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 ↑)
  - **Reduction** – gain of **e$^-$** (oxidation state ↓)

- **Half-reactions** – focus on oxidation and reduction separately

Example: $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$

→$CaCl_2(s)$ consists of Ca^{2+} and Cl^- ions

$$\oplus \begin{array}{|l} Ca(s) \rightarrow Ca^{2+}(s) + 2e^- \text{ (loss of } 2e^-\text{, oxidation)} \\ Cl_2(g) + 2e^- \rightarrow 2Cl^-(s) \text{ (gain of } 2e^-\text{, reduction)} \end{array}$$

$$Ca(s) + Cl_2(g) + \cancel{2e^-} \rightarrow Ca^{2+}(s) + \cancel{2e^-} + 2Cl^-(s)$$

→Adding the half-reactions gives the overall reaction

→Ca is oxidized (Ca is the reducing agent)

→Cl_2 is reduced (Cl_2 is the oxidizing agent)

➢Generalized expressions for half reactions:

➢**Red → Ox + *n*e$^-$** or **Ox + *n*e$^-$ → Red**

➢**Ox/Red** form a **redox couple** (Ex: Ca^{2+}/Ca; Cl_2/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 **H_2O**
   - ➢ 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 is balanced)

$V^{3+} + 2H_2O \rightarrow VO_2^+$ (balance O)

$V^{3+} + 2H_2O \rightarrow VO_2^+ + 4H^+$ (balance H)

→ $V^{3+} + 2H_2O \rightarrow VO_2^+ + 4H^+ + 2e^-$ (balance charge)

$Ce^{4+} \rightarrow Ce^{3+}$ (Ce, O and H are balanced)

→ $Ce^{4+} + 1e^- \rightarrow Ce^{3+}$ (balance charge)

3. Multiply the 2nd half-reaction by 2 to get $2e^-$

$2Ce^{4+} + 2e^- \rightarrow 2Ce^{3+}$

4. Add the half-reactions

$$\begin{array}{l} V^{3+} + 2H_2O \rightarrow VO_2^{+} + 4H^{+} + 2e^{-} \\ 2Ce^{4+} + 2e^{-} \rightarrow 2Ce^{3+} \end{array}$$

$$V^{3+} + 2H_2O + 2Ce^{4+} + \cancel{2e^{-}} \rightarrow VO_2^{+} + 4H^{+} + \cancel{2e^{-}} + 2Ce^{3+}$$

$$\boxed{\Rightarrow \mathbf{V^{3+} + 2Ce^{4+} + 2H_2O \rightarrow VO_2^{+} + 2Ce^{3+} + 4H^{+}}}$$

Note: If H_3O^+ is required in the equation instead of H^+, add as many water molecules on both sides as the # of H^+ ions

$$\Rightarrow \mathbf{V^{3+} + 2Ce^{4+} + 6H_2O \rightarrow VO_2^{+} + 2Ce^{3+} + 4H_3O^{+}}$$

- **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

Example: Balance the following skeleton equation in basic solution: $CrO_2^{-} + BrO_4^{-} \rightarrow CrO_4^{2-} + BrO_3^{-}$

1. Redox couples: CrO_4^{2-}/CrO_2^{-} and BrO_4^{-}/BrO_3^{-}

Half-reactions: $CrO_2^{-} \rightarrow CrO_4^{2-}$ and $BrO_4^{-} \rightarrow BrO_3^{-}$

2. $CrO_2^{-} \rightarrow CrO_4^{2-}$ (Cr is balanced)

$CrO_2^{-} + 2H_2O \rightarrow CrO_4^{2-}$ (balance O)

$CrO_2^{-} + 2H_2O \rightarrow CrO_4^{2-} + 4H^{+}$ (balance H)

$\rightarrow CrO_2^{-} + 2H_2O \rightarrow CrO_4^{2-} + 4H^{+} + 3e^{-}$ (balance charge)

$BrO_4^{-} \rightarrow BrO_3^{-}$ (Br is balanced)

$BrO_4^{-} \rightarrow BrO_3^{-} + H_2O$ (balance O)

$BrO_4^{-} + 2H^{+} \rightarrow BrO_3^{-} + H_2O$ (balance H)

$\rightarrow BrO_4^{-} + 2H^{+} + 2e^{-} \rightarrow BrO_3^{-} + H_2O$ (balance charge)

3. Multiply the 1st half-reaction by 2 and the 2nd by 3 to get $6e^-$ in both half-reactions

$$\begin{array}{l} 2CrO_2^{-} + 4H_2O \rightarrow 2CrO_4^{2-} + 8H^{+} + 6e^{-} \\ 3BrO_4^{-} + 6H^{+} + 6e^{-} \rightarrow 3BrO_3^{-} + 3H_2O \end{array}$$

4. Add the half-reactions

$$2CrO_2^{-} + 4H_2O + 3BrO_4^{-} + 6H^{+} + \cancel{6e^{-}} \rightarrow$$
$$\rightarrow 2CrO_4^{2-} + 8H^{+} + \cancel{6e^{-}} + 3BrO_3^{-} + 3H_2O$$

$$\Rightarrow \mathbf{2CrO_2^{-} + 3BrO_4^{-} + H_2O \rightarrow 2CrO_4^{2-} + 3BrO_3^{-} + 2H^{+}}$$

5. Add $2OH^-$ on both sides of the equation

$$2CrO_2^{-} + 3BrO_4^{-} + H_2O + 2OH^{-} \rightarrow$$
$$\rightarrow 2CrO_4^{2-} + 3BrO_3^{-} + \overbrace{2H^{+} + 2OH^{-}}^{2H_2O}$$

$$\boxed{\mathbf{2CrO_2^{-} + 3BrO_4^{-} + 2OH^{-} \rightarrow 2CrO_4^{2-} + 3BrO_3^{-} + H_2O}}$$

21.2 Galvanic (Voltaic) Cells

- Produce electricity from a spontaneous chemical reaction

  Example: Zn metal reacts spontaneously with Cu^{2+} solutions to yield metallic Cu and Zn^{2+} ions

  $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$ (SO_4^{2-} counter ions)

$\rightarrow$The two half-reactions are:

$Zn(s) \rightarrow Zn^{2+} + 2e^{-}$ (oxidation)

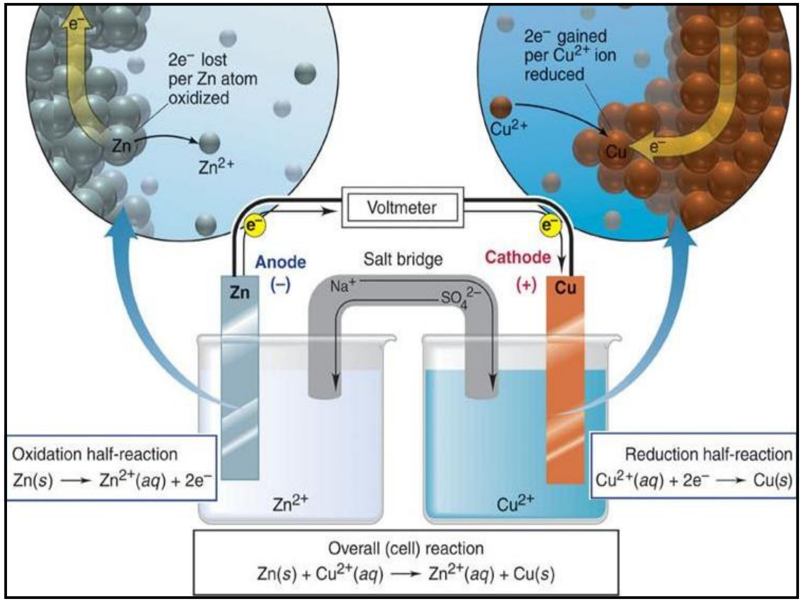
$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$ (reduction)

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

$\rightarrow$**Half-cells** $\rightarrow$ where the half-reactions occur

$\rightarrow$**Anode** half-cell $\rightarrow$ where **oxidation** occurs

$\rightarrow$**Cathode** half-cell $\rightarrow$ 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**