Unit 1

ELECTROCHEMISTRY

Redox Reactions

Biological CO_2 reduction

2 Steps

1. Take CO_2 from atmosphere
2. Turn it into fuel, structures, & information

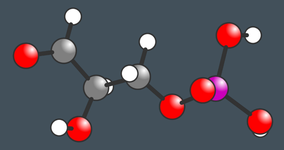
Photosynthesis

$$2H_2O + 2NADP^+ + 3ADP + 3P_i \rightarrow 2NADPH + H^+ + 3ATP + O_2$$ Light RXN

red oxid

$$3CO_2 + 9ATP + 6NADPH \rightarrow G3P + 9P_i + 6NADP^+ + 3H_2O$$ Dark RXN

oxid red



Net Reaction: $3CO_2 + H_2O \rightarrow [CH_2O]_n + O_2$ (1-5% efficiency)

Downstream Yields: Glucose, Cellulose…

Electrochemical CO_2 reduction

2 Steps

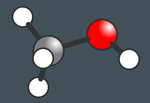
1. Take CO_2 from atmosphere
2. Turn it into fuel more efficiently?

Electrochemical Methods

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \text{ (2e}^-\text{)}$$

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \text{(2e}^-\text{)}$$

$$CO_2 + 2H_2O \rightarrow CH_3OH + \frac{3}{2}O_2 \text{ (6e}^-\text{)}$$



Other products:

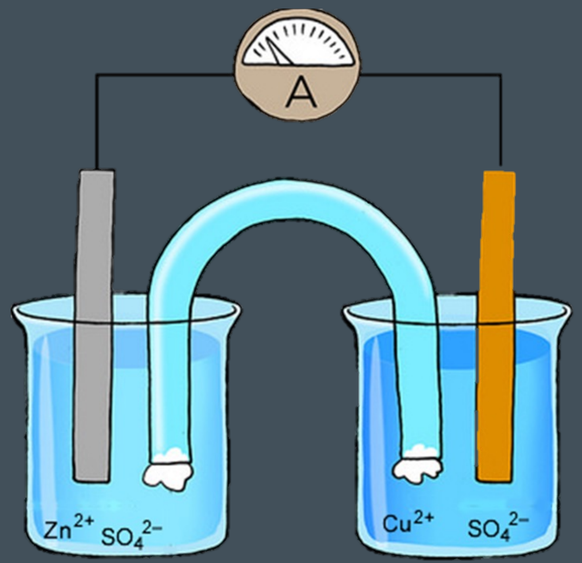
CH_4 Formic Acid C_2H_6 C_2H_4

Trillion Tree Project: US to plant 51 billion trees by 2030.

Large scale CO_2 reduction reactors planned: Zero.

Topics

1. Balancing redox reactions
2. Redox in aqueous acids
3. Redox in aqueous base
4. Electricity: terms and units
5. Cell shorthand notation



ID: redox reactions, reductants, & oxidants

$MnCl_2 + H_2$ -------- > $Mn + 2\ HCl$

$N_2H_4 + N_2O_2$ -------- > $2\ H_2O + 2\ N2$

$4\ CH_3NHNH_2 + 5\ N_2O_4$ -------- > $9\ N_2 + 4\ CO_2 + 12\ H_2O$

$Pb + PbO_2$ $\xrightarrow{H_2SO_4\ (aq)}$ --------- > $2\ PbSO_4$

Orion Service Module

Half reactions

Half reaction

- A complete reaction is separated into a pure reduction or a pure oxidation by consuming electrons (left side, reduction) or yielding electrons (right side, oxidation)

Half cell

- A species is either oxidized or reduced at this physical location in an experiment. Oxidation and reduction will generally not occur at the same electrode at the same time / voltage.

Downs Process

$$NaCl(l) \rightarrow Na(l) + Cl_2(g)$$

Special Types of Redox Reactions

Comproportionation – 2 oxidation state in 1 oxidation state out

$$CuCl_2 + Cu + heat \rightarrow CuCl$$

Disproportionation – 1 oxidation state in 2 oxidations states out

$$Hg_2Cl_2(s) + heat \rightarrow Hg(l) + HgCl_2$$

Half Reactions

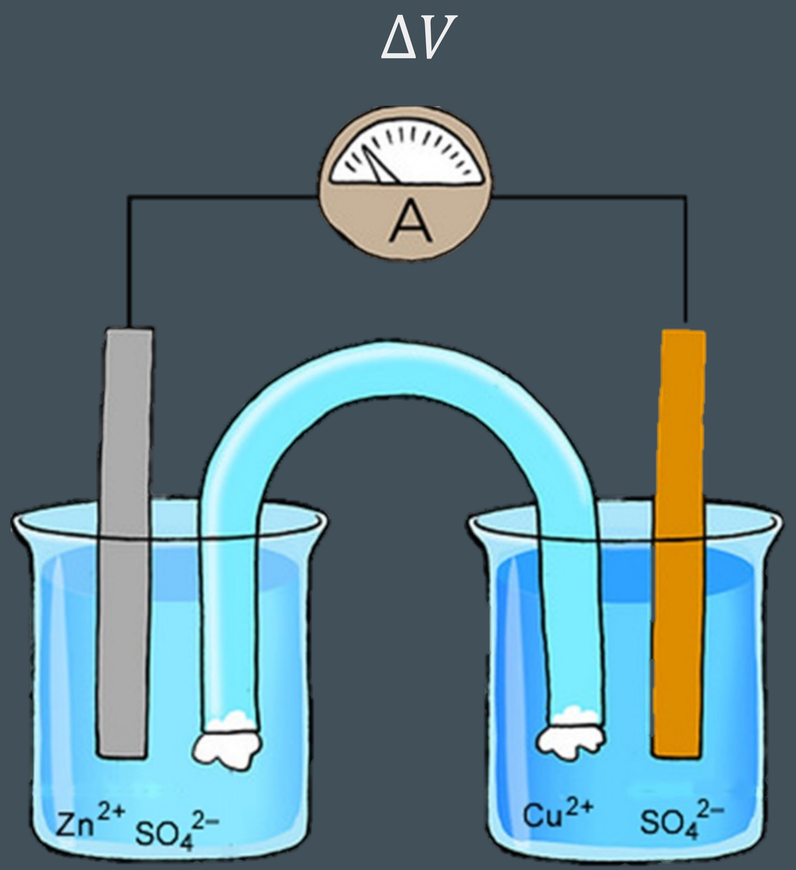
Derive the two half reactions:

$$MnO_4^- (aq) + I^- (aq) \rightarrow MnO_2 (s) + I_2 (s)$$

Basic Conditions

Two half-cells = electrochemical **c**ell

Where are the half reactions?



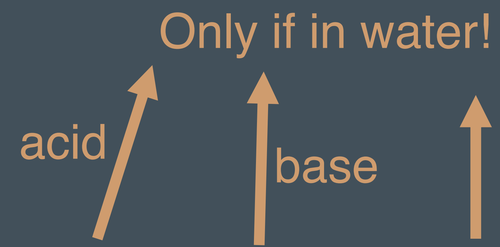
After the reaction

Balancing Redox Reactions

1. Identify reactants and products
   - solvent (water), pH (acidic vs basic)
   - other additives and conditions

2. Identify reductant and oxidant.
   - Assign formal oxidation states

3. Write the ½ reactions
   - Mass and charge balance with e^-, H^+, OH^-, and H_2O



4. Combine ½ reactions to cancel electrons (Hess's Law)

Balancing redox equations in aqueous acid

Acidic Conditions

Separate the overall equation into two half-reactions. For each half-reaction:

1. Balance the main atom
2. Add H_2O to balance O
3. Add H^+ to balance H
4. Balance the charge using electrons
5. Adjust the equations to have the same number of electrons in each half-reaction
6. Add the two half-reactions. The electrons should all cancel out

Example

$MnO^{4-} + HSO_3^{1-}$ ------ > Mn^{2+} (*aq*) + SO_4^{2-} (*aq*)

Acidic Conditions

Example

Acidic Conditions

Balancing redox equations in aqueous base

Basic Conditions

Separate the overall equation into two half-reactions. For each half-reaction:

1. Balance the main atom
2. Add H_2O to balance O
3. Add H^+ to balance H
4. Add OH^- to both sides of the half-reaction
5. Balance the charge using electrons
6. Adjust the equations to have the same number of electrons in each half-reaction
7. Add the two half-reactions. The electrons should all cancel out.
8. Combine any H^+ and OH^- ions that are on the same side of the overall equation.

Example

$$MnO_4^- (aq) + I^- (aq) \rightarrow MnO_2 (s) + I_2 (s)$$

Basic Conditions

In class practice: Lead acid battery

In the Lab

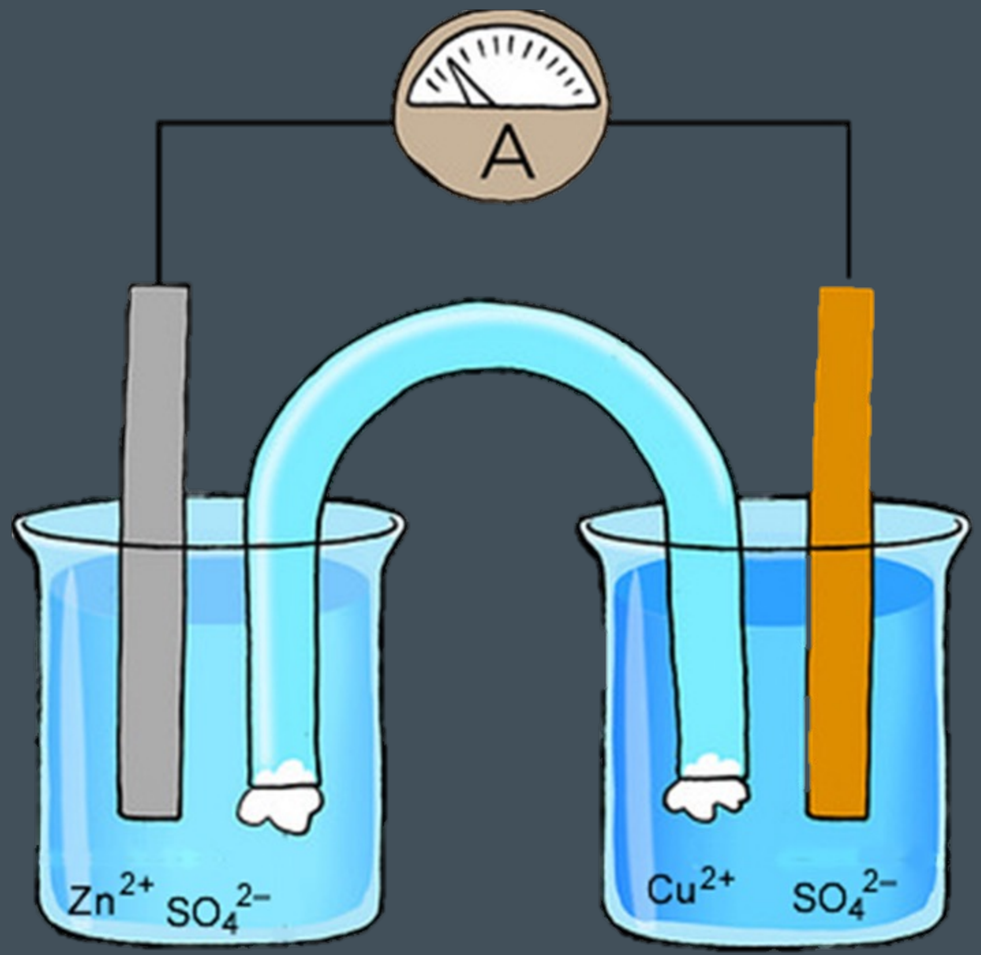
Half cell

- The location in a cell where **either** a species is oxidized **or** reduced

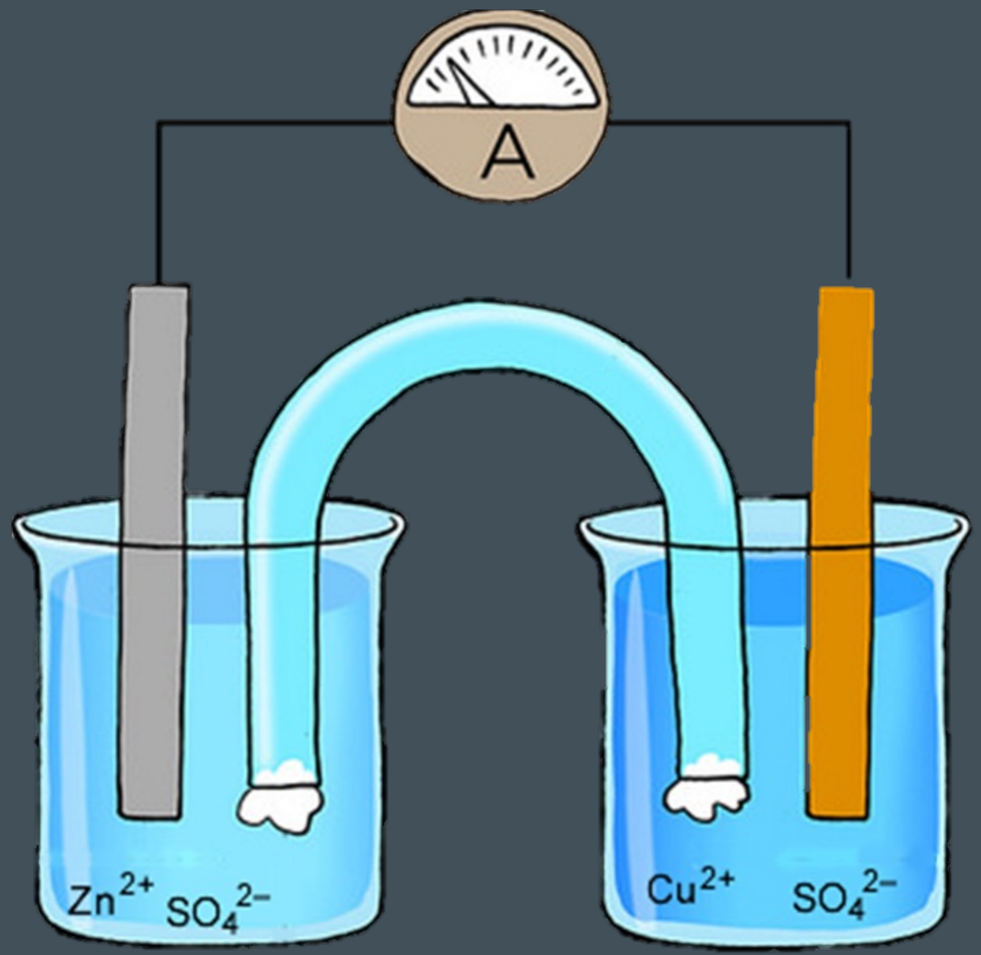
Half Reaction

- A partial reaction showing describing **either** reduction (electronation) **or** oxidation (de-electronation)

Two Half-Cells = Electrochemical Cell

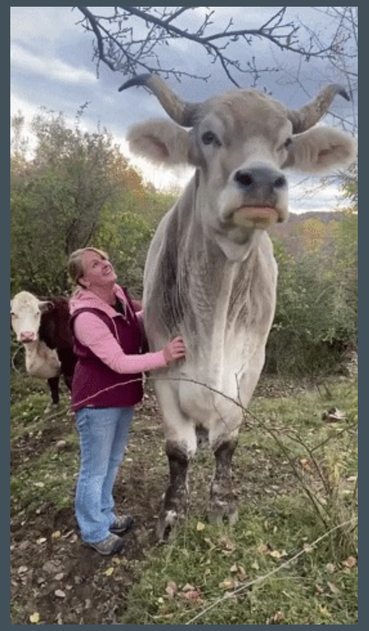


After The Reaction



Oxidation is at the anode & Reduction is at the cathode

An ox

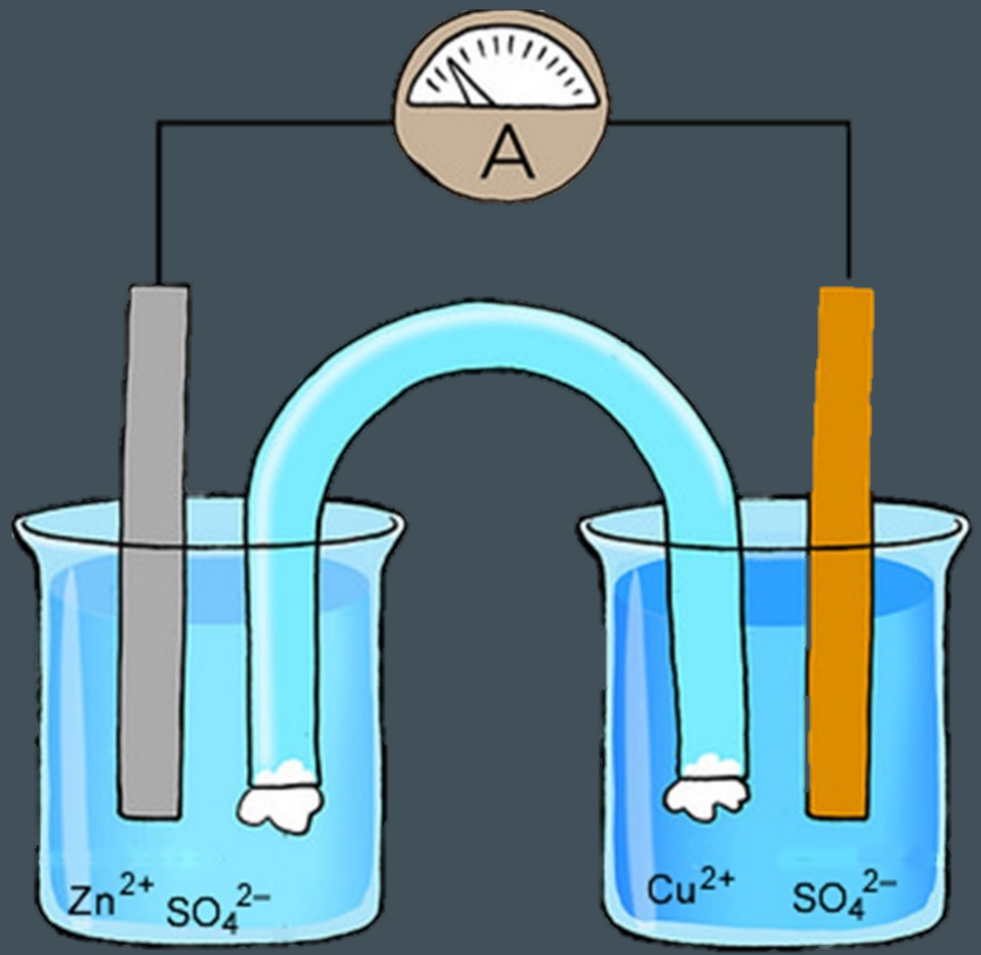


Anode is oxidation

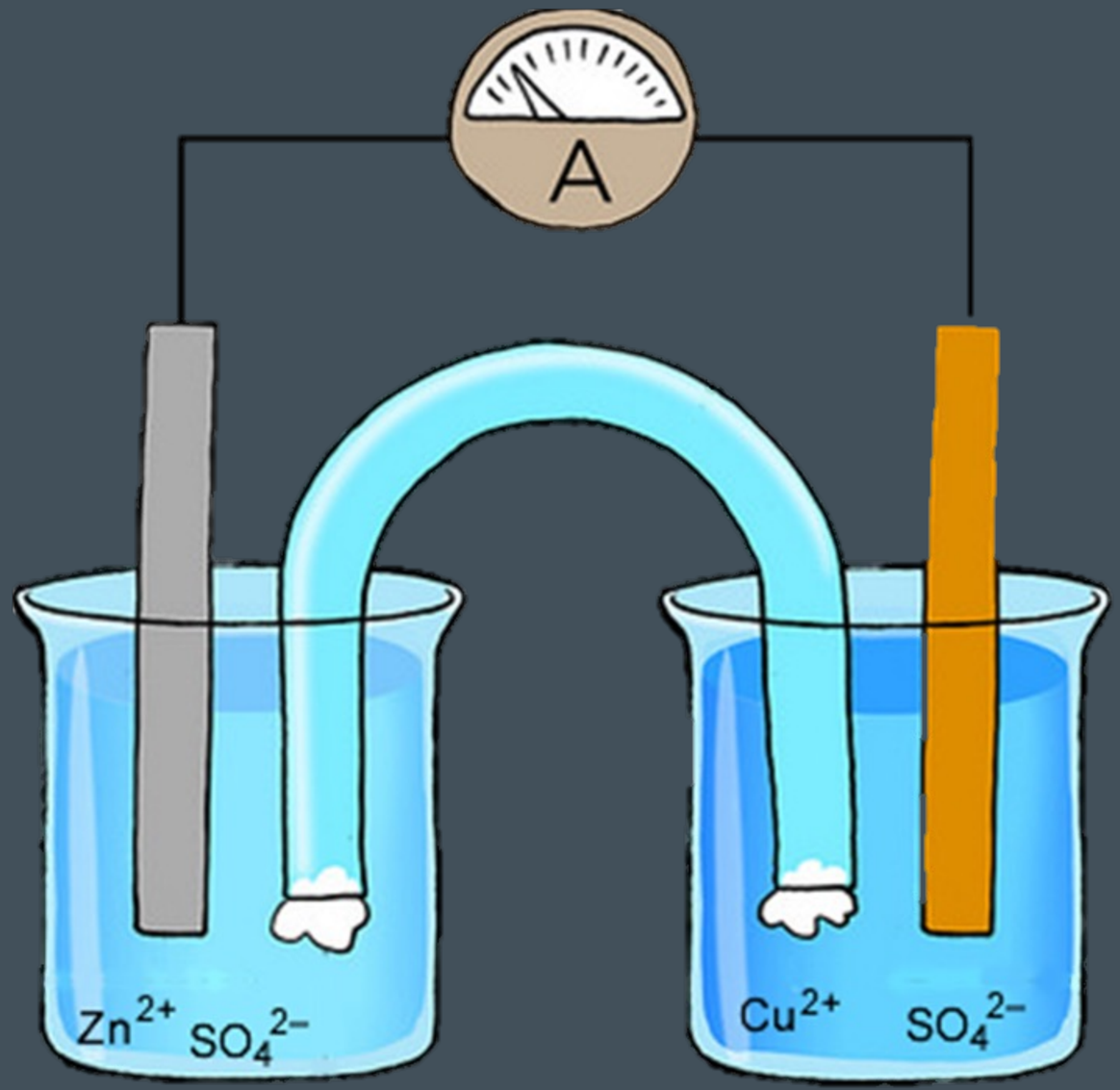
Red cat

Reduction is **cat**hode

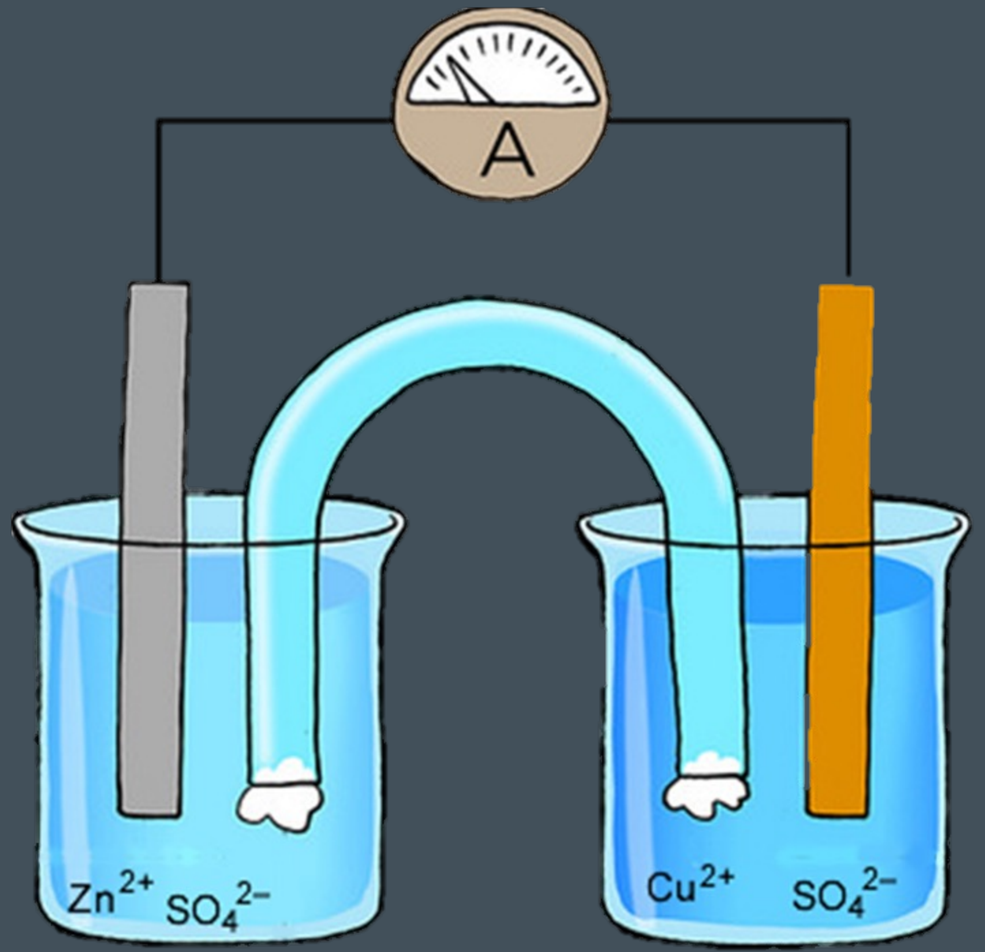
The salt bridge



The flow of electrons and ions



Shorthand notation



Cell shorthand notation rules

1. The anode is listed on the far left, and the cathode is on the far right.
2. The salt bridge divides the cell in half, and is represented by $\|$.
3. A phase boundary (such as solid/liquid, or liquid/gas) is represented by a single vertical line |.
4. Concentrations are listed in parentheses (sometimes omitted when 1 M).
5. If there is more than one ion in a solution, the ions are separated by a comma.

Shorthand Notation Example

Write the shorthand notation for the below reaction with cells that contain 0.2 M $Al_2(SO_4)_3$ and 0.1 M $SnCl_2$.

$$2Al + 3Sn^{2+} \rightarrow 2Al^{3+} + 3Sn$$

Terminology Alert

Review: Important Definitions

DEF Electrochemistry | Interaction of molten salts or ionic solutions with electric currents.

DEF Voltage | How hard electrons are ‘pushing’ to move between two locations. The amount of energy (J) gained or lost per electron transferred between two locations. Units: Volt = V = J/C.

DEF Current | How many or how fast electrons are flowing. Units: Amp=A=C/s.

DEF Charge | A fundamental property of subatomic particles as in p^+ and e^-. The origin of electricity. Units: C=coulomb.

DEF Cell Potential | A voltage measured between chemically distinct locations at zero current. Units: Volt = V.

DEF Electrolysis | A chemical reaction induced by *applying* a voltage.

DEF Oxidation | A net *loss* of electrons relating a reactant to a product.

DEF Reduction | A net *gain* of electrons relating a reactant to a product.

DEF Half Reaction | A chemical reaction that explicitly shows a gain (reduction) or loss (oxidation) of electrons in the reaction scheme.

DEF Electrochemical Cell | A device that forces electrons through one path (usually an external circuit) and ions through another (the electrolyte)

DEF Cathode | The electrode in an electrochemical cell where reduction occurs.

DEF Anode | The electrode in an electrochemical cell where oxidation occurs.

DEF Electrolyte | The medium (usually a liquid) in an electrochemical cell that conducts ions but not electrons

DEF Salt Bridge | A specialized device that allows a common ion to conduct between two electrolyte solutions while minimizing the mixing of all other ions between two half cells.

DEF Faraday | The amount of charge in 1 mol of electrons. 1 F = 96,485 C

Next Time

Section 8.2

- Reaction stoichiometry
- Standard Reduction Potentials
- Atomistic models for understanding an electrochemical reaction