Chapter 13
Electrochemistry and Cell Voltage

• 13-1 The Gibbs Function and Cell Voltage
• 13-2 Half Cell Potentials
• 13-3 Oxidizing and Reducing Agents
• 13-4 Concentrations and the Nernst Equations
• 13-5 Equilibrium Constants from Electrochemistry
• 13-6 (Skip) Batteries and Fuel Cells
• 13-7 (Skip) Corrosion and Its Prevention
Chapter 13
Electrochemistry and Cell Voltage

• Important Chapter - ties together several concepts from previous Chapters
  – Oxidation-Reduction
  – Electrochemical Cells
  – Acid-Base
  – Solubility
  – Equilibrium constants

• Practical Importance
  – Energy storage – batteries
  – Energy conversion – solar cells
  – Chemical conversion
    • E.g., printed circuits – metal deposition
    • Corrosion
    • Corrosion prevention
The Gibbs Function and Cell Voltage

\[ e^- \text{ flow } \rightarrow \]

Anode

(-)

Oxidation

Cathode

(+)

Reduction

\[ Q = \text{charge} \]

There exists “potential” or potential difference, called \( \Delta E \), between the cells.
For a **Galvanic Cell**, a spontaneous reaction takes place.

For the Galvanic cell the cell performs electrical work on the surroundings (acts as a battery)

For an **Electrolytic Cell**, a non-spontaneous reaction takes place.

For the electrolytic cell, the cell performs electrical work on the system
\[ W_{\text{elec}} = - Q \Delta E \]

<table>
<thead>
<tr>
<th>Type Cell</th>
<th>( \Delta E )</th>
<th>( W_{\text{elec}} )</th>
<th>Performs work:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanic</td>
<td></td>
<td></td>
<td>on surroundings</td>
</tr>
<tr>
<td>Electrolytic</td>
<td></td>
<td></td>
<td>on system</td>
</tr>
</tbody>
</table>
\[ W_{\text{elec}} = - Q \Delta E \]

\( W \) units is Joules \quad \Delta \mathcal{E} \) units is Joules/coulomb

recall \( Q = I \times t \)

Substituting gives

**Common unit for** \( W_{\text{elec}} \)

1 kilowatt-hour = \( 3.6 \times 10^6 \) Joules
Consider a Galvanic Cell (recall that this is a spontaneous reaction)

Let’s related $\Delta G$ (The Gibbs Function or Gibbs free energy) to $W_{\text{elec}}$

$$\Delta G = W_{\text{elec, max}} \text{ (at constant } T,P)$$

Max. means theoretical max, some energy is lost as heat

Remember Faradays constant?

$$F = 96,485 \text{ coulombs/mole electrons}$$

If $n$ moles of electrons pass through our Galvanic Cell

$$\Delta G = \text{ (at constant } T,P)$$
Standard States and Cell Voltages

Standard States usually at 25°C, all reactants and products at standard states.

Example 13-2 and Exercise 13-2 give a straightforward example of calculating $\Delta G^\circ$ for a chemical reaction in a cell

TRY THEM
<table>
<thead>
<tr>
<th>Term</th>
<th>Oxidation Number Change</th>
<th>Electron Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>Increase</td>
<td>Loss of Electrons</td>
</tr>
<tr>
<td>Reduction</td>
<td>Decrease</td>
<td>Gain of Electrons</td>
</tr>
<tr>
<td>Oxidizing Agent, does the oxidizing <strong>and</strong> becomes reduced</td>
<td>Decrease</td>
<td>Picks Up electrons</td>
</tr>
<tr>
<td>Reducing Agent, does the reducing <strong>and</strong> becomes oxidized</td>
<td>Increase</td>
<td>Supplies Electrons</td>
</tr>
<tr>
<td>Substance Oxidized</td>
<td>Increase</td>
<td>Loses Electrons</td>
</tr>
<tr>
<td>Substance Reduced</td>
<td>Decrease</td>
<td>Gains Electrons</td>
</tr>
</tbody>
</table>
$\Delta \varepsilon^\circ = 0.602 \text{ V}$
13-2 Half Cell Potentials

This section introduces **Standard half cell reduction potentials**

Tables that list half cell reactions as **reductions**. (This table from 3rd Ed OFB is slightly different than 4th edition)

**Table 13–1**

<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential $\varepsilon^\circ$(V)</th>
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</thead>
<tbody>
<tr>
<td>F$_2$ + 2 e$^-$ → 2F$^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>Au$^{3+}$ + 3 e$^-$ → Au</td>
<td>1.42</td>
</tr>
<tr>
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</tr>
<tr>
<td>Br$_2$ + 2 e$^-$ → 2 Br$^-$</td>
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</tr>
<tr>
<td>Hg$^{2+}$ + 2 e$^-$ → Hg</td>
<td>0.851</td>
</tr>
<tr>
<td>Ag$^+$ + e$^-$ → Ag</td>
<td>0.800</td>
</tr>
<tr>
<td>I$_2$ + 2 e$^-$ → 2 I$^-$</td>
<td>0.535</td>
</tr>
<tr>
<td>Cu$^{2+}$ + 2 e$^-$ → Cu</td>
<td>0.340</td>
</tr>
<tr>
<td>2 H$^+$ + 2 e$^-$ → H$_2$</td>
<td>0</td>
</tr>
<tr>
<td>Pb$^{2+}$ + 2 e$^-$ → Pb</td>
<td>-0.126</td>
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</tr>
<tr>
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<td>-0.409</td>
</tr>
<tr>
<td>Cr$^{3+}$ + 3 e$^-$ → Cr</td>
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<td>Li$^+$ + e$^-$ → Li</td>
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</table>
Standard Reduction potentials $E^\circ$

$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni (s)} \quad -0.257 \text{ Volts}$

$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu (s)} \quad +0.345 \text{ Volts}$

Now if we combine these as two separate cells (as we did in chapter 12)

$\text{Cu}^{2+}$ reduction potential is more positive (+0.34) therefore it is reduced (cathode) and Ni is oxidized (anode)

*Notice that we want the opposite of the Nickel reduction potential, therefore the minus sign*
By international convention

\[ 2H^+ + 2e^- \rightarrow H_2 (g) \]

\[ E = 0.0 \text{ volts} \]

### Table 13-1
Some Standard Reduction Potentials in Aqueous Solution at 25°C

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<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential ( E^\circ ) (V)</th>
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</thead>
<tbody>
<tr>
<td>Strongest oxidizing agent</td>
<td></td>
</tr>
<tr>
<td>( \text{F}_2 + 2e^- \rightarrow 2\text{F}^- )</td>
<td>2.87</td>
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<td>_pb{}^{2+} + 2e^- \rightarrow \text{Pb}</td>
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7/5/2003 OFB Chapter 13
$$\Delta E^\circ = E^\circ \text{ (cathode)} - E^\circ \text{ (anode)}$$

Note: The number of electrons appearing in half-equations do not figure in to computation of the potential difference of a cell

Why?

$E^\circ$ is a ratio

Units are $\frac{\text{Joules}}{\text{Coulomb}}$
Chapter 13
Electrochemistry and Cell Voltage

• Typical problem (Chapter 13 #10 end of chapter)
A Galvanic cell is constructed in which at Pt|Fe$^{2+}$, Fe$^{3+}$ half cell is connected to a Cd$^{2+}$|Cd half cell.
(a) By referring to Appendix E, write balanced chemical equations for the half reaction at the anode and the cathode and for the overall reaction
(b) Calculate the cell voltage, assuming that all reactions and products are in standard state at 298.15°K.
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Look up **Reduction** Potentials in Appendix E

For Fe$^{3+}$ to Fe$^{2+}$ and Cd$^{2+}$ to Cd

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

Need to balance electrons and stoichiometry
A Galvanic cell is constructed in which at Pt|Fe$^{2+}$, Fe$^{3+}$ half cell is connected to a Cd$^{2+}$|Cd half cell.

(b) Calculate the cell voltage, assuming that all reactions and products are in standard state at 298.15°K.

Fe$^{3+}$ reduction potential is more positive (+0.771) therefore it is **reduced** (cathode) and Cd (-0.403) is **oxidized** (anode)

Notice that the numbers of electrons appearing in half-equations do not figure in the computation of the potential difference of a cell
# Oxidizing and Reducing Agents

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Some Standard Reduction Potentials in Aqueous Solution at 25°C

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• Good oxidizing Agent
  – More positive on the Reduction Potential scale

\[
O_2 \, + \, 4H^+ \, + \, 4e^- \, \rightarrow \, 2H_2O
\]

\[E^o = +1.229V\]

• Even better oxidizing agent

\[
O_3 \, (g) \, + \, 2H^+ \, + \, 2e^- \, \rightarrow \, O_2 \, + \, 2H_2O
\]

\[E^o = +2.07V\]

Ozone is a great bleach for pulp

And sterilizing agent for water to remove algae and organic impurities

Peroxides are good oxidizing agents too (Clorox, e.g., H₂O₂ \[E^o = +1.776V\])
In general, Good **Reducing Agents** (undergo Oxidation, lose electrons) and are to the left of the periodic table

\[ \text{reduction potential } E^\circ < 0 \]

(e.g., \(\text{Li} \rightarrow \text{Li}^+ + e^-\))

In general, Good **Oxidizing agents** (undergo Reduction, gain electrons) and are to the right of the periodic table

\[ \text{reduction potential } E^\circ > 0 \]

(e.g., \(\text{F}_2 + 2e^- \rightarrow 2\text{F}^-\))
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<thead>
<tr>
<th>Strength of oxidizing agent</th>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential $\mathcal{E}^\circ$(V)</th>
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Figure 13-5
Example 13-5

(a) Determine whether 1.00 M H₃PO₃ (aq) and 1.00 M SO₂ (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

(b) Determine which is the stronger reducing agent under these conditions. Refer to 13-5 for necessary data.
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(b) Determine which is the stronger reducing agent under these conditions. Refer to 13-5 for necessary data.

This is a disproportionation problem, write to get both H₃PO₃ on the left and then add and calculated ΔE.

\[
\begin{align*}
H₃PO₃ + 2H^+ + 2e^- &\rightarrow H₃PO₂ + H₂O \\
H₃PO₃ + H₂O &\rightarrow H₃PO₄ + 2H^+ + 2e-
\end{align*}
\]
Example 13-5

(a) Determine whether 1.00 M \( \text{H}_3\text{PO}_3 \) (aq) and 1.00 M \( \text{SO}_2 \) (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

Only two half reactions involving \( \text{H}_3\text{PO}_3 \)

\[
\text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \quad \text{E}= (-0.499) \text{ V} \\
\text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \quad \text{E}= (-0.276) \text{ V}
\]

This is disproportionation, write to get both \( \text{H}_3\text{PO}_3 \) on the left and then add and calculated \( \Delta \text{E} \)

\[
\text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \quad \text{Reduction} \\
\text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^- \quad \text{Oxidation}
\]
Disproportionation is

\[ 2 \text{H}_3\text{PO}_3 \rightarrow \text{H}_3\text{PO}_2 + \text{H}_3\text{PO}_4 \]

\[ \Delta \mathcal{E} = \mathcal{E} \text{ (cathode)} - \mathcal{E} \text{ (anode)} \]

\[ = -0.499 - (-0.276) = -0.223 \therefore \text{stable} \]

Why stable?

Recall

For an **Electrolytic Cell**, a non-spontaneous reaction takes place.

For the electrolytic cell, the cell performs electrical work on the system.
Example 13-5

(a) Determine whether 1.00 M H$_3$PO$_3$ (aq) and 1.00 M SO$_2$ (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

Only two half reactions involving SO$_2$

\[
2\text{SO}_2 + 2\text{H}^+ + 4\text{e}^- \rightarrow \text{S}_2\text{O}_3^{\text{-2}} + \text{H}_2\text{O}
\]

\[
\text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}
\]

Disproportionation of SO$_2$

Rewrite to get both SO$_2$ on the left, balance electrons and stoichiometry and add
Example 13-5

(a) Determine whether 1.00 M $\text{H}_3\text{PO}_3$ (aq) and 1.00 M $\text{SO}_2$ (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

Disproportionation of $\text{SO}_2$

$$4 \text{SO}_2 + 3 \text{H}_2\text{O} \rightarrow 2 \text{HSO}_4^- + \text{S}_2\text{O}_3^{2-} + 4\text{H}^+$$

$$\Delta \mathcal{E} = \mathcal{E} (\text{cathode}) – \mathcal{E} (\text{anode})$$

$$= 0.40 – (+ 0.172) = +0.228 \therefore \text{unstable}$$

Why unstable? It’s a spontaneous reaction.

Recall

For a **Galvanic Cell**, a spontaneous reaction takes place.

For the Galvanic cell the cell performs electrical work on the surroundings (acts as a battery)
Example 13-5

(a) Determine whether 1.00 M H₃PO₃ (aq) and 1.00 M SO₂ (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

\[ \text{H}_3\text{PO}_3 \text{ is stable} \]
\[ \text{(non-spontaneous disproportionation)} \]

and

\[ \text{SO}_2 \text{ is unstable} \]
\[ \text{(spontaneous disproportionation)} \]

(b) Determine which is the stronger reducing agent under these conditions. Refer to 13-5 for necessary data
Example 13-5

(a) Determine whether 1.00 M \( \text{H}_3\text{PO}_3 \) (aq) and 1.00 M \( \text{SO}_2 \) (aq) are stable with respect to disproportionation in acidic solution (pH 0 at 25°C).

(b) Determine which is the stronger reducing agent under these conditions. Refer to 13-5 for necessary data.

Only two half reactions involving \( \text{H}_3\text{PO}_3 \)

\[
\text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \quad \text{E}= (0.499) \text{ V}
\]

\[
\text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \quad \text{E}= (0.276) \text{ V}
\]

Only two half reactions involving \( \text{SO}_2 \)

\[
2\text{SO}_2 + 2\text{H}^+ + 4\text{e}^- \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \quad \text{E}= +0.40 \text{ V}
\]

\[
\text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O} \quad \text{E}= +0.172 \text{ V}
\]

Which is the most negative?
13-4 Concentration Effects and the Nernst Equation

- For Electrochemical Cells which are NOT at standard states (1M or 1 atm)
- From Chapter 11

  - Where Q is the reaction quotient

- From Chapter 13

Can substitute \(-nF \Delta E^\circ\) for \(\Delta G^\circ\) and \(-nF \Delta E\) for \(\Delta G\), and rearranging, becomes the Nernst Equation
If Temp. at 25C and
R = 8.3 JK\(^{-1}\)mol\(^{-1}\) and
F = 96,485 C mol\(^{-1}\) and use
J/C = V,
then the equation becomes

\[ \text{Nernst Equation} \]
Example 13-6

The cell

\[ \text{Zn} \mid \text{Zn}^{2+} \ || \ \text{MnO}_4^- \mid \text{Mn}^{2+} \mid \text{Pt} \]

Anode (oxidation) | cathode (reduction)

(the same cell used in Example 3-3) is setup at 298.15 K with the following non-standard concentrations: \([\text{H}^+] = 0.010\text{M}\) (i.e., acidic \(\text{pH}=2\)), \([\text{MnO}_4^-] = 0.12\text{M}\), \([\text{Mn}^{2+}] = 0.0010\text{M}\), and \([\text{Zn}^{2+}] = 0.015\text{M}\). Calculate the cell voltage.

This is a Nernst equation problem

1. Balanced the two half reactions
2. Determined overall \# electrons transferred
3. Calculate \(\Delta E^\circ\) for standard conditions (1M)
4. Using the Nernst equation, use \(\Delta E^\circ\) and substitute the non-standard concentrations and solve.
This is a Nernst equation problem

1. Balanced the two half reactions and determined overall # electrons transferred

2. Calculate $\Delta E^\circ$ for standard conditions (1M)

3. Using the Nernst equation, use $\Delta E^\circ$ and substitute the non-standard concentrations and solve.
1. Balanced the two half reactions and determine # electrons transferred

\[
\text{Zn} | \text{Zn}^{2+} \ || \ \text{MnO}_4^- | \text{Mn}^{2+} | \text{Pt}
\]

\text{Anode (oxidation)} | \text{cathode (reduction)}

\text{Cathode (Reduction)}

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

\text{Anode (Oxidation)}

\[
\text{Zn} \rightarrow \text{Zn}^{2+}
\]
Overall reaction is

\[ 2 \text{MnO}_4^{-1} + 5 \text{Zn} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5 \text{Zn}^{2+} + 8 \text{H}_2\text{O} \]

This is a Nernst equation problem

1. Balanced the two half reactions and determined overall # electrons transferred

2. Calculate \( \Delta E^\circ \) for standard conditions (1M)

Next calculate \( \Delta E^\circ \) (look-up in tables)
This is a Nernst equation problem

1. Balanced the two half reactions and determined overall # electrons transferred

2. Calculate $\Delta E^\circ$ for standard conditions (1M)

3. Using the Nernst equation, use $\Delta E^\circ$ and substitute the non-standard concentrations and solve.

Overall reaction is

$$2 \text{MnO}_4^{-1} + 5 \text{Zn} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5 \text{Zn}^{2+} + 8 \text{H}_2\text{O}$$
\[ \Delta E = \Delta E^* - \frac{0.0592 \ V}{n} \log_{10} Q \]

\[ Q = \frac{[Mn^{2+}]^2[Zn^{2+}]^5}{[MnO_4^{-1}]^2[H^+]^{16}} \]

\[ \Delta E = 2.25V - \frac{0.0592 \ V}{10} \log_{10} \frac{[Mn^{2+}]^2[Zn^{2+}]^5}{[MnO_4^{-1}]^2[H^+]^{16}} \]

\[ \Delta E = 2.25V - \frac{0.0592 \ V}{10} \log_{10} \frac{[10^{-3}]^2[1.5\times10^{-2}]^5}{[0.12]^2[0.01]^{16}} \]
**Review  Example 13-6**

The cell

\[
\text{Zn} | \text{Zn}^{2+} || \text{MnO}_4^- | \text{Mn}^{2+} | \text{Pt}
\]

(the same cell used in Example 3-3) is setup at 298.15 K with the following non-standard concentrations: \([H^+] = 0.010\text{M} \) (i.e., acidic \( \text{pH}=2 \)), \([\text{MnO}_4^-] = 0.12\text{M} \), \([\text{Mn}^{2+}] = 0.0010\text{M} \), and \([\text{Zn}^{2+}] = 0.015\text{M} \). Calculate the cell voltage.

\[
\Delta E = \Delta E^o - \frac{0.0592V}{n} \log_{10} Q
\]

\[
\Delta E = 2.25V - \frac{0.0592V}{10} \log_{10} (5.3 \times 10^{18})
\]

\[
\Delta E = 2.16 \text{ Volts (Cell voltage)}
\]
Thus far we have used the Nernst equation to calculate the potential difference in a cell.

If given a voltage for a cell, we can calculate an \([X]\) or unknown concentration given the concentrations of the other species

$$
\Delta E = \Delta E^\circ - \frac{0.0592 V}{n} \log_{10} Q
$$

Rearrange the Nernst Equation
\[ \log_{10} Q = \frac{n}{0.0592V} [\Delta E^\circ - \Delta E] \]

Q is the reaction quotient

e.g. for the general reaction,

\[ a \, A + b \, B \rightarrow c \, C + d \, D \]

\[ Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]
• Try example 13-7, and its exercise
  – Practice in finding an unknown concentration in a cell

• Ph Meters
  – Are H\(^+\) ion specific selective electrodes that determine \([H^+]\)
13-5 Equilibrium Constants from Electrochemistry

Previously

\[
\Delta E = \Delta E^\circ - \left( \frac{RT}{nF} \right) \ln Q
\]

If at Temp. = 25°C or standard temperature and a reaction is at equilibrium (Q=K), after rearrangement this becomes

We can now use cell reactions to find Equilibrium constant for Redox reactions, which are difficult to determine directly.
If Temp. at 25C and

$R = 8.3 \text{ JK}^{-1}\text{mol}^{-1}$ and

$F = 96,485 \text{ C mol}^{-1}$ and use

$\frac{J}{C} = V$

then the equation becomes
Example 13-8

Calculate the equilibrium constant of the Redox reaction

\[ 2 \text{MnO}_4^- + 5 \text{Zn} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5 \text{Zn}^{2+} + 8\text{H}_2\text{O} \]

At 25C using the standard potential difference established in Example 13-3

The cell

\[ \text{Zn} | \text{Zn}^{2+} || \text{MnO}_4^- | \text{Mn}^{2+} | \text{Pt} \]

Anode (oxidation) | cathode (reduction)

\[ \Delta E^\circ = 2.27 \text{ volts} \]

\[ N = 10 \text{ electrons} \]
An enormous equilibrium constant, which means this reaction equilibrium lies to the right.

$$2 \text{MnO}_4^{-1} + 5 \text{Zn} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5 \text{Zn}^{2+} + 8 \text{H}_2\text{O}$$

Permanganate is an extremely strong oxidizing agent and Zinc is an extremely strong reducing agent.
Permanganate is an extremely strong oxidizing agent and Zinc is an extremely strong reducing agent

\[
K = \frac{[Mn^{2+}]^2[Zn^{2+}]^5}{[MnO_4^{-1}]^2[H^+]}^{16} = \frac{10^{380}}{1}
\]
• Electrolytic Cells can also be used to measure
  – Acidity constants
  – Basicity constants
  – Solubility product constants

\[
\text{AgCl (s) excess} \rightarrow \text{Ag}^{+1} + \text{Cl}^{-1}
\]

To determine \(K_{\text{sp}}\), just find the [Ag\(^{+1}\)] in an electrolytic cell containing a known amount of [Cl\(^{-1}\)]
Example 13-9

A galvanic cell consists of a standard hydrogen half-cell (with platinum electrode) operating as the anode, and a silver half-cell:

\[ \text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{H}^+ (1 \text{ M}) | \text{Ag}^+ | \text{Ag} \]

The Ag\(^+\) (aq) in the cathode compartment is in equilibrium with some solid AgCl and Cl\(^-\) (aq); the concentration of the Cl\(^-\) (aq) is 0.00100 M. The measured cell voltage is \( \Delta E = 0.398 \text{V} \). Calculate the silver-ion concentration in the cell and the \( K_{sp} \) of silver chloride at 25°C.
\[ \text{Pt|H}_2 (1 \text{ atm})|\text{H}^+ (1\text{M})||\text{Ag}^+|\text{Ag} \]

\[ \log_{10} Q = \frac{n}{0.0592V} \left[ \Delta E^\circ - \Delta E \right] \]
\[
\log_{10} Q = \frac{2}{0.0592V} \left[ \Delta \mathcal{E}^\circ - 0.397 \right]
\]

Pt|H$_2$ (1 atm)|H$^+$ (1M)||Ag$^+$|Ag
Overall reaction

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

\[ Q = \frac{[H^+]^2[\text{Ag}]^2}{[\text{Ag}^+]^2 \text{P}_{\text{H}_2}} \]

For [H+] Given:

\[ Q = \frac{[1]^2 \cdot 1}{[\text{Ag}^+]^2 \cdot 1} = 4 \times 10^{13} \]

For [Ag+] Given:

\[ Q = \frac{1}{[\text{Ag}^+]^2} = 4 \times 10^{13} \]

\[ [\text{Ag}^+] = 1.6 \times 10^{-7} \]

\[ K_{sp}^{\text{AgCl}} = [\text{Ag}^+][\text{Cl}^-] \]

\[ K_{sp}^{\text{AgCl}} = [1.6 \times 10^{-7}][1 \times 10^{-3}] \]

\[ K_{sp}^{\text{AgCl}} = 1.6 \times 10^{-10} \]
Chapter 13 Summary

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\[ \Delta G = - Q \Delta \mathcal{E} = -n \ F \Delta \mathcal{E} \]

(at constant T,P)

\( \Delta G = \) change in Gibbs Energy  
\( Q = \) charge  
\( \Delta \mathcal{E} = \) potential difference 
\( N = \# \) electrons transferred  
\( F = \) Faraday constant

\[ \Delta \mathcal{E}^\circ = \mathcal{E}^\circ \text{ (cathode)} - \mathcal{E}^\circ \text{ (anode)} \]

\[ \log_{10} Q = \frac{n}{0.0592 V} \left[ \Delta \mathcal{E}^\circ - \Delta \mathcal{E} \right] \]
13-6 (skip) Batteries and Fuel Cells
Battery Chemistry

Lead-acid cells
Anode: Sponge metallic lead
Cathode: Lead dioxide (PbO₂)
Electrolyte: Aqueous sulfuric acid

Half-cell reactions:
Pb + SO₄²⁻ → PbSO₄ + 2e⁻
PbO₂ + SO₄²⁻ + 4H⁺ + 2e⁻ → PbSO₄ + 2H₂O

Alkaline cells
Anode: Zinc powder
Cathode: Manganese dioxide (MnO₂) powder
Electrolyte: Potassium hydroxide (KOH)

Half reactions:
Zn + 2OH⁻ → ZnO + H₂O + 2e⁻
2MnO₂ + H₂O + 2e⁻ → Mn₂O₃ + 2OH⁻

Nickel/cadmium cells
Anode: Cadmium
Cathode: Nickel oxyhydroxide Ni(OH)₂
Electrolyte: Aqueous potassium hydroxide (KOH)

Reactions:
Cd + 2OH⁻ → Cd(OH)₂ + 2e⁻
NiO₂ + 2H₂O + 2e⁻ → Ni(OH)₂ + 2OH⁻
Zinc/air cells
Anode: Amalgamated zinc powder and electrolyte
Cathode: Oxygen ($O_2$)

Half reactions:
$Zn_2^+ + 2OH^- \rightarrow Zn(OH)_2$
$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Solid cathode lithium cells
Anode: Lithium
Cathode: A heat-treated $MnO_2$
Electrolyte: Propylene carbonate and 1,2-dimethoxyethane

Half reactions:
$Li \rightarrow Li^+ + e$
$Mn^{IV}O_2 + Li^+ + e \rightarrow Mn^{III}O_2(Li^+)$

Lithium ion cells
Anode: Carbon compound
Cathode: Lithium oxide
Electrolyte: LiPF$_6$

Chemistry: Based on “intercalation”, the reversible insertion of guest atoms like lithium into host solids like the battery electrode materials.
Chapter 13
Electrochemistry and Cell Voltage

• Examples /exercises

• Problems
  3, 5, 9, 11, 15, 19, 29, 31, 35, 37, 41, 45