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## Chapter 13 Electrochemistry

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## Chapter Objectives

- Describe at least three types of **corrosion** and identify chemical reactions responsible for corrosion.
- Define **oxidation** and **reduction**.
- Write and balance **half-reactions** for simple **redox** processes.
- Describe the differences between **galvanic** and **electrolytic cells**.
- Use **standard reduction potentials** to calculate **cell potentials** under both **standard** and **nonstandard conditions**.

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## Chapter Objectives

- Use standard reduction potentials to predict the spontaneous direction of a redox reaction.
- Calculate the amount of metal plated, the amount of current needed, or the time required for an **electrolysis** process.
- Distinguish between **primary** and **secondary batteries**.
- Describe the chemistry of some common battery types and explain why each type of battery is suitable for a particular application.
- Describe at least three common techniques for preventing corrosion.

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## Corrosion

- **Corrosion** is the degradation of metals by chemical reactions with the environment.
  - **Uniform corrosion** occurs evenly over a large portion of the surface area of a metal.
  - **Galvanic corrosion** occurs when two different metals contact each other in the presence of an appropriate electrolyte.
  - **Crevice corrosion** occurs when two pieces of metal touch each other, leaving a small gap or crevice between the metals.

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## Corrosion

- Different metals corrode differently.
  - Aluminum has a greater tendency to corrode than iron, but corrosion of aluminum is not problematic compared to iron.
    - The aluminum oxide corrosion product forms a protective layer on the surface of aluminum metal.
    - The iron oxide corrosion product flakes off the surface of iron, exposing fresh iron to corrosion.

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## Corrosion



- Corrosion occurs in a variety of forms. The chain shows uniform corrosion. The grill cover shows crevice corrosion where the handle is attached.

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### Oxidation-Reduction Reactions and Galvanic Cells

- Special conditions must be present before iron reacts with oxygen to form iron(III) oxide.
  - Rust formation is a slow process, so the basics of electrochemistry must be investigated using more easily observed reactions.
- Reactions that transfer electrons between reactants are known as **oxidation-reduction** or **redox reactions**.
  - Oxidation** is the loss of electrons from some chemical species.
  - Reduction** is the gain of electrons to some chemical species.

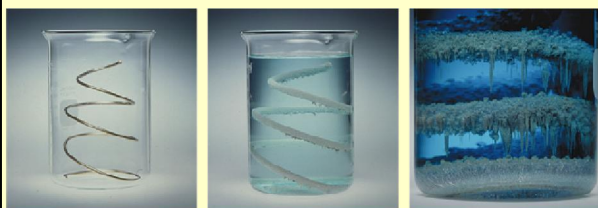
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### Oxidation-Reduction and Half-Reactions

- For an oxidation-reduction reaction to occur, one reactant must be oxidized and one reactant must be reduced.
  - Oxidation cannot occur without reduction.
- When copper wire is placed in a silver nitrate solution, a redox reaction occurs.
  - A reaction is observed to occur because the solution changes color and crystals form on the surface of the copper wire.

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### Oxidation-Reduction and Half-Reactions

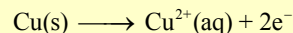


- When a clean copper wire is placed into a colorless solution of silver nitrate, it is quickly apparent that a chemical reaction occurs.

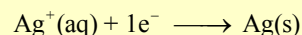
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### Oxidation-Reduction and Half-Reactions

- The solution's blue color is indicative of  $\text{Cu}^{2+}$  ions in solution.
  - $\text{Cu}^{2+}$  is formed when a copper atom loses two electrons.
  - The copper metal is oxidized.



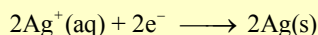
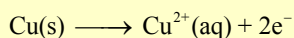
- The crystals forming on the surface of the copper wire are silver metal.
  - Silver is formed when a silver cation gains an electron.
  - The silver cation is reduced.



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### Oxidation-Reduction and Half-Reactions

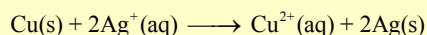
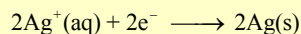
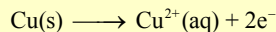
- For the reaction between silver cation and copper metal, two **half-reactions** are written.
  - One for the oxidation of copper and one for the reduction of silver.
  - Neither half-reaction can occur without the other.
- The half-reactions as written indicate that  $\text{Ag}^{+}$  only accepts one electron whereas Cu loses two electrons.
  - The electron transfer must balance, so the reduction half-reaction is multiplied by 2.



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### Oxidation-Reduction and Half-Reactions

- Add the two half-reactions together, the electrons cancel out, leaving the **net ionic equation** for the redox reaction.



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## Oxidation-Reduction and Half-Reactions

- The species undergoing oxidation is referred to as a **reducing agent**.
  - The Cu was oxidized and is the reducing agent.
  - The Cu facilitated the reduction of  $\text{Ag}^+$  by losing electrons.
- The species undergoing reduction is referred to as an **oxidizing agent**.
  - The  $\text{Ag}^+$  was reduced and is the oxidizing agent.
  - The  $\text{Ag}^+$  facilitated the oxidation of Cu by gaining electrons.

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## Building a Galvanic Cell

- A **galvanic cell** is any electrochemical cell in which a spontaneous chemical reaction can be used to generate an electric current.
  - The name **electrochemistry** comes from the observation of electric currents in galvanic cells.
- To harness electricity from a galvanic cell, each half-reaction is prepared separately in half-cells.
  - Cu metal immersed in  $\text{Cu}^{2+}$  solution is one half-cell.
  - Ag metal immersed in  $\text{Ag}^+$  solution is the second half-cell.

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## Building a Galvanic Cell

- Current flows by the migration of ions in solution.
  - To transfer current between the half-cells, a salt bridge is used.
  - The **salt bridge** contains a strong electrolyte that allows either cations or anions to migrate into the solution where they are needed to maintain charge neutrality.
  - A metal wire cannot transport ions and cannot be used.

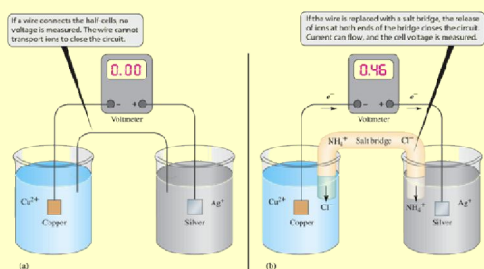
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## Building a Galvanic Cell

- For a salt bridge composed of  $\text{NH}_4\text{Cl}$ :
  - $\text{NH}_4^+$  will flow into the  $\text{Ag}^+$  beaker to offset the removal of  $\text{Ag}^+$  from solution.
  - $\text{Cl}^-$  will flow into the  $\text{Cu}^{2+}$  beaker to offset the production of  $\text{Cu}^{2+}$  in solution.
- The circuit is completed by connecting wires to each metal strip.
  - A voltage potential of 0.46 V will be measured for the described cell.

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## Building a Galvanic Cell



- A salt bridge is crucial to a galvanic cell. The salt bridge allows **ions** to flow between each half-cell, completing the circuit.

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## Terminology for Galvanic Cells

- Electrodes** are the electrically conducting sites at which either oxidation or reduction occurs.
  - The electrode where oxidation occurs is the **anode**.
  - The electrode where reduction occurs is the **cathode**.
- Cell notation** - a shorthand notation for the specific chemistry of an electrochemical cell.
  - Cell notation lists the metals and ions involved in the reaction.
  - A vertical line, |, denotes a **phase boundary**.
  - A double vertical line, ||, denotes a salt bridge.
  - The anode is written on the left, the cathode on the right.

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## Terminology for Galvanic Cells

- General form of cell notation  
anode | anode electrolyte || cathode electrolyte | cathode
- For the previous example of copper and silver  
$$\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) (1 \text{ M}) || \text{Ag}^+(\text{aq}) (1 \text{ M}) | \text{Ag}$$
  - The electrolyte concentration is also given.
- An electrochemical cell is at its **standard state** when the electrolyte concentrations are 1 M.
- For half-cells that generate or consume a gas, a partial pressure of 1 atm is required for the standard state.

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## Atomic Perspective on Galvanic Cells

- Before half-cells are connected by a salt bridge, a small build up of charge occurs for each half-cell at the interface between the electrode and the electrolyte.
  - At the anode, some oxidation occurs and cations dissolve into solution, leaving a negative charge on the anode.
  - At the cathode, some reduction occurs and cations are removed from solution, leaving a positive charge on the cathode.

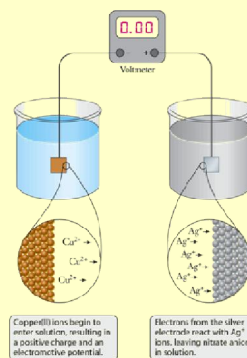
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## Atomic Perspective on Galvanic Cells

- An equilibrium can be described for each half-cell, the **half-reaction equilibrium**.
  - Not an oxidation-reduction equilibrium.
- The build up of charge on the electrode means there is potential for electrical work.
  - This potential is the **cell potential**, or **electromotive force (EMF)**.
- EMF is related to the maximum work obtainable from an electrochemical cell.
  - $w_{\text{max}} = qE$
  - $q$  is the charge,  $E$  is the cell potential.

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## Atomic Perspective on Galvanic Cells



- Without a salt bridge to close the circuit, local charges build up around both electrodes. Neither electrode reaction can proceed to any significant extent, so no cell voltage can be measured.

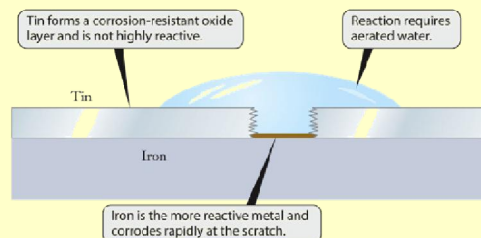
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## Galvanic Corrosion and Uniform Corrosion

- Metals in contact with a solution establish an oxidation half-reaction equilibrium.
  - If the solution contains a substance that can undergo reduction, a redox reaction may occur.
- For two metals in contact, such as a tin-plated steel can, exposure to air and moisture results in rapid corrosion.
  - The half-reaction equilibrium for the tin facilitates the process by which iron is oxidized.
  - This is an example of galvanic corrosion.

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## Galvanic Corrosion and Uniform Corrosion



- A "tin can" is usually tin-plated steel. If the tin coating is scratched to expose the underlying steel, iron in the steel will corrode rapidly.

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## Galvanic Corrosion and Uniform Corrosion

- Metal not in contact with another metal can also corrode.
  - A nonmetal is involved in the second half-cell.
- For the corrosion of iron, iron is one half-cell and oxygen dissolved in water is the second half-cell.
- The electrode for the oxygen half-cell is the iron itself.
- Dissolved salts facilitate the corrosion reaction.
- This is an example of **uniform corrosion**.

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## Cell Potentials

- The relative corrosivities of various plated steels can be expressed as **cell potential**.
- A **voltmeter** measures the size of the electrical potential and also its polarity - the locations of the negative charge (negative pole) and the positive charge (positive pole).
- An electric potential has a fixed polarity and voltage.
  - Reversing the poles of a battery with respect to a voltmeter changes the sign on the measured voltage but does not influence the electrochemical reaction in the battery.

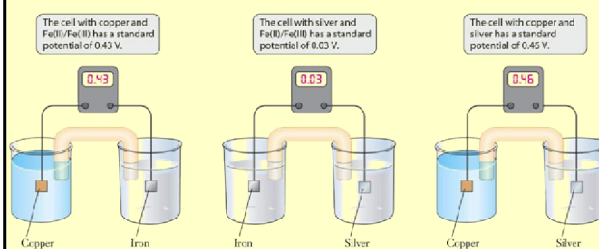
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## Measuring Cell Potential

- When a voltmeter is connected to the previously described copper/silver cell, a potential of 0.462 V is measured.
- Connecting the copper half-cell to a reducing iron(III)/iron(II) half-cell, a cell potential of 0.434 V is measured.
- Connecting the iron(III)/iron(II) half-cell to the silver half-cell results in a cell potential of 0.028 V.
- For the three cell potentials measured, the fact that  $0.462\text{ V} = 0.434\text{ V} + 0.028\text{ V}$  suggests two things:
  - The behavior of cell potentials is akin to state functions.
  - If a specific standard electrode is chosen, comparison to all other electrodes will result in a practical system for determining cell potential.

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## Measuring Cell Potential

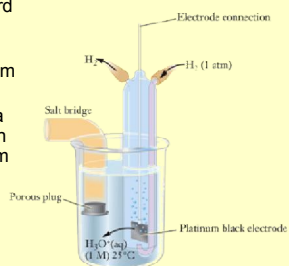


- Measurement of standard cell voltages for various combinations of the same half-reactions suggests that a characteristic potential can be associated with a particular half-reaction.

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## Measuring Cell Potential

- The **standard hydrogen electrode (SHE)** is the choice for the standard component in cell potential measurements.
- The cell is constructed of a platinum wire or foil as the electrode.
  - The electrode is immersed in a 1 M HCl solution through which  $\text{H}_2$  gas with a pressure of 1 atm is bubbled.
- The SHE has been chosen as the reference point for the scale of standard reduction potentials, and assigned a potential of exactly zero volts.



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## Measuring Cell Potential

- For the Standard Hydrogen Electrode
  - The half-reaction for the SHE is:  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ .
  - The half-cell notation is:  $\text{Pt}(\text{s}) | \text{H}_2(\text{g}, 1\text{ atm}) | \text{H}^+(1\text{ M})$ .
  - The half-cell is assigned a potential of exactly zero volts.
  - The cell potential is attributed to the other half-reaction.

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## Measuring Cell Potential

- For some galvanic cells, the SHE acts as the anode and for other galvanic cells, the SHE acts as the cathode.
- The anode is the site of oxidation, releasing electrons and creating a negatively charged electrode.
  - If the anode is connected to the positive terminal of the voltmeter, a negative potential is measured.
- The cathode is the site of reduction, consuming electrons and creating a positively charged electrode.
  - If the cathode is connected to the positive terminal of the voltmeter, a positive potential is measured.

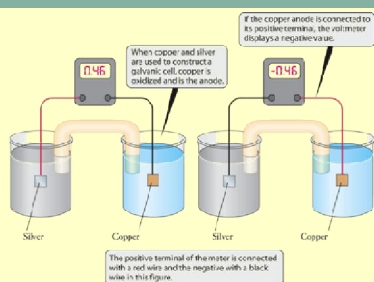
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## Measuring Cell Potential

- When the SHE is always connected to the positive terminal, the sign of the potential tells us the direction of the redox reaction.
  - When the potential is negative, the SHE is the anode, and  $\text{H}_2$  is oxidized to  $\text{H}^+(\text{aq})$ .
  - When the potential is positive, the SHE is the cathode, and  $\text{H}^+(\text{aq})$  is reduced to  $\text{H}_2$ .

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## Measuring Cell Potential



- Just like a commercial battery, a galvanic cell has a fixed polarity. Electrons flow through the external circuit from the anode to the cathode. Reversing the leads of the voltmeter changes the sign of the reading, but does not influence the flow of current.

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## Standard Reduction Potentials

- To compare the oxidation-reduction trends of species used in electrochemistry, all half-cell potentials are written as reductions.
  - A table of [standard reduction potentials](#) lists the potential of any half-reaction when connected to a SHE.
  - All materials are 1 M for aqueous species and 1 atm partial pressure for gases.

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## Standard Reduction Potentials

Table 13.1

Standard reduction potentials for several of the half-reactions involved in the cells discussed in the text. A more extensive table of potentials appears in Appendix I.

Half-Reaction	Standard Reduction Potential (V)
$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$	-0.763
$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$	-0.44
$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$	0.000
$\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$	+0.337
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.771
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.7794

- Standard reduction potentials for several half-reactions involved in the cells discussed in the text.

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## Standard Reduction Potentials

- Although the half-reactions are listed as reductions in the table, one half-reaction in any electrochemical cell must be an oxidation and, therefore, reversed from what appears in the table.
  - The cell potential sign must be changed when writing the half-reaction as an oxidation.
- Some half-reactions have positive potentials, whereas others have negative potentials.

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## Standard Reduction Potentials

- All potentials are measured with a SHE connected to the negative terminal.
  - If the voltage is positive, the SHE is the anode, the oxidation site.
  - A positive standard reduction potential means the half-reaction proceeds as written (reduction occurs).
  - If the voltage is negative, the SHE is the cathode, the reduction site.
  - A negative standard reduction potential means the half-reaction proceeds as an oxidation.

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## Standard Reduction Potentials

- The tendency for the chemicals involved in a half-reaction to be an oxidation or reduction depends on the value of the reduction potential.
  - A large, positive value for the standard reduction potential implies the substance is reduced readily and a good oxidizing agent.
  - A large, negative value for the standard reduction potential implies the substance is oxidized readily and a good reducing agent.

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## Standard Reduction Potentials

- For a galvanic cell, the half-reaction with the more positive reduction potential will be the cathode.
  - The half-reaction with the more negative reduction potential will be the anode.
- The standard reduction potential for any pair of half-reactions,  $E_{\text{cell}}^{\circ}$ , is calculated from the standard reduction potentials for the cathode and anode.

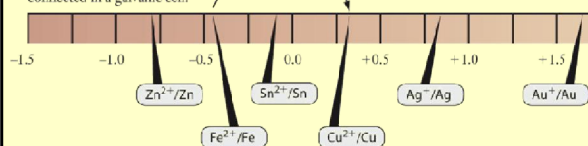
$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ}$$

- $E_{\text{red}}^{\circ}$  is the standard reduction potential for the cathode and  $E_{\text{ox}}^{\circ}$  is the standard reduction potential for the anode.

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## Standard Reduction Potentials

Iron is oxidized and copper is reduced when they are connected in a galvanic cell.

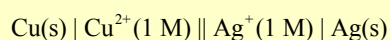


- For standard reduction potentials arranged horizontally, the anode and cathode for a galvanic cell can easily be determined. The reduction potential furthest to the left is the anode.

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## Example Problem 13.1

- Using standard reduction potentials, identify the anode and the cathode and determine the cell potential for a galvanic cell composed of copper and iron. Assume standard conditions.
- Confirm that the potential of the following galvanic cell is 0.462 V:



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## Nonstandard Conditions

- The cell potential at nonstandard conditions is calculated using the [Nernst equation](#).

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

- $Q$  is the reaction quotient,  $F$  is the [Faraday constant](#), and  $n$  is the number of electrons transferred in the reaction.
- $F = 96,485 \text{ J V}^{-1} \text{ mol}^{-1}$  or  $96,485 \text{ C mol}^{-1}$

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## Corrosion Prevention

- The following observations can be used to reduce corrosion in a number of ways.
  - Corrosion is a pervasive reaction, with a large, negative free energy change.
  - It is possible to predict what materials will corrode and use this information to protect a material such as iron.
  - Some materials, like aluminum, corrode readily, but the product, in this case  $\text{Al}_2\text{O}_3$ , forms a protective layer that eliminates further corrosion.

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## Coatings

- Applying a protective coating to a material is the most common way of protecting against corrosion.
  - A coating can be applied with electroplating or painting.
  - The coating protects the underlying material from exposure to water and oxygen.

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## Coatings

- Rust inhibitors can be added to paint to further inhibit corrosion.
  - Many of the common inhibitors contain the following ions: phosphate, borosilicate, chromate, or phosphosilicate.
  - All of these ions, as part of a paint coating, form compounds with oxidized iron that inhibit further rust formation.
  - This process is called **passivation**.

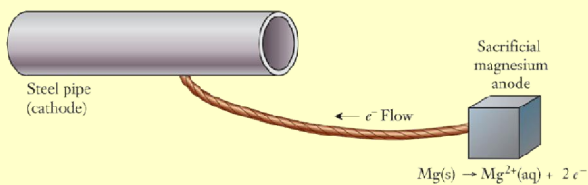
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## Cathodic Protection

- Some materials are more easily oxidized than iron, which provides a way to construct galvanic corrosion conditions intended to protect the iron.
  - Mg has a reduction potential more negative than Fe.
  - When combined, Mg will oxidize and Fe will be reduced.
- Magnesium can be used to prevent iron corrosion.
  - The piece of magnesium is called a **sacrificial anode**.
  - Connecting magnesium to iron forces iron to be the cathode, preventing iron from oxidizing.
  - This process is called **cathodic protection**.
  - The sacrificial anode must be replaced periodically to be effective.

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## Cathodic Protection



- Sacrificial anodes are one effective method of corrosion prevention. The anode is preferentially oxidized relative to the protected metal.

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## Preventing Corrosion in space

- Corrosion prevention is a concern for NASA.
  - Corrosion prevention at the launch site is a major concern.
  - Batteries used in the International Space Station (ISS) must be prevented from corroding in the ISS's earth-like atmosphere.
  - The corrosivity of a planet's atmosphere must be known before a craft can land safely.

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