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 Batteries and Fuel Cells
• 13-7 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⁻ flow →

Anode

(-)

Oxidation

Cathode

(+)

Reduction

Q = charge

There exists “potential” or potential difference, called ΔE, 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  \( \Delta E \) units is Joules/coulomb

Recall \( Q = I \times t \)

Substituting gives
Consider a Galvanic Cell (recall that this is a spontaneous reaction)

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

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

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

Remember Faraday's constant?

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

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

$$\Delta G = \ldots$$

(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
\[ \varepsilon^\circ \] (V)

\[ \begin{align*}
0.345 & \quad \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \\
0.000 & \quad 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \\
-0.257 & \quad \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)
\end{align*} \]

\[ \Delta \varepsilon^\circ = 0.602 \text{ V} \]
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>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential $\xi^\circ$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strongest oxidizing agent</strong></td>
<td></td>
</tr>
<tr>
<td>$F_2 + 2 e^- \rightarrow 2F^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>$Au^{3+} + 3 e^- \rightarrow Au$</td>
<td>1.42</td>
</tr>
<tr>
<td>$Cl_2 + 2 e^- \rightarrow 2 Cl^-$</td>
<td>1.358</td>
</tr>
<tr>
<td>$Br_2 + 2 e^- \rightarrow 2 Br^-$</td>
<td>1.065</td>
</tr>
<tr>
<td>$Hg^{2+} + 2 e^- \rightarrow Hg$</td>
<td>0.851</td>
</tr>
<tr>
<td>$Ag^+ + e^- \rightarrow Ag$</td>
<td>0.800</td>
</tr>
<tr>
<td>$I_2 + 2 e^- \rightarrow 2 I^-$</td>
<td>0.535</td>
</tr>
<tr>
<td>$Cu^{2+} + 2 e^- \rightarrow Cu$</td>
<td>0.340</td>
</tr>
<tr>
<td>$2 H^+ + 2 e^- \rightarrow H_2$</td>
<td>0</td>
</tr>
<tr>
<td>$Pb^{2+} + 2 e^- \rightarrow Pb$</td>
<td>-0.126</td>
</tr>
<tr>
<td>$Sn^{2+} + 2 e^- \rightarrow Sn$</td>
<td>-0.136</td>
</tr>
<tr>
<td>$Ni^{2+} + 2 e^- \rightarrow Ni$</td>
<td>-0.23</td>
</tr>
<tr>
<td>$Cd^{2+} + 2 e^- \rightarrow Cd$</td>
<td>-0.403</td>
</tr>
<tr>
<td>$Fe^{2+} + 2 e^- \rightarrow Fe$</td>
<td>-0.409</td>
</tr>
<tr>
<td>$Cr^{3+} + 3 e^- \rightarrow Cr$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 e^- \rightarrow Zn$</td>
<td>-0.763</td>
</tr>
<tr>
<td>$Al^{3+} + 3 e^- \rightarrow Al$</td>
<td>-1.706</td>
</tr>
<tr>
<td>$Mg^{2+} + 2 e^- \rightarrow Mg$</td>
<td>-2.375</td>
</tr>
<tr>
<td>$Na^+ + e^- \rightarrow Na$</td>
<td>-2.71</td>
</tr>
<tr>
<td>$Ca^{2+} + 2 e^- \rightarrow Ca$</td>
<td>-2.76</td>
</tr>
<tr>
<td>$K^+ + e^- \rightarrow K$</td>
<td>-2.92</td>
</tr>
<tr>
<td>$Li^+ + e^- \rightarrow Li$</td>
<td>-3.04</td>
</tr>
</tbody>
</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>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential $E^\circ(V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongest oxidizing agent</td>
<td></td>
</tr>
<tr>
<td>$F_2 + 2e^- \rightarrow 2F^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>$Au^{3+} + 3e^- \rightarrow Au$</td>
<td>1.42</td>
</tr>
<tr>
<td>$Cl_2 + 2e^- \rightarrow 2Cl^-$</td>
<td>1.358</td>
</tr>
<tr>
<td>$Br_2 + 2e^- \rightarrow 2Br^-$</td>
<td>1.065</td>
</tr>
<tr>
<td>$Hg^{2+} + 2e^- \rightarrow Hg$</td>
<td>0.851</td>
</tr>
<tr>
<td>$Ag^+ + e^- \rightarrow Ag$</td>
<td>0.800</td>
</tr>
<tr>
<td>$I_2 + 2e^- \rightarrow 2I^-$</td>
<td>0.535</td>
</tr>
<tr>
<td>$Cu^{2+} + 2e^- \rightarrow Cu$</td>
<td>0.340</td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightarrow H_2$</td>
<td>0</td>
</tr>
<tr>
<td>Weakest reducing agent</td>
<td></td>
</tr>
<tr>
<td>$Pb^{2+} + 2e^- \rightarrow Pb$</td>
<td>$-0.126$</td>
</tr>
<tr>
<td>$Sn^{2+} + 2e^- \rightarrow Sn$</td>
<td>$-0.136$</td>
</tr>
<tr>
<td>$Ni^{2+} + 2e^- \rightarrow Ni$</td>
<td>$-0.23$</td>
</tr>
<tr>
<td>$Cd^{2+} + 2e^- \rightarrow Cd$</td>
<td>$-0.403$</td>
</tr>
<tr>
<td>$Fe^{2+} + 2e^- \rightarrow Fe$</td>
<td>$-0.409$</td>
</tr>
<tr>
<td>$Cr^{3+} + 3e^- \rightarrow Cr$</td>
<td>$-0.74$</td>
</tr>
<tr>
<td>$Zn^{2+} + 2e^- \rightarrow Zn$</td>
<td>$-0.763$</td>
</tr>
<tr>
<td>$Al^{3+} + 3e^- \rightarrow Al$</td>
<td>$-1.706$</td>
</tr>
<tr>
<td>$Mg^{2+} + 2e^- \rightarrow Mg$</td>
<td>$-2.375$</td>
</tr>
<tr>
<td>$Na^+ + e^- \rightarrow Na$</td>
<td>$-2.71$</td>
</tr>
<tr>
<td>$Ca^{2+} + 2e^- \rightarrow Ca$</td>
<td>$-2.76$</td>
</tr>
<tr>
<td>$K^+ + e^- \rightarrow K$</td>
<td>$-2.92$</td>
</tr>
<tr>
<td>$Li^+ + e^- \rightarrow Li$</td>
<td>$-3.04$</td>
</tr>
</tbody>
</table>

Strength of oxidizing agent

Strength of reducing agent
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°C.
A Galvanic cell is constructed in which at Pt|Fe2+, Fe3+ half cell is connected to a Cd2+|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

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\textsuperscript{2+}, Fe\textsuperscript{3+} half cell is connected to a Cd\textsuperscript{2+}|Cd half cell.

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

Fe\textsuperscript{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

<table>
<thead>
<tr>
<th>Term</th>
<th>Oxidation Number Change</th>
<th>Electron Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Oxidation</td>
<td>Increase</td>
<td>Loss of Electrons</td>
</tr>
<tr>
<td>2. Reduction</td>
<td>Decrease</td>
<td>Gain of Electrons</td>
</tr>
<tr>
<td>3. Oxidizing Agent, does the oxidizing</td>
<td>Decrease</td>
<td>Picks Up electrons</td>
</tr>
<tr>
<td>4. Reducing Agent, does the reducing</td>
<td>Increase</td>
<td>Supplies Electrons</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential $\Delta(E^\circ)(V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strongest oxidizing agent</strong></td>
<td></td>
</tr>
<tr>
<td>$F_2 + 2 \text{e}^- \rightarrow 2F^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>$Au^{3+} + 3 \text{e}^- \rightarrow Au$</td>
<td>1.42</td>
</tr>
<tr>
<td>$Cl_2 + 2 \text{e}^- \rightarrow 2 Cl^-$</td>
<td>1.358</td>
</tr>
<tr>
<td>$Br_2 + 2 \text{e}^- \rightarrow 2 Br^-$</td>
<td>1.065</td>
</tr>
<tr>
<td>$I_{2g}^{2+} + 2 \text{e}^- \rightarrow I_{2g}$</td>
<td>0.851</td>
</tr>
<tr>
<td>$Ag^+ + \text{e}^- \rightarrow Ag$</td>
<td>0.800</td>
</tr>
<tr>
<td>$I_2 + 2 \text{e}^- \rightarrow 2 I^-$</td>
<td>0.535</td>
</tr>
<tr>
<td>$Cu^{2+} + 2 \text{e}^- \rightarrow Cu$</td>
<td>0.340</td>
</tr>
<tr>
<td>$2 H^+ + 2 \text{e}^- \rightarrow H_2$</td>
<td>0</td>
</tr>
<tr>
<td>$Pb^{2+} + 2 \text{e}^- \rightarrow Pb$</td>
<td>$-0.126$</td>
</tr>
<tr>
<td>$Sn^{2+} + 2 \text{e}^- \rightarrow Sn$</td>
<td>$-0.136$</td>
</tr>
<tr>
<td>$Ni^{2+} + 2 \text{e}^- \rightarrow Ni$</td>
<td>$-0.23$</td>
</tr>
<tr>
<td>$Cd^{2+} + 2 \text{e}^- \rightarrow Cd$</td>
<td>$-0.403$</td>
</tr>
<tr>
<td>$Fe^{2+} + 2 \text{e}^- \rightarrow Fe$</td>
<td>$-0.409$</td>
</tr>
<tr>
<td>$Cr^{3+} + 3 \text{e}^- \rightarrow Cr$</td>
<td>$-0.74$</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 \text{e}^- \rightarrow Zn$</td>
<td>$-0.763$</td>
</tr>
<tr>
<td>$Al^{3+} + 3 \text{e}^- \rightarrow Al$</td>
<td>$-1.706$</td>
</tr>
<tr>
<td>$Mg^{2+} + 2 \text{e}^- \rightarrow Mg$</td>
<td>$-2.375$</td>
</tr>
<tr>
<td>$Na^+ + \text{e}^- \rightarrow Na$</td>
<td>$-2.71$</td>
</tr>
<tr>
<td>$Ca^{2+} + 2 \text{e}^- \rightarrow Ca$</td>
<td>$-2.76$</td>
</tr>
<tr>
<td>$K^+ + \text{e}^- \rightarrow K$</td>
<td>$-2.92$</td>
</tr>
<tr>
<td>$Li^+ + \text{e}^- \rightarrow Li$</td>
<td>$-3.04$</td>
</tr>
</tbody>
</table>

3/23/20
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.
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

This is a disproportionation problem, write to get both H₃PO₃ on the left and then add and calculated $\Delta E$

\[ H₃PO₃ + 2H^+ + 2e^- \rightarrow H₃PO₂ + H₂O \]
\[ H₃PO₃ + H₂O \rightarrow H₃PO₄ + 2H^+ + 2e^- \]
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 calculate $\Delta\text{E}$

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

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

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

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

Only two half reactions involving SO₂

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

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

Disproportionation of SO₂
Rewrite to get both SO₂ on the left, balance electrons and stoichiometry and add
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).

Disproportionation of SO$_2$

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

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

\[ = 0.40 - (+0.172) = +0.228 \therefore \text{unstable} \]

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 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).

H$_3$PO$_3$ is stable
(non-spontaneous disproportionation)

and

SO$_2$ is unstable
(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 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

Only two half reactions involving H₃PO₃

H₃PO₃ + 2H⁺ + 2e⁻ → H₃PO₂ + H₂O  E = (0.499) V
H₃PO₄ + 2H⁺ + 2e⁻ → H₃PO₃ + H₂O  E = (0.276) V

Only two half reactions involving SO₂

2SO₂ + 2H⁺ + 4e⁻ → S₂O₃⁻² + H₂O  E = +0.40 V
HSO₄⁻ + 3H⁺ + 2e⁻ → SO₂ + 2H₂O  E = +0.172 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 \(-n \, F \, \Delta E^\circ\) for \(\Delta G^\circ\) and \(-n \, F \, \Delta E\) for \(\Delta G\), and rearranging, becomes the Nernst Equation
Nernst Equation

If Temp. at 25°C and
R = 8.3 JK⁻¹mol⁻¹ and
F = 96,485 C mol⁻¹ and use
J/C = V,
then the equation becomes

Nernst Equation
Example 13-6

The cell

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

Anode (oxidation) \mid 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

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

Anode (oxidation) | cathode (reduction)

Cathode (Reduction)

\[ \text{MnO}_4^{-1} \rightarrow \text{Mn}^{2+} \]

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

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

\[ Q = \frac{[\text{Mn}^{2+}]^2 [\text{Zn}^{2+}]^5}{[\text{MnO}_4^{-1}]^2 [\text{H}^+]^{16}} \]

\[ \Delta E = 2.25V - \frac{0.0592 V}{10} \log_{10} \frac{[\text{Mn}^{2+}]^2 [\text{Zn}^{2+}]^5}{[\text{MnO}_4^{-1}]^2 [\text{H}^+]^{16}} \]

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

The cell

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

(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.

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

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

\[
\Delta E = 2.16\text{ Volts (Cell voltage)}
\]
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
\[ \log_{10} Q = \frac{n}{0.0592 V} [\Delta E^\circ - \Delta E] \]

Q is the reaction quotient

e.g. for the general reaction,

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

\[ Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]
13-5 Equilibrium Constants from Electrochemistry

Previously

\[
\ln K = \frac{-\Delta G^\circ_r}{RT}
\]

\[
\Delta G_r^\circ = -n \mathcal{F} \Delta E^\circ
\]

If a reaction is at equilibrium, after rearrangement this becomes

\[
\ln K = \left(\frac{n \mathcal{F}}{RT}\right) \Delta E^\circ
\]

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

\( J/C = V, \)

then the equation becomes

\[
\log_{10} K = \left( \frac{n}{0.0592 V} \right) \Delta E^\circ
\]
Example 13-8

Calculate the equilibrium constant of the Redox reaction

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

At 25°C 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)

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

\[ N = 10 \text{ electrons} \]
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.
2 MnO$_4^{-1}$ + 5 Zn + 16H$^+$

$\rightarrow$ 2Mn$^{2+}$ + 5 Zn$^{2+}$ + 8 H$_2$O

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

AgCl (s) excess → Ag$^{+1}$ + Cl$^{-1}$

To determine $K_{sp}$, 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:

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

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
Pt|H₂ (1 atm)|H⁺ (1M)||Ag⁺|Ag

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

Pt|H₂ (1 atm)|H⁺ (1M)||Ag⁺|Ag
Pt\(|\text{H}_2\ (1 \text{ atm})|\text{H}^+\ (1\text{M})|\text{Ag}^+|\text{Ag}\)

Overall reaction

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

\[Q = \frac{[H^+]^2[Ag]^2}{[Ag^+]^2P_{H_2}}\]

\[Q = \frac{[1]^21}{[Ag^+]^21} = 4 \times 10^{13}\]

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

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

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

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

\[K_{sp}^{AgCl} = 1.6 \times 10^{-10}\]

Answer
Chapter 13 Summary

<table>
<thead>
<tr>
<th>Term</th>
<th>Δ Oxidization</th>
<th>ΔElectron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td>Increase</td>
<td>Loss</td>
</tr>
<tr>
<td>Reduction</td>
<td>Decrease</td>
<td>Gain</td>
</tr>
<tr>
<td>Oxidizing Agent</td>
<td>Decrease</td>
<td>Picks</td>
</tr>
<tr>
<td>Reducing Agent</td>
<td>Increase</td>
<td>Supplies</td>
</tr>
</tbody>
</table>

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

(at constant T,P)

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

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

\[
\log_{10} Q = \frac{n}{0.0592 \mathcal{V}} \left[ \Delta \mathcal{E}^\circ - \Delta \mathcal{E} \right]
\]
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$^{-}$ → Zn(OH)$_2$
$\frac{1}{2}$O$_2$ + H$_2$O + 2e$^{-}$ → 2OH$^{-}$

Solid cathode lithium cells
Anode: Lithium
Cathode: A heat-treated MnO$_2$
Electrolyte: Propylene carbonate and 1,2-dimethoxyethane

Half reactions:
Li → Li$^+$ + e$^{-}$
Mn$^{IV}$O$_2$ + Li$^+$ + e$^{-}$ → 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