Electrochemistry

- Interplay between electricity and chemical reactions

- Spontaneous (voltaic)
  - Spontaneous flow of electrons
  - Provides electrical energy

- Non-spontaneous (electrolytic)
Oxidation-Reduction Reactions

- Oxidation-reduction reactions are chemical reactions in which one or more substances experience a change of oxidation number.

- An oxidation-reduction (or redox) reaction can be identified by tracking the oxidation numbers of all the elements involved in the chemical reaction.

- The transfer of electrons that occurs in a redox reaction produces energy in the form of electricity.

- In any redox reaction, both oxidation and reduction must occur.
Assigning Oxidation Numbers

- To track electrons in a redox reaction, charges are assigned to atoms by attributing shared electrons to the more electronegative species.

- Rules for assigning oxidation numbers.
Oxidizing and Reducing Agents

- An oxidizing agent (or oxidant) is a substance that makes it possible for another substance to be oxidized
- A reducing agent (or reductant) is a substance that makes it possible for another substance to be reduced

Example: Identify important features in the following reaction

\[
\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)
\]
Oxidizing and Reducing Agents

Example: Identify the elements that undergo a change in oxidation number

\[
\text{Ba}^{2+} \text{(aq)} + 2 \text{OH}^{-} \text{(aq)} + \text{H}_2\text{O}_2 \text{(aq)} + 2 \text{ClO}_2 \text{(aq)} \rightarrow \text{Ba(ClO}_2\text{)}_2 \text{(s)} + 2 \text{H}_2\text{O(l)} + \text{O}_2\text{(g)}
\]

A – Ba, O
B – O, Cl, H
C – Cl, Ba
D – O, Cl
E – Ba, H
Half-Reactions

- It is convenient to separate a redox reaction into separate oxidation and reduction processes.
- For the reaction 
  \[ \text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g) \]
  - the oxidation half-reaction is 
  - the reduction half-reaction is 

- For the oxidation process, the electrons are shown as products. For the reduction process, the electrons are shown as reactants.
Balancing Redox Reactions

There are a variety of techniques for balancing oxidation-reduction reactions. We will use the methods developed in CEM151:

- assign oxidation numbers
- identify oxidized/reduced species
- write the balanced half-reactions
- include electrons as reactant/products where appropriate
- balance the half-reactions so that the number of electrons lost in the oxidation half-reaction equals the number gained in the reduction half-reaction
- Add the half-reactions and cancel like terms
- Balance the charges by adding $H^+$ (if acidic solution) or $OH^-$ (if basic solution)
- For reaction in aqueous solution, complete the procedure by adding $H_2O$ to the side which is oxygen and hydrogen deficient
Redox Reaction in Acidic Solution I

Example: Complete and balance the redox reaction below which occurs in acidic solution

\[ \text{Cu}(s) + \text{NO}_3^-(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{NO}_2(g) \]

- assign oxidation numbers

- identify oxidized/reduced species

- write the balanced half-reactions
- include electrons as reactant/products where appropriate
Example: Balance the redox reaction $\text{Cu(s)} + \text{NO}_3^-(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{NO}_2(g)$

balance the half-reactions so that the number of electrons lost in the oxidation half-reaction equals the number gained in the reduction half-reaction

Add the half-reactions and cancel like terms
Example: Balance the redox reaction \( \text{Cu}(s) + \text{NO}_3^-(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{NO}_2(g) \)

Balance the charges by adding \( \text{H}^+ \) (if acidic solution) or \( \text{OH}^- \) (if basic solution)

For reaction in aqueous solution, complete the procedure by adding \( \text{H}_2\text{O} \) to the side which is oxygen and hydrogen deficient

the right side is deficient by 4H and 2O
Example: Complete and balance the redox reaction below which occurs in basic solution

\[ \text{Cr(OH)}_3(s) + \text{ClO}^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}_2(g) \]

- assign oxidation numbers

- identify oxidized/reduced species

- write the balanced half-reactions
- include electrons as reactant/products where appropriate
Example: Balance the redox reaction

\[ \text{Cr(OH)}_3(s) + \text{ClO}^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}_2(g) \]

balance the half-reactions so that the number of electrons lost in the oxidation half-reaction equals the number gained in the reduction half-reaction

Add the half-reactions and cancel like terms
Example: Balance the redox reaction

\[
\text{Cr(OH)}_3(s) + \text{ClO}^{-}(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}_2(g)
\]

Balance the charges by adding H\(^+\) (if acidic solution) or OH\(^-\) (if basic solution)

For reaction in aqueous solution, complete the procedure by adding H\(_2\)O to the side which is oxygen and hydrogen deficient

the right side is deficient by 4H and 2O
Redox Reactions

- Balance the following equations:
  - \( \text{As}_2\text{O}_3(s) + \text{NO}_3^- (aq) \rightarrow \text{H}_3\text{AsO}_4(aq) + \text{N}_2\text{O}_3(aq) \) (acidic solution)
  - \( \text{MnO}_4^- (aq) + \text{Br}^- (aq) \rightarrow \text{MnO}_2(s) + \text{BrO}_3^- (aq) \) (basic solution)
True/False

Which of the following statements are true?
1. If something is reduced, it is formally losing electrons.
2. A reducing agent is oxidized as it reacts
3. Oxidizing agents can convert CO into CO$_2$.
4. The oxidation number of Xe(g) is always 0.

- A – 1, 2, 4
- B – 2, 3, 4
- C – 3, 2
- D – 1, 3
- E – 2, 4
Voltaic Cells

- The energy released in a spontaneous redox reaction can be used to perform electrical work.
- Oxidation occurs at the anode.
- Reduction occurs at the cathode.
The redox reaction

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

is a spontaneous process where

The redox reaction can be carried out using a voltaic cell, where the electrons flow through an external circuit.
Zn/Cu Voltaic Cell
Summary of Voltaic Cell

- Oxidation at anode - electron source
- Reduction at cathode - electron sink
- Electrons flow spontaneously from the negative anode to the positive cathode
- The electrical circuit is completed by the movement of ions in solution

- Solution compartments are joined by a salt bridge, which provides a migration path for the electrolytes
- The anode electrode is consumed (loses mass), while the cathode electrode gains mass
For the Cu/Zn voltaic cell discussed earlier

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

where the reactants and products were ZnSO\(_4\) and CuSO\(_4\), the cell can be represented in shorthand notation by

\[ \text{Zn(s)}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu(s)} \]

The oxidation reaction appears on the left and the reduction reaction appears on the right.

The double vertical line denotes an interface for which the junction potential has been eliminated (for example, a salt bridge).
A voltaic cell is described by
Al(s)|Al^{3+}(aq)||Ni^{2+}(aq)|Ni(s)

Draw the voltaic cell and indicate
- The cathode and anode
- The balanced half reactions at the cathode and anode
- The number of electrons transferred
- The direction of electron flow
Electromotive Force

- Electrons spontaneously flow from anode to cathode in a voltaic cell because there is a potential energy difference between the two electrodes.

- The potential difference between the electrodes for a given electric charge is measured in units of volts.

- In a voltaic cell, since the potential difference between electrodes “drives” electrons from the anode to the cathode, it is called the electromotive force (or emf).
Cell Potential

- The electromotive force of a voltaic cell is called the cell potential, $E_{\text{cell}}$
- $E_{\text{cell}}$ will depend on

- $E_{\text{cell}}^0$ is the standard emf (or standard cell potential) under the conditions

- For the Zn/Cu voltaic cell
The standard cell potential, $E_{\text{cell}}^o$, is the difference between two electrode potentials.

Standard electrode potentials for a given electrode are tabulated for reduction reactions.

The standard reduction potentials $E_{\text{red}}^o$ are measured in reference to a standard hydrogen electrode (SHE), where

$$E_{\text{cell}} = E_{\text{red}}^o(\text{cathode}) - E_{\text{red}}^o(\text{anode}) = 0.0 \text{ V} - E_{\text{red}}^o(\text{anode})$$

A voltaic cell consisting of a SHE as the cathode can be used to determine $E_{\text{red}}^o$ for the anode material.
### Standard Reduction Potentials

<table>
<thead>
<tr>
<th>$E^\circ_{\text{red}}$ (V)</th>
<th>Reduction half reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2.87</td>
<td>$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^- (aq)$</td>
</tr>
<tr>
<td>+0.54</td>
<td>$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^- (aq)$</td>
</tr>
<tr>
<td>+0.34</td>
<td>$\text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu}(s)$</td>
</tr>
<tr>
<td>0.00</td>
<td>$2\text{H}^+ (aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
</tr>
<tr>
<td>-0.76</td>
<td>$\text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn}(s)$</td>
</tr>
<tr>
<td>-1.66</td>
<td>$\text{Al}^{3+} (aq) + 3e^- \rightarrow \text{Al}(s)$</td>
</tr>
<tr>
<td>-3.05</td>
<td>$\text{Li}^+ (aq) + e^- \rightarrow \text{Li}(s)$</td>
</tr>
</tbody>
</table>
Example: For the voltaic cell

\[ \text{Zn|ZnSO}_4(aq)||\text{CuSO}_4(aq)|\text{Cu} \]

\[ E^{\circ}_{\text{cell}} = +1.10 \text{ V.} \quad \text{Given } E^{\circ}_{\text{red}(\text{Zn})} = -0.76 \text{ V, calculate } E^{\circ}_{\text{red}} \text{ for the reduction of } \text{Cu}^{2+} \]

This standard reduction potential is identical to that listed in the previous table.
Standard Potentials and Stoichiometry

Example: Calculate the standard emf for a cell that employs the following reaction

\[ 2\text{Al}(s) + 3\text{I}_2(s) \rightarrow 2\text{Al}^{3+}(aq) + 6\text{I}^-(aq) \]

the standard reduction potentials are

- \( \text{Al}^{3+}(aq) \) to \( \text{Al}(s) \) \( E^\circ_{\text{red}} = -1.66 \text{ V} \)
- \( \text{I}_2(s) \) to \( 2\text{I}^-(aq) \) \( E^\circ_{\text{red}} = +0.54 \text{ V} \)

\[ E^\circ_{\text{cell}} = E^\circ_{\text{red \ (cathode)}} - E^\circ_{\text{red \ (anode)}} \]

\[ E^\circ_{\text{cell}} = +0.54 \text{ V} - (-1.66 \text{ V}) = +2.20 \text{ V} \]

A – -2.2 V
B – -1.12 V
C – 1.12 V
D – 2.2 V
E – 0 V
Standard Potentials

Of the following four half-reactions, determine which combination leads to the highest and the lowest positive emf.

1. \( \text{Ag}^+ (aq) + e^- \rightarrow \text{Ag} (s) \) \( E_{\text{red}}^o = 0.799 \)
2. \( \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \) \( E_{\text{red}}^o = 0.337 \)
3. \( \text{Ni}^{2+} (aq) + 2e^- \rightarrow \text{Ni} (s) \) \( E_{\text{red}}^o = -0.280 \)
4. \( \text{Cr}^{3+} (aq) + 3e^- \rightarrow \text{Cr} (s) \) \( E_{\text{red}}^o = -0.740 \)

In each of the two cases identify the material at the anode and the cathode.
Electrochemical cells

- Use the following reduction potentials
  - $\text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn} (s) \quad E^{\circ}_{\text{red}} = -0.76 \text{ V}$
  - $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu} (s) \quad E^{\circ}_{\text{red}} = 0.34 \text{ V}$
  - $\text{Al}^{3+} + 3e^{-} \rightarrow \text{Al} (s) \quad E^{\circ}_{\text{red}} = -1.66 \text{ V}$
  - $\text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni} (s) \quad E^{\circ}_{\text{red}} = -0.23 \text{ V}$
  - $\text{Fe}^{2+} + 2e^{-} \rightarrow \text{Fe} (s) \quad E^{\circ}_{\text{red}} = -0.44 \text{ V}$
  - $\text{Fe}^{3+} + 3e^{-} \rightarrow \text{Fe} (s) \quad E^{\circ}_{\text{red}} = -0.036 \text{ V}$
Trends in Standard Reduction Potentials

- The more positive the $E_{\text{red}}^0$ value for a half-reaction, the greater the tendency for the reactant of the half-reaction to be reduced.

- The substance with the most positive value of $E_{\text{red}}^0$ is $F_2$:
  
  $$F_2(g) + 2e^- \rightarrow 2F^-(aq) \quad E_{\text{red}}^0 = +2.87 \text{ V}$$

  - $F_2$ is the most easily reduced species and the strongest oxidizing agent.
  - $F^-$ is a weak reducing agent.

- The list of $E_{\text{red}}^0$ values provides an ordering of substance to act as oxidizing or reducing agents.
Flashlight and Alkaline Batteries

- Probably the most common commercial voltaic cell is the dry cell (or flashlight battery)

- A graphite rod serves as the cathode, and the nature of the cathode material (typically a paste) means only a small portion is electrochemically active

- An alkaline battery typically has better performance as the ammonium ion in the dry cell is replaced by KOH
Nickel-Cadmium Batteries

- The half-reactions occurring in a Ni-Cd battery are

  - Cathode: \( \text{NiO}_2 + 2\text{H}_2\text{O}^{(\ell)} + 2\text{e}^- \rightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^- (aq) \)

  - Anode: \( \text{Cd}(s) + 2\text{OH}^- (aq) \rightarrow \text{Cd(OH)}_2(s) + 2\text{e}^- \)

  - Ni is reduced, and Cd is oxidized
  - The products of the redox reaction are solids which adhere to the electrodes
  - No gases are produced in the forward or reverse reactions
Lead-Storage Battery

- A automobile battery is also rechargeable

- The solid products remain on the electrodes, and the system can be readily recharged using a generator driven by the car engine

- The cell potential is

\[ E_0 = E_{\text{red (reduction)}} - E_{\text{red (oxidation)}} \]

\[ E_0 = +1.685 - (-0.356) = +2.041 \text{ V} \]
Spontaneity of Redox Reactions

- Voltaic cells use redox reactions which occur spontaneously
- We have already discussed the relation
  
a more general relation can be written
- In general,