Electrochemistry
-- Electrochemistry deals with the relationship between chemical change and electricity

-- Electrochemical cells (two types)
  • Galvanic cells -- use a spontaneous ($\Delta G < 0$) reaction to produce electricity (batteries)
  • Electrolytic cells -- use a source of electricity to drive a non-spontaneous ($\Delta G > 0$) reaction (electrolysis)

21.1 Redox Half-Reactions

• Redox reactions involve $e^-$ transfer
  -- Oxidation -- loss of $e^-$ (oxidation state $\uparrow$)
  -- Reduction -- gain of $e^-$ (oxidation state $\downarrow$)

• Half-reactions -- focus on oxidation and reduction separately

Example: Ca(s) + Cl2(g) $\rightarrow$ CaCl2(s)

→ CaCl2(s) consists of Ca$^{2+}$ and Cl$^-$ ions

→ Ca(s) → Ca$^{2+}$ + 2e$^-$ (loss of 2e$, oxidation)

→ Cl2(g) + 2e$^-$ $\rightarrow$ 2Cl$^-$ (gain of 2e$, reduction)

Adding the half-reactions gives the overall reaction

Ca(s) + Cl2(g) + 2e$^-$ $\rightarrow$ Ca$^{2+}$ + 2e$^-$ + 2Cl$^-$

⇒ Ca is oxidized (Ca is the reducing agent)
⇒ Cl2 is reduced (Cl2 is the oxidizing agent)

Generalized expressions for half reactions:

Red/ → Ox + $n e^-$

Ox/Red form a redox couple (Ex: Ca$^{2+}$/Ca; Cl2/Cl$^-$)

Balancing Redox Reactions

• Half-reaction method -- divides the overall reaction into two half-reactions

• Balancing in acidic solutions

1. Identify the redox couples and write the half-reactions
2. Balance each half-reaction separately:
   - 1st, balance all elements other than O and H
   - 2nd, balance O by adding H2O
   - 3rd, balance H by adding H$^+$
   - 4th, balance the charge by adding e$^-$
3. Multiply the half-reactions by integers to equal the # of e$^-$ in them
4. Add the half-reactions and cancel the e$^-$

Example: Balance the following skeleton equation in acidic solution: V$^{3+}$ + Ce$^{4+}$ $\rightarrow$ VO$^{2+}$ + Ce$^{3+}$

1. Redox couples: VO$^{2+}$/V$^{3+}$ and Ce$^{4+}$/Ce$^{3+}$
   Half-reactions: V$^{3+}$ $\rightarrow$ VO$^{2+}$ and Ce$^{4+}$ $\rightarrow$ Ce$^{3+}$

2. V$^{3+}$ $\rightarrow$ VO$^{2+}$
   V$^{3+}$ + 2H$^+_2$O → VO$^{2+}$ + 4H$^+$ + 2e$^-$ (balance charge)

3. Multiply the 2nd half-reaction by 2 to get 2e$^-$
   2Ce$^{4+}$ + 2e$^-$ $\rightarrow$ 2Ce$^{3+}$

4. Add the half-reactions

V$^{3+}$ + 2H$^+_2$O + 2Ce$^{4+}$ + 2e$^-$ $\rightarrow$ VO$^{2+}$ + 2Ce$^{3+}$ + 4H$^+$

⇒ V$^{3+}$ + 2Ce$^{4+}$ + 2H$^+_2$O $\rightarrow$ VO$^{2+}$ + 2Ce$^{3+}$ + 4H$^+$

Note: If H3O$^+$ is required in the equation instead of H$^+$, add as many water molecules on both sides as the # of H$^+$ ions

⇒ V$^{3+}$ + 2Ce$^{4+}$ + 6H$^+_2$O $\rightarrow$ VO$^{2+}$ + 2Ce$^{3+}$ + 4H$^+_3$O$^+$

• Balancing in basic solutions

   - The same four steps are used plus a fifth step:
   - 5. Add OH$^-$ on both sides of the equation in order to neutralize the H$^+$, and cancel the water molecules if necessary
3. Multiply the 1st half-reaction by 2 and the 2nd by 3 to get 6e⁻ in both half-reactions

\[
\begin{align*}
&2\text{CrO}_2^- + 4\text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- \\
&3\text{BrO}_4^- + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{BrO}_3^- + 3\text{H}_2\text{O}
\end{align*}
\]

4. Add the half-reactions

\[
\begin{align*}
2\text{CrO}_2^- + 4\text{H}_2\text{O} + 3\text{BrO}_4^- + 6\text{H}^+ + 6\text{e}^- & \rightarrow \\
2\text{CrO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- + 3\text{BrO}_3^- + 3\text{H}_2\text{O}
\end{align*}
\]

5. Add 2OH⁻ on both sides of the equation

\[
\begin{align*}
2\text{CrO}_2^- + 3\text{BrO}_4^- + \text{H}_2\text{O} + 2\text{OH}^- & \rightarrow \\
2\text{CrO}_4^{2-} + 3\text{BrO}_3^- + 2\text{H}^+ + 2\text{OH}^-
\end{align*}
\]

\[
2\text{CrO}_2^- + 3\text{BrO}_4^- + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + 3\text{BrO}_3^- + \text{H}_2\text{O}
\]

21.2 Galvanic (Voltaic) Cells

- Produce electricity from a spontaneous chemical reaction

**Example:** Zn metal reacts spontaneously with Cu²⁺ solutions to yield metallic Cu and Zn²⁺ ions

\[
\begin{align*}
\text{Zn(s)} & \rightarrow \text{Zn}^{2+} + 2\text{e}^- \\
\text{Cu}^{2+} + 2\text{e}^- & \rightarrow \text{Cu(s)}
\end{align*}
\]

The two half-reactions are:

\[
\begin{align*}
\text{Zn(s)} & \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad \text{(oxidation)} \\
\text{Cu}^{2+} + 2\text{e}^- & \rightarrow \text{Cu(s)} \quad \text{(reduction)}
\end{align*}
\]

- The two half-reactions can be **physically separated** by placing them in separate containers (half-cells)

- **Galvanic Cells** → where the half-reactions occur
  - Anode half-cell → where oxidation occurs
  - Cathode half-cell → where reduction occurs

- **Electrodes** → in contact with the electrolyte solutions and the external electrical circuit
  - **Anode** (oxidation)
  - **Cathode** (reduction)

  - In voltaic cells, the anode is (-) and the cathode is (+)
  - The e⁻s flow from the anode toward the cathode

- **Salt bridge** → completes the electrical circuit and maintains electrical neutrality of the half-cells (porous material soaked in a concentrated electrolyte solution)

  - **Anions** in the salt bridge flow toward the anode
  - **Cations** in the salt bridge flow toward the cathode

  - By convention, the anode half-cell appears on the left

Galvanic Cell Notation

- **Half-cell notation**
  - Different phases are separated by vertical lines
  - Species in the same phase are separated by commas

- **Types of electrodes**
  - **Active** electrodes – involved in the electrode half-reaction (most metal electrodes)
  - **Inactive (inert)** electrodes – not involved in the electrode half-reaction (inert solid conductors; serve as a contact between the solution and the external el. circuit)

**Example:** Pt electrode in Fe³⁺/Fe²⁺ soln.

\[
\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad \text{(as reduction)}
\]

- Notation: \(\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt(s)}\)

  - Electrodes involving metals and their slightly soluble salts

**Example:** Ag/AgCl electrode

\[
\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^- \quad \text{(as reduction)}
\]

- Notation: \(\text{Cl}^- | \text{AgCl(s)} | \text{Ag(s)}\)
Electrodes involving gases – a gas is bubbled over an inert electrode

Example: H₂ gas over Pt electrode
H₂(g) → 2H⁺ + 2e⁻ (as oxidation)
Notation: Pt(s) | H₂(g) | H⁺

• Cell notation
  – The anode half-cell is written on the left of the cathode half-cell
  – The electrodes appear on the far left (anode) and far right (cathode) of the notation
  – Salt bridges are represented by double vertical lines

Example: A combination of the Pt(s) | H₂(g) | H⁺ and Cl⁻ | AgCl(s) | Ag(s) half-cells leads to:
H₂(g) → 2H⁺ + 2e⁻ (anode, oxidation)
AgCl(s) + e⁻ → Ag(s) + Cl⁻ (cathode, reduction)
2AgCl(s) + H₂(g) → 2Ag(s) + 2H⁺ + 2Cl⁻
⇒ Pt(s) | H₂(g) | H⁺, Cl⁻ | AgCl(s) | Ag(s)

Example: A combination of the Zn(s) | Zn²⁺ and Fe³⁺, Fe²⁺ | Pt(s) half-cells leads to:
⇒ Zn(s) | Zn²⁺ || Fe³⁺, Fe²⁺ | Pt(s)

Example: Write the cell reaction and the cell notation for a cell consisting of a graphite cathode immersed in an acidic solution of MnO₄⁻ and Mn²⁺ and a graphite anode immersed in a solution of Sn⁴⁺ and Sn²⁺.
Write the half reactions (a list of the most common half-reactions is given in Appendix D)
Sn²⁺ → Sn⁴⁺ + 2e⁻ ×5 (oxidation)
MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O(l) ×2 (reduction)
5Sn²⁺ + 2MnO₄⁻ + 16H⁺ + 10e⁻ → 5Sn⁴⁺ + 2Mn²⁺ + 8H₂O(l)
The graphite (C) electrodes are inactive
⇒ C(s) | Sn²⁺, Sn⁴⁺ || H⁺, MnO₄⁻, Mn²⁺ | C(s)

Why Do Galvanic Cells Work?
• Consider a cell made of two active metal electrodes, M₁ and M₂, and their ions.
  ➢ If the cell circuit is open, the two metals are in equilibrium with their ions
1) M₁ ⇌ M₁⁺ + e⁻
2) M₂ ⇌ M₂⁺ + e⁻
  ➢ The produced electrons accumulate in the metal electrodes and produce electrical potentials
  ➢ If M₁ has a greater tendency to give out its electrons, the first equilibrium is shifted further to the right and the potential of M₁ is more negative
  ➢ When the circuit is closed, electrons flow from the more negative M₁ (anode) toward the less negative M₂ (cathode)

21.3 Cell Potentials
• Electromotive force (emf) – drives the electrons in the el. circuit
  ➢ emf is the difference between the electrical potentials of the two electrodes (voltage)
• Cell potential (Eᵢ_cell) → Eᵢ_cell = emf
  ➢ Units → volts (V) → (1 V = 1 J/C since the electrical work is equal to the applied voltage times the charge moving between the electrodes)
• Standard cell potential (E°ᵢ_cell) – the cell potential at standard-state conditions (gases → 1 atm, solutions → 1 M, liquids & solids → pure)
E_cell is measured with a voltmeter

If the (+) terminal of the voltmeter is connected to the (+) electrode (cathode), the voltmeter shows a positive reading

E_cell characterizes the overall cell reaction

If E_cell > 0, the cell reaction is spontaneous

If E_cell < 0, the cell reaction is non-spontaneous

If E_cell = 0, the cell reaction is at equilibrium

Example: Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s)

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

E^o_{cell} = +1.10 V > 0 \rightarrow \text{spontaneous reaction}

Electrode potentials (E) – characterize the individual electrodes (half-reactions)

The cell potential is the difference between the electrode potentials of the cathode and anode

E^o_{cell} = E^o_{cathode} - E^o_{anode}

Standard electrode potentials (E^o) – electrode potentials at the standard-state

E^o_{cell} = E^o_{cathode} - E^o_{anode}

- E^o values are reported for the half-reaction
  written as reduction (standard reduction potentials) \rightarrow listed in Appendix D

Absolute values for E and E^o can’t be measured

⇒ A reference electrode (half-cell) is needed

- The potentials of all electrodes are measured relative to the reference electrode

Standard hydrogen electrode – used as a reference electrode \rightarrow E^o_{ref} = 0 V (assumed)

H^+(1M) | H_2(g, 1atm) || Pt(s)

2H^+(1M) + 2e^- \rightarrow H_2(g, 1atm)

- To find the potential of any electrode, a cell is constructed between the unknown electrode and the reference electrode
- The cell potential is directly related to the unknown electrode potential

Determination of Electrode Potentials

- Electrode potentials can be determined by measurements versus the standard H-electrode or other electrodes with known potentials

Example: E^o_{cell} = +0.46 V for the reaction:

Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)

If E^o = +0.34 V for the Cu^{2+}/Cu redox couple, what is E^o for the Ag^+/Ag redox couple?

⇒ Split into half-reactions:

Cu(s) \rightarrow Cu^{2+} + 2e^- \hspace{1cm} E^o_{Cu} = +0.34 V \hspace{1cm} \text{(anode, ox)}

Ag^+ + e^- \rightarrow Ag(s) \hspace{1cm} E^o_{Ag} = ??? V \hspace{1cm} \text{(cathode, red)}

E^o_{cell} = E^o_{Ag} - E^o_{Cu} = E^o_{Ag} - (+0.34) = +0.46

⇒ E^o_{Ag} = +0.46 + (+0.34) = +0.80 V

Using Cell Potentials in Calculations

- Cell potentials are additive
  - If two reactions are added, their potentials are added too

- Cell potentials are intensive properties – remain independent of the system size
  - If a reaction (or a half-reaction) is multiplied by a number, its potential remains the same

Example:

Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)

E^o_{cell} = +0.46 V

3Ag(s) + Au^{3+} \rightarrow 3Ag^+ + Au(s)

E^o_{cell} = +0.70 V

3Cu(s) + 2Au^{3+} \rightarrow 3Cu^{2+} + 2Au(s)

E^o_{cell} = +0.46 + 0.70 = +1.16 V

Example:

Pt(s) | H_2(g, 1atm) || H^+(1M), Cl^-(1M) | AgCl(s) | Ag(s)

H^+/H_2 \rightarrow \text{anode}

Ag/AgCl \rightarrow \text{cathode}

E^o_{cell} = E^o_{Ag/AgCl} - E^o_{ref}

E^o_{Ag/AgCl} = +0.22 V

\[ E^o_{cell} = +0.46 + (-0.22) = +0.24 V \]

Pt(s) | H_2(g, 1atm) || H^+(1M), Cl^-(1M) | AgCl(s) | Ag(s)

H^+/H_2 \rightarrow \text{anode}

Ag/AgCl \rightarrow \text{cathode}

E^o_{cell} = E^o_{Ag/AgCl} - E^o_{ref}

E^o_{Ag/AgCl} = +0.22 V
**Strengths of Oxidizing and Reducing Agents**

- \( E^o \) values are always tabulated for reduction
  
  \[ \text{Ox} + n\text{e}^- \rightarrow \text{Red} \quad (E^o) \]
  
  - Ox is an oxidizing agent; Red is a reducing agent
  
  - \( E^o \) is a measure for the tendency of the half-reaction to undergo reduction
  
  \( \Rightarrow \) Higher (more positive) \( E^o \) means
    - Greater tendency for reduction
    - Lower tendency for oxidation
  
  \( \Rightarrow \) Higher (more positive) \( E^o \) means
    - Stronger oxidizing agent (Ox) \( \rightarrow \) Ox is reduced
    - Weaker reducing agent (Red) \( \rightarrow \) Red is oxidized

- In a spontaneous redox reaction, the stronger oxidizing and reducing agents react to produce the weaker oxidizing and reducing agents
  
  Stronger Red\(_1\) + Stronger Ox\(_2\) \rightarrow Weaker Ox\(_1\) + Weaker Red\(_2\)

**Example:**

Given the following half-reactions:

- \( \text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^- \quad E^o = +1.36 \text{ V} \)
- \( \text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l) \quad E^o = +1.23 \text{ V} \)
- \( \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad E^o = +0.77 \text{ V} \)
- \( \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(s) \quad E^o = -0.44 \text{ V} \)

\( \text{Cl}_2(g) + 2\text{e}^- \rightarrow 2\text{Cl}^- \quad (E^o) \)

\( \text{O}_2(g) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l) \quad (E^o) \)

\( \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad (E^o) \)

\( \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(s) \quad (E^o) \)

**a)** Rank the oxidizing and reducing agents by strength

\( \text{Ox} \) agents on the left; \( \text{Red} \) agents on the right

- \( \text{Oxidizing} \rightarrow \) (Top) \( \text{Cl}_2 > \text{O}_2 > \text{Fe}^{3+} > \text{Fe}^{2+} \) (Bottom)
- \( \text{Reducing} \rightarrow \) (Bottom) \( \text{Fe} > \text{Fe}^{3+} > \text{H}_2\text{O} > \text{Cl}^- \) (Top)

**d)** Is the reaction of disproportionation (simultaneous oxidation and reduction) of \( \text{Fe}^{3+} \) to \( \text{Fe}^{3+} \) and \( \text{Fe}(s) \) spontaneous at standard conditions?

→ Need the sign of \( E^o_{\text{cell}} \)

\( \Rightarrow \) \( \text{Fe}^{2+}/\text{Fe}(s) \) undergoes reduction

\( \Rightarrow \) \( \text{Fe}^{3+}/\text{Fe}^{2+} \) undergoes oxidation (reverse equation)

\( \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(s) \quad (\text{reduction}) \quad E^o = -0.44 \text{ V} \)

\( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \quad \times 2 \quad (\text{oxidation}) \quad E^o = +0.77 \text{ V} \)

\( 3\text{Fe}^{3+} + 2\text{e}^- \rightarrow \text{Fe}(s) + 2\text{Fe}^{2+} + 2\text{e}^- \)

\( E^o_{\text{cell}} = E^o_{\text{cath}} - E^o_{\text{anod}} = -0.44 - (+0.77) = -1.21 \text{ V} \)

\( \Rightarrow E^o_{\text{cell}} < 0 \) \( \rightarrow \) the reaction is non-spontaneous at standard conditions

**Relative Reactivity of Metals**

- The *activity series* of metals – ranks metals based on their ability to displace \( \text{H}_2 \) from acids or water or displace each other’s ions in solution

- **Metals that can displace \( \text{H}_2 \) from acids**

  - The reduction of \( \text{H}^+ \) from acids to \( \text{H}_2 \) is given by the standard hydrogen half-reaction
    \( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(g) \quad E^o = 0 \text{ V} \)

  - In order for this half-reaction to proceed as written, the metal must have lower reduction potential (the metal must be below \( \text{H}^+/\text{H}_2 \) in Appendix D)

  \( \Rightarrow \) If \( E^o_{\text{metal}} < 0 \), the metal **can** displace \( \text{H}_2 \) from acids

  \( \Rightarrow \) If \( E^o_{\text{metal}} > 0 \), the metal **cannot** displace \( \text{H}_2 \)

- **Electrochemical series** – an arrangement of the redox couples in order of decreasing reduction potentials \( (E^o) \) \( \rightarrow \) Appendix D

  - The most positive \( E^o \)s are at the top of the table
  
  - The most negative \( E^o \)s are at the bottom of the table

  \( \Rightarrow \) The **strongest oxidizing agents** (Ox) are at the top of the table as reactants

  \( \Rightarrow \) The **strongest reducing agents** (Red) are at the bottom of the table as products

  - Every redox reaction is a sum of two half-reactions, one occurring as oxidation and another as reduction

    \( \text{Red}_1 \rightarrow \text{Ox}_1 + n\text{e}^- \quad \text{Ox}_2 + n\text{e}^- \rightarrow \text{Red}_2 \)

    \( \text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2 \)
Example: Can Fe and Cu be dissolved in HCl(aq)?
→ Fe$^{2+}$/Fe is below and Cu$^{2+}$/Cu is above H$_2$/H$^+$

\[ \begin{align*}
2H^+ + 2e^- &\rightarrow H_2(g) \quad \text{(reduction)} \quad E^o = 0.00 \text{ V} \\
\text{Fe(s)} &\rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(oxidation)} \quad E^o = -0.44 \text{ V}
\end{align*} \]

\[ \begin{align*}
2H^+ + 2e^- + \text{Fe(s)} &\rightarrow H_2(g) + \text{Fe}^{2+} + 2e^- \\
E^o_{\text{cell}} &= E^o_{\text{cath}} - E^o_{\text{anod}} = 0.00 - (-0.44) = +0.44 \text{ V}
\end{align*} \]

⇒ $E^o_{\text{cell}} > 0$ → spontaneous (Fe dissolves in HCl)

\[ \begin{align*}
2H^+ + 2e^- + \text{Cu(s)} &\rightarrow H_2(g) + \text{Cu}^{2+} + 2e^- \\
E^o_{\text{cell}} &= E^o_{\text{cath}} - E^o_{\text{anod}} = 0.00 - (+0.34) = -0.34 \text{ V}
\end{align*} \]

⇒ $E^o_{\text{cell}} < 0$ → non-spontaneous (Cu doesn’t dissolve)

### 21.4 Free Energy and Electrical Work

**Relationship Between $E_{\text{cell}}$ and $\Delta G$**

- **Electrical work ($w$)**
  \[ w = \text{(charge transferred)} \times \text{(voltage)} \]
  \[ -n \rightarrow \# \text{ mol } e^- \text{ transferred} \]
  \[ F = \text{charge of 1 mol } e^- \]

\[ w = -nFE_{\text{cell}} \quad \text{(voltage)} = E_{\text{cell}} \]

⇒ If the process is carried out reversibly ($w = w_{\text{max}}$)

\[ \Delta G_r = -nFE_{\text{cell}} \quad \text{and} \quad \Delta G_r^o = -nFE_{\text{cell}}^o \]

\[ F = 96485 \text{ C/mol} \rightarrow \text{Faraday constant} \]

- **Metals that can displace H$_2$ from water**
  - The reduction of H$_2$O to H$_2$ is given by:
  \[ 2H_2O(l) + 2e^- + 2K^+ + 2e^- \rightarrow 2H_2(g) + 2OH^- \quad E^o = -0.42 \text{ V} \]
  - The value of E is for pH = 7 (nonstandard state)

⇒ Metals that are below H$_2$O/H$_2$OH$^-$ in Appendix D can displace H$_2$ from water at standard conditions

⇒ Metals that have $E^o_{\text{metal}} < -0.42$ can displace H$_2$ from water at pH = 7

**Example:** Potassium, K, dissolves readily in water

\[ 2H_2O(l) + 2e^- + K^+ + e^- \rightarrow 2OH^- + 2K^+ \quad E^o = -2.93 \text{ V} \]

\[ 2K(s) + H_2O(l) \rightarrow 2OH^- + 2K^+ + 2e^- \quad E^o_{\text{cell}} = -0.42 - (-2.93) = +2.51 > 0 \quad \text{(spontaneous)} \]

- **Faraday’s constant**

\[ F = 96485 \text{ C/mol} \]

- **The reduction of H$_2$O to H$_2$ is given by:**

\[ 2H_2O(l) + 2e^- + 2K^+ + 2e^- \rightarrow 2H_2(g) + 2OH^- \quad E^o = -0.42 \text{ V} \]

- **Metals that can displace H$_2$ from water**
  - The reduction of H$_2$O to H$_2$ is given by:
  \[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E = -0.42 \text{ V} \]
  - The value of E is for pH = 7 (nonstandard state)

- **Metals that are below H$_2$O/H$_2$OH$^-$ in Appendix D can displace H$_2$ from water at standard conditions**

- **Metals that have $E^o_{\text{metal}} < -0.42$ can displace H$_2$ from water at pH = 7**

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- **The reduction of H$_2$O to H$_2$ is given by:**

\[ 2H_2O(l) + 2e^- + 2K^+ + 2e^- \rightarrow 2H_2(g) + 2OH^- \quad E^o = -0.42 \text{ V} \]

- **Metals that can displace H$_2$ from water**
  - The reduction of H$_2$O to H$_2$ is given by:
  \[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E = -0.42 \text{ V} \]
  - The value of E is for pH = 7 (nonstandard state)

⇒ Metals that are below H$_2$O/H$_2$OH$^-$ in Appendix D can displace H$_2$ from water at standard conditions

⇒ Metals that have $E^o_{\text{metal}} < -0.42$ can displace H$_2$ from water at pH = 7

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\[ 2K(s) + H_2O(l) \rightarrow 2OH^- + 2K^+ + 2e^- \quad E^o_{\text{cell}} = -0.42 - (-2.93) = +2.51 > 0 \quad \text{(spontaneous)} \]

- **Faraday’s constant**

\[ F = 96485 \text{ C/mol} \]

- **The reduction of H$_2$O to H$_2$ is given by:**

\[ 2H_2O(l) + 2e^- + 2K^+ + 2e^- \rightarrow 2H_2(g) + 2OH^- \quad E^o = -0.42 \text{ V} \]

- **Metals that can displace H$_2$ from water**
  - The reduction of H$_2$O to H$_2$ is given by:
  \[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- \quad E = -0.42 \text{ V} \]
  - The value of E is for pH = 7 (nonstandard state)

⇒ Metals that are below H$_2$O/H$_2$OH$^-$ in Appendix D can displace H$_2$ from water at standard conditions

⇒ Metals that have $E^o_{\text{metal}} < -0.42$ can displace H$_2$ from water at pH = 7

**Example:** Potassium, K, dissolves readily in water

\[ 2H_2O(l) + 2e^- + K^+ + e^- \rightarrow 2OH^- + 2K^+ \quad E^o = -2.93 \text{ V} \]

\[ 2K(s) + H_2O(l) \rightarrow 2OH^- + 2K^+ + 2e^- \quad E^o_{\text{cell}} = -0.42 - (-2.93) = +2.51 > 0 \quad \text{(spontaneous)} \]
Example: Using $E^o$ values from appendix D, calculate $K$ at 298 K for the reaction:

$$2\text{Cr}^{2+} + \text{Br}_2(l) \rightarrow 2\text{Cr}^{3+} + 2\text{Br}^-$$

$\rightarrow$ This is the reverse of the reaction in the previous example ($E^o_{cell} = -1.47 \text{ V}$ from previous example)

$\rightarrow E_{reverse} = -E_{forward}$

$\Rightarrow E^o_{cell} = E^o_{cell} - (-1.47 \text{ V}) = +1.47 \text{ V}$

$\Rightarrow E^o_{cell} > 0 \rightarrow$ the reaction is spontaneous at standard conditions

$\Rightarrow K >> 1 \rightarrow$ the products are favored at equilibrium

---

Example: Calculate $K_{sp}$ of PbSO$_4$ at 298 K.

PbSO$_4$(s) $\rightarrow$ Pb$^{2+}$ + SO$_4^{2-}$ $K_{sp} = ?$

$\rightarrow$ Not a redox reaction, but it can be represented as a sum of two redox half-reactions

PbSO$_4$(s) + 2e$^-$ $\rightarrow$ Pb(s) + SO$_4^{2-}$ (reduction) $E^o = -0.36 \text{ V}$

Pb(s) $\rightarrow$ Pb$^{2+}$ + 2e$^-$ (oxidation) $E^o = -0.13 \text{ V}$

$$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.36 - (-0.13) = -0.23 \text{ V}$$

$\Rightarrow K_{sp} = e^{rac{nE^o_{cell}}{RT}} = e^{-0.0257} = 1.7 \times 10^{-8}$

$\Rightarrow E^o_{cell} < 0 \rightarrow$ the dissolution of PbSO$_4$ is non-spontaneous at 298 K ($K_{sp} << 1$)

---

The Nernst equation applies also to half-reactions ($E$ and $E^o$ are used instead of $E_{cell}$ and $E^o_{cell}$)

Example: Calculate the electrode potential of the Cu$^{2+}$/Cu redox couple at 298 K, if the concentration of Cu$^{2+}$ is 0.025 M.

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s) \quad E^o = +0.34 \text{ V}$$

$\rightarrow$ Use the Nernst eq. to get $E$

$\rightarrow Q = 1/[\text{Cu}^{2+}] = 1/0.025$ and $n = 2$

$$E = E^o - \frac{0.0257}{n} \ln Q = +0.34 - \frac{0.0257}{2} \ln \left(\frac{1}{0.025}\right)$$

$E = +0.34 - 0.047 = 0.29 \text{ V}$

---

The Effect of Concentration on $E_{cell}$

$\bullet$ The Nernst equation – gives the variation of the cell potential with composition

$$\Delta G_r = \Delta G^o_r + RT \ln Q$$

$$\Delta G_r = -nFE^o_{cell}$$

$\Rightarrow -nFE^o_{cell} = -nFE^o_{cell} + RT \ln Q$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q$$

$\rightarrow$ At 298 K

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n} \ln Q$$

$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q$

$E_{cell}$ in Relation to $Q$ and $K$

$\Rightarrow$ From $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$:

$\Rightarrow$ If $Q < 1$ (more reactants), $\ln Q < 0$, and $E_{cell} > E^o_{cell}$

$\Rightarrow$ If $Q > 1$ (more products), $\ln Q > 0$, and $E_{cell} < E^o_{cell}$

$\Rightarrow$ If $Q = 1$ (standard state), $\ln Q = 0$, and $E_{cell} = E^o_{cell}$

$\Rightarrow$ Combining $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$ with $E^o_{cell} = (RT/nF) \ln K$ leads to:

$$\rightarrow E_{cell} = (RT/nF) \ln K - (RT/nF) \ln Q$$

$\Rightarrow$ If $Q < K$, $E_{cell} > 0$ $\rightarrow$ forward reaction is spontaneous

$\Rightarrow$ If $Q > K$, $E_{cell} < 0$ $\rightarrow$ reverse reaction is spontaneous

$\Rightarrow$ If $Q = K$, $E_{cell} = 0$ $\rightarrow$ reaction is at equilibrium
Concentration Cells

- **Concentration cell** – contains the same redox couple in both the anode and cathode half-cells
  - The anode and cathode are the same
  - The concentrations of the components are different in the two half-cells
    \[ E_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0 \]

**Example:** Cu\(^{2+}\)/Cu concentration cell (\(E^{\circ}_{\text{Cu}} = 0.34\) V)

\[ \text{Cu}^{2+}(1.0\text{ M}) + 2e^- \rightarrow \text{Cu}(s) \]  
(cathode, reduction)

\[ \text{Cu}(s) \rightarrow \text{Cu}^{2+}(0.1\text{ M}) + 2e^- \]  
(anode, oxidation)

\[ \text{Cu}^{2+}(1.0\text{ M}) + 2e^- + \text{Cu}(s) \rightarrow \text{Cu}(s) + \text{Cu}^{2+}(0.1\text{ M}) + 2e^- \]

\[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}} - E^{\circ}_{\text{Cu}} = +0.34 - (+0.34) = 0 \text{ V} \]

Ion-selective electrodes – have potentials that are directly related to the concentration of specific ions such as H\(^+\) (pH), K\(^+\), F\(^-\), Cl\(^-\), Br\(^-\), …

**Example:** Calculate the pH of a solution in which the potential of the H\(^+\) | H\(_2\)(g,1atm) | Pt electrode is \(E = -0.15 \text{ V}\).

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g,1\text{atm}) \]

\[ E^{\circ} = 0.00 \text{ V} \]

\[ Q = \frac{P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{1 \text{ atm}}{[\text{H}^+]^2} \]

\[ n = 2 \]

\[ E = E^{\circ} - \frac{0.0592}{n} \log Q = -0.15 \text{ V} \]

Galvanic Cells as Batteries

- **Primary cells** – can’t be recharged
  - The battery dies when the reactants are exhausted

**Example:** The alkaline battery – a dry cell

Cathode (reduction):
\[ 2\text{MnO}_2(s) + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Mn}_2\text{O}_3(s) + 2\text{OH}^- \]

Anode (oxidation):
\[ \text{Zn}(s) + 2\text{OH}^- \rightarrow \text{ZnO}(s) + \text{H}_2\text{O} + 2e^- \]

Overall:
\[ 2\text{MnO}_2(s) + \text{Zn}(s) \rightarrow 2\text{Mn}_2\text{O}_3(s) + \text{ZnO}(s) \]

Since all reactants and products are solids (dry cell) \(Q = 1\)

\[ E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln 1 = E^{\circ}_{\text{cell}} \approx 1.5 \text{ V} \]

Secondary cells – can be recharged
- The cell is periodically converted to an electrolytic cell in order to convert some of the products back to reactants

**Example:** The lead-acid battery

Cathode (reduction):
\[ \text{Pb}_3\text{O}_4(s) + 3\text{H}^+ + 2e^- \rightarrow 3\text{PbSO}_4(s) + 2\text{H}_2\text{O} \]

Anode (oxidation):
\[ \text{Pb}(s) + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(s) + \text{H}_2\text{O} \]

Overall (cell) reaction:
\[ 2\text{Pb}_3\text{O}_4(s) + 2\text{Pb}(s) + 2\text{H}_2\text{SO}_4(aq) \rightarrow 6\text{PbSO}_4(s) + 2\text{H}_2\text{O} \]

\[ E^{\circ}_{\text{cell}} = 1.685 - (-0.356) = 2.041 \approx 2 \text{ V} \]

\[ E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257}{2} \ln \left( \frac{1}{[\text{H}_2\text{SO}_4]^2} \right) \]

\[ \rightarrow \text{As H}_2\text{SO}_4 \text{ is consumed, } E_{\text{cell}} \text{ drops} \]

\[ \Rightarrow \text{The cell needs to be recharged} \]
• Fuel cells – use combustion reactions
  – The cell must be continuously provided with fuel and oxygen (flow cells)

Example: The hydrogen fuel cell

\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cath}} - E^{\circ}_{\text{anod}}
\]
\[
E^{\circ}_{\text{cell}} = 1.23 - (0.00) \approx 1.2 \text{ V}
\]

\[
Q = \frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}}
\]
\[
E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257}{2} \ln Q
\]

\[
\Rightarrow \uparrow P_{H_2} \text{ and } \uparrow P_{O_2}
\]

leads to \( \Rightarrow E_{\text{cell}} \)

– At pH < 7 (acid rain, etc.), the reduction potentials of H₂O and O₂ are even higher

⇒ Easier oxidation of the metal

Example: Rusting of iron (Fe \( \rightarrow \) E° = -0.44 V)

Cathode, reduction:

\[\text{O}_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) \quad E^\circ = +0.82 \text{ V} \quad (pH = 7)\]

Anode, oxidation:

\[\text{Fe}(s) \rightarrow \text{Fe}^{2+} + 2e^- \quad (x2) \quad \ E^\circ = -0.44 \text{ V} \]

Overall:

\[2\text{Fe}(s) + \text{O}_2(g) + 4H^+ \rightarrow 2\text{Fe}^{2+} + 2H_2O(l) \]

\[E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cath}} - E^{\circ}_{\text{anod}} = +0.82 - (-0.44) = +1.26 \text{ V} \]

⇒ E°_{\text{cell}} > 0 \rightarrow \text{spontaneous reaction}

→ Further oxidation:

\[2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2(g) + (n+2)H_2O(l) \rightarrow \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}(s) + 4H^+\]

21.6 Corrosion

• Unwanted oxidation of metals in the environment
  – If the metal (M) is in contact with water

Cathode, reduction:

\[2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \quad E^\circ = -0.83 \text{ V} \quad \text{at } pH = 7 \]

\[\rightarrow E = -0.42 \text{ V} \]

Anode, oxidation:

\[M(s) \rightarrow M^{n+} + ne^- \quad E^\circ < -0.42 \text{ V} \]

⇒ Any metal with E° < -0.42 V can be oxidized by H₂O

Cathode, reduction:

\[\text{O}_2(g) + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}(l) \quad E^\circ = +1.23 \text{ V} \quad \text{at } pH = 7 \]

\[\rightarrow E = +0.82 \text{ V} \]

Anode, oxidation:

\[M(s) \rightarrow M^{n+} + ne^- \quad E^\circ < +0.82 \text{ V} \]

⇒ Any metal with E° < +0.82 V can be oxidized by H₂O in the presence of O₂

→ Overall rusting process:

\[2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}(l) \]

\[2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2(g) + (n+2)\text{H}_2\text{O}(l) \rightarrow \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}(s) + 4\text{H}^+ \]

Corrosion is enhanced by acidic conditions (\( \uparrow [\text{H}^+] \)) and by salty solutions (improved conductivity)

• Corrosion protection
  – Anodic protection – preoxidation of the metal by formation of a thin layer of protective metal oxide
  – Cathodic protection – connecting the metal to a more strongly reducing metal with lower E° value called sacrificial anode

Example: Protecting Fe construction elements by connecting them to blocks of Mg or Al (sacrificial anodes)

\[E^\circ_{\text{Mg}} = -2.36 \text{ V} \]

\[E^\circ_{\text{Fe}} = -0.44 \text{ V} \]

Example: Galvanization of Fe by coating it with Zn

\[E^\circ_{\text{Zn}} = -0.76 \text{ V} \]

21.7 Electrolytic Cells and Electrolysis

• Electrolytic cells – use external electrical source to drive a non-spontaneous reaction
Electrolytic cells act in reverse (non-spontaneous) direction compared to galvanic cells:

- $E^\circ_{\text{cell}} < 0$ and $\Delta G > 0$ (non-spontaneous reaction)
- The anode is positive and the cathode is negative
- There are some similarities between electrolytic and galvanic cells:
  - Oxidation is always on the anode and reduction is always on the cathode
  - Electrons always flow from anode toward cathode

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>$\Delta G$</th>
<th>$E_{\text{cell}}$</th>
<th>Electrode</th>
<th>Name</th>
<th>Process</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltaic</td>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>Anode</td>
<td>Oxidation</td>
<td>Reduction</td>
<td>-</td>
</tr>
<tr>
<td>Electrolytic</td>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>Anode</td>
<td>Oxidation</td>
<td>Reduction</td>
<td>+</td>
</tr>
</tbody>
</table>

Electrolysis – the passage of electrical current through an electrolyte by applying external voltage (the process in electrolytic cells):

- Electrolysis causes a non-spontaneous reaction (often a splitting of a substance to its elements)
- The applied voltage must be greater than the cell potential of the reverse spontaneous reaction
- The electrolyte can be a molten salt or an aqueous electrolyte solution
- Salt bridges are often not necessary
- During electrolysis the cations are attracted to the cathode (negative) and the anions are attracted to the anode (positive)

Predicting the Products of Electrolysis

- The cations (+) are attracted to the cathode (-) and the anions (-) are attracted to the anode (+)

Electrolysis of molten salts – used for industrial isolation of the most active elements (Na, Li, Mg, Al, …; F₂, Cl₂, Br₂, …)

- The cation is reduced at the cathode
- The anion is oxidized at the anode

Example: Isolation of Na and Cl₂ by electrolysis of molten NaCl

\[
\begin{align*}
\text{Na}^+(l) + e^- & \rightarrow \text{Na}(l) \quad (\times 2) \quad \text{cathode, reduction} \\
2\text{Cl}^-(l) & \rightarrow \text{Cl}_2(g) + 2e^- \quad \text{anode, oxidation} \\
2\text{Na}^+(l) + 2\text{Cl}^-(l) & \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)
\end{align*}
\]

Electrolysis of mixed molten salts

- The cation with higher $E^\circ$ value (the stronger oxidizing agent) is reduced at the cathode
- The anion with lower $E^\circ$ value (the stronger reducing agent) is oxidized at the anode

Note: $E^\circ$ values in appendix D are for aqueous ions and can be used only as approximate guidance. Instead, $EN$ values can be used to estimate the stronger oxidizing and reducing agents.

Example: Predict the products of the electrolysis of a molten mixture of NaCl and AlF₃

- Possible cathode half-reactions (reduction)
  1) Reduction of Na⁺ and 2) Reduction of Al³⁺

→ Al³⁺ is the stronger oxidizing agent because Al is more $EN$ than Na, so Al³⁺ gains electrons easier

⇒ Cathode half-reaction: $\text{Al}^3^+(l) + 3e^- \rightarrow \text{Al}(l)$

⇒ Possible anode half-reactions (oxidation)

1) Oxidation of F⁻ and 2) Oxidation of Cl⁻

→ Cl⁻ is the stronger reducing agent because Cl is less $EN$ than F, so Cl⁻ looses electrons easier

⇒ Anode half-reaction: $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-$

\[
\begin{align*}
\text{Al}^3^+(l) + 3e^- & \rightarrow \text{Al}(l) \quad (\times 2) \quad \text{cathode, reduction} \\
2\text{Cl}^-(l) & \rightarrow \text{Cl}_2(g) + 2e^- \quad (\times 3) \quad \text{anode, oxidation} \\
2\text{Al}^3^+(l) + 6e^- + 6\text{Cl}^-(l) & \rightarrow 2\text{Al}(l) + 2\text{Cl}_2(g) + 6e^-
\end{align*}
\]

⇒ The products are Al(l) and Cl₂(g)
**Electrolysis of water**
- Pure water is hard to electrolyze (low conductivity), so a small amount of a non-reactive salt (NaNO₃) is added (can be neglected)

→ H₂O is reduced at the cathode:

\[ 2H₂O(l) + 2e^- \rightarrow H₂(g) + 2OH^- \quad E^o = -0.83 \text{ V} \]

(at pH = 7) \[ E = -0.42 \text{ V} \]

→ H₂O is oxidized at the anode:

\[ 2H₂O(l) \rightarrow O₂(g) + 4H^+ + 4e^- \quad E^o = +1.23 \text{ V} \]

(at pH = 7) \[ E = +0.82 \text{ V} \]

4H₂O(l) + 4e⁻ + 2H₂O(l) → 2H₂(g) + 4OH⁻ + O₂(g) + 4H⁺ + 4e⁻

→ Overall: \[ 2H₂O(l) \rightarrow 2H₂(g) + O₂(g) \]

\[ E_{cell} = E_{cath} - E_{anod} = -0.42 - (+0.82) = -1.24 \text{ V} \]

→ \( E_{cell} < 0 \) ⇒ non-spontaneous reaction
⇒ To drive the reaction, the external voltage must be greater than 1.24 V

**Overvoltage** – the extra voltage (in the case of water over 1.24) needed to drive the reaction
- For H₂O on most inert electrodes, the overvoltage is 0.4 to 0.6 V per electrode

→ Cathode, reduction:

\[ E = -0.42 - 0.6 \approx -1.0 \text{ V} \]

→ Anode, oxidation:

\[ E = +0.82 + 0.6 \approx +1.4 \text{ V} \]

→ Total: \[ E_{cell} = -1.0 - (+1.4) \approx -2.4 \text{ V} \]

**Example:** Predict the products of the electrolysis of a mixture of 1M NaCl(aq) and 1M KNO₃(aq) with inert electrodes at pH = 7.

→ Possible cathode half-reactions (reduction)
1. Reduction of \( H₂O \)
   \[ 2H₂O(l) + 2e^- \rightarrow H₂(g) + 2OH^- \quad E = -0.42 \text{ V} \]
   → with overvoltage \[ E \approx -1.0 \text{ V} \]
2. Reduction of cations in the solution
   \[ Na^+ + e^- \rightarrow Na(s) \quad E^o = -2.71 \text{ V} \]
   \[ K^+ + e^- \rightarrow K(s) \quad E^o = -2.93 \text{ V} \]

→ Half-reaction (1) has the highest (most positive) \( E \) value ⇒ \( H₂O \) is reduced to \( H₂ \) on the cathode

→ Possible anode half-reactions (oxidation)
1. Oxidation of \( H₂O \)
   \[ 2H₂O(l) \rightarrow O₂(g) + 4H^+ + 4e^- \quad E^o = +1.36 \text{ V} \]
   → with overvoltage \[ E \approx +1.4 \text{ V} \]
2. Oxidation of active metal electrodes – none
3. Oxidation of anions in the solution
   \[ 2Cl^- \rightarrow Cl₂(g) + 2e^- \quad E^o = +1.36 \text{ V} \]

\[ \text{Note: NO}_3^- \text{ can’t be further oxidized (not a product in any half-reaction in appendix D)} \]
→ Half-reaction (3) has the lowest \( E^o \) value ⇒ \( Cl^- \) is oxidized to \( Cl₂ \) on the anode

→ Overall: \[ 2H₂O(l) + 2Cl^- \rightarrow H₂(g) + 2OH^- + Cl₂(g) \]

\[ \text{Note: Without the overvoltage, } H₂O \text{ would be oxidized to } O₂ \text{ at the anode} \]
Electrolysis of aqueous solutions is often used for production or purification of less active elements:

- Cations of **less active metals** (Cu, Ag, Au, Pt, …) are reduced on the cathode.
- Anions of **less active nonmetals** (I₂, Br₂, …) are oxidized on the anode (including Cl₂ due to the overvoltage of water).
- Cations of **more active metals** (Na, K, Mg, Ca, …) are not reduced (H₂O is reduced to H₂ instead) → can’t be produced by electrolysis of aqueous soln.
- Anions of **more active nonmetals** (F⁻) and oxoanions of elements in their highest oxidation state (NO₃⁻, CO₃²⁻, SO₄²⁻, …) are not oxidized.

---

**The Stoichiometry of Electrolysis**

- **Faraday’s law** – the amount of substance produced on each electrode is directly proportional to the amount of charge transferred through the cell:
  \[ I \rightarrow \text{el. current} \quad t \rightarrow \text{time of electrolysis} \]
  \[ Q \rightarrow \text{charge transferred} \quad n \rightarrow \# \text{mol e⁻ transferred} \]
  \[ I = \frac{Q}{t} \quad \Rightarrow \quad Q = I \times t \]
  \[ Q = nF \rightarrow \quad n = \frac{Q}{F} \]

→ \( n \) is related to the amount of substance through the stoichiometry of the half-reaction
→ Allows the determination of the amount of substance produced by measuring \( I \) and \( t \)

---

**Example:** During electrorefining of Cu, how much time is needed to produce 250 g Cu on the cathode if the current is kept at 11 A?

\[ I = 11 \text{ A} = 11 \text{ C/s} \]

**Half-reaction:** \( \text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu(s)} \)

\[ n = \frac{250 \text{ g Cu}}{63.55 \text{ g Cu/mol}} \times \frac{2 \text{ mol e⁻}}{1 \text{ mol Cu}} = 7.9 \text{ mol} \]

\[ n = \frac{I \times t}{F} \quad \Rightarrow \quad t = \frac{n \times F}{I} \]

\[ t = \frac{7.9 \text{ mol} \times 96485 \text{ C/mol}}{11 \text{ C/s}} = 6.9 \times 10^4 \text{ s} = 19 \text{ hr} \]