

Chapter 20. Electrochemistry

Common Student Misconceptions

- Students often think that *oxidation* must necessarily mean *adding oxygen*.
- Students often have trouble balancing redox equations.
- Students often think that pure polar solvents, such as water, conduct electricity.
- Students commonly think that electrons flow through the salt-bridge (or the porous barrier) and through solutions.
- Students often do not consider water as a participant in the redox reactions.
- Students often think that, since individual electrode potentials cannot be measured, there are no processes taking place when a metal is immersed in an electrolyte.
- Many students think that a measured potential for a galvanic cell cannot be negative; it can, in which case one can re-connect the leads of the voltmeter to the opposite electrodes and obtain a positive reading.
- Students often think that cell potentials are independent of concentrations (and pressures) of ions (and gases) in the electrochemical reaction.
- Students find it difficult to understand that electrochemical potentials are relative in nature.
- Students often do not realize that electrochemical processes can be viewed as reversible; this allows us to make a connection between E°_{cell} , ΔG° , and K .

Teaching Tips

- Students should be encouraged to review section 4.4.
- Many authors have suggested mnemonics for oxidation and reduction. One of the most common is “*LEO goes GER*,” for lose electrons = oxidation and gain electrons = reduction.
- One of the most frequent errors students make when balancing redox reactions by the method of half-reactions is to incorrectly count up the charges on each side of the reaction.

Lecture Outline

20.1 Oxidation States and Oxidation-Reduction Reactions^{1,2}

- Chemical reactions in which the oxidation state of one or more substances change are called **oxidation-reduction reactions** (*redox reactions*).
 - Recall:
 - Oxidation involves loss of electrons (OIL).
 - Reduction involves gain of electrons (RIG).
 - Also:
 - Oxidation involves an *increase* of an oxidation number.
 - Reduction involves a *decrease* of an oxidation number.
- **Electrochemistry** is the branch of chemistry that deals with relationships between electricity and chemical reactions.
- Consider the spontaneous reaction that occurs when Zn is added to HCl.

$$\text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$$
 - The oxidation numbers of Zn and H^+ have changed.
 - The oxidation number of Zn has increased from 0 to +2.

¹ “Oxidation-Reduction Reactions—Part I” Animation from Instructor’s Resource CD/DVD

² “Oxidation-Reduction Reactions—Part II” Animation from Instructor’s Resource CD/DVD

- The oxidation number of H has decreased from +1 to 0.
 - Therefore, Zn is oxidized to Zn^{2+} , while H^+ is reduced to H_2 .
- H^+ causes Zn to be oxidized.
 - Thus, H^+ is the **oxidizing agent**, or **oxidant**.
- Zn causes H^+ to be reduced.
 - Thus, Zn is the **reducing agent**, or **reductant**.
- Note that the reducing agent is oxidized and the oxidizing agent is reduced.

FORWARD REFERENCES

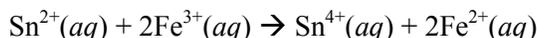
- Oxidation numbers of transition metals will be covered again in Chapters 23 (section 23.1) for metal complexes.

20.2 Balancing Redox Equations^{3,4}

- Recall the *law of conservation of mass*: The amount of each element present at the beginning of the reaction must be present at the end.
- *Conservation of charge*: Electrons are not lost in a chemical reaction.
- Some redox equations may be easily balanced by inspection.
 - However, for many redox reactions we need to look carefully at the transfer of electrons.

Half-Reactions

- **Half-reactions** are a convenient way of separating oxidation and reduction reactions.
- Consider the reaction:

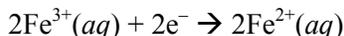


- The oxidation half-reaction is:



- Note that electrons are a product here.

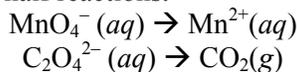
- The reduction half-reaction is:



- Note that electrons are a reactant here. These are the same two electrons as in the oxidation half-reaction above.

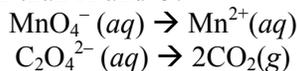
Balancing Equations by the Method of Half-Reactions^{5,6}

- Consider the titration of an acidic solution of $\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate, colorless) with KMnO_4 (deep purple).
 - MnO_4^- is reduced to Mn^{2+} (pale pink), while the $\text{C}_2\text{O}_4^{2-}$ is oxidized to CO_2 .
 - The equivalence point is indicated by the presence of a pale pink color.
 - If more KMnO_4 is added, the solution turns purple due to the excess KMnO_4 .
- What is the balanced chemical equation for this reaction?
- We can determine this using the method of half-reactions:
 - Write down the two incomplete half reactions.



- Balance each half reaction.

- First, balance elements other than H and O.



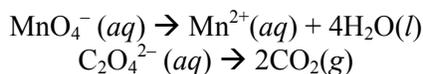
- Then balance O by adding water.

³ “Redox Balancing without Puzzling” from Further Readings

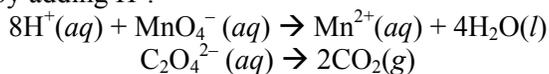
⁴ “Ask the Historian: Balancing Redox Equations” from Further Readings

⁵ “Balancing Redox Equations in Acid” Activity from Instructor’s Resource CD/DVD

⁶ “Hydronium Ion” 3-D Model from Instructor’s Resource CD/DVD



- Then balance H by adding H^+ .

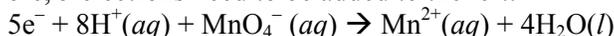


- Finish by balancing charge by adding electrons.

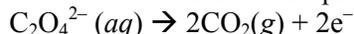
- This is an easy place to make an error!

- For the permanganate half-reaction, note that there is a charge of 7+ on the left and 2+ on the right.

- Therefore, 5 electrons need to be added to the left:



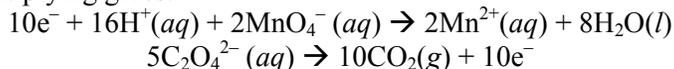
- In the oxalate half-reaction, there is a 2- charge on the left and a 0 charge on the right, so we need to add two electrons to the products:



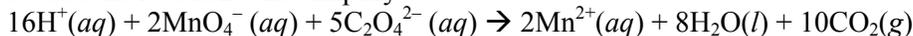
- Multiply each half-reaction to make the number of electrons equal.

- To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both.

- Multiplying gives:



- Now add the reactions and simplify.



- The equation is now balanced!

- Note that all of the electrons have cancelled out!

Balancing Equations for Reactions Occurring in Basic Solution⁷

- The same method as above is used, but OH^- is added to “neutralize” the H^+ used.
- The equation must again be simplified by canceling like terms on both sides of the equation.

FORWARD REFERENCES

- Redox reactions involving transition metals will be covered in Chapter 23 (section 23.1).

20.3 Voltaic Cells^{8,9,10,11,12,13,14,15,16,17}

- The energy released in a spontaneous redox reaction may be used to perform electrical work.
- **Voltaic**, or **galvanic cells**, are devices in which electron transfer occurs via an external circuit.
- Voltaic cells utilize spontaneous reactions.
- If a strip of Zn is placed in a solution of CuSO_4 , Cu is deposited on the Zn and the Zn dissolves by forming Zn^{2+} .

⁷ “Balancing Redox Equations in Base” Activity from Instructor’s Resource CD/DVD

⁸ “Common Student Misconceptions in Electrochemistry: Galvanic, Electrolytic and Concentration Cells” from Further Readings

⁹ “Alleviating the Common Confusion Caused by Polarity in Electrochemistry” from Further Readings

¹⁰ “Voltaic Cells I: The Copper-Zinc Cell” Animation from Instructor’s Resource CD/DVD

¹¹ “Visible Oxidation-Reduction in Electrochemical Cells” from Live Demonstrations

¹² “Redox Chemistry of Iron and Copper” Movie from Instructor’s Resource CD/DVD

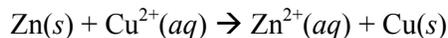
¹³ “Formation of Silver Crystals” Movie from Instructor’s Resource CD/DVD

¹⁴ Figure 20.5 from Transparency Pack

¹⁵ “Electrochemical Errors” from Further Readings

¹⁶ “Dental Filling Discomforts Illustrate Electrochemical Potentials of Metals” from Further Readings

¹⁷ “Using a Teaching Model to Correct Known Misconceptions in Electrochemistry” from Further Readings



- Zn is spontaneously oxidized to Zn^{2+} by Cu^{2+} .
- The Cu^{2+} is spontaneously reduced to Cu^0 by Zn.
- The entire process is spontaneous.
- Each of the two compartments of a voltaic cell is called a *half-cell*.
- This voltaic cells consists of:
 - The two solid metals are the *electrodes* (cathode and anode).
 - An oxidation half-reaction:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$$
 - Oxidation takes place at the **anode**.
 - A reduction half-reaction:

$$\text{Cu}^{2+}(aq) + 2e^{-} \rightarrow \text{Cu}(s)$$
 - Reduction takes place at the **cathode**.
- As oxidation occurs, Zn is converted to Zn^{2+} and $2e^{-}$.
 - The electrons flow toward the cathode where they are used in the reduction reaction.
 - We expect the Zn electrode to lose mass and the Cu electrode to gain mass.
- Electrons flow from the anode to the cathode.
 - Therefore, the anode is negative and the cathode is positive.
 - Electrons cannot flow through the solution; they have to be transported through an external wire.
- Anions and cations move through a porous barrier,, or a *salt bridge*.
 - A salt bridge is filled with a saturated solution of an electrolyte and is used to maintain the electrical neutrality of the solutions in both half-cells.
 - Cations from the salt bridge electrolyte move towards the cathode to neutralize the excess of negatively charged ions (Cathode: $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}$, so the counter ion of Cu, e.g., NO_3^{-} , is in excess).
 - Anions from the salt bridge electrolyte move towards the anode to neutralize the excess Zn^{2+} ions formed by oxidation.

20.4 Cell Potentials Under Standard Conditions

- The flow of electrons from anode to cathode is spontaneous.
 - What is the “driving force”?
- Electrons flow from anode to cathode because the cathode has a lower electrical potential energy than the anode.
 - *Potential difference* is the difference in electrical potential.
 - The potential difference is measured in volts.
 - One volt (V) is the potential difference required to impart one joule (J) of energy to a charge of one coulomb (C):

$$1\text{V} = 1 \frac{\text{J}}{\text{C}}$$

- **Electromotive force (emf)** is the force required to push electrons through the external circuit.
 - **Cell potential:** E_{cell} is the emf of a cell.
 - This is known as the *cell voltage*.
 - E_{cell} is > 0 for a spontaneous reaction.
- For 1M solutions or 1 atm pressure for gases at 25°C (standard conditions), the **standard emf (standard cell potential)** is called E°_{cell} .
 - For example, for the reaction:

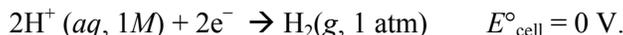
$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$
 - $E^{\circ}_{\text{cell}} = +1.10 \text{ V}$

Standard Reduction Potentials^{18,19,20,21}

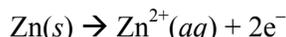
- We can conveniently tabulate electrochemical data.
- Standard reduction potentials**, E°_{red} are measured relative to a standard.
- The emf of a cell can be calculated from standard reduction potentials:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

- We use the following half-reaction as our standard:



- This electrode is called a **standard hydrogen electrode** (SHE) or the normal hydrogen electrode (NHE).
- The SHE is *assigned* a standard reduction potential of zero.
- Consider the half-reaction:



- We can *measure* E°_{cell} relative to the SHE (cathode):
 - It consists of a Pt electrode in a tube placed in 1 M H^+ solution.
 - H_2 is bubbled through the tube.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

$$0.76 \text{ V} = 0 \text{ V} - E^\circ_{\text{red}}(\text{anode}).$$

- Therefore, $E^\circ_{\text{red}}(\text{anode}) = -0.76 \text{ V}$.
- Standard reduction potentials must be written as reduction reactions:

$$\text{Zn}^{2+}(aq, 1M) + 2e^- \rightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76 \text{ V.}$$
 - Since $E^\circ_{\text{red}} = -0.76 \text{ V}$, we conclude that the *reduction* of Zn^{2+} in the presence of the SHE is *not* spontaneous.
 - However, the *oxidation* of Zn with the SHE *is* spontaneous.
- The standard reduction potential is an intensive property.
 - Therefore, changing the stoichiometric coefficient does not affect E°_{red} .

$$2\text{Zn}^{2+}(aq) + 4e^- \rightarrow 2\text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76 \text{ V}$$
- Reactions with $E^\circ_{\text{red}} > 0$ are spontaneous reductions relative to the SHE.
 - Reactions with $E^\circ_{\text{red}} < 0$ are spontaneous oxidations relative to the SHE.
 - The larger the difference between E°_{red} values, the larger E°_{cell} .
- The more positive the value of E°_{red} , the greater the driving force for reduction.

Strengths of Oxidizing and Reducing Agents²²

- Consider a table of standard reduction potentials.
- We can use this table to determine the relative strengths of reducing (and oxidizing) agents.
 - The more positive the E°_{red} , the stronger the oxidizing agent (written in the table as a reactant).
 - The more negative the E°_{red} , the stronger the reducing agent (written as a product in the table).
 - We can use this to predict if one reactant can spontaneously oxidize another.
 - For example:
 - F_2 can oxidize H_2 or Li.
 - Ni^{2+} can oxidize $\text{Al}(s)$.
 - We can use this table to predict if one reactant can spontaneously reduce another.
 - For example:
 - Li can reduce F_2 .

¹⁸ “Voltaic Cells II: The Zinc-Hydrogen Cell” Animation from Instructor’s Resource CD/DVD

¹⁹ Table 20.1 from Transparency Pack

²⁰ Figure 20.9 from Transparency Pack

²¹ “Standard Reduction Potential” Animation from Instructor’s Resource CD/DVD

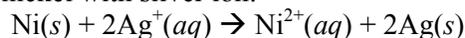
²² Figure 20.12 from Transparency Pack

20.5 Free Energy and Redox Reactions^{23,24}

- For any electrochemical process

$$E^\circ = E^\circ_{\text{red}}(\text{reduction process}) - E^\circ_{\text{red}}(\text{oxidation process}).$$

- A positive E° indicates a spontaneous process (galvanic cell).
- A negative E° indicates a nonspontaneous process.
- The above equation is used to understand the activity series of metals.
 - Consider the reaction of nickel with silver ion:



- The standard cell potential is:

$$\begin{aligned} E^\circ &= E^\circ_{\text{red}}(\text{Ag}^+/\text{Ag}) - E^\circ_{\text{red}}(\text{Ni}^{2+}/\text{Ni}) \\ &= (0.80 \text{ V}) - (-0.28 \text{ V}) = 1.08 \text{ V} \end{aligned}$$

- This value indicates that the reaction is spontaneous.

EMF, Free Energy and the Equilibrium Constant

- We can show that:

$$\Delta G = -nFE$$

- where ΔG is the change in free energy, n is the number of moles of electrons transferred, F is **Faraday's constant**, and E is the emf of the cell.
- We define F as:

$$1F = 96,500 \frac{\text{C}}{\text{mol e}^-} = 96,500 \frac{\text{J}}{(\text{V})(\text{mol e}^-)}$$

- Since n and F are positive, if $\Delta G < 0$ then $E > 0$, and the reaction will be spontaneous.
- When the reactants and products are in their standard states:

$$\Delta G^\circ = -nFE^\circ$$
- Since ΔG° is related to the equilibrium constant, K , we can relate E° to K :

$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RT \ln K}{-nF} = \frac{RT}{nF} \ln K$$

Electrical Work

- Free energy is a measure of the maximum amount of useful work that can be obtained from a system.
 - We know:

$$\Delta G = w_{\text{max}}$$

- and:

$$\Delta G = -nFE$$

- thus:

$$w_{\text{max}} = -nFE$$

- If E_{cell} is positive, w_{max} will be negative.
 - Work is done *by* the system *on* the surroundings.
- The emf can be thought of as being a measure of the driving force for a redox process.
 - In an electrolytic cell an external source of energy is required to force the reaction to proceed.

$$w = nFE_{\text{external}}$$

- In order to drive the nonspontaneous reaction, the external emf must be greater than E_{cell} .
- From physics we know that work is measured in units of watts:

$$1 \text{ W} = 1 \text{ J/s}$$

- Electric utilities use units of kilowatt-hours: $\text{kWh} = 3.6 \times 10^6 \text{ J}$.

²³ “Activity Series for Some Metals” from Live Demonstrations

²⁴ “An Activity Series: Zinc, Copper, and Silver Half Cells” from Live Demonstrations

20.6 Cell Potentials Under Nonstandard Conditions

- A voltaic cell is functional until $E = 0$ at which point equilibrium has been reached.
 - The cell is then “dead.”
- The point at which $E = 0$ is determined by the concentrations of the species involved in the redox reaction.

The Nernst Equation²⁵

- We can calculate the cell potential under nonstandard conditions.
- Recall that:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- We can substitute in our expression for the free energy change:

$$-nFE = -nFE^\circ + RT \ln Q$$

- Rearranging, we get the **Nernst equation**:

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

or

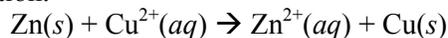
- Note that there is a change from natural logarithm to log base 10.

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

- The Nernst equation can be simplified by collecting all the constants together and using a temperature of 298 K:

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

- Example: If we have the reaction:



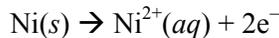
- If $[\text{Cu}^{2+}] = 5.0 \text{ M}$ and $[\text{Zn}^{2+}] = 0.050 \text{ M}$:

$$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0592}{2} \log \frac{0.050}{5.0} = 1.16 \text{ V}$$

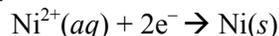
Concentration Cells²⁶

- A **concentration cell** is one whose emf is generated solely because of a concentration difference.
- Example: Consider a cell with two compartments, each with a Ni(s) electrode but with different concentrations of $\text{Ni}^{2+}(aq)$.
 - One cell has $[\text{Ni}^{2+}] = 1.0 \text{ M}$ and the other has $[\text{Ni}^{2+}] = 0.001 \text{ M}$.
 - The standard cell potential is zero.
 - But this cell is operating under nonstandard conditions!
 - The driving force is the difference in Ni^{2+} concentrations.

- Anode (dilute Ni^{2+}):



- Cathode (concentrated Ni^{2+}):



- Using the Nernst equation we can calculate a cell potential of +0.0888 V for this concentration cell.

²⁵ “Nernst Equation” Activity from Instructor’s Resource CD/DVD

²⁶ “Using the Biological Cell in Teaching Electrochemistry” from Further Readings

20.7 Batteries and Fuel Cells^{27,28,29,30,31,32}

- A **battery** is a portable, self-contained electrochemical power source consisting of one or more voltaic cells.
 - *Primary* cells: cannot be recharged.
 - *Secondary* cells: can be recharged from an external power source after its voltage has dropped.

Lead-Acid Battery³³

- A 12 V car battery consists of six cathode/anode pairs each producing 2 V.
- Cathode: PbO₂ on a metal grid in sulfuric acid:

$$\text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3\text{H}^+(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$
- Anode: Pb:

$$\text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^-$$
- The overall electrochemical reaction is

$$\text{PbO}_2(s) + \text{Pb}(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$
- The standard cell potential for this reaction is:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

$$= (+1.685 \text{ V}) - (-0.356 \text{ V}) = +2.041 \text{ V}$$
- Wood or glass-fiber spacers are used to prevent the electrodes from touching.
- An advantage of these cells is that they can be recharged.
 - An external source of energy is used to reverse the process.

Alkaline Battery

- The most common nonrechargeable battery is the alkaline battery.
- Powdered zinc metal is immobilized in a gel in contact with a concentrated solution of KOH.
- Thus, these batteries are *alkaline*.
- The reaction at the anode is:



- The reaction at the cathode is the reduction of MnO₂:

$$2\text{MnO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{MnO}(\text{OH})(s) + 2\text{OH}^-(aq)$$
- The cell potential of these batteries is 1.55 V at room temperature.

Nickel-Cadmium, Nickel-Metal-Hydride, and Lithium-Ion Batteries³⁴

- A common rechargeable battery is the nickel-cadmium (NiCad) battery.
 - The reaction at the cathode is:

$$2\text{NiO}(\text{OH})(s) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{Ni}(\text{OH})_2(s) + 2\text{OH}^-(aq)$$
 - The reaction at the anode is:

$$\text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd}(\text{OH})_2(s) + 2e^-$$
 - The cell potential of this battery is about 1.30 V at room temperature.
 - Cadmium is a toxic heavy metal.
 - There are environmental concerns to be addressed regarding the disposal of such batteries.
- Other rechargeable batteries have been developed.

²⁷ “Batteries: Full Speed Ahead” from Further Readings

²⁸ “Structure and Content of Some Primary Batteries” from Further Readings

²⁹ “Making a Simple Battery: The Gerber Cell” from Live Demonstrations

³⁰ “Batteries” Activity from Instructor’s Resource CD/DVD

³¹ “Time to Recharge” from Further Readings

³² “Batteries, from Cradle to Grave” from Further Readings

³³ Figure 20.19 from Transparency Pack

³⁴ “Lithium Batteries: A Practical Application of Chemical Principles” from Further Readings

- NiMH batteries (nickel-metal-hydride).
- Li-ion batteries (lithium-ion batteries).

Hydrogen Fuel Cells^{35,36}

- Direct production of electricity from fuels occurs in a **fuel** cell.
- An example is a hydrogen fuel cell.
 - At the cathode:

$$2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4e^- \rightarrow 4\text{OH}^-(aq)$$
 - At the anode:

$$2\text{H}_2(g) + 4\text{OH}^-(aq) \rightarrow 4\text{H}_2\text{O}(l) + 4e^-$$
- This cell is known as a PEM fuel cell (proton exchange membrane).
- The anode and cathode are separated by a polymer membrane that is permeable to protons but not electrons; it acts as a salt bridge.

FORWARD REFERENCES

- Hydrogen economy will be further mentioned in Chapter 22 (section 22.2).

20.8 Corrosion

- An example of an undesirable redox reaction is the **corrosion** of metals.
- Metal is attacked by a substance in the environment and converted to an unwanted compound.

Corrosion of Iron (Rusting)^{37,38}

- Consider the rusting of iron:
 - Since $E^\circ_{\text{red}}(\text{Fe}^{2+}) < E^\circ_{\text{red}}(\text{O}_2)$, iron can be oxidized by oxygen.
 - Cathode: $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$ $E^\circ_{\text{red}} = 1.23 \text{ V}$.
 - Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$ $E^\circ_{\text{red}} = -0.44 \text{ V}$.
- Dissolved oxygen in water usually causes the oxidation of iron.
- The Fe^{2+} initially formed can be further oxidized to Fe^{3+} , which forms rust, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(s)$.
- Oxidation occurs at the site with the greatest concentration of O_2 .
- Other factors are the pH, presence of salts, stress on the iron, and contact with other metals.

Preventing Corrosion of Iron^{39,40}

- Corrosion can be prevented by coating the iron with paint or another metal.
 - This prevents oxygen and water from reacting at the surface of the iron.
 - *Galvanized iron* is coated with a thin layer of zinc.
 - Zinc protects the iron since Zn is the anode and Fe is the cathode:

$$\begin{array}{ll} \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) & E^\circ_{\text{red}} = -0.76 \text{ V} \\ \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s) & E^\circ_{\text{red}} = -0.44 \text{ V} \end{array}$$
 - The standard reduction potentials indicate that Zn is easier to oxidize than Fe.
 - This process is **cathodic protection** (the *sacrificial anode* is destroyed).
- We can use something similar to protect underground pipelines.
 - Often, Mg is used as a sacrificial anode:

$$\begin{array}{ll} \text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s) & E^\circ_{\text{red}} = -2.37 \text{ V} \\ \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s) & E^\circ_{\text{red}} = -0.44 \text{ V} \end{array}$$

³⁵ “Vehicle of Change” from Further Readings

³⁶ “Hydrogen” 3-D Model from Instructor’s Resource CD/DVD

³⁷ “Evaluation of Corrosion Susceptibility of a Metal: Student Corrosion Experiment II” from Further Readings

³⁸ Figure 20.22 from Transparency Pack

³⁹ Figure 20.23 from Transparency Pack

⁴⁰ “Prevention of Corrosion” Activity from Instructor’s Resource CD/DVD

20.9 Electrolysis^{41,42,43,44,45}

- **Electrolysis reactions** are nonspontaneous reactions that require an external current in order to force the reaction to proceed.
 - They take place in **electrolytic cells**.
- In voltaic and electrolytic cells, reduction occurs at the cathode and oxidation occurs at the anode.
 - However, in electrolytic cells, electrons are forced to flow from the anode to the cathode.
 - In **electrolytic cells**, the anode is positive and the cathode is negative.
 - In voltaic cells, the anode is negative and the cathode is positive.
- Example: The decomposition of molten NaCl.
 - Cathode: $2\text{Na}^+(l) + 2e^- \rightarrow 2\text{Na}(l)$
 - Anode: $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-$.
 - Industrially, electrolysis is used to produce metals like Al.
- Electrolysis of high-melting ionic substances requires very high temperatures.
 - Do we get the same products if we electrolyze an aqueous solution of the salt?
 - Water complicates the issue!
 - Example: Consider the electrolysis of NaF(aq):

$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$	$E^\circ_{\text{red}} = -2.71 \text{ V}$
$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	$E^\circ_{\text{red}} = -0.83 \text{ V}$

 - Thus, water is more easily reduced than the sodium ion.

$2\text{F}^-(aq) \rightarrow \text{F}_2(g) + 2e^-$	$E^\circ_{\text{red}} = +2.87 \text{ V}$
$2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$	$E^\circ_{\text{red}} = +1.23 \text{ V}$

 - Thus, it is easier to oxidize water than the fluoride ion.
- Electrolysis does not always involve *inert* electrodes.
 - *Active* electrodes are electrodes that take part in electrolysis.
 - An example is *electroplating*.
 - Consider an active Ni electrode and another metallic electrode (steel) placed in an aqueous solution of NiSO₄:
 - Anode (nickel strip): $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^-$
 - Cathode (steel strip): $\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$
 - Ni plates on the inert electrode.
 - Electroplating is important in protecting objects from corrosion.

Quantitative Aspects of Electrolysis^{46,47,48}

- We want to know how much material we obtain with electrolysis.
- Consider the reduction of Cu²⁺ to Cu.

$$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s).$$
- 2 moles of electrons will plate 1 mol of Cu.
- The charge of one mol of electrons is 96,500 C (1 F).
 - A *coulomb* is the amount of charge passing a point in one second when the current is one ampere.
- The amount of Cu can be calculated from the current (*amperes*) and time required to plate.

$$\text{Coulombs} = \text{amperes} \times \text{seconds}$$

⁴¹ “Electroplating” Movie from Instructor’s Resource CD/DVD

⁴² “Electrolytic Cells in Series: A Red, White, and Blue Electrolysis” from Live Demonstrations

⁴³ “Electroplating Copper” from Live Demonstrations

⁴⁴ Figure 20.25 from Transparency Pack

⁴⁵ “Floating Pennies” from Live Demonstrations

⁴⁶ “Electrolysis” Activity from Instructor’s Resource CD/DVD

⁴⁷ “Electrolysis Calculation Example” Activity from Instructor’s Resource CD/DVD

⁴⁸ Figure 20.27 from Transparency Pack

Further Readings:

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3. Lee R. Summerlin and James L. Ealy, Jr., "Activity Series for Some Metals," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 1* (Washington: American Chemical Society, **1988**), p. 150. This overhead projector demonstration employs hydrogen gas formation.
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