Chemistry 12 - Notes on Unit 5 Electrochemistry

Oxidation – Reduction

Introduction
-Demonstration of oxidation – reduction reactions

Definitions: (species means atom, ion or molecule)

**Oxidation** – a species undergoing oxidation loses electrons
(charge becomes more positive)

**Reduction** – a species undergoing reduction gains electrons
(charge becomes more negative)

**Oxidizing agent** – The species being reduced
(gains electrons, causes the other one to be oxidized)

**Reducing agent** – The species being oxidized
(loses electrons, causes the other one to be reduced)

\[ 2 \text{ e}^- \]

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

**Redox** – Short for Oxidation – Reduction

Redox identification

Charge on neutral atom or molecule = 0

**Oxidation** – Charge gets more + (loses electrons)

**Reduction** – Charge gets more – (gains electrons)

Reduction (charge decreases)

E.g.) \[ \text{Pb}^{2+} (aq) + \text{Mg}^0 (s) \rightarrow \text{Pb}^0 (s) + \text{Mg}^{2+} (aq) \]

Oxidation (Charge increases)
**Half-Reactions**

- Redox reactions can be broken up into oxidation & reduction half reactions.

  e.g.) Redox rx: \( \text{Pb}^{2+} (\text{aq}) + \text{Zn} (\text{s}) \rightarrow \text{Pb} (\text{s}) + \text{Zn}^{2+} (\text{aq}) \)

  The \( \text{Pb}^{2+} \) gains 2 electrons.

**Reduction Half-rx:** \( \text{Pb}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Pb} (\text{s}) \)

Electrons on the LEFT side (or GER) Means REDUCTION

**Oxidation numbers**

- Real or apparent charge on an atom in a molecule or ion

**Rules to find oxidation number of an atom**

1) **In elemental form:**
   - (Single atoms of monatomic elements) or (diatomic molecules of diatomic elements)
   - Oxidation number of atoms = 0
   - Eg) Mn, Cr, N\(_2\), F\(_2\), Sn, O\(_2\), etc.

   ![The oxidation # of each atom = 0](image)

2) **In monatomic ions:** oxidation # = charge
   - Eg) In \( \text{Cr}^{3+} \) - oxidation # of Cr = +3
     - \( \text{S}^{2-} \) - oxidation # of S = -2

3) **In ionic compounds**
   a) the oxidation # of **Alkali Metals** is always +1
      - eg) \( \text{NaCl} \quad \text{K}_2\text{CrO}_4 \)

      ![Ox # of Na & K = +1](image)

   b) the oxidation # of **Halogens** when at the end (right side) of the formula is always –1
      - eg) \( \text{CaCl}_2 \quad \text{AlBr}_3 \quad \text{KF} \)

      ![Ox # of Cl, Br and F = -1](image)
Note: Halogens are not always –1! (Only when it is written last in formula.)

4) In molecules or polyatomic ions:
   a) Ox. # of oxygen is almost always –2
      
      e.g.) KOH, CrO₄²⁻, Li₃PO₄

      Ox # of O is –2

   b) An exception is Peroxides in which ox. # of O = -1

      Hydrogen Peroxide: H₂O₂

      Alkali Peroxides: Na₂O₂

5) In molecules or ions:
   a) Hydrogen is almost always +1
      
      e.g.) HNO₃, H₂SO₄, HPO₄²⁻ Every “H” has an ox # of +1

   b) An exception is metallic hydrides, which have an ox # of -1
      
      e.g.) NaH, CaH₂ (In each one of these Ox. # of H = -1)

Finding oxidation numbers of each atom in a molecule or PAI

In a neutral molecule the total charge = 0
      
      e.g.) NH₃ ← Total charge = 0 (no charge)

In a polyatomic ion – the total ionic charge is written on the top right
      
      e.g.) CrO₄²⁻ ← Total ionic charge (TIC) = -2

Oxidation numbers of all atoms add up to total ionic charge (TIC)
      
      e.g.) Find the oxidation # of Cr in CrO₄²⁻:

      (Let x = ox # of one Cr atom)

      CrO₄²⁻:

      \[ X + 4 [\text{# of “O” atoms}] -2 [\text{charge of oxygen}] = -2 [\text{total ionic charge}] \]

      \[ X - 8 = -2 \]

      X = -2 + 8
$X = +6$  So ox # of Cr here $= +6$

e.g.) Find ox # of Cl in HClO$_4$

\[
\text{HClO}_4 \quad \quad +1 + x + 4 (-2) = 0 \\
1 + x - 8 = 0 \\
x - 7 = 0 \\
x = +7
\]

e.g.) Find Ox # of Cr in Cr$_2$O$_7^{2-}$

\[
\text{Cr}_2\text{O}_7^{2-} \quad \quad 2x + 7(-2) = -2 \\
2x - 14 = -2 \\
2x = +12 \\
x = +6
\]

e.g.) Find ox # of P in Li$_3$PO$_4$

\[
\text{Li}_3\text{P}_4 \quad \quad 3(+1) + x + 4(-2) = 0 \\
3 + x - 8 = 0 \\
x - 5 = 0 \\
x = +5
\]

**Changes in oxidation numbers**

When an atom's oxidation # is **increased**, it is **oxidized**.

e.g.) Half-rx: Fe$^{2+} \rightarrow$ Fe$^{3+} + e^-$

More complex:

-When Mn$^{3+}$ changes to MnO$_4^-$, is Mn oxidized or reduced?

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

- In this process, Mn is oxidized.
**Reduction** – When an atom’s oxidation # is **decreased**, it is **reduced**.

e.g.) Cu(NO₃)₂ → Cu(s) Ox # **decreases** (reduction)

<table>
<thead>
<tr>
<th>Ox # of Cu in Cu(NO₃)₂</th>
<th>Ox # of Cu in Cu(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>0</td>
</tr>
</tbody>
</table>

**Redox ID using oxidation #'s**

Given a more complex equation – identify atoms which **do not change ox #'s** (often “O” or “H” but not always!)

e.g.) \[3\text{SO}_2 + 3\text{H}_2\text{O} + \text{ClO}_3^- \rightarrow 3\text{SO}_4^{2-} + 6\text{H}^+ + \text{Cl}^-\]

There are no O₂ molecules or peroxides, so “O” in all these has an ox # = -2

Again:

\[3\text{SO}_2 + 3\text{H}_2\text{O} + \text{ClO}_3^- \rightarrow 3\text{SO}_4^{2-} + 6\text{H}^+ + \text{Cl}^-\]

H is (+1) in both of these so it doesn’t change

The only atoms left are “S” and “Cl”. Find the Ox #’s of S and Cl⁻ in species that contain them. (Ox # of 1 atom in each case)

\[3\text{SO}_2 \rightarrow 3\text{SO}_4^{2-}\]

Ox # of S is +4

Coefficients are just for balancing.

\[\text{SO}_2 \rightarrow \text{SO}_4^{2-}\]

Ox # of S is +6

Ox # of S **increases** so S is being **oxidized**
Note:
- R.A.O., the reducing agent is oxidized
- The species SO₂ is acting as the reducing agent.
- The element S is being oxidized so S is losing electrons.

Look at the species with Cl:

\[
\text{ClO}_3^- \rightarrow \text{Cl}^-
\]

<table>
<thead>
<tr>
<th>Ox. # of Cl</th>
<th>Ox. # of Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5</td>
<td>-1</td>
</tr>
</tbody>
</table>

Decrease in ox # so Cl is being reduced

(They may also ask for the atom acting as the oxidizing agent – this would be Cl in ClO₃⁻)

Notes:
- For hydrocarbons it's best to rewrite them as simple molecular formulas.
- All O's are in molecules or ions, no O₂ & no peroxides so O remains unchanged as -2
- All H's are in molecules or ions, no H₂ or metallic hydrides so H remains unchanged as +1
- The atoms to check for changes are C and Cr.

\[
2\text{CrO}_4^{2-} + 3\text{CH}_2\text{O} + 2\text{H}_2\text{O} \rightarrow 2\text{Cr(OH)}_3 + 3\text{HCO}_2^- + \text{OH}^-
\]

So…
- a) the species being oxidized is (CH₂O) HCHO (inc. in ox #)
- b) the reducing agent is (CH₂O) HCHO (RAO)
- c) The species being reduced is CrO₄²⁻ (decrease in ox #)
- d) The oxidizing agent is CrO₄²⁻ (OAR)
- e) The species losing e⁻'s is (CH₂O) HCHO (LEO)
- f) The species gaining e⁻'s is CrO₄²⁻ (GER)

**Using oxidation numbers to identify half-reactions**

They don't have to be balanced

e.g.) If NO₂⁻ \(\rightarrow\) NO₃⁻

("O" does not change it's ox # (no O₂ or peroxides)) so find ox # of N on both sides.

\[
\text{NO}_2^- \rightarrow \text{NO}_3^-
\]

<table>
<thead>
<tr>
<th>Ox. #</th>
<th>Ox. #</th>
</tr>
</thead>
<tbody>
<tr>
<td>+3</td>
<td>+5</td>
</tr>
</tbody>
</table>

\(\Delta\text{O.N.} = +2\) Since ox # increases, this is an oxidation
NOTE: When asked if a given reaction is a redox or not:

Look for a change from an element → compound or compound→ an element

These will always be redox, because in elemental form ox. # = 0 and in compounds usually ox. # is not = 0

Eg.) Is the reaction: Zn + Cl₂ → ZnCl₂ a redox reaction?

Answer: It must be because ΔON of Zn (0 → +2 = +2) and ΔON of Cl (0 → -1 = -1)

Half-reactions and the reduction table

- Look at “Standard Reduction Table”

<table>
<thead>
<tr>
<th>Ox agents on left + e⁻'s</th>
<th>⇄</th>
<th>Reducing agents on right</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂ + 2e⁻ ⇄ 2F⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag⁺ + e⁻ ⇄ Ag (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu²⁺ + 2e⁻ ⇄ Cu(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn²⁺ + 2e⁻ ⇄ Zn (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li⁺ + e⁻ ⇄ Li (s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- So F₂ is a stronger ox agent than Ag⁺, etc.

Help in Hunting
- Solid metals mostly on bottom right (less active ones Ag, Au, farther up on the right side)
- Halogens (e.g. Cl₂) and oxyanions e.g. BrO₃⁻, MnO₄⁻, IO₃⁻ found near top left
- Some metal ions found on both sides e.g. Fe²⁺, Sn²⁺, Cu⁺, Mn³⁺ can act as OA’s or RA’s

All the half-rx’s are written as reductions:

e.g.) F₂ + 2e⁻ ⇄ 2F⁻
Ag⁺ + e⁻ ⇌ Ag(s)

- The double arrow implies that oxidation's can also take place (reverse of reductions)

Specifically just reduction

Specifically just oxidation

e.g.) reduction of Ag⁺ (Same as table- single arrow)

oxidation of Ag (Reverse of that on table- single arrow)

Using the reduction table to predict which reactions are spontaneous

- An oxidizing agent will react spontaneously with (oxidize) a reducing agent below it on the right

Look at your reduction chart!

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂(g) + 2e⁻ ⇌ 2F⁻</td>
<td>F₂. the strongest OA. oxidize (react spontaneously</td>
</tr>
<tr>
<td>S₂O₈²⁻ + 2e⁻ ⇌ 2SO₄²⁻</td>
<td>with) all species below it on the right side from</td>
</tr>
<tr>
<td>Li⁺ + e⁻ ⇌ Li(s)</td>
<td>SO₄²⁻ (near top right) will reduce only F₂.</td>
</tr>
</tbody>
</table>

Look at the 4th half rx from the bottom

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺ + e⁻ ⇌ K(s)</td>
<td>K⁺ will oxidize only Rb(s), Cs(s) and Li(s), nothing else on the chart.</td>
</tr>
<tr>
<td>Rb⁺ + e⁻ ⇌ Rb(s)</td>
<td></td>
</tr>
<tr>
<td>Cs⁺ + e⁻ ⇌ Cs(s)</td>
<td></td>
</tr>
<tr>
<td>Li⁺ + e⁻ ⇌ Li(s)</td>
<td></td>
</tr>
</tbody>
</table>

- A reducing agent on the right will react spontaneously with (reduce) any oxidizing agent on the left above it

e.g.) Li(s) (bottom right) will reduce all species on the left side except Li⁺. SO₄²⁻ (near top right) will reduce only F₂.

- An OA on the left will not react spontaneously with a RA on the right above it!

e.g.) Au³⁺ will not oxidize (or react spontaneously with) SO₄²⁻.

Some points...

1) Be very careful with charges e.g. Li⁺ is a totally different thing than Li(s).

2) Things don’t react with species which are only on the same side (these are impossible – not just non-spontaneous.)

   E.g.) K⁺ (4th from bottom on the left) will not oxidize Rb⁺ or Cs⁺ Li⁺ etc. –because they are on the same side only. (Impossible)

   E.g.) Li(s) will not reduce Cs(s), Rb(s), K(s), etc. because they are all on the same side only.

3) Some elements with multiple oxidation numbers e.g.) Sn, Cu, Mn, Fe have ions on both sides of the chart!

   –Look carefully at your table to find these.
Notice: Fe$^{2+}$ is on the left (OA) at – 0.45
Fe$^{2+}$ is on the right (RA) at + 0.77
Sn$^{2+}$ is on the left (OA) at – 0.14
Sn$^{2+}$ is on the right (RA) at + 0.15

A word about Cu...

Notice: Cu$^+$ is on the left at + 0.52
Cu$^+$ is on the right at + 0.15
- recall that anything on the left will oxidize a species below it on the right.

\[
\begin{align*}
\text{Cu}^+ + e^- &= \text{Cu} & \text{E}_o = 0.52 \\
\text{Cu}^{2+} + e^- &= \text{Cu}^+ & \text{E}_o = 0.15
\end{align*}
\]

Since Cu$^+$ oxidizes and reduces itself, any water solution of Cu$^+$ is unstable – it won’t remain Cu$^+$ very long!

(demo Cu in HNO$_3$)

Notice: Mn$^{2+}$ is on the left at $E^o$ = -1.19
Mn$^{2+}$ is on the right at $E^o$ = +1.22
Also notice: Cr$^{3+} + e^- = \text{Cr}^{2+}$ - 0.41
Cr$^{3+} + 3e^- = \text{Cr}(s)$ - 0.74

If a redox reaction is non-spontaneous, then the reverse reaction will be spontaneous!

e.g.) The reaction Sr$^{2+} + \text{Ca}(s) \rightarrow \text{Ca}^{2+} + \text{Sr}(s)$ is non-spontaneous because Ca is above Sr$^{2+}$ on the right side.

But the rx: Ca$^{2+} + \text{Sr}(s) \rightarrow \text{Sr}^{2+} + \text{Ca}(s)$ is spontaneous because Sr$_{(s)}$ is below Ca$^{2+}$ on the right side.

Acidified solutions

- Any reactions on the table with H$^+$ in them are acidified or acid solutions.

e.g.) Look at these: at $E^o$ = +1.51 (4th from the top)

\[
\text{MnO}_4^- + 8H^+ + 5e^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}
\]

Called acidified permanganate solution

Note: Names of many ions can be found on the ion table!
Nitric, Sulphuric & Phosphoric acids

- These acids are shown in ionized form on the table.
- Nitric acid (HNO₃) is found in two places on the left side.

\[ \text{NO}_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \quad E^0 = +0.96 \text{ v} \]

\[ 2\text{NO}_3^- + 4H^+ + 2e^- \rightleftharpoons \text{N}_2\text{O}_4 + 2H_2O \quad E^0 = +0.80 \text{ v} \]

Don’t worry about coefficients yet. They are only used for balancing.

- Sulphuric acid is found at + 0.17 v

\[ \text{SO}_4^{2-} + 4H^+ + 2e^- \rightleftharpoons \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \quad E^0 = +0.17 \text{ v} \]

A note about water

- On the top of the table it says "ionic concentrations are at 1M"
- This includes \([H^+] = 1 \text{M}\) with two exceptions:
  - Neutral water is found on the shaded lines at + 0.82 v and − 0.41 v
  - Neutral water as a reducing agent is on the right side at + 0.82 v
  - Neutral water as an oxidizing agent is on the left side at − 0.41 v

Finding products of spontaneous reactions

eg) Given \(\text{Sn}^{4+} + \text{H}_2\text{S}\) – find the products

See the table at + 0.15 v and + 0.14 v

\[ \text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+} \quad + 0.15 \text{ v} \]

\[ \text{S(s)} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{S} \quad + 0.14 \text{ v} \]

The higher reaction will be reduction (\(\rightarrow\)), the lower reaction will proceed to the left (\(\leftarrow\)) and be an oxidation.

\[ \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \]

\[ \text{S(s)} + 2\text{H}^+ + 2e^- \leftarrow \text{H}_2\text{S} \quad \text{(reversed! Lower one is reversed-is an oxidation)} \]

- So the products are \(\text{Sn}^{2+}\), \(\text{S}\), and \(\text{H}^+\)

(at this point don’t worry about coefficients yet.)
Using data to make your own simple Redox table

Example problem:

1) Four metals A, B, C, & D were tested with separate solutions of A^{2+}, B^{2+}, C^{2+} & D^{2+}. Some of the results are summarized in the following table:

<table>
<thead>
<tr>
<th>Metal</th>
<th>A^{2+}</th>
<th>B^{2+}</th>
<th>C^{2+}</th>
<th>D^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td>(1) no reaction</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td>(3) reaction</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>(2) reaction</td>
<td></td>
<td>(4) no reaction</td>
<td></td>
</tr>
</tbody>
</table>

List the ions in order from the strongest to weakest oxidizing agent.

Using data

1) – Since B^{2+} does not oxidize A : B^{2+} must be below A on the table.

\[
\begin{align*}
A^{2+} + 2e^- &= A \\
B^{2+} + 2e^- &= B
\end{align*}
\]

2) – Since C^{2+} reacts with A: C^{2+} must be above A:

\[
\begin{align*}
C^{2+} + 2e^- &= C \\
A^{2+} + 2e^- &= A \\
B^{2+} + 2e^- &= B
\end{align*}
\]

3) – Since A^{2+} reacts with D: A^{2+} must be above D on the table. But is D^{2+} above or below B^{2+}? We don’t know yet.

\[
D^{2+} \quad \text{Here} \quad A^{2+} \quad \text{Or here?}
\]

Let’s look at the next information:

4) – D^{2+} does not react with B

- Now we know that D^{2+} must be below B on the table

So now we have our complete table:

<table>
<thead>
<tr>
<th>Oxidizing agents</th>
<th>Reducing agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>C^{2+} + 2e^- = C</td>
<td></td>
</tr>
<tr>
<td>A^{2+} + 2e^- = A</td>
<td></td>
</tr>
<tr>
<td>B^{2+} + 2e^- = B</td>
<td></td>
</tr>
<tr>
<td>D^{2+} + 2e^- = D</td>
<td></td>
</tr>
</tbody>
</table>

- At this point it’s good to go back and recheck that all the data given is consistent with your table.
- So now we have our answer; The ions in order of strongest to weakest oxidizing agent is: C^{2+}, A^{2+}, B^{2+}, D^{2+}
- Just in case you’re asked, you can see that the order of reducing agent from strongest to weakest is D, B, A, C.
Another example –

Four non-metal oxidizing agents X₂, Y₂, Z₂ and W₂ are combined with solutions of ions: X⁻, Y⁻, Z⁻ and W⁻.

The following results were obtained:

1. X₂ reacts with W⁻ and Y⁻ only.
2. Y⁻ will reduce W₂

List the reducing agents from strongest to weakest

1. X₂ will be above W⁻ & Y⁻, but below Z⁻

OA’s                       RA’s
Z₂ + 2e⁻ ⇌ 2Z⁻
X₂ + 2e⁻ ⇌ 2X⁻
W₂ + 2e⁻ ⇌ 2W⁻
Y⁻ + 2e⁻ ⇌ 2Y⁻

(2) Since Y⁻ reduces W₂, Y⁻ must be lower on the right of W₂.

To answer the question:

The reducing agents from strongest to weakest are: Y⁻, W⁻, X⁻, Z⁻

Balancing half-reactions

- Some half-rx’s are on the table, but not all.
- Given if the soln. Is acidic or basic.
- Think of Major Hydroxide (Major → O → H → - (charge))
- Major atoms → atoms other than O & H

Acid Soln.  E.g.) S₉O₈²⁻ → HSO₃⁻ (acid soln.)

(1) Balance Major Atoms (S in this case)

S₉O₈²⁻ → 2HSO₃⁻

(2) Balance “O” atoms, by adding H₂O (to the side with less O’s)

S₉O₈²⁻ → 2HSO₃⁻ + 2H₂O

(3) Balance “H” atoms by adding H⁺ (to the side with less H’s)

S₉O₈²⁻ + 6H⁺ → 2HSO₃⁻ + 2H₂O
(4) Balance charge by adding e⁻’s (to the more + side)

\[
S_2O_8^{2-} + 6H^+ \rightarrow 2HSO_3^- + 2H_2O
\]

- The left side needs 6 e⁻’s to get a –2 charge

So the final balanced half-rx is:

\[
S_2O_8^{2-} + 6H^+ + 6 e^- \rightarrow 2HSO_3^- + 2H_2O
\]

- Always double-check these!
- Don’t miscopy charges, etc.

In basic solution

- Do the first steps of the balancing just like an acid

E.g.) MnO₂ → MnO₄⁻ (basic solution)

Major (Mn already balanced)
- Oxygen: \(2H_2O + MnO_2 \rightarrow MnO_4^-\)
- Hydrogen: \(2H_2O + MnO_2 \rightarrow MnO_4^- + 4H^+\)
- Charge: \(2H_2O + MnO_2 \rightarrow MnO_4^- + 4H^+ + 3e^-\)

In basic solution: write the reaction \(H^+ + OH^- \rightarrow H_2O\) or \(H_2O \rightarrow H^+ + OH^-\)

- In whichever way is needed to cancel out the H⁺’s
- Add to the half-rx

E.g.) \(\frac{2H_2O + MnO_2 \rightarrow MnO_4^- + 4H^+ + 3e^-}{4H^+ + 4OH^- \rightarrow 4H_2O}\)

We need 4H⁺ on the left to cancel the 4H⁺ on the left side

You must write the whole water equation

(Take away 2H₂O’s from both sides)

\[MnO_2 + 4OH^- \rightarrow MnO_4^- + 2H_2O + 3e^-\]

Double-check everything!

- Reactions without H’s or O’s are done in neutral soln
Balancing overall redox reactions using the half-reaction (half-cell) method

1. Break up Rx into 2 half-rx’s.
2. Balance each one (in acidic or basic as given)
3. Multiply each half rx by whatever is needed to cancel out e⁻’s
   (Note: balanced half-rx have e⁻’s (on left reduction on right oxidation) Balanced redox don’t have e⁻’s)
4. Add the 2 half-rx’s canceling e⁻’s and anything else (usually H₂O’s, H⁺’s or OH⁻’s) in order to simplify.

Example: \( \text{U}^{4+} + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \text{UO}_2^{2+} \) (acidic)

Balance each ½ rx

\( \text{U}^{4+} \rightarrow \text{UO}_2^{2+} \) (Major (U) balanced already)
\( \text{Oxygen} \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} \)
\( \text{Hydrogen} \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} + 4\text{H}^+ \)
\( \text{Charge} \rightarrow \text{U}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \)

\( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \) (Major (Mn) balanced already)
\( \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \)
\( \text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \)

Multiply by 5 to get 10e⁻

\( (\text{U}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- ) \times 5 \)
\( (\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} ) \times 2 \)

\( 5\text{U}^{4+} + 10\text{H}_2\text{O} + 2\text{MnO}_4^- + 16\text{H}^+ + 10\text{e}^- \rightarrow 5\text{UO}_2^{2+} + 20\text{H}^+ + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{e}^- \)

To simplify: -Take away 10e⁻ from both sides
- Take away 16H⁺’s from both sides
- Take away 8H₂O’s from both sides

Quick check by finding TIC’s on both sides

\( 5\text{U}^{4+} + 2\text{H}_2\text{O} + 2\text{MnO}_4^- \rightarrow 5\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{Mn}^{2+} \)
\[ +20 + 0 - 2 \]
\[ \text{TIC} = +18 \]

Quick notes

- Some redox equations have just one reactant
  - Use this as the reactant in both half-rx’s.
  - These are called “self-oxidation-reduction” or Disproportionation reactions.
Redox titrations

- same as in other units (solubility/acids-bases)
- coefficient ratios for the “mole bridge” are obtained by the balanced redox equation:

![TITRATIONS Table]

Finding a suitable solution titrate a sample

Use redox table:
- If sample is on the left (OA) Use something below it on the right (RA)
- If sample is on the right (RA) use something above it on the left (OA)
- Good standards will change colour as they react

Acidified MnO₄⁻ (purple) = Mn²⁺ (clear)
Acidified Cr₂O₇²⁻ (orange) = Cr³⁺ (pale green)
Electrochemical Cells

(Cu/Zn Cell)

Definitions

**Electrochemical cell** – A device which converts chemical energy into electrical energy

**Electrode** – A conductor (usually a metal) at which a half-cell reaction occurs.

**Anode** - The electrode at which oxidation occurs. (A & O are both vowels) LEOA

**Cathode** – The electrode at which reduction occurs. (R & C are both consonants) GERC

Half-cell reactions

**Anode – Oxidation half-rx**

Zn(s) → Zn^{2+} (aq) + 2e^{-}

Metal atoms are changed to + ions. Metal dissolves and anode loses mass as the cell operates.

**Cathode – Reduction half-rx**

Cu^{2+} + 2e^{-} → Cu

+ ions are changed to metal atoms. New metal is formed so the cathode gains mass.
**Flow of electrons**
-Since the anode loses e⁻'s, (LEOA) and the cathode gains e⁻'s (GERC)

-Electrons flow from the anode toward the cathode in the wire (conducting solid)

Flow of ions in the salt bridge
-Salt bridge contains any electrolyte (conducting solution)

**Flow of electrons**

Anode: Zn → Zn²⁺ + 2e⁻

Cathode: Cu²⁺ + 2e⁻ → Cu

Common things which contain electrolytes, e.g.) potatoes, apples, oranges, lemons, frogs, people

If there was no SB + ions (cations) would build up at the anode
If there was no SB + ions are used up, so there would be an excess of – ions (anions) at the cathode
Identifying the anode and cathode
- Look at the reduction table
- All half-rx’s are reversible (can go forward or backward)
- All are written as reductions (GERC)
- Their reverse would be oxidations (LEOA)
- The half-rx with the greater potential to be reduced is higher on the table
  (higher reduction potential \(E^\circ\))
So the higher half-rx is the cathode (HIC)
(Notice \(\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}\) is higher than \(\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}\) so \(\text{Cu}\) gets to be the cathode)
Also notice that the Anode reaction is Reversed (AIR)
(Anode rx: \(\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-\))

**Standard reduction potentials and voltages**

**Voltage** – The tendency for e’s to flow in an electrochemical cell. (Note: a cell may have a high voltage even if no e’s are flowing. It is the tendency (or potential) for e’s to flow.
- Can also be defined as the potential energy per coulomb. (Where 1C = the charge carried by \(6.25\times10^{18}\) e’)
  \(1\ \text{Volt} = 1\ \text{Joule/Coulomb}\)

**Reduction potential of half-cells**
- The tendency of a half-cell to be reduced. (take e’s)
Voltage only depends on the difference in potentials not the absolute potentials.

<table>
<thead>
<tr>
<th></th>
<th>before buying calculator</th>
<th>after buying calculator</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mrs. A</td>
<td>$2000</td>
<td>$1980</td>
<td>$20</td>
</tr>
<tr>
<td>Mrs. B</td>
<td>$50</td>
<td>$30</td>
<td>$20</td>
</tr>
</tbody>
</table>

-Both people spent $20 on the calculator.
Relative potentials of half-cells can only be determined by connecting with other half-cells and reading the voltage.

E.g.) How good a basketball team is can only be determined by playing with other teams and looking at points (scores).

- A “standard” half-cell was arbitrarily chosen to compare other half-cells with.
- It was assigned a “reduction potential” of 0.000 v
- It is: \[ 2H^+ (aq) + 2e^- \rightarrow H_2(g) \quad E^o = 0.000 \text{ v} \]

- Since potential depends on gas pressure, temp. and \([H^+]\) this half cell is assigned a value of 0.000 v at “standard state” which is 25°C, 101.3 kPa and \([H^+] = 1.0 \text{ M}\)

The standard half-cell acts as an anode (LEOA) or cathode (GERC) depending on what it is connected to. For example, when the standard half-cell is connected to the Ag/Ag⁺ half-cell.

For this cell, the voltage is 0.80 volts with the electrons flowing toward the Ag.

So the cathode is the Ag/Ag⁺ half-cell
The anode is the H₂/H⁺ half-cell

\begin{align*}
\text{(GERC) Cathode half-rx} & \quad \text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E^o = ? \\
\text{(LEOA) Anode half-rx} & \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad E^o = 0.00 \text{ volts} \\
\text{Voltage of cell} & = 0.80 \text{ volts}
\end{align*}
-From this we can see that the $E^\circ$ for the Ag/Ag$^+$ half-cell must be 0.80 V different than that of the standard half-cell. Since the Ag/Ag$^+$ is the one which is reduced, we say it has a higher reduction potential than the standard. Therefore the reduction potential of the Ag/Ag$^+$ half-cell is +0.80 V.

Consider the following cell:

![Diagram of a voltaic cell](image)

The voltage on the voltmeter is 0.45 volts.

a) Write the equation for the half-reaction taking place at the anode. Include the $E^\circ$.

\[
\text{______________________________________________ E}^\circ: \text{__________v}
\]

b) Write the equation for the half-reaction taking place at the cathode.

\[
\text{______________________________________________ E}^\circ: \text{__________v}
\]

c) Write the balanced equation for the redox reaction taking place as this cell operates. Include the $E^\circ$.

\[
\text{______________________________________________ E}^\circ: \text{__________}
\]

d) Determine the reduction potential of the ion $X^{2+}$.

\[
E^\circ: \text{__________v}
\]

e) Toward which beaker ($X(NO_3)_2$) or (Cr(NO_3)$_3$) do NO$_3^-$ ions migrate?

\[
\text{__________________________ _}
\]

f) Name the actual metal “X” ________________________________
Consider the following cell:

The initial cell voltage is 1.20 Volts

a) Write the equation for the half-reaction which takes place at the cathode. Include the $E^0$

$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd} \quad E^0 = \ldots \text{v}$

b) Write the equation for the half-reaction taking place at the anode:

$\text{Ag}^{+} + e^- \rightarrow \text{Ag} \quad E^0 = \ldots \text{v}$

c) Write the balanced equation for the overall redox reaction taking place. Include the $E^0$.

$\text{Cd}^{2+} + \text{Ag} \rightarrow \text{Cd} + \text{Ag}^{+} \quad E^0 = \ldots \text{v}$

d) Find the oxidation potential for Cd: $E^0 = \ldots \text{v}$

e) Find the reduction potential for Cd$^{2+}$: $E^0 = \ldots \text{v}$

f) Which electrode gains mass as the cell operates? _______

g) Toward which beaker (AgNO$_3$ or Cd(NO$_3$)$_2$) do K$^+$ ions move? _______

h) The silver electrode and AgNO$_3$ solution is replaced by Zn metal and Zn(NO$_3$)$_2$ solution.

What is the cell voltage now? _______ Which metal now is the cathode? _______
Consider the following electrochemical cell:

[Diagram of an electrochemical cell with Ni and Cu electrodes, Ni(NO₃)₂ and Cu(NO₃)₂ solutions, and a salt bridge labeled with 1.0 M KNO₃.]

a) Write the equation for the half-reaction taking place at the nickel electrode. Include the $E^0$

b) Write the equation for the half-reaction taking place at the Cu electrode. Include the $E^0$.

c) Write the balanced equation for the redox reaction taking place.

d) What is the initial cell voltage? ________________ 

e) Show the direction of electron flow on the diagram above with an arrow with an "e−" written above it.

f) Show the direction of flow of cations in the salt bridge using an arrow with "Cations" written above it.

(***If you are having any difficulty with this you need to contact your teacher before you move on*********)
Voltages at non-standard conditions

Note: When cells are first constructed, they are not at equilibrium. All the voltages calculated by the reduction table are initial voltages.

- As the cells operate, the concentrations of the ions change:
  eg) For the cell: \( \text{Cu(NO}_3\text{)}_2/\text{Cu}||\text{Zn/Zn(NO}_3\text{)}_2 \)
  - The cathode \( \frac{1}{2} \) reaction is: \( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E^0 = +0.34 \text{ v} \)
  - The anode \( \frac{1}{2} \) reaction is: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E^0 = +0.76 \text{ v} \)
  - The overall reaction is: \( \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+} \quad E^0 = +1.10 \text{ v} \)

All electrochemical cells are exothermic (they give off energy) \( \text{strong tendency to form products} \)

Initially: \( \text{Cu}^{2+} + \text{Zn} \rightleftharpoons \text{Cu} + \text{Zn}^{2+} + \text{energy} \quad \text{Voltage} = 1.10 \text{ v} \)

- As the cell operates [\( \text{Cu}^{2+} \)] decreases (reactants used up) & [\( \text{Zn}^{2+} \)] increases (products formed). Both these changes tend to push the reaction to the left (LeChateliers Principle)
  \( \text{Cu}^{2+} + \text{Zn} \rightleftharpoons \text{Cu} + \text{Zn}^{2+} + \text{energy} \quad \text{Voltage} < 1.10 \text{ v} \)

Eventually, these tendencies will be equal. At this point, the cell has reached equilibrium. At equilibrium the cell voltage becomes 0.00 v.

Predicting spontaneity from \( E^0 \) of a redox reaction

| If \( E^0 \) for any redox (overall) reaction is > 0 (positive) the reaction is Spontaneous. |
| If \( E^0 \) is < 0 (negative) the reaction is Non-spontaneous |
| When a reaction is reversed the sign of \( E^0 \) changes |

Example:

a) Find the standard potential (\( E^0 \)) for the following reaction:
\( 2\text{MnO}_4^- + 4\text{H}_2\text{O} + 3\text{Sn}^{2+} \rightarrow 2\text{MnO}_2 + 8\text{OH}^- + 3\text{Sn}^{4+} \)

b) Is this reaction as written (forward rx) spontaneous? _____

c) Is the reverse reaction spontaneous? _____ \( E^0 = _____ \)

Solution:

a) Find the two half-rx’s which add up to give this reaction. Write them so what’s on the left of the overall rx is on the left of the half-rx. (& what’s on right is on the right)  The half-rx for \( \text{MnO}_4^- \rightarrow \text{MnO}_2 \) in basic soln. is at + 0.60. To keep \( \text{MnO}_4^- \) on the left, this \( \frac{1}{2} \)rx is written as it is on the table.

\[ \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2 + 4\text{OH}^- \quad E^0 = +0.60 \]

The rest of the overall rx involves \( \text{Sn}^{2+} \) changing to \( \text{Sn}^{4+} \). The \( \frac{1}{2} \) reaction for that must be reversed as well as its \( E^0 \). Since \( \text{Sn}^{2+} \) must stay on the left side, the half-rx on the table must be reversed as well as its \( E^0 \).

\[ \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^- \quad E^0 = -0.15 \text{ V} \]

-Now, add up the 2 \( \frac{1}{2} \)-rx”s to get the overall (Multiply by factors to balance e”s –and add up \( E^0 \)’s.

Unit 5-Oxidation-Reduction NOTES
(MnO₄⁻ + 2H₂O + 3e⁻ → MnO₂ + 4OH⁻) \( \text{E}^0 = +0.60 \text{ v} \)
(Sn²⁺ → Sn⁴⁺ 2e⁻) \( \text{E}^0 = -0.15 \text{ v} \)

\[
2\text{MnO}_4^- + 4\text{H}_2\text{O} + 3\text{Sn}^{2+} \rightarrow 2\text{MnO}_2 + 8\text{OH}^- + 3\text{Sn}^{4+} \quad \text{E}^0 = +0.45 \text{ V}
\]

So \( \text{E}^0 \) for the overall redox reaction = \( +0.45 \text{ v} \)

b) Since \( \text{E}^0 \) is positive, this reaction is spontaneous as written.
c) The \( \text{E}^0 \) for the reverse reaction would be \(-0.45 \text{ v}\) so the reverse reaction is non-spontaneous.

The Lead-Acid Storage Battery (Automobile battery)

Anode (Pb Plate)

\[
Pb(s) + \text{HSO}_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^- \\
\text{Ox #} = 0 \quad \rightarrow \quad \text{Ox #} = +2
\]

You can tell this is oxidation because ox # of Pb increases and electrons are lost. (LEOA)

Cathode (PbO₂ plate)

\[
PbO_2(s) + \text{HSO}_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2\text{H}_2\text{O}(l) \\
\text{Ox # of Pb} = +4 \quad \rightarrow \quad \text{Ox # of Pb} = +2 \quad \text{GERC}
\]
The overall redox reaction: (discharging or operating)

\[
Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) + \text{electrical energy}
\]

Notes: As cell discharges the anode (Pb) and cathode (PbO₂) disintegrate and the white solid (PbSO₄) forms on both plates. Originally, [H⁺] & [HSO₄⁻] is high. i.e.) [H₂SO₄] is high. H₂SO₄ is denser than H₂O therefore the density (specific gravity) of the electrolyte is high to start with. As the cell discharges, H₂SO₄ (H⁺ & HSO₄⁻) is used up and H₂O is formed. Therefore, electrolyte gets less dense as the battery discharges. Condition of the battery can be determined using a "hydrometer" or battery tester. (Higher the float, the denser the electrolyte)

Adding electrical energy to this reaction will reverse it (recharging)

Charging Reaction:

\[
\text{Electrical energy} + 2PbSO_4(s) + H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq)
\]

The E° for the discharging rx, is +2.04 volts. A typical car battery has 6 of these in series to give a total voltage =12.24V.

The Zinc-Carbon battery (LeClanche-Cell, Common Dry cell, or regular carbon battery. Often called "Heavy Duty")
Cathode ½ reaction:
(GERC) \[ 2\text{MnO}_2(\text{s}) + 2\text{NH}_4^+ + 2\text{e}^- \rightarrow 2\text{MnO(OH)}(\text{s}) + 2\text{NH}_3(\text{aq}) \]
Or simplified: \[ \text{Mn}^{4+} + \text{e}^- \rightarrow \text{Mn}^{3+} \]

Anode ½ reaction:
(LEOA) \[ \text{Zn}(\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow \text{Zn(NH}_3)_4^{2+} + 2\text{e}^- \]
Or simplified: \[ \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+} + 2\text{e}^- \]

**The alkaline dry cell**
- Operates under **basic** conditions
- Delivers much **greater current**
- Voltage remains constant
- More **expensive**
- Lasts longer

Cathode ½ reaction (GERC) \[ 2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^- \]
Anode ½ reaction (LEOA) \[ \text{Zn}(\text{s}) + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \]

**Fuel cells**
- Fuel cells are continuously fed fuel and they convert the **chemical** energy in fuel to **electrical** energy
- More **efficient** (70-80%) than burning gas or diesel to run generators (30-40%)
- No pollution – only produces **water**
- Can use **H}_2 and \text{O}_2 or **hydrogen rich fuels** (e.g. methane CH\text{}_4) and \text{O}_2.
- Used in space capsules – \text{H}_2 & \text{O}_2 in tanks \text{H}_2\text{O} produced used for drinking

**Anode ½ reaction:**
\[ 2\text{H}_2(\text{g}) + 4\text{OH}^- (\text{aq}) \rightarrow 4\text{H}_2\text{O(l)} + 4\text{e}^- \]

**Cathode ½ reaction:**
\[ \text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq}) \]

**Overall reaction:**
\[ 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)} \]
Applied electrochemistry—The Breathalyzer Test

After drinking, breath contains ethanol $\text{C}_2\text{H}_5\text{OH}$. Acidified dichromate (at $E^0 = 1.23$ on the reduction table) will oxidize alcohol. The unbalanced formula equation is:

$$\text{C}_2\text{H}_5\text{OH} + K_2\text{Cr}_2\text{O}_7 + H_2\text{SO}_4 \rightarrow \text{CH}_3\text{COOH} + \text{Cr}_2(\text{SO}_4)_3 + K_2\text{SO}_4 + H_2\text{O}$$

-K$_2$Cr$_2$O$_7$ is yellow (orange at higher concentrations)
-Cr$_2$(SO$_4$)$_3$ is green

-Exhaled air is mixed with standardized acidified dichromate
-Put in a spectrophotometer set at the wavelength of green light
-More alcohol produces more green Cr$_2$(SO$_4$)$_3$ (green)
-Machine is calibrated with known concentration samples of alcohol to ensure accuracy

Electrolytic Cells (ELC’s)

Electrolysis – uses an external power source to cause a non-spontaneous redox reaction to occur.

In BOTH Electrochemical Cells (ECC’s) and Electrolytic Cells (ELC’s):

- **OXIDATION** takes place at the **ANODE** (LEOA)
- **REDUCTION** takes place at the **CATHODE** (GERC)

There are three main types of Electrolytic Cells:

1. Electrolysis of **Molten** Salts (no H$_2$O) with **Unreactive** (Inert) Electrodes
2. Electrolysis of **Aqueous** Salts (H$_2$O solution) with **Unreactive** (Inert) Electrodes
3. Electrolysis of **Aqueous** Salts (H$_2$O solution) with **Reactive** Electrodes
Type 1 - Electrolysis of Molten Salts (no H₂O) with Unreactive (Inert) Electrodes

All molten (melted) salts consist of mobile ions.

Eg.) \[ \text{NaI(l)} \rightarrow \text{Na}^+(l) + \text{I}^-(l) \]
\[ \text{NaCl(l)} \rightarrow \text{Na}^+(l) + \text{Cl}^-(l) \]

An example of a “Type 1” ELC: Electrolysis of molten NaCl (NaCl(l))

Diagram:

CATHODE
Reduction of Na⁺ happens here (GERC)

ANODE
Oxidation of Cl⁻ happens here (LEOA)

\[ \text{Na}^+(l) + \text{e}^- \rightarrow \text{Na}(s) \quad E^o = -2.71 \text{ v} \]

\[ 2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2\text{e}^- \quad E^o = -1.36 \text{ v} \]

Cathode Half-Reaction (Reduction of the Cation)
Looking near the bottom of the Reduction Table, we see the half-reaction for the reduction of Na⁺

Anode Half-Reaction (Oxidation of the Anion)
To write the oxidation of Cl⁻, we find Cl⁻ on the Right Side and REVERSE the half-reaction:

2 Cl⁻ → Cl₂(g) + 2e⁻ \( E^o = -1.36 \text{ v} \) (the sign on the E^o is changed since the rx. is reversed.)
To find the overall redox reaction with its $E^\circ$, we add up the half reactions as follows:

\[(\text{Na}^+ + e^- \rightarrow \text{Na}_\text{s}) \ 2\]  
\[E^\circ = -2.71 \text{ v}\]  
\[2 \text{ Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2e^- \]  
\[E^\circ = -1.36 \text{ v}\]  
\[2 \text{ Na}^+ + 2 \text{ Cl}^- \rightarrow 2 \text{ Na}_\text{s} + \text{Cl}_2(\text{g}) \]  
\[E^\circ = -4.07 \text{ v}\]  

The Product at the Cathode is $\text{Na}_\text{s}$  
The Product at the Anode is $\text{Cl}_2(\text{g})$

The industrial application of this cell is called a Down's Cell.

A quick method for writing half-reactions for Type 1 Electrolytic Cells (electrolysis of molten salts with unreactive electrodes)

1. Dissociate the salt into its ions
2. Underneath the Cation, write $\text{C}^-$ (representing the Cathode)
3. Underneath the Anion, write $\text{A}^+$ (representing the Anode)
4. Draw arrow showing where each ion goes
5. The half-reactions must start with the ion (the ion must be the reactant)
6. For the Cathode Half-Reaction, write the reduction of the cation (same as on table)
7. For the Anode Half-Reaction, write the oxidation of the anion (reversed from table)

Type 2 Electrolytic Cells – Electrolysis of Aqueous Salts and Non-reactive Electrodes

Because the salts are aqueous, water is present. Looking at the top and bottom shaded lines on the reduction table, you can see that water can be oxidized or reduced:

- $\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \ E^\circ = -0.82 \text{ v}$
- is the oxidation of water and could take place at the ANODE.
- This half-reaction, the way it’s written, is the reduction of water and could take place at the CATHODE.
To find the Half-Reaction at the CATHODE (reduction)

Due to the “Overpotential Effect”, the “Arrow on the Left” tells us whether:
1. The Cation is reduced? or
2. Water is reduced?

To find the Half-Reaction at the ANODE (Oxidation)

Look at the “overpotential arrow on the RIGHT side of the table
A method for finding the Half-Reactions (Oxidation at the Anode) and (Reduction at the Cathode) in this type of cell is:

1. Dissociate the salt into its ions
2. Write “H₂O” between the two ions.
3. Underneath the Cation, write (representing the Cathode)
4. Underneath the Anion, write (representing the Anode)
5. Using the rules about the “Overpotential Arrows” determine what is reduced at the Cathode (the cation or water) and what is oxidized at the Anode (the anion or water).
6. Complete the half-reactions at the Cathode and the Anode (with their E₀’s)
7. Add half-reactions to get the overall redox reaction if you are asked to.

Let’s do an example: A major industrial process is the electrolysis of brine (NaCl (aq)):

NaCl (aq) → Na⁺ + H₂O + Cl⁻

Cathode Half-Reaction: 2 H₂O + 2e⁻ → H₂(g) + 2 OH⁻  \(E^0 = -0.41 \text{ v}\)

For the Anode, look at the “overpotential arrow” on the RIGHT side. Notice that the Cl⁻ is BELOW the arrow. This means Cl⁻ will be oxidized (rather than H₂O). So…

Anode Half-Reaction: 2 Cl⁻ → Cl₂(g) + 2e⁻  \(E^0 = -1.36 \text{ v}\)

Overall Redox Reaction: 2 Cl⁻ + 2 H₂O → Cl₂(g) + H₂(g) + 2 OH⁻  \(E^0 = -1.77 \text{ v}\)

The Products at the Cathode would be H₂(g) + 2 OH⁻ (the pH near the cathode would ___crease)
The Product at the Anode would be Cl₂(g)

There would be bubbles observed at both electrodes! Draw them into the diagram above!
The **minimum voltage required** to carry this reaction out would be 1.77 v (just enough to overcome the –1.77 v $E^0$)

**Type 3 Electrolytic Cells – Electrolysis of Aqueous Salts with Reactive Electrodes**

In this type of cell, the electrodes are normal **metals**, not inert ones like platinum or carbon.

Something that’s important:

The metal that the **Cathode** is made from is **NOT reduced**. That’s because **metals cannot gain electrons** and become negative metal ions (no such ion as Fe$^{2-}$!)

The **Cathode** metal is **NOT oxidized**. That’s because **oxidation does not take place at the cathode**!

To summarize: **THE CATHODE METAL NEVER REACTS!!**

The Cathode only supplies the **SURFACE** for the **reduction** of the Cation (+ ion) or for the **reduction of water** (depending on whether the cation is above or below the left overpotential arrow.) Here’s an example:

An **aqueous** solution containing the Cu$^{2+}$ ion is electrolyzed. The cathode is made of **Iron**.

Write the equation for the Half-Reaction taking place at the **Cathode**:

The Iron will not react! (It only provides the surface—so there is no half-rx. involving Fe!)

The Cu$^{2+}$ ion is ABOVE the overpotential arrow on the left, so Cu$^{2+}$ will be reduced!

The Half-Reaction at the Cathode would be: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)}$ $E^0 = +0.34$ v

When this happens, the Iron Cathode will become coated with copper, and will turn reddish in colour. (But remember, the iron itself does NOT react!)

**In a Type 3 cell, there are 3 possibilities for Oxidation at the ANODE:**

1. The **anion** in the solution is **oxidized**
2. **Water** is **oxidized**
3. The **Anode Metal** is **oxidized**

The one with the **Highest Oxidation Potential** (The LOWEST one on the RIGHT of the table) will be the one that is Oxidized. (Treat water as if it were at the right overpotential arrow.)

- $\text{Br}_2 + \text{2e}^- \rightarrow 2\text{Br}^-$ **$E^0 = +1.08$** v
- $\text{Cl}_2 + \text{2e}^- \rightarrow 2\text{Cl}^-$ **$E^0 = +1.35$** v
- $\text{Fe}_2\text{O}_3 + \text{2e}^- \rightarrow \text{2Fe}^0 + \text{3H}_2\text{O}$ **$E^0 = +1.36$** v
- $\text{C}_6\text{H}_5\text{O}_7^-$ + $14\text{H}^+$ + $8e^-$ **$E^0 = +1.23$**

---

-Water behaves as if it were here.
Let’s do an example:

An aqueous solution containing the Cl⁻ ion is electrolyzed. The anode is made of silver. Write the equation for the Half-Reaction taking place at the Anode:

\[
\textbf{BrO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{Br}_2 + 3\text{H}_2\text{O}, \quad E^\circ = +1.48 \\
\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}, \quad E^\circ = +1.39 \\
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}, \quad E^\circ = +1.23 \\
\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}, \quad E^\circ = +1.23 \\
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}, \quad E^\circ = +1.22 \\
2\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}, \quad E^\circ = +1.20 \\
\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}^{3+}, \quad E^\circ = +1.09 \\
\text{AuCl}_4^- + 4\text{e}^- \rightarrow \text{Au}^{0} + 4\text{Cl}^-, \quad E^\circ = +1.00 \\
3\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO}_2 + 2\text{H}_2\text{O}, \quad E^\circ = +0.96 \\
\frac{1}{2}\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}^{0}, \quad E^\circ = +0.85 \\
\frac{1}{2}\text{O}_2 + 2\text{H}^+ ([\text{I}^-]), 2\text{e}^- \rightarrow \text{H}_2\text{O}, \quad E^\circ = +0.82 \\
2\text{NO}_3^- + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2\text{O}_4 + 2\text{H}_2\text{O}, \quad E^\circ = +0.80 \\
\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^{0}, \quad E^\circ = +0.80 \\
\frac{1}{2}\text{Hg}_2^{2+} + \text{e}^- \rightarrow \text{Hg}, \quad E^\circ = +0.77 \\
\]

The one with the highest oxidation potential. (The lowest on the RIGHT side) is Ag (the anode)

So the Half-Reaction at the Anode is the oxidation of Ag: \[ \text{Ag}^{0} \rightarrow \text{Ag}^+ + \text{e}^- \quad E^\circ = -0.80 \text{v} \]

Here’s an example question. Given the following cell:

Identify the Anode ___________________ the Cathode ___________________
Write an equation for the half-rx. at the Anode ______________________
E°= __________

Write an equation for the half-rx. at the Cathode ______________________
E°= __________

Write an equation for the overall redox rx. ___________________________ E°= _______

Product at Anode _____ Product at Cathode _____ Minimum voltage necessary _______

(*****If you are having any difficulty with this you need to contact your teacher before you move on ************)

Electrorefining

In Electrorefining, an impure metal is refined by making it the ANODE. The pure metal is the CATHODE.

Eg.) An ANODE made of IMPURE COPPER could have something like the following make-up:
- Mostly copper
- Some Ag or Au (above Cu on the reduction table)
- Some Zn (below Cu on the reduction table)
- Some “dirt” –any non-metal impurities

The CATHODE would be made of PURE COPPER

The SOLUTION is an aqueous solution of a compound containing Cu^{2+} (eg CuSO_4)

Remember, for Electrorefining: IMPURE ANODE → PURE CATHODE (PC)
Use your Reduction Table to help you explain all the information shown in the diagram:

First, we look at the **Anode**:

- **Au and Ag will NOT oxidize as long as Cu is present. As the Cu oxidizes around it, they fall down, with the dirt, to become part of the Anode Mud (sludge)**.

- **Zn will oxidize first (highest Ox. Potential), putting Zn^{2+} ions into the solution. Zn \rightarrow Zn^{2+} + 2e^-**

- **Once Zn is gone, Cu^{2+} (the next highest Ox. Potential) will start oxidizing:**
  
  \[ Cu \rightarrow Cu^{2+} + 2e^- \]

- **The solution contains only Cu^{2+}, SO_4^{2-}, and Zn^{2+} ions. Metals above Cu (Au & Ag) have fallen to the Anode mud **not** oxidized into ions!**

- **The solution is CuSO_4(aq)**
  
  So there are lots of Cu^{2+} ions there to begin with.

- **Going towards the Cathode**

- **Anode Mud**

- **IMPURE ANODE**
Now, let’s look at the **CATHODE**

Coming from the Anode

An Excess of e’s are forced onto the Cathode by the external power supply. The Cathode thus becomes Negative.

Electroplating

An application of an electrolytic cell is Electroplating. In **Electroplating**:

- The **object to be Plated** is the **Cathode** (attached to the Negative Terminal of the Battery)
- The **Electrolyte** must contain the **Cation of the Metal** to be Plated on the Object
- The **Best Anode** is the **Metal to be Plated** onto the Object
Example: We wish to plate and Iron ring with Copper.

- The **Iron Ring** (made by Dwarfs?) is made the **Cathode** (connected to the **negative**)
- The **Anode** is **Copper** (to keep supplying Cu$^{2+}$ ions as it is oxidized)
- The **Electrolyte** is aqueous CuSO$_4$ (supplies Cu$^{2+}$ to start with. SO$_4^{2-}$ does not react here.)

Here is the diagram of the set-up:

**Electrowinning**

The name given to the **reduction of ores** to produce **metals** in industry.

Eg.)  \[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}_{(s)} \]

Comes from Zinc ores like ZnS, ZnCl$_2$ etc.

Zinc Metal
**Aluminum Production**

Looking at the reduction table:

We see that Al$^{3+}$ is BELOW the left overpotential arrow. Therefore, Al$^{3+}$ CANNOT be reduced from an aqueous (water) solution.

In order to reduce Al$^{3+}$ to its metal Al, you must electrolyze a MOLTEN salt of aluminum.

The main ore used to produce Aluminum is called **Bauxite** – Hydrated Aluminum Oxide or Al$_2$O$_3$$\cdot$3H$_2$O.

When this is heated, the water is forced off: Al$_2$O$_3$$\cdot$3H$_2$O $\xrightarrow{\text{heat}}$ Al$_2$O$_3$ $+$ 3H$_2$O

The melting point of Alumina (Al$_2$O$_3$) is much too high to melt it economically. (mp. $=$ 2072 °C)

So Alumina (Al$_2$O$_3$) is mixed with Cryolite (Na$_3$AlF$_6$)

The melting point of this mixture is $\approx$ 1000 °C.

Some of the ions present in this mixture of molten salts are: Al$^{3+}$, O$^{2-}$, F$^-$ and Na$^+$

The Half-Reaction at the Cathode is the Reduction of Al$^{3+}$ ions to Al metal:

**Cathode** Half-Reaction: Al$^{3+}$(l) $+$ 3e$^-$ $\rightarrow$ Al(l)

(At these high temperatures both Al$^{3+}$ & Al are liquids)

The Half-Reaction at the Anode is the Oxidation of oxide ions using Carbon Electrodes:

**Anode** Half-Reaction: C(s) $+$ 2O$^{2-}$ $\rightarrow$ CO$_2$(g) $+$ 4e$^-$

Some texts state more simply: 2O$^{2-}$ $\rightarrow$ O$_2$ $+$ 4e$^-$

Remember, there is NO water in this mixture. It is molten.
This process is carried out by Alcan in Kitimat, B.C. It uses 10 million amps of electricity. Alcan has their own power generating plant at Kemano B.C.

Because of high temperature and great amounts of electrical energy used, production of Al is expensive! Recycling Al used a lot less energy!

**Corrosion**

Corrosion is Undesirable Oxidation of a metal (usually Fe)

**Oxygen** from the air is reduced at the **Cathode**

The Fe becomes the **Anode** (is oxidized)

**Moisture** can provide a solution for these processes to take place in. O₂ from the air dissolves in the water droplet. The dissolved O₂ is reduced at the Cathode and the iron surface becomes the Anode. The series of reactions that take place are as follows:

1. Fe → Fe²⁺ + 2e⁻ (iron is oxidized to Fe²⁺)
2. ½ O₂ + H₂O + 2e⁻ → 2 OH⁻ (O₂ picks up e⁻ from the Fe and is reduced to OH⁻)
3. Fe²⁺ + 2 OH⁻ → Fe(OH)₂(s) (the Fe²⁺ from Rx.1 and the OH⁻ from Rx.2 form the ppt. (Fe(OH)₂(s)) Oxidized by O₂ and H₂O
4. Fe(OH)₂ → Fe(OH)₃(s)
5. Some Fe(OH)₃(s) Reacts with H₂O to produce Fe₂O₃·3H₂O(s) (Hydrated Iron(III) Oxide)

A mixture of Fe(OH)₃(s) and Fe₂O₃·3H₂O(s) is called **RUST**

**Preventing Corrosion**

✓ Keep the Fe (or steel) surface protected from moisture and oxygen – Paint or other Coatings

✓ Keep the Fe away from metals which are higher on the Reduction Table. (eg.) When Fe and Cu are in close proximity and the conditions are right—moisture is present and there are some dissolved salts—a type of Electrochemical Cell can form in which Cu becomes the Cathode and Fe becomes the Anode (and Fe is oxidized)
✔ Use what’s called **Cathodic Protection**

**In Cathodic Protection:**
A metal lower on the Reduction Table (higher oxidation potential) is attached to or brought near to the Fe.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reaction</th>
<th>Oxidation Potential (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe⁺⁺</td>
<td>Fe⁺⁺⁺</td>
<td>-0.45</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>Ag⁺⁺</td>
<td>-0.69</td>
</tr>
<tr>
<td>Cr⁺⁺</td>
<td>Cr⁺⁺⁺</td>
<td>-0.74</td>
</tr>
<tr>
<td>Zn⁺⁺</td>
<td>Zn⁺⁺⁺</td>
<td>-0.76</td>
</tr>
<tr>
<td>Ti⁺⁺⁺</td>
<td>Ti⁺⁺⁺⁺</td>
<td>-0.79</td>
</tr>
<tr>
<td>H⁺⁺⁺⁺</td>
<td>H⁺⁺⁺⁺⁺</td>
<td>-0.83</td>
</tr>
<tr>
<td>Mn⁺⁺</td>
<td>Mn⁺⁺⁺</td>
<td>-1.19</td>
</tr>
<tr>
<td>Al⁺⁺</td>
<td>Al⁺⁺⁺</td>
<td>-1.66</td>
</tr>
<tr>
<td>Mg⁺⁺</td>
<td>Mg⁺⁺⁺</td>
<td>-2.37</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Na⁺⁺⁺</td>
<td>-2.71</td>
</tr>
<tr>
<td>Ca⁺⁺⁺</td>
<td>Ca⁺⁺⁺⁺</td>
<td>-2.87</td>
</tr>
<tr>
<td>Sr⁺⁺⁺</td>
<td>Sr⁺⁺⁺⁺</td>
<td>-2.99</td>
</tr>
<tr>
<td>Ba⁺⁺⁺</td>
<td>Ba⁺⁺⁺⁺</td>
<td>-2.91</td>
</tr>
<tr>
<td>K⁺</td>
<td>K⁺⁺⁺⁺</td>
<td>-2.93</td>
</tr>
<tr>
<td>Rb⁺⁺⁺</td>
<td>Rb⁺⁺⁺⁺</td>
<td>-2.98</td>
</tr>
<tr>
<td>Cs⁺⁺⁺</td>
<td>Cs⁺⁺⁺⁺</td>
<td>-3.03</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Li⁺⁺⁺⁺⁺</td>
<td>-3.04</td>
</tr>
</tbody>
</table>

An example would be Mg

In the presence of O₂ or any other oxidizing agent, Mg (with an oxidation potential = +2.37 v) will give up e⁻’s more readily than Fe (oxidation potential = +0.45 v).

This saves the Fe from being oxidized!

**Some common examples of Cathodic Protection:**
✔ Plates of Mg are attached to the hulls of ships. When Mg is oxidized it is replaced.

✔ Galvanized Steel is Steel (mainly Fe) coated or mixed with Zn (oxidation potential = +0.76v)

\[ \text{Zn} \rightarrow \text{Zn}^{2⁺} + 2e⁻ \quad \text{a strong coating of ZnO is formed, protecting the metal from further oxidation.} \]

✔ Stainless Steel contains Fe with other metals like Cr etc.

**Impressed Current**
A voltage is applied with an external power supply to keep the Fe slightly negative. Thus, the Fe surface has excess e⁻’s so it doesn’t have to oxidize in order to supply e⁻’s to O₂.

*The End of Chem 12 Notes!* *(And you thought we’d never get there!)*