Electrochemistry

Study of the interchange of chemical and electrical energy

- Electron transfer reactions are called oxidation-reduction reactions or REDOX reactions.
- Electrochemical processes that result in the generation of an electric current (electricity) or can be caused by imposing an electric current.

Redox Reactions

- **OXIDATION NUMBER**: Assigned charge on an atom
- **OXIDATION**: Loss of electrons (increase in oxidation number or charge... "+")
- **REDUCTION**: Gain of electrons (decrease in oxidation number or charge... "-")

Redox Reactions

- **OXIDATION NUMBER**: Assigned charge on an atom
- **OXIDATION**: Loss of electrons (increase in oxidation number or charge... "+")
- **REDUCTION**: Gain of electrons (decrease in oxidation number or charge... "-")

Redox Reactions

**LEO THE LION GOES GER!**

Redox Reactions

**OIL RIG!**
Redox Reactions

• **OXIDIZING AGENT**: electron acceptor... species that is reduced (an agent facilitates something / ex: travel agent)

• **REDUCING AGENT**: electron donor... species that is oxidized

Placing a piece of Zn in a solution with Cu<sup>2+</sup> ions...
Make note of what is taking place at the molecular level

Redox Reactions

• Oxidation and reduction go hand in hand... need one to have the other

• Cannot have 2 oxidations or 2 reductions in the same equation

• Written as two **HALF-REACTIONS** (one for oxidation and one for reduction)

\[
2 \text{Mg}(s) + \text{O}_2(g) \rightarrow 2 \text{MgO}(s) \quad \text{Overall}
\]

\[
2 \text{Mg} \rightarrow 2 \text{Mg}^{2+} + 4 \text{e}^- \quad \text{OXIDATION}
\]

\[
\text{O}_2 + 4 \text{e}^- \rightarrow 2 \text{O}_2^- \quad \text{REDUCTION}
\]

Oxidation Numbers

**Assigned charge on an atom**

1) Elements not bonded to another different element have an oxidation number of **ZERO** (ex: Na, Fe, O<sub>2</sub>, N<sub>2</sub>)

2) In monatomic ions, oxidation number is equal to the charge on the ion (ex: Li<sup>+</sup> = +1, Fe<sup>3+</sup> = +3, P<sup>3-</sup> = -3)

3) Oxidation number of oxygen is **USUALLY** -2... in H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> it is -1

Oxidation Numbers

**Assigned charge on an atom**

4) Oxidation number of hydrogen is +1 **EXCEPT** when bonded to metals in binary compounds then it is -1 (ex: CaH<sub>2</sub>, LiH)

5) Group IA metals are always +1, IIA always +2, etc... remember transition metals vary

6) Oxidation numbers of a molecule must add up to **ZERO** or add up to the charge on a polyatomic ion

**Ex**: HCO<sub>3</sub><sup>-</sup>
Oxidation Numbers

Assigned charge on an atom

Examples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>(−4)</td>
</tr>
<tr>
<td>CO</td>
<td>(−2)</td>
</tr>
<tr>
<td>C</td>
<td>(0)</td>
</tr>
<tr>
<td>CH₄</td>
<td>(−4)</td>
</tr>
<tr>
<td>H₂</td>
<td>(0)</td>
</tr>
<tr>
<td>Cl₂</td>
<td>(0)</td>
</tr>
<tr>
<td>HCl</td>
<td>(−1)</td>
</tr>
<tr>
<td>NaCl</td>
<td>(−1)</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>(−7)</td>
</tr>
<tr>
<td>ZnO</td>
<td>(−2)</td>
</tr>
<tr>
<td>CaF₂</td>
<td>(−2)</td>
</tr>
<tr>
<td>O₂</td>
<td>(0)</td>
</tr>
<tr>
<td>O₃</td>
<td>(0)</td>
</tr>
<tr>
<td>HO₂</td>
<td>(−1)</td>
</tr>
<tr>
<td>H₂O</td>
<td>(0)</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>(−1)</td>
</tr>
<tr>
<td>F₂</td>
<td>(0)</td>
</tr>
</tbody>
</table>

Practice

• EXAMPLE:
  Identify which is being oxidized and which is being reduced in the following.

  2 Ca(s) + O₂(g) → 2 CaO(s)
  Mg(s) + 2 HCl(aq) → MgCl₂(aq) + H₂(g)
  2 Na(s) + 2 H₂O(l) → 2 NaOH(aq) + H₂(g)

Writing a Redox Reaction

1) Write the NET IONIC equation
2) Assign oxidation numbers
3) Determine what is being oxidized and reduced

• EXAMPLE: Lead foil is immersed in silver nitrate

  Pb(s) + 2 Ag⁺(aq) → Pb²⁺(aq) + 2 Ag(s)
  0 +1 +2 0

Balancing a Redox Reaction

1) Write the half reactions
2) Balance the non H⁺ and O's first
3) Use H₂O to balance the O's and use H⁺ to balance the H's
4) Use e⁻ to balance the charges
5) Get common multiple for e⁻ and multiply
6) Cancel and add up the half reactions (e⁻ must cancel as well as all like species).
   Verify # of atoms and charges are balanced
7) In basic solutions, add OH⁻ to BOTH sides for every H⁺ in final equation... make H₂O

• EXAMPLE:
  Write the balanced equation for the oxidation of Fe²⁺ to Fe³⁺ by Cr₂O₇²⁻ in acidic solution.

  Fe²⁺ → Fe³⁺
  Cr₂O₇²⁻ → Cr³⁺

  STEP #1

• EXAMPLE:
  Write the balanced equation for the oxidation of Fe²⁺ to Fe³⁺ by Cr₂O₇²⁻ in acidic solution.

  Fe²⁺ → Fe³⁺
  Cr₂O₇²⁻ → 2 Cr³⁺

  STEP #2
Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the oxidation of Fe^{2+} to Fe^{3+} by Cr_2O_7^{2-} to Cr^{3+} in acidic solution.

  \[
  \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}
  \]
  \[
  \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
  \]

  **STEP #3**

Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the oxidation of Fe^{2+} to Fe^{3+} by Cr_2O_7^{2-} to Cr^{3+} in acidic solution.

  \[
  \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}
  \]
  \[
  14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
  \]

  **STEP #3**

Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the oxidation of Fe^{2+} to Fe^{3+} by Cr_2O_7^{2-} to Cr^{3+} in acidic solution.

  \[
  \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1 \text{e}^-
  \]
  \[
  6 \text{e}^- + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
  \]

  **STEP #4**

Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the oxidation of Fe^{2+} to Fe^{3+} by Cr_2O_7^{2-} to Cr^{3+} in acidic solution.

  \[
  6 \text{Fe}^{2+} \rightarrow 6 \text{Fe}^{3+} + 6 \text{e}^-
  \]
  \[
  6 \text{e}^- + 14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
  \]

  **STEP #5**

Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the oxidation of Fe^{2+} to Fe^{3+} by Cr_2O_7^{2-} to Cr^{3+} in acidic solution.

  \[
  6 \text{Fe}^{2+} \rightarrow 6 \text{Fe}^{3+} + 6 \text{e}^-
  \]
  \[
  14 \text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}
  \]

  **STEP #6**

  Are all atoms and charges balanced? 

Balancing a Redox Reaction

• **EXAMPLE:**
  Write the balanced equation for the following reaction in **BASIC** solution:

  \[
  \text{ClO}_3^- + \text{SO}_2 \rightarrow \text{Cl}_2 + \text{SO}_4^{2-}
  \]

  Practice

• **EXAMPLES:**
  Write the balanced equation for the following reaction in **ACIDIC** solution:

  \[
  \text{MnO}_4^- + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+}
  \]

  Write the balanced equation for the following reaction in **BASIC** solution:

  \[
  \text{ClO}_3^- + \text{SO}_2 \rightarrow \text{Cl}_2 + \text{SO}_4^{2-}
  \]
**Practice**

**EXAMPLE:**
Write the balanced equation for the following reaction in BASIC solution:
\[ \text{CN}^- + \text{MnO}_4^- \rightarrow \text{CNO}_2^- + \text{MnO}_2 \]

**Electrochemical Cells**

**Galvanic (Voltaic) Cell**
Thermodynamically favorable chemical reactions (battery)

**Electrolytic Cell**
Thermodynamically unfavorable and require external e- source (current or DC power source)

**Galvanic or Voltaic Cell**
- **ANODE**: Electrode where oxidation occurs (can become smaller over time)
- **CATHODE**: Electrode where reduction occurs (can become larger over time)
- **INERT ELECTRODE**: Used when gas involved or going from ion to ion instead of solid (made of Pt or graphite)
- **SALT BRIDGE**: Used to maintain electrical neutrality in the cell (can be filled with agar or porous disk used)
- **ELECTRON FLOW**: ALWAYS through wire from ANODE to CATHODE (alphabetical order)
- **VOLTMETER**: Measures cell potential in volts

**You MUST be able to set up, label all the parts, and know what is happening in the cell!**
Galvanic or Voltaic Cell

Metal electrodes are placed in 1.0 M solutions (standard conditions) that contain ions of itself (i.e. Zn placed in solution of Zn(NO₃)₂).... Pt is used as electrode if solid metal not being used!

AN OX: Oxidation occurs at the Anode

RED CAT: Reduction occurs at the Cathode

CAHODE: Cathode is positive (voltaic cells)

ANODE: Anode is negative

Salt Bridge
Connection between electrochemical cells whose purpose is to PROVIDE IONS TO BALANCE THE CHARGE in the cell

- Maintains electrical NEUTRALITY in the cell
- Filled with a salt solution or agar (paste) such as KNO₃ so that no precipitation occurs
- Porous disk may be present instead

FAT CAT: Electrons in a voltaic cell ALWAYS flow From the Anode To the Cathode

What would happen if the salt bridge was removed?
Calculated Voltage

- Some energy is lost as heat

VOLT (V): unit of electrical potential

VOLTMETER: measures electrical potential

Some energy is lost as heat (Resistance) which makes voltmeter readings a smidge lower than actual or calculated voltage

**Galvanic or Voltaic Cell**

- Shorthand Cell Diagram (Line Notation):
  \[
  \text{Zn(s)} + \text{Cu}^{2+}(aq) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(aq)
  \]
  \( [\text{Cu}^{2+}] = 1 \text{ M} \) & \( [\text{Zn}^{2+}] = 1 \text{ M} \)

**Cell Potential**

Measure of the electromotive force or the “pull” of the electrons as they travel from anode to the cathode

- Denoted \( E_{\text{cell}} \), Emf, or called cell voltage
- \( \text{VOLT (V)} \): unit of electrical potential
- \( \text{VOLTMETER} \): measures electrical potential
- Some energy is lost as heat (Resistance) which makes voltmeter readings a smidge lower than actual or calculated voltage

**Standard Reduction Potentials**

- Always given as reduction half reactions but can be reversed (and FLIP the sign of the voltage) to get oxidation potentials
- **MOST** positive... most easily **REDUCED** (generally nonmetals)
- **LEAST** positive... most easily **OXIDIZED** (metals)
- Can also be used as an activity series with less positive metals being more active

**Cell Potential**

Measure of the electromotive force or the “pull” of the electrons as they travel from anode to the cathode

- Each half reaction has an electrical potential
- Each potential is measured against a standard... Hydrogen electrode assigned a value of 0.00 V
- Standard conditions are 1 atm, 1.0 M, and 25°C (use \( E_{\text{cell}} \) to denote)

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^\circ ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 + 2 \text{H}^+ \rightarrow 2 \text{H}_2 \text{O} )</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag} )</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{H}_2 \text{O} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{H}_2 \text{O} )</td>
<td>0.82</td>
</tr>
<tr>
<td>( \text{mg} \text{Cl}_2 + \text{e}^- \rightarrow \text{mg} + 2 \text{Cl}^- )</td>
<td>0.27</td>
</tr>
<tr>
<td>( \text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^- )</td>
<td>0.22</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} )</td>
<td>0.70</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Cu}^{2+} + 2 \text{H}_2 \text{O} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{O} + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2 \text{O} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + \text{e}^- \rightarrow \text{Zn} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{MnO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2 \text{O} )</td>
<td>0.51</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} )</td>
<td>0.22</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{H}_2 \text{O} + 2 \text{e}^- \rightarrow \text{Cu} + 4 \text{H}^+ + 2 \text{O} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{Zn} + \text{H}_2 \text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{H}_2 \text{SO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4 + 2 \text{H}_2 )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{MnO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2 \text{O} )</td>
<td>0.51</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{H}_2 \text{SO}_4 + \text{Ag} \rightarrow \text{AgSO}_4 + 2 \text{H}_2 \text{O} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{Cu} + \text{Fe}^{2+} \rightarrow \text{Cu}^{2+} + \text{Fe} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{Cd} + \text{Ni}^{2+} \rightarrow \text{Ni} + \text{Cd}^{2+} )</td>
<td>0.38</td>
</tr>
<tr>
<td>( \text{Zn} + \text{Ni}^{2+} \rightarrow \text{Ni} + \text{Zn}^{2+} )</td>
<td>0.38</td>
</tr>
</tbody>
</table>

**Shorthand Cell Diagram (Line Notation):**

- **Zn(s) | Zn^{2+}(1 M) || Cu^{2+}(1 M) | Cu(s)**

- **Phase boundary**
- **Salt bridge**

ANOGE written first followed by CATHODE!!
Standard Reduction Potentials

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ$ (V)</th>
<th>Half-Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$IO_3^- + 6 H^+ + 5e^- \rightarrow \frac{1}{2} I_2 + 3 H_2O$</td>
<td>-1.20</td>
<td>$Cu^2+ + 2 e^- \rightarrow Cu$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$Fe^3+ + 3 e^- \rightarrow Fe$</td>
<td>-0.77</td>
<td>$Cr^3+ + 3 e^- \rightarrow Cr$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$Br_2 + 2 e^- \rightarrow 2 Br^-$</td>
<td>-1.07</td>
<td>$Zn^2+ + 2 e^- \rightarrow Zn$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$VO_2^+ + 2 H^+ + e^- \rightarrow VO^2+ + H_2O$</td>
<td>-1.00</td>
<td>$ClO_2^- + e^- \rightarrow ClO_2^-$</td>
<td>-0.95</td>
</tr>
<tr>
<td>$2 Hg^2+ + 2 e^- \rightarrow 2 Hg$</td>
<td>-0.85</td>
<td>$H_2 + 2 e^- \rightarrow 2 H^-$</td>
<td>-2.23</td>
</tr>
<tr>
<td>$La^3+ + 3 e^- \rightarrow La$</td>
<td>-0.86</td>
<td>$Al^3+ + 3 e^- \rightarrow Al$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$H_2O_2 + 2 e^- \rightarrow 2 H^+ + 2 OH^-$</td>
<td>0.83</td>
<td>$MnO_4^- + e^- \rightarrow MnO_4^2-$</td>
<td>0.56</td>
</tr>
<tr>
<td>$Ca^2+ + 2 e^- \rightarrow Ca$</td>
<td>-2.37</td>
<td>$K^+ + e^- \rightarrow K^-$</td>
<td>-2.92</td>
</tr>
<tr>
<td>$Cu^2+ + e^- \rightarrow Cu$</td>
<td>-0.85</td>
<td>$Ag^+ + e^- \rightarrow Ag$</td>
<td>0.80</td>
</tr>
<tr>
<td>$2 Hg + 2 e^- \rightarrow 2 Hg^2+$</td>
<td>-1.07</td>
<td>$I_2 + 2 e^- \rightarrow 2 I^-$</td>
<td>-0.53</td>
</tr>
<tr>
<td>$La^3+ + 3 e^- \rightarrow La$</td>
<td>-1.18</td>
<td>$NO_3^- + 4 H^+ + 3 e^- \rightarrow NO + 2 H_2O$</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Calculating Cell Potential

$E^\circ_{cell} = E^\circ_{oxidation} + E^\circ_{reduction}$

Metal with the MORE POSITIVE reduction potential gets to be REDUCED when setting up a voltaic cell if no reaction is given!!

1) Decide which element is oxidized and which is reduced using reduction potentials (more positive gets to be reduced if no reaction is given)

2) Write both equations with voltages... REVERSE the equation that will be oxidized and FLIP the sign of the voltage

3) Balance the half-reactions... DO NOT MULTIPLY POTENTIALS BY A COEFFICIENT (because it's a ratio)

4) Add reactions and voltages together

Calculating Cell Potential

**EXAMPLE:**

Consider the galvanic cell based on the reaction:

$Al^3+(aq) + Mg(s) \rightarrow Al(s) + Mg^2+(aq)$

Give the balanced cell reaction, calculate $E^\circ_{cell}$, and write the shorthand diagram for the cell.

**EXAMPLE:**

Consider the galvanic cell based on the reaction:

$Ag^+(aq) + Zn(s) \rightarrow Ag(s) + Zn^{2+}(aq)$

Give the balanced cell reaction, calculate $E^\circ_{cell}$, and draw a diagram of the cell and label completely.
Favorability

\[ +E_{\text{cell}}^\circ = \text{Thermodynamically favorable} \]

\[ -E_{\text{cell}}^\circ = \text{Thermodynamically unfavorable} \]

\[ E_{\text{cell}}^\circ = 0...\text{Equilibrium (DEAD BATTERY)} \]

\[ \Delta G^\circ = -nFE^\circ \]

\( n \) = \# of moles (# e- transferred in BALANCED equation)

\( F \) = 96,485 coulombs/mol (Faraday’s constant)

\( E^\circ \) = Standard reaction potential (V... same as J/C)

\[ \text{EXAMPLE:} \]

Calculate the \( \Delta G \) value for the reaction below under standard conditions:

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

\( E^\circ = +1.56 \text{V} \)

The \# of e- transferred = \# of moles!!

Applications of Voltaic Cells

• Lead-Storage Batteries (car)
• Dry Cell Batteries (use paste)
• Fuel Cells (reactants continuously supplied.. Spacecraft)

Nonstandard Conditions

• Voltaic cells at NONstandard conditions follow LE CHATELIER’S PRINCIPLE when \[ \] is changed

• Increase in \[ \] of REACTANT favors the FORWARD

• Increase in \[ \] of PRODUCT favors the REVERSE

• EXAMPLE:

For the reaction below, predict whether \( E_{\text{cell}} \) is larger or smaller than \( E_{\text{cell}}^\circ \) for the following:

a) \([\text{Al}^{3+}] = 2.0 \text{ M}, [\text{Mn}^{2+}] = 1.0 \text{ M} \]

b) \([\text{Al}^{3+}] = 1.0 \text{ M}, [\text{Mn}^{2+}] = 3.0 \text{ M} \]

\[ 2 \text{Al(s)} + 3 \text{ Mn}^{2+}(aq) \rightarrow 2 \text{Al}^{3+}(aq) + 3 \text{ Mn(s)} \]

Nonstandard Conditions

• NERNST EQUATION (at 298 K):

\[ E = E^\circ - \frac{0.0592}{n} \log Q \]

\( n \) = \# of electrons exchange in BALANCED rxn

\( Q = \frac{[\text{Products}]^n}{[\text{Reactants}]^n} \)

\( E \) = Energy produced by the reaction
Nonstandard Conditions

• EXAMPLE:
  Calculate the cell potential at 298 K generated by the reaction below at the following conditions:
  \[ [\text{Cr}_2\text{O}_7^{2-}] = 2.0 \, \text{M}, \quad [\text{H}^+] = 1.0 \, \text{M}, \quad [\text{I}^-] = 1.0 \, \text{M}, \quad \text{and} \quad [\text{Cr}^{3+}] = 1.0 \times 10^{-5} \, \text{M}. \]

  \[
  \text{Cr}_2\text{O}_7^{2-}(aq) + 14 \, \text{H}^+(aq) + 6 \, \text{I}^-(aq) \rightarrow 2 \, \text{Cr}^{3+}(aq) + 3 \, \text{I}_2(s) + 7 \, \text{H}_2\text{O}(l)
  \]

Nonstandard Conditions

• EXAMPLE:
  If the voltage of the cell below is 0.45 V at 25°C when \([\text{Zn}^{2+}] = 1.0 \, \text{M}\) and \(P_{\text{H}_2} = 1.0 \, \text{atm}\), what is the concentration of \(\text{H}^+\)?

  \[
  \text{Zn}(s) + 2 \, \text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)
  \]

  Be careful with the math!

Nonstandard Conditions

• EXAMPLE:
  Consider the galvanic cell based on the reaction:
  \[
  \text{Ag}^+(aq) + \text{Zn}(s) \rightarrow \text{Ag}(s) + \text{Zn}^{2+}(aq) \quad E^\circ = 1.56 \, \text{V}
  \]

  If 2.00 g of NaI(s) are added to each half-cell, what happens to the cell voltage? Explain.

Electrolysis

Application of electric current to bring about chemical change

2 \, \text{H}_2\text{O}(aq) + \text{energy} \rightarrow 2 \, \text{H}_2(g) + \text{O}_2(g)

Electrolytic cells are thermo. unfavored!

Electrolysis

Application of electric current to bring about chemical change

Important differences between Voltaic and Electrolytic Cells:

1) Electrolytic requires external energy source
2) Electrolytic cell occurs in a SINGLE container
3) Voltaic IS a battery... Electrolytic needs a battery
4) AN OX / RED CAT still apply for electrolytic but the charge is reversed (cathode = "-" / anode = "+")
5) Electrolytic usually use inert electrodes (Pt)

Electrolysis Potential

If WATER is present with an ionic compound in the electrolytic cell:

• Compare the REDUCTION potential of the cation with that of water... More positive is the one that occurs

• Compare the OXIDATION potential of the anion with that of water... More positive is the one that occurs

If just a molten ionic compound is present in the electrolytic cell... cation is reduced and anion is oxidized!
Electrolysis Potential

• EXAMPLE:
An electrolytic cell is created from a solution of nickel (II) chloride in water. Determine the potential for the cell.

\[ \text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni(s)} \quad E^\circ = -0.25 \text{ V} \]
\[ 2 \text{H}_2\text{O(l)} + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^- \quad E^\circ = -0.83 \]

Ni is more positive… occurs!

Electrolysis Potential

• EXAMPLE:
An electrolytic cell is created from a solution of nickel (II) chloride in water. Determine the potential for the cell.

\[ 2 \text{Cl}^- \rightarrow \text{Cl}_2(g) + 2 \text{e}^- \quad E^\circ = -1.36 \text{ V} \]
\[ 2 \text{H}_2\text{O(l)} \rightarrow \text{O}_2(g) + 4 \text{H}^+ + 4 \text{e}^- \quad E^\circ = -1.23 \]

H\(_2\)O is more positive… occurs!

Electrolysis Potential

• EXAMPLE:
An electrolytic cell is created from a solution of nickel (II) chloride in water. Determine the potential for the cell.

Compare reduction potentials of cation and water first!

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Ni is more positive… occurs!

Electrolysis Potential

\[ E = -0.25 + -1.23 \text{ V} \]
\[ -1.48 \text{ V} \]

Electroplating

Use of electrolysis to deposit a thin layer of one metal on another to improve its look or prevent corrosion

• Three types of questions about this:
1) How many grams of a metal could be plated out?
2) How long would it take to plate out a given mass?
3) What is the average current?

Electroplating

Use of electrolysis to deposit a thin layer of one metal on another to improve its look or prevent corrosion

\[ I = \frac{q}{t} \]

1 Amp = 1 C/s
96,485 C/mol e-

I = current (amperes, A)
qu = charge (coulombs, C)
t = time (sec)
**Electroplating**

Use of electrolysis to deposit a thin layer of one metal on another to improve its look or prevent corrosion.

**To find # of grams plated out:**

- Use stoich to get time to seconds and use the current (C/s) to get charge.
- Use 1 mol e⁻ / 96,485 C to get to amount of e⁻ involved.
- Use half-reaction of metal to figure out # moles of the metal are plated out for certain # moles of e⁻.
- Get moles to grams.

**EXAMPLE:**

How many minutes must a current of 5.00 A be applied to a solution of Ag⁺ to produce 10.5 g of silver metal?

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

**Use This!**

**Practice**

- **EXAMPLE:**
  
  How much Ca will be produced in an electrolytic cell of molten CaCl₂ if a current of 0.452 A is passed through the cell for 1.5 hours?

  \[ \text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{Ca(s)} \]