Guide to Chapter 18. Electrochemistry

We will spend three lecture days on this chapter. During the first class meeting we will review oxidation and reduction. We will introduce balancing redox equations in acidic media. To round out the first lecture, we will learn about galvanic cells.

For the second lecture, we will learn about standard reduction potentials and the Nernst equation. We will tie the cell potential to $\Delta G$ and $\Delta G^\circ$.

The third day we will discuss electrolytic cells.

Read the introductory paragraph to Chapter 18.

Reading Section 18.1 Galvanic Cells and 18.2. Shorthand Notation for Galvanic Cells.

Learning Objective 1: Be able to determine oxidation numbers of elements involved in oxidation-reduction (redox) reactions. Be able to identify oxidation, reduction, oxidizing agents, and reducing agents. Review Chapter 4 if necessary.

Learning Objective 2: Be able to balance redox equations.

Learning Objective 3: Know the abbreviated notation used for electrochemical cells.

Learning Objective 4: Know the components of an electrochemical cell (anode, cathode, salt bridge, negative and positive electrode. Be able to write the reaction occurring at each electrode.

Do Problems 1 – 4 at the end of these sections.

Do the following end-of-chapter problems: 24, 26, 32, 36 (a and b only); 38, 40, 42

Problem Club Question A. Balance the following reactions in acidic solution:

- a. $\text{NO}_3^-(aq) + \text{Cl}^-(aq) \rightarrow \text{NO}(g) + \text{Cl}_2(g)$
- b. $\text{AuCl}_4^-(aq) + \text{Fe}^{2+}(aq) \rightarrow \text{Au}(s) + \text{Cl}^-(aq) + \text{Fe}^{3+}(aq)$
- c. $\text{H}_2\text{O}_2(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{SO}_3^{2-}(aq) + \text{O}_2(g)$

(Hint: In $\text{H}_2\text{O}_2$, the oxidation number for hydrogen should be assigned first. What would happen if you assigned oxygen’s first?)

Answer: 1a. $2 \text{NO}_3^-(aq) + 6 \text{Cl}^-(aq) + 8 \text{H}^+(aq) \rightarrow 2 \text{NO}(g) + 3 \text{Cl}_2(g) + 4 \text{H}_2\text{O}$

b. $\text{AuCl}_4^-(aq) + 3 \text{Fe}^{2+}(aq) \rightarrow \text{Au}(s) + 4 \text{Cl}^-(aq) + 3 \text{Fe}^{3+}(aq)$

c. $\text{H}_2\text{O}_2(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{SO}_3^{2-}(aq) + \text{O}_2(g) + \text{H}_2\text{O}(aq)$; if you assigned ox number to hydrogen peroxide’s oxygens first, the hydrogens would have to be +2 which is impossible.

Problem Club Question B. Balance the following reactions in basic solution:

- a. $\text{NO}_3^-(aq) + \text{Cl}^-(aq) \rightarrow \text{NO}(g) + \text{Cl}_2(g)$

Answer: $2 \text{NO}_3^-(aq) + 6 \text{Cl}^-(aq) + 4 \text{H}_2\text{O} \rightarrow 2 \text{NO}(g) + 3 \text{Cl}_2(g) + 8 \text{OH}^-(aq)$

Problem Club Question C. Consider the reaction: $\text{Pb}(s) + 2 \text{Ag}^+(aq) \rightarrow \text{Pb}^{2+}(aq) + 2 \text{Ag}(s)$

a. Sketch this galvanic cell using two beakers and a salt bridge.

b. Label the cathode and the anode.

c. Which electrode is gaining mass as the cell discharges?

d. Which solution is increasing in concentration as the reaction proceeds?

e. What is the oxidation half reaction? The reduction half reaction?

f. What is the oxidizing agent? The reducing agent?

g. What is being oxidized? Being reduced?

Answer: a. see text; b. cathode = Ag; anode = Pb; c. silver; d. $\text{Pb}^{2+}(aq)$

e. Oxidation: $\text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2 \text{e}^-$  Reduction: $\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s)$
f. Oxidizing agent = Ag⁺; reducing agent = Pb; g. Being oxidized: Pb; Being reduced: Ag⁺

Problem Club Question D. (ACS style) Answer: A

Problem Club Question E. (ACS style) Answer: C

Problem Club Question F. (ACS style) Answer: B

Problem Club Question G. (ACS style) Answer: C

Problem Club Question H. (ACS style) Answer: B

Problem Club Question I. (ACS style) Answer: A

Read Section 18.3. Cell Potentials and Free Energy Changes for Cell Reactions

Learning Objective 5: Given either $E^0$ or $\Delta G^0$, be able to calculate the other.

Do Problem 5 at the end of the section.

Do the following end-of-chapter problems: 44, 46, 48, 50, 52,

Problem Club Question J. Which of the following are spontaneous ($\Delta G < 0$) at standard conditions?

Calculate $E^0$

a. $Zn(s) + 2 Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2 Fe^{2+}(aq)$

b. $O_2(g) + 4 H^+(aq) + 4 Cl^-(aq) \rightarrow 2 H_2O + 2 Cl_2(g)$

Answers: a. Spontaneous, $E^0 = +1.53 V$; b. Non-spontaneous, $E^0 = -0.13 V$


Answers: a. $n = 2; \Delta G = -295 kJ \quad Kp = 5.1 \times 10^{+51};$ b. $n = 4; \Delta G = +50 kJ \quad Kp = 1.7 \times 10^{-9}$

Problem Club Question L. For a certain cell, $\Delta G$ at 25°C is -47 kJ. Calculate the standard cell potential, $E^0$ if $n=2$. Repeat for $n = 3$.

Answers: a. $n = 2: E^0 = +0.24 V$; b. $n = 3: E^0 = +0.16 V$

Problem Club Question M. Which of the following will be oxidized by 1 M HCl (Remember: HCl is 100% dissociated.)?

a. Ag  b. Al  c. Cu  d. Zn

Answers: a. No; b. Yes; c. No; d. Yes

Problem Club Question N. Which of the following will be oxidized by 1 M HNO₃?

a. I⁻  b. Mg  c. Al  d. F⁻

Answers: a. Yes; b. Yes; c. Yes; d. No

Problem Club Question O. (ACS style) Answer: C

Problem Club Question P. (ACS style) Answer: A

Problem Club Question Q. (ACS style) Answer: C

Read Section 18.4. Standard Reduction Potentials and Section 18.5. Using Standard Reduction Potentials.

Learning Objective 6: Be able to calculate $E^0$ for a reaction from a table of standard reduction potentials. Be able to identify the chemical from the table of SRPs that is most easily oxidized/reduced.
Do Problems 6 – 9 at the end of these sections.

Do the following end-of-chapter problems: 54, 56, 60, 62

Problem Club Question R. Use a table of standard reduction potentials to calculate \( E^0 \) for these galvanic/voltaic cells.

\[
\begin{align*}
\text{a. } & Pb(s) + 2 \text{Ag}^+(aq) \rightleftharpoons Pb^{2+}(aq) + 2 \text{Ag(s)} \\
\text{b. } & MnO_2(s) + 4 H^+(aq) + 2 \text{I}^-(aq) \rightleftharpoons Mn^{2+}(aq) + 2 H_2O + I_2(s)
\end{align*}
\]

Answers: a. \( E^0 = +0.93 \) V;  b. \( E^0 = +0.67 \) V

Problem Club Question S. Consider this partial table of standard reduction potentials for some transition metals:

<table>
<thead>
<tr>
<th>( E^0 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ag^+ + e^- \rightleftharpoons Ag )</td>
</tr>
<tr>
<td>( Cu^{+2} + 2 e^- \rightleftharpoons Cu )</td>
</tr>
<tr>
<td>( Fe^{+3} + 3 e^- \rightleftharpoons Fe )</td>
</tr>
<tr>
<td>( Pb^{+2} + 2 e^- \rightleftharpoons Pb )</td>
</tr>
<tr>
<td>( Cr^{+3} + 3 e^- \rightleftharpoons Cr )</td>
</tr>
</tbody>
</table>

a. What is the strongest oxidizing agent? Reducing agent?
b. What is the most easily oxidized? Reduced?
c. With which species will \( Fe^{+3} \) react?
d. With which species will \( Fe \) react?
e. List the two species that will not react with any other species in the table.
f. What species can oxidize chromium but cannot oxidize copper?
g. Rank species in the table from weakest reducing agent to strongest reducing agent.

Answers: a. Strongest oxidizing agent = \( Ag^+ \);  Strongest reducing agent = \( Cr \);  b. Most easily oxidized = \( Cr \);  Most easily reduced = \( Ag^+ \);  c. \( Pb \) and \( Cr \);  d. \( Ag^+ \) and \( Cu^{+2} \);  e. \( Ag^+ \) and \( Cr^{+3} \);  g. \( Fe^{+3} \); \( Pb^{+2} \) and \( Cu^{+2} \);  h. \( Ag < Cu < Fe < Pb < Cr \)

Problem Club Question T. Which species in each pair is the better oxidizing agent?

\[
\begin{align*}
\text{a. } & Br_2 \text{ or } H_2O_2 \\
\text{b. } & SO_4^{2-} \text{ or } MnO_4^- \\
\text{c. } & Cl_2 \text{ or } Br_2
\end{align*}
\]

Answers: a. \( H_2O_2 \)  b. \( MnO_4^- \)  c. \( Cl_2 \)

Problem Club Question U. Which species in each pair is the better reducing agent?

\[
\begin{align*}
\text{a. } & Ca \text{ or } Mg \\
\text{b. } & Cu^+ \text{ or } Fe^{+2} \\
\text{c. } & Cl^- \text{ or } Br^-
\end{align*}
\]

Answers: a. \( Ca \)  b. \( Cu^+ \)  c. \( Br^- \)

Problem Club Question V. Use the table of SRPs to select:

\[
\begin{align*}
\text{a. } & \text{a reducing agent that will convert } Pb^{+2} \text{ to } Pb \text{ but will not reduce } Cd^{+2} \text{ to } Cd. \\
\text{b. } & \text{an oxidizing agent that converts } Br^- \text{ to } Br_2 \text{ but not } Cl^- \text{ to } Cl_2
\end{align*}
\]

Answers: a. \( Pb^{+2} \rightleftharpoons Pb: \text{ SRP} = -0.13 \) V \( Cd^{+2} \rightleftharpoons Cd: \text{ SRP} = -0.40 \) V

Select a species that has an SOP > + 0.13 V but < +0.40 V. For example, \( Ni^{+2} + 2e \) has an SOP = +0.23 V;  b. there are several rxns that could be used. They are the ones that have SRPs > 1.09 V but < 1.36 V.

Problem Club Question W. Which is the strongest oxidizing agent?

<table>
<thead>
<tr>
<th>Standard Oxidation Potentials</th>
<th>( E^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Na \rightleftharpoons Na^+ + e^- )</td>
<td>2.71 V</td>
</tr>
<tr>
<td>( Cd \rightleftharpoons Cd^{+2} + 2e^- )</td>
<td>0.40 V</td>
</tr>
</tbody>
</table>
H₂ → 2H⁺ + 2e⁻  0.00 V
Ag → Ag⁺ + e⁻  -0.80 V

(A) Na⁺  (B) H₂  (C) Cd⁰  (D) Ag⁺
Answer: D

*(Problem Club Question X.*) What new substances or ions are formed when metallic copper, in excess, is placed in a solution containing ZnSO₄ and HgCl₂ in equal concentration?

<table>
<thead>
<tr>
<th>Substance</th>
<th>Standard Oxidation Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na→Na⁺+e⁻</td>
<td>2.71 V</td>
</tr>
<tr>
<td>Zn→Zn²⁺+2e⁻</td>
<td>0.76 V</td>
</tr>
<tr>
<td>Fe→Fe³⁺+2e⁻</td>
<td>0.4 V</td>
</tr>
<tr>
<td>Pb→Pb²⁺+2e⁻</td>
<td>0.13 V</td>
</tr>
<tr>
<td>H₂→2H⁺+2e⁻</td>
<td>0.00 V</td>
</tr>
<tr>
<td>Cu→Cu²⁺+2e⁻</td>
<td>-0.34 V</td>
</tr>
<tr>
<td>Hg→Hg²⁺+2e⁻</td>
<td>-0.85 V</td>
</tr>
<tr>
<td>Ag→Ag⁺+e⁻</td>
<td>-0.80 V</td>
</tr>
</tbody>
</table>

(A) Cu²⁺ and Zn  (D) Cl⁻ and Cu²⁺
(B) Cu²⁺ and Hg  (E) Hg²⁺ and Cu²⁺
(C) SO₄²⁻ and Cu
Answer: B

*(Read Section 18.6. Cell Potentials and Composition of the reaction Mixture: The Nernst Equation.)*

Learning Objective 7: Use the Nernst equation to calculate the concentration of chemical involved in the reaction.

Do Problems 10 and 11 at the end of this section.

Do the following end-of-chapter problems: 30, 64, 66, 68, 70

*(Problem Club Question Y.*) Consider the galvanic cell in which the following reaction occurs:

Sn⁴⁺(aq) + Zn(s) → Sn(s) + Zn⁺²(aq)

a. Write the Nernst equation for the cell.
b. Calculate E⁰
c. Calculate E when [Zn⁺²] = 0.045 M and [Sn⁴⁺²] = 0.82 M
d. Calculate E when [Zn⁺²] is twice as large as [Sn⁴⁺²].

Answers: a. E = E⁰ - (0.0592/z)log([Zn⁺²]/[Sn⁺²])
b. E⁰ = +0.620 V
c. E = +0.620 - (0.0592/z)log([0.045]/[0.82]) = 0.657 V
d. E = +0.620 - (0.0592/z)log([2]/[1]) = 0.611 V.

*(Problem Club Question Z. (ACS style) Answer: B)*

*(Read Sections 18.7. Electrochemical Determination of pH.)*

Learning Objective 8: Use the Nernst equation to calculate pH.

Do Problem 12 at the end of this section.
Read Section 18.8 Standard Cell Potentials and Equilibrium Constants.
Learning Objective 9: Use the Nernst equation to calculate the equilibrium constant, $K$.

Do Problems 13 and 14 at the end of this section.

Do the following end-of-chapter problems: 72, 74, 78

Read Sections 18.9 and 18.10.
Learning Objective 10: Be familiar with common batteries.

Read Section 18.11. Electrolysis and Electrolytic Cells and Section 18.12. Commercial Applications of Electrolysis
Learning Objective 11: Know the products of hydrolysis of aqueous solutions.

Learning Objective 12: Be familiar with corrosion - its causes, the reactions involved and methods of prevention.

Learning Objective 13: Be familiar with important electrochemical processes such as the Downs cell, the chlor-alkali process and the Hall process.

Do Problem 18 at the end of this section.

Do the following end-of-chapter problems: 28, 88, 90, 92

Problem Club Question AA. Consider the electrolysis of a water solution of MgBr$_2$

a. Write the equation for the cathode half-reaction.
b. Write the equation for the anode half reaction.
c. Write the equation for the overall reaction and
d. Calculate the minimum applied voltage required for electrolysis.

Answers: a. $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$
b. $2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-$
c. $2 \text{H}_2\text{O} + 2 \text{Br}^- \rightarrow \text{H}_2 + 2 \text{OH}^- + \text{Br}_2$
d. $E = 1.91 \text{ V}$

Problem Club Question BB. (ACS style) Answer: B


Learning Objective 14: Be able to relate units of electricity (current, time, amperes, coulombs, and watts) to the amount (moles or grams) of material (produced or consumed) in an electrochemical reaction.

Do Problems 20 and 21 at the end of this section.

Do the following end-of-chapter problems: 86, 94, 96, 98

Problem Club Question CC. An electrolytic cell is producing aluminum from Al$_2$O$_3$ at a rate of 1.00 kg per day. Assuming a yield of 100%,
a. How many electrons must pass through the cell per day?
b. What is the current passing through the cell?
c. How much oxygen is being produced simultaneously?

Answers: a. $6.7 \times 10^{25}$; b. 124 amps; c. 890 g O$_2$ ($= 27.8$ moles of O$_2$)
Problem Club Question DD. How long would it take to plate out 5.0 g Ag from Ag\(^+\) using a current of 10.0 amps?
Answers: 450 seconds = 7.5 minutes;

How much chromium (in grams) can be plated out of a solution of Cr\(^{3+}\) using a current of 15 amps for 1.00 hr?
Answer: 4.8 g Cr

Problem Club Question EE. Consider the Downs cell.
   a. Write the cathode and anode reactions that occur in the electrolysis of molten NaCl.
   b. Write the overall reaction.
   c. What quantity of sodium would be produced per day if the current is 30 amps?
   d. What volume of chlorine at STP is produced per day if the current is 30 amps?

   Answers: a. Cathode reaction: \(Na^+ + e^- \rightarrow Na(l)\)  Anode reaction: \(2 Cl^- \rightarrow Cl_2 + 2 e^-\)
   b. \(2 NaCl \rightarrow 2 Na(l) + Cl_2(g)\)  c. 27 mol Na = 621 g Na  d. 301 L Cl\(_2\)

Problem Club Question FF. (ACS style) Answer: D

Problem Club Question GG. (ACS style) Answers: C

Problem Club Question HH. (ACS style) Answer: B

Problem Club Question II. (ACS style) Answer: B