{A}_D^c \mathcal{A}_B^d}}{\mathcal{A}_A^{\mathcal{A}_B^b}} \right) \quad \text{or at } T = 298.15 \text{ K (25 C)}
\]

\[
E = E^\circ - 0.05916 \frac{n}{\log \left( \frac{\mathcal{A}_C^{\mathcal{A}_D^c \mathcal{A}_B^d}}{\mathcal{A}_A^{\mathcal{A}_B^b}} \right)}
\]

Where \( n \) = the number of moles of electrons transferred in the balanced redox reaction.

Standard Potentials (\( E^\circ \)) – analogous to \( \Delta G^\circ \)

The cell voltage when the activities of all reactants and products are unity

Standard half cell reduction potentials (Table in back of book) –

\( E^\circ \) for \( 2H^+ + 2e^- \leftrightarrow H_2 \) is arbitrarily set to 0 V.

\[
\begin{align*}
\text{MnO}_4^- + 8H^+ + 5e^- & \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} & + 1.507 \text{ V} \\
+ \text{voltage, spontaneous at unit activities, implies } \text{Ag}^+ \text{ is a strong oxidizing} \\
\text{agent}) \\
\text{Cd}^{2+} + 2e^- & \leftrightarrow \text{Cd(s)} & -0.402 \text{ V} \\
- \text{voltage, nonspontaneous at unit activities, implies } \text{Cd}^{2+} \text{ is a weak} \\
\text{oxidizing agent})
\end{align*}
\]

Using the Nernst Equation

For example 2

\[
\begin{align*}
\text{Cd(s)} \leftrightarrow \text{Cd}^{2+} + 2e^- & \quad \text{Oxidation} \\
2\text{Ag}^+ + 2e^- & \leftrightarrow 2\text{Ag(s)} & \quad \text{Reduction} \\
\text{Cd(s)} + 2\text{Ag}^+ & \leftrightarrow \text{Cd}^{2+} + 2\text{Ag(s)}
\end{align*}
\]
\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

**The Nernst equation for a half-cell reaction is always written as a reduction!!!!**

\[ E_{\text{cell}} = \{E^{\circ}_{\text{cathode}} - (0.05916/2)\log(1/[Ag^+]^2)\} - \{E^{\circ}_{\text{anode}} - (0.05916/2)\log(1/[Cd^{2+}])\} \]

\[ = (E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}) - (0.05916/2)\log([Cd^{2+}]/[Ag^+]) \]

\[ [Cd^{2+}]/[Ag^+]^2 = Q \text{ (the reaction quotient)} \]

So in general,

\[ E = E^\circ - (0.05916/n)\log Q \]

When \( E = 0 \), we are at equilibrium. Therefore,

\[ E^\circ = (0.05916/n)\log K \text{ at 25 C} \]

Or \[ K = 10^{nE^\circ/0.05916} \text{ at 25 C} \]

Adding together two half reactions to obtain a new half reaction. To do this it is best to convert to \( \Delta G_s \)

14.22
You must determine which reactions you must to add together to obtain the reaction in question.

\[ \text{HOBr} \rightarrow \text{Br}_2(aq) \]
\[ \text{Br}_2(aq) \rightarrow \text{2Br}^-(aq) \]
\[ \text{HOBr} \rightarrow \text{2Br}^-(aq) \]

balance reaction between HOBr and Br⁻ in an acidic solution

balancing the half-cell reaction:
step 1: add H⁺ to the reactant side and water to the product side
\[ \text{HOBr} + \text{H}^+ \leftrightarrow \text{Br}^- + \text{H}_2\text{O} \]
Step 2: Stoichiometrically balance the reaction. It already is in this case!
Step 3: balance the charge by adding electrons
\[ \text{HOBr} + 2e^- + H^+ \leftrightarrow \text{Br}^- + \text{H}_2\text{O} \]

Repeat for the reactions that you must add to obtain the above rxn. When you add to half-rxns to obtain a third half-rxn, the safe thing to do is to add the \( \Delta Gs \).

\[ \begin{align*}
\text{HOBr} + \text{H}^+ + e^- &\leftrightarrow \frac{1}{2}\text{Br}_2 + \text{H}_2\text{O} & \Delta G_1 &= -F(1.584) \\
\frac{1}{2}\text{Br}_2 + e^- &\leftrightarrow \text{Br}^- & \Delta G_2 &= -F(1.098) \\
\end{align*} \]

\[ \Delta G_3 = \Delta G_1 + \Delta G_1 = -2F(E^0) \]

\[-F(1.584) + -F(1.098) = -2F(E^0) \]

\[ E^0 = \frac{1.584 + 1.098}{2} = 1.341 \text{ V} \]

14-29

You are forming a half-reaction. It is safest to add together multiply Ks (or add \( \Delta Gs \)).

\[ \begin{align*}
Pd(\text{OH})_2(s) &\leftrightarrow \text{Pd}^{2+} + 2\text{OH}^- & K_{sp} &= 3 \times 10^{-28} \\
Pd^{2+} + 2e^- &\leftrightarrow \text{Pd(s)} & K_1 &= 10^{(nE^°/0.05916)} = 8.9 \times 10^{30} \\
Pd(\text{OH})_2(s) + 2e^- &\leftrightarrow \text{Pd(s)} + 2\text{OH}^- & K &= K_{sp}K_1 \\
K &= 3 \times 10^3 \\
\log K &= -nE^°/0.05916 \\
E^° &= -(0.05916/2)\log(3 \times 10^3) = 0.103 \text{ V} \]