

Chapter 20. Electrochemistry

20.1 Oxidation-Reduction Reactions

- Chemical reactions in which the oxidation state of one or more substances changes are called **oxidation-reduction reactions** (*redox reactions*).
 - Recall:
 - Oxidation involves loss of electrons (OIL).
 - Reduction involves gain of electrons (RIG).
 - 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.
 - 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.

20.2 Balancing Oxidation-Reduction Equations

- 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:
$$\text{Sn}^{2+}(aq) + 2\text{Fe}^{3+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq)$$
 - The oxidation half-reaction is:
$$\text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2e^-$$
 - Note that electrons are a product here.
 - The reduction half-reaction is:
$$2\text{Fe}^{3+}(aq) + 2e^- \rightarrow 2\text{Fe}^{2+}(aq)$$
 - Note that electrons are a reactant here.

Balancing Equations by the Method of Half-Reactions

- 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 given 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:

$$\text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq)$$

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{CO}_2(g)$$
- Balance each half-reaction:
 - First, balance elements other than H and O.

$$\text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq)$$

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{CO}_2(g)$$
 - Then balance O by adding water.

$$\text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$$

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{CO}_2(g)$$
 - Then balance H by adding H^+ .

$$8\text{H}^+(aq) + \text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$$

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{CO}_2(g)$$
 - 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:

$$5e^- + 8\text{H}^+(aq) + \text{MnO}_4^-(aq) \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$$
 - In the oxalate reaction, there is a 2- charge on the left and a 0 charge on the right, so we need to add two electrons:

$$\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{CO}_2(g) + 2e^-$$
 - Multiply each half reaction to make the number of electrons gained equal to the number of electrons lost.
 - To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both.
 - Multiplication gives:

$$10e^- + 16\text{H}^+(aq) + 2\text{MnO}_4^-(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O}(l)$$

$$5\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 10\text{CO}_2(g) + 10e^-$$
 - Now add the reactions and simplify.

$$16\text{H}^+(aq) + 2\text{MnO}_4^-(aq) + 5\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O}(l) + 10\text{CO}_2(g)$$
 - The equation is now balanced!
 - Note that all the electrons have canceled out!

Balancing Equations for Reactions Occurring in Basic Solution

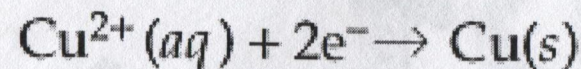
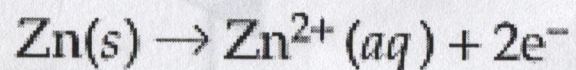
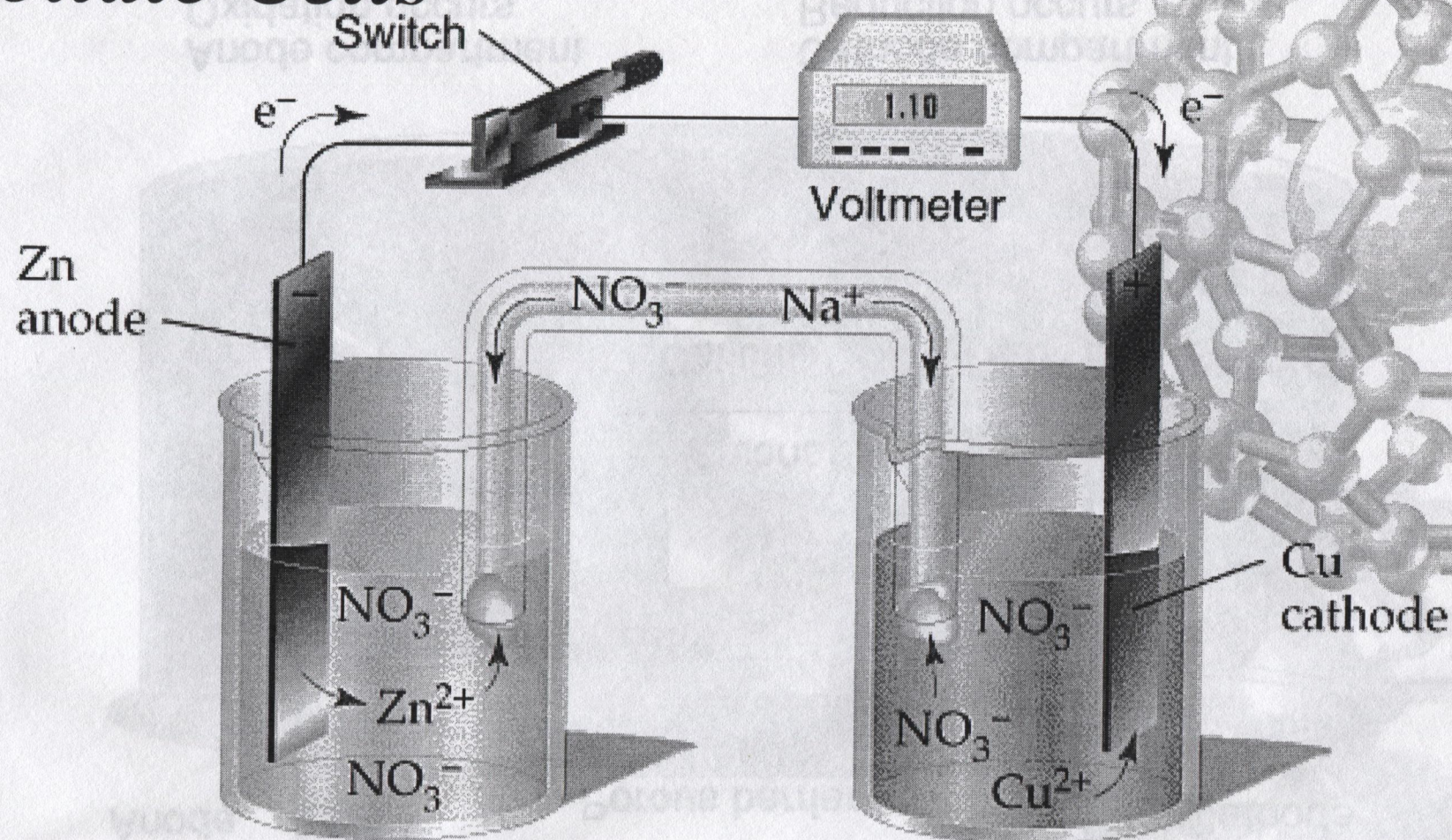
- We use OH^- and H_2O rather than H^+ and H_2O .
- The same method is used as in an acid solution, but OH^- is added to "neutralize" the H^+ used.
- The equation must again be simplified by canceling like terms on both sides of the equation.

20.3 Voltaic Cells

- 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+} .

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$
- Zn is spontaneously oxidized to Zn^{2+} by Cu^{2+} .
- The Cu^{2+} is spontaneously reduced to Cu^0 by Zn.

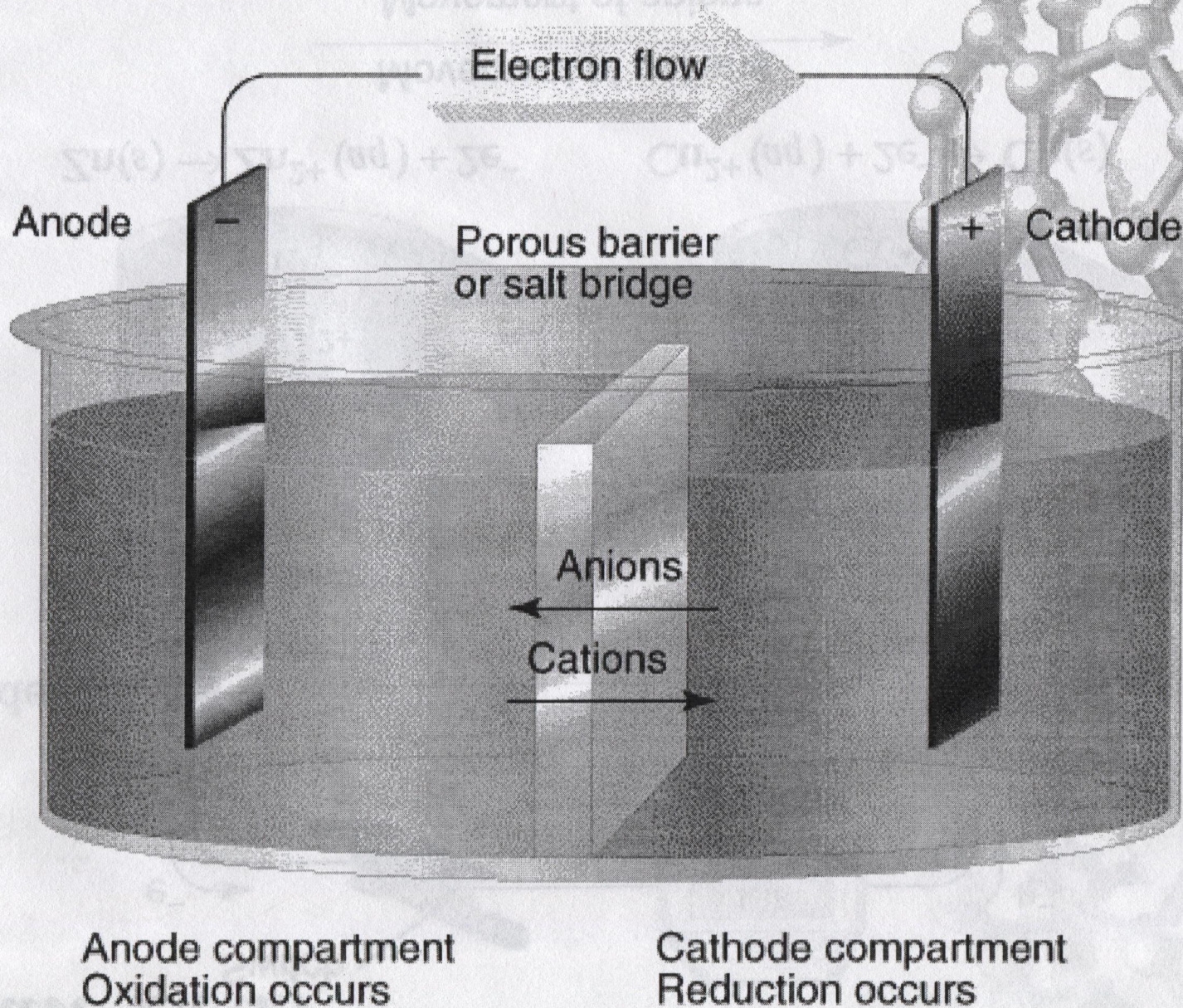
Voltaic Cells



Movement of cations

Movement of anions

Voltaic Cells



- The entire process is spontaneous.
- This voltaic cell consists of:
 - 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**.
 - A salt bridge (used to complete the electrical circuit).
 - Cations move from anode to cathode.
 - Anions move from cathode to anode.
 - The two solid metals are the **electrodes** (cathode and anode).
 - 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 salt bridge.
 - Cations move into the cathodic compartment to neutralize the excess negatively charged ions (Cathode: $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}$, so the counter ion of Cu is in excess).
 - Anions move into the anodic compartment to neutralize the excess Zn^{2+} ions formed by oxidation.

A Molecular View of the Electrode Process

- "Rules" of voltaic cells:
 - At the anode electrons are products.
 - Oxidation occurs at the anode.
 - At the cathode electrons are reactants.
 - Reduction occurs at the cathode.

20.4 Cell EMF

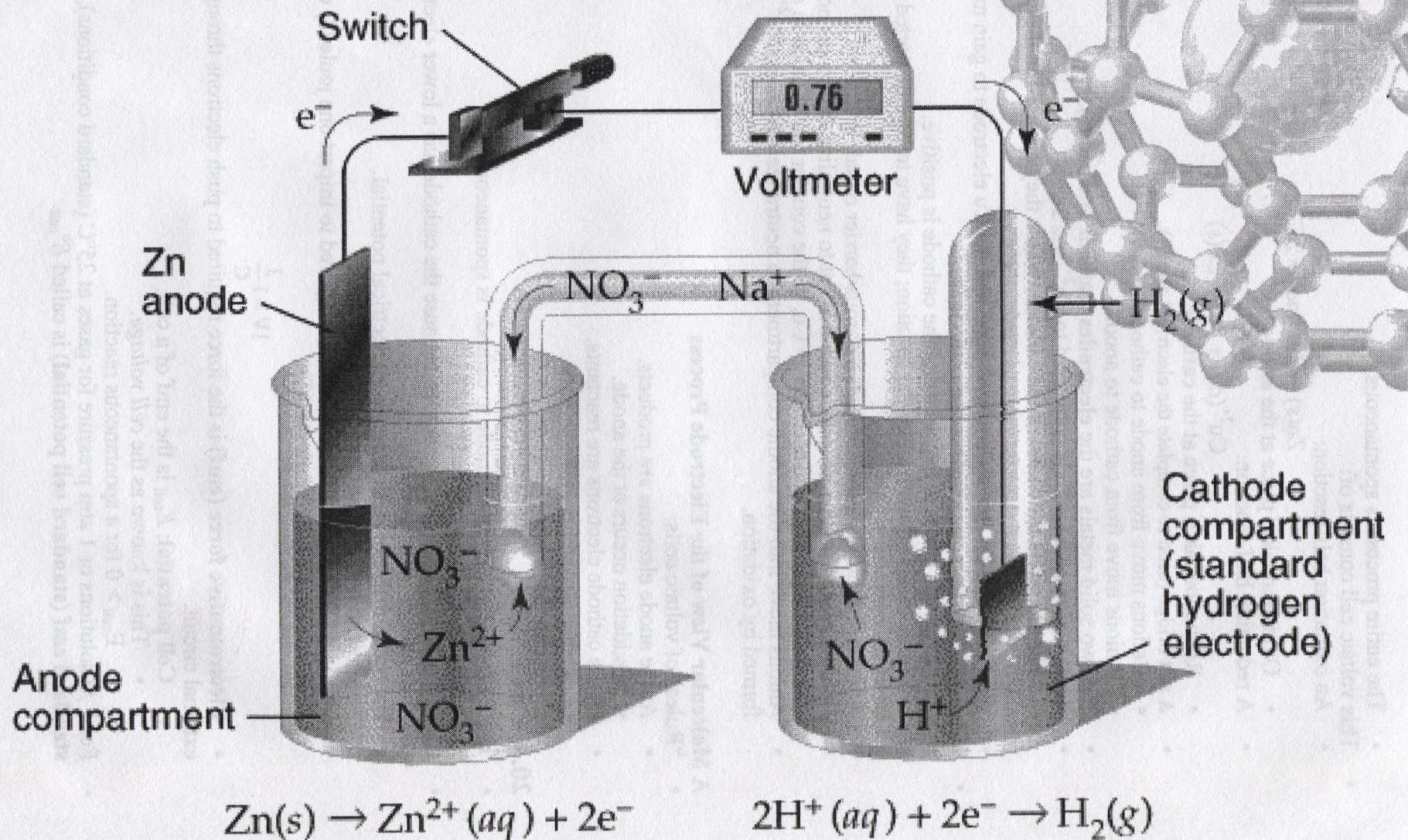
- The flow of electrons from anode to cathode is spontaneous.
 - What is the "driving force"?
- Electrons flow from anode to cathode because the cathode has a lower electrical potential energy than the anode.
 - **Potential difference:** difference in electrical potential.
 - The potential difference 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):

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

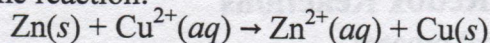
- **Electromotive force (emf)** is the force required to push electrons through the external circuit.
 - **Cell potential:** E_{cell} is the emf of a cell.
 - This is known as the *cell voltage*.
 - $E_{\text{cell}} > 0$ for a spontaneous reaction.
- For 1 M solutions or 1 atm pressure for gases at 25°C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

Cell EMF

Standard Reduction Potentials



- For example, for the reaction:



- $E^\circ_{\text{cell}} = +1.10 \text{ V}$.

Standard Reduction Potentials

- 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:

$$2\text{H}^+(aq, 1 \text{ M}) + 2e^- \rightarrow \text{H}_2(g, 1 \text{ atm}) \quad E^\circ_{\text{cell}} = 0 \text{ V}$$
 - This electrode is called a **standard hydrogen electrode** (SHE).
 - The SHE is *assigned* a standard reduction potential of zero.
- Consider the half-reaction:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$$
 - We can *measure* E°_{cell} relative to the SHE.
 - In this cell the SHE is the 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:

$$\text{Zn}^{2+}(aq, 1 \text{ M}) + 2e^- \rightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76 \text{ V}$$
 - 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 the E°_{cell} .
- The more positive the value of E°_{red} , the greater the driving force for reduction.

Oxidizing and Reducing Agents

- Consider a table of standard reduction potentials.
- We can use this table to determine the relative strength 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 table to predict if one reactant can spontaneously oxidize another.
 - 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.
 - Example:
 - Li can reduce F_2 .

20.5 Spontaneity of Redox Reactions

- 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 (voltaic cell).
- A negative E° indicates a nonspontaneous process.
- This equation is used to understand the activity series of metals.
 - Consider the reaction of nickel with silver ion:
$$\text{Ni}(s) + 2\text{Ag}^{+}(aq) \rightarrow \text{Ni}^{2+}(aq) + 2\text{Ag}(s)$$
 - The standard cell potential is:
$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{red}}(\text{Ag}^{+}/\text{Ag}) - E^{\circ}_{\text{red}}(\text{Ni}^{2+}/\text{Ni}) \\ &= (0.80 \text{ V}) - (-0.28 \text{ V}) \\ &= 1.08 \text{ V} \end{aligned}$$
 - This value indicates that the reaction is spontaneous.

EMF and Free-Energy Change

- 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:

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

- Since n and F are positive, if $\Delta G < 0$, then $E > 0$, and the reaction will be spontaneous.

20.6 Effect of Concentration on Cell EMF

- 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 Equation

- 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**:

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

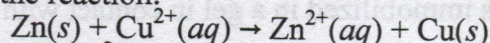
or

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

- Note the change from natural logarithm to log base-10.
- The Nernst equation can be simplified by collecting all the constants together 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 Cells

- 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 $\text{Ni}(s)$ 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: the difference in Ni^{2+} concentrations.
 - Anode (dilute Ni^{2+}): $\text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^-$
 - Cathode (concentrated Ni^{2+}): $\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$
- Using the Nernst equation we can calculate a cell potential of +0.0888 V for this concentration cell.

Cell EMF and Chemical Equilibrium

- A system is at equilibrium when $\Delta G = 0$.
- From the Nernst equation, at equilibrium

$$\log K = \frac{nE^\circ}{0.0592}$$

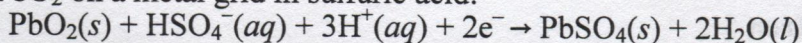
- Thus, if we know the cell emf, we can calculate the equilibrium constant.

20.7 Batteries

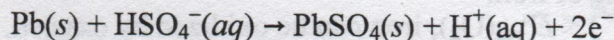
- A **battery** is a portable, self-contained electrochemical power source consisting of one or more voltaic cells.

Lead-Acid Battery

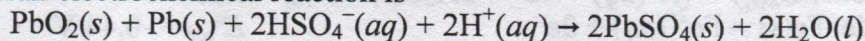
- A 12-V car battery consists of six cathode/anode pairs, each producing 2 V.
- Cathode: PbO_2 on a metal grid in sulfuric acid:



- Anode: Pb:



- The overall electrochemical reaction is



- The cell potential for this reaction is:

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode}) \\ &= (+1.685 \text{ V}) - (-0.356 \text{ V}) \\ &= +2.041 \text{ V} \end{aligned}$$

- 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:

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^{-}$$
- The reaction at the cathode is the reduction of MnO_2 :

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

Nickel–Cadmium, Nickel–Metal–Hydride, and Lithium–Ion Batteries

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

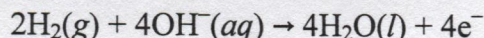
$$2\text{NiO}(\text{OH})(s) + 2\text{H}_2\text{O}(l) + 2e^{-} \rightarrow 2\text{Ni}(\text{OH})_2(s) + 2\text{OH}^{-}(aq)$$
 - The reaction at the anode is:

$$\text{Cd}(s) + 2\text{OH}^{-}(aq) \rightarrow \text{Cd}(\text{OH})_2(s) + 2e^{-}$$
 - 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 with respect to disposal of such batteries.
- Other rechargeable batteries have been developed.
 - NiMH batteries (nickel–metal–hydride)
 - Li-ion batteries (lithium-ion batteries).

Fuel Cells

- Direct production of electricity from fuels occurs in a **fuel cell**.
- Cathode: reduction of oxygen:

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



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

- 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 to consider are the pH, presence of salts, stress on the iron, and contact with other metals.

Preventing the Corrosion of Iron

- Corrosion can be prevented by coating the iron with paint or another metal.
 - This prevents oxygen and water from reacting at the iron surface.
 - Galvanized iron is coated with a thin layer of zinc.

- Zinc protects the iron, since Zn is the anode and Fe the cathode:

$$\begin{array}{ll} \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn}(\text{s}) & E^{\circ}_{\text{red}} = -0.76 \text{ V} \\ \text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}(\text{s}) & E^{\circ}_{\text{red}} = -0.44 \text{ V} \end{array}$$
- 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 a similar process to protect underground pipelines.
 - Often, Mg is used as a sacrificial anode:

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

20.9 Electrolysis

- **Electrolysis reactions** are nonspontaneous reactions that require an external current in order to force the reaction to proceed.
- 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 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.

Electrolysis of Aqueous Solutions

- Example: decomposition of molten NaCl.
 - Cathode: $2\text{Na}^{+}(\text{l}) + 2\text{e}^{-} \rightarrow 2\text{Na}(\text{l})$
 - Anode: $2\text{Cl}^{-}(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^{-}$
- 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):

$$\begin{array}{ll} \text{Na}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Na}(\text{s}) & E^{\circ}_{\text{red}} = -2.71 \text{ V} \\ 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^{-}(\text{aq}) & E^{\circ}_{\text{red}} = -0.83 \text{ V} \end{array}$$
 - Thus water is more easily reduced than sodium ion.

$$\begin{array}{ll} 2\text{F}^{-}(\text{aq}) \rightarrow \text{F}_2(\text{g}) + 2\text{e}^{-} & E^{\circ}_{\text{red}} = +2.87 \text{ V} \\ 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} & E^{\circ}_{\text{red}} = +1.23 \text{ V} \end{array}$$
 - Thus it is easier to oxidize water than fluoride ion.

Electrolysis with Active Electrodes

- Active electrodes: electrodes that take part in electrolysis.
 - Example: electroplating.
- Consider an active Ni electrode and another metallic electrode (steel) placed in an aqueous solution of NiSO_4 :
 - Anode: $\text{Ni}(\text{s}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-}$
 - Cathode: $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni}(\text{s})$.
- Ni plates on the inert electrode.
- Electroplating is important in protecting objects from corrosion.

Quantitative Aspects of Electrolysis

- We want to know how much material we obtain with electrolysis.
- Consider the reduction of Cu^{2+} to Cu.

$$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$$
 - 2 mol of electrons will plate 1 mol of Cu.

- The charge of 1 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 and time taken to plate.

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

$$\text{Mol } e^- = \text{Coulombs} \times \left(\frac{1 \text{ mol } e^-}{96,500 \text{ C}} \right)$$

$$\text{Mol Cu} = \text{Moles } e^- \times \left(\frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \right)$$

- The molar mass of Cu is used to convert moles Cu to grams Cu.

Electrical Work

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

$$\Delta G = w_{\max}$$
 - And:

$$\Delta G = -nFE$$
 - Thus:

$$w_{\max} = -nFE$$
 - 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: work is measured in of watts:

$$1 \text{ W} = 1 \text{ J/s}$$
- Electric utilities use units of kilowatt-hours:

$$1 \text{ kWh} = (1000 \text{ W})(1 \text{ hour}) = \left(\frac{3600 \text{ s}}{1 \text{ hour}} \right) \left(\frac{1 \text{ J/s}}{1 \text{ W}} \right) = 3.6 \times 10^6 \text{ J}$$

The Meaning of Reduction and Oxidation

[Return to Redox Menu](#)

I. Oxidation Numbers

Every atom, ion or polyatomic ion has a formal oxidation number associated with it. This value compares the number of protons in an atom (positive charge) and the number of electrons assigned to that atom (negative charge).

In many cases, the oxidation number reflects the actual charge on the atom, but there are many cases where it does not. Think of oxidation numbers as a bookkeeping exercise simply to keep track of where electrons go.

II. Reduction

Reduction means what it says: the oxidation number is reduced in reduction.

This is accomplished by adding electrons. The electrons, being negative, reduce the overall oxidation number of the atom receiving the electrons.

III. Oxidation

Oxidation is the reverse process: the oxidation number of an atom is increased during oxidation.

This is done by removing electrons. The electrons, being negative, make the atom that lost them more positive.

IV. Some Information

There are rules to help you determine the oxidation number. Here is a [lesson on the rules](#).

I remember this phrase: LEO the lion says GER.

LEO = Loss of Electrons is Oxidation

GER = Gain of Electrons is Reduction

Another way is to simply remember that reduction is to reduce the oxidation number. Therefore, oxidation must increase the value.

V. Some Definitions

Oxidizing Agent - that substance which oxidizes somebody else. It is reduced in the process.

Reducing Agent - that substance which reduces somebody else. It is oxidized in the process.

It helps me to remember these definitions by the opposite nature of what happens. By that, I mean the oxidizing agent gets reduced and the reducing agent gets oxidized.

Redox Rules

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I Rule Number One

All free, uncombined elements have an oxidation number of zero.

This includes diatomic elements such as O_2 or others like P_4 and S_8 .

II. Rule Number Two

Hydrogen, in all its compounds except hydrides, has an oxidation number of +1 (positive one)

III. Rule Number Three

Oxygen, in all its compounds except peroxides, has an oxidation number of -2 (negative two).

Now, some examples:

1. What is the oxidation number of Cl in HCl?

Since $H = +1$, the Cl must be -1 (minus one).

2. What is the oxidation number of Na in Na_2O ?

Since $O = -2$, the two Na must each be +1.

3. What is the oxidation number of Cl in ClO^- ?

The O is -2, but since a -1 must be left over, then the Cl is +1.

4. What is the oxidation number for each element in $KMnO_4$?

$K = +1$ because KCl exists. We know the $Cl = -1$ because HCl exists. $O = -2$ by definition
 $Mn = +7$. There are 4 oxygens for a total of -8, K is +1, so Mn must be the rest.

5. What is the oxidation number of S in SO_4^{2-} ?

$O = -2$. There are four oxygens for -8 total. Since -2 must be left over, the S must be +6.

Some practice problems:

1. N in NO_3^-

2. C in CO_3^{2-}

3. Cr in CrO_4^{2-}

4. Cr in $Cr_2O_7^{2-}$

5. Fe in Fe_2O_3

Redox Rules Answers

basic_model.html

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1. N in NO_3^-

The O is -2 and three of them makes -6. Since -1 is left over, the N must be +5

2. C in CO_3^{2-}

The O is -2 and three of them makes -6. Since -2 is left over, the C must be +4

3. Cr in CrO_4^{2-}

The O is -2 and four of them makes -8. Since -2 is left over, the Cr must be +6

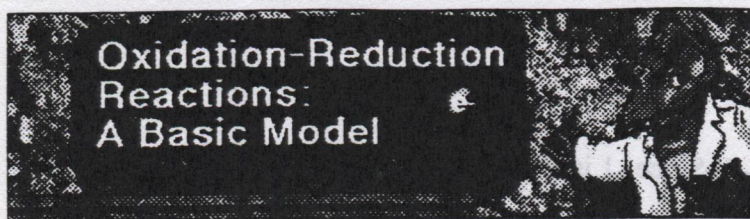
4. Cr in $\text{Cr}_2\text{O}_7^{2-}$

The O is -2 and seven of them makes -14. Since -2 is left over, the two Cr must each be +6

5. Fe in Fe_2O_3

The O is -2 and three of them makes -6. Each Fe must be +3

Charge of	Group	Period
+1	I	1
+2	II	2
+3	III	3
+4	IV	4



Assigning all atoms an oxidation state of zero serves as an important reference point, as oxidation-reduction reactions always involve a change in the oxidation state of the atoms or ions involved. This change in oxidation state is due to the "loss" or "gain" of electrons. The loss of electrons from an atom produces a positive oxidation state, while the gain of electrons results in negative oxidation states.

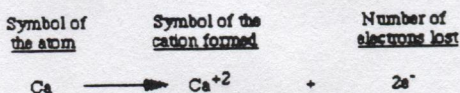
The changes that occur in the oxidation state of certain elements can be predicted quickly and accurately by the use of simple guidelines. These guidelines are based on the behavior of the Representative Elements, which can be divided into two classes; the metals and nonmetals.

All metal atoms are characterized by their tendency to be oxidized, losing one or more electrons, forming a positively charged ion, called a cation. During this oxidation reaction, the oxidation state of the metal always increases from zero to a positive number, such as "+1, +2, +3....", depending on the number of electrons lost. The number of electrons lost by these Representative metals and the charge of the cation formed are always equal to the Group number of the metal as summarized below.

Group Number	Number of Electrons Lost	Charge of Cation Formed
I	1	+1
II	2	+2
III	3	+3
IV	4	+4

The group numbers also correspond to the electrons that are found in the outermost energy levels of these atoms. These electrons are often called valence electrons.

By convention oxidation reactions are written in the following form using the element, Calcium, as an example



Note that the oxidation state increases from zero to a positive number (from "0" to "+2" in the above example) and is always numerically equal to the number of electrons lost. See Exercise 1

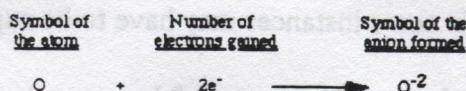
The electrons lost by the metal are not destroyed but gained by the nonmetal, which is said to be reduced. As the nonmetal gains the electrons lost by the metal, it forms a negatively charged ion, called an anion. During this reduction reaction, the oxidation state of the nonmetal always decreases from zero to a negative value (-1, -2, -3 ...) depending on the number of electrons gained. The number of electrons gained by any Representative nonmetal and the charge of the anion formed, can be predicted

by use of the following guidelines.

Group Number	Number of Electrons Gained	Charge of Anion Formed
IV	4	-4
V	3	-3
VI	2	-2
VII	1	-1
VIII	0	no tendency to form anions

Note, the GROUP VIII nonmetals have no tendency to gain additional electrons, hence they are unreactive in terms of oxidation-reduction. This is one the reasons why this family of elements was originally called the Inert Gases.

By convention reduction reactions are written in the following way:



Note that the charge of anion formed is always numerically equal to the number of electrons gained. See exercise 2

One important fact to remember in studying oxidation-reduction reactions is that the process of oxidation cannot occur without a corresponding reduction reaction. Oxidation must always be "coupled" with reduction, and the electrons that are "lost" by one substance must always be "gained" by another as matter (such as electrons) cannot be destroyed or created. Hence, the terms "lost or gained", simply mean that the electrons are being transferred from one particle to another.

Redox Reactions Involving Nonmetals Only

The situation is a bit more complex when nonmetals atoms are involved. As all nonmetals have similarly high electronegativity values, it is unreasonable to assume that there will be a transfer of electrons between them in an oxidation-reduction reaction. In these instances the valence electrons involved can no longer be thought of as being "lost or gained" between the atoms, but instead, are only partially transferred, moving closer to that atom which has the higher electronegativity (and away from the atom of lower electronegativity). This "shift" of electrons results in an unequal distribution of charge, as the more electronegative atom becomes more "negative" and the atom of lower electronegativity becomes more "positive".

The accurate determination of the distribution of charge resulting from these "electron shifts" is very difficult, but guidelines have been devised to simplify the process. In general, these guidelines assign the more electronegative atom a negative oxidation state, and the atom with the lower electronegativity, a positive oxidation state. One should be aware that these guidelines are at best, arbitrary approximations, and in some instances may have to be supplemented by additional methods.

Guidelines - Oxidation States of Nonmetals

1. When two, nonmetals react with each other, the more electronegative element is assigned the negative oxidation state.
 - a. Fluorine, the most electronegative element, is always assigned an oxidation state of "-1" when combined with any other element.
 - b. Hydrogen, whenever it is combined in a molecule, is assigned an oxidation state of "+1".
 - c. When hydrogen combines with metals in forming compounds called, metal hydrides, it is assigned an oxidation state of (-1)
2. Oxygen, in most compounds, is usually assigned an oxidation state of "-2".
 - a. However, when it is found in peroxides ("O - O bonds ") it is assigned a value of "-1"; or when combined with fluorine, it is assigned a value of "+1".
3. The sum of the oxidation states of every element in a substance or species (it may be an ion or a molecule) must always equal the electrical charge indicated for that substance or species.
 - a. any monatomic ion has an oxidation state equal to its charge
 - b. the sum of the oxidation states of all atoms in a compound must equal zero.
 - c. the sum of the oxidation states of all atoms in a polyatomic ion must equal the charge of the ion.

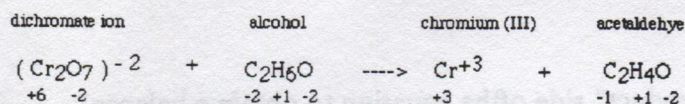
See exercise 5

Balancing Redox Reactions Using the Half Reaction Method

Many redox reactions occur in aqueous solutions or suspensions. In this medium most of the reactants and products exist as charged species (ions) and their reaction is often affected by the pH of the medium. The following provides examples of how these equations may be balanced systematically. The method that is used is called the ion-electron or "half-reaction" method.

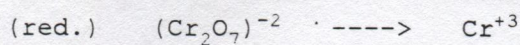
Example 1 -- Balancing Redox Reactions Which Occur in Acidic Solution

Organic compounds, called alcohols, are readily oxidized by acidic solutions of dichromate ions. The following reaction, written in net ionic form, records this change. The oxidation states of **each atom in each compound** is listed in order to identify the species that are oxidized and reduced, respectively.

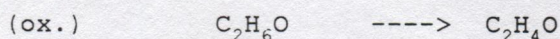
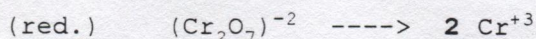


An examination of the oxidation states, indicates that carbon is being oxidized, and chromium, is being reduced. To balance the equation, use the following steps:

- First, divide the equation into two halves; an oxidation half-reaction and reduction half-reaction by grouping appropriate species.



- Second, if necessary, balance both equations by inspection. In doing this ignore any oxygen and hydrogen atoms in the formula units. In other words, balance the non-hydrogen and non-oxygen atoms only. By following this guideline in the example above, only the **reduction half-reaction** needs to be balanced by placing the coefficient, **2**, in front of Cr^{+3} as shown below.



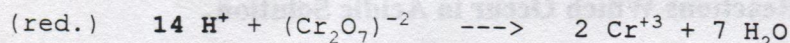
(as there are equal numbers of carbon atoms on both sides of this equation, skip this step for this half-reaction. Remember, in this step, one concentrates on balancing only non-hydrogen and non-oxygen atoms)

- The third step involves balancing oxygen atoms. To do this, one must use water (H_2O) molecules. Use 1 molecule of water for each oxygen atom that needs to be balanced. Add the appropriate number of water molecules to that side of the equation required to balance the oxygen atoms as shown below.



(as there are equal numbers of oxygen atoms, skip this step for this half-reaction)

4. The fourth step involves balancing the hydrogen atoms. To do this one must use hydrogen ions (H^+). Use one (1) H^+ ion for every hydrogen atom that needs to be balanced. Add the appropriate number of hydrogen ions to that side of the equation required to balance the hydrogen atoms as shown below

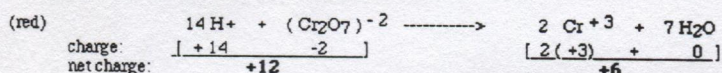


(as there are 14 hydrogen atoms in 7 water molecules, 14 H^+ ions must be added to the opposite side of the equation)

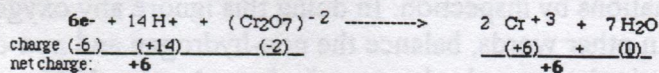


(2 hydrogen ions must be added to the "product" side of the equation to obtain a balance)

5. The fifth step involves the balancing of positive and negative charges. This is done by adding electrons (e^-). Each electron has a charge equal to (-1). To determine the number of electrons required, find the net charge of each side of the equation.

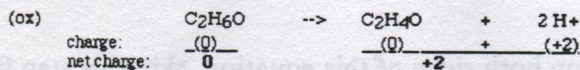


The electrons must always be added to that side which has the greater positive charge as shown below.

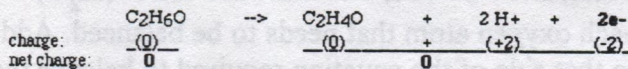


note: the net charge on each side of the equation does not have to equal zero.

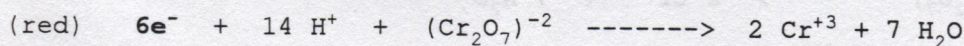
The same step is repeated for the oxidation half-reaction.



As there is a net charge of +2 on the product side, two electrons must be added to that side of the equation as shown below.

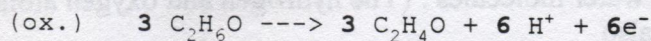


At this point the two half-reactions appear as:

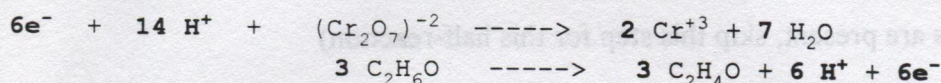


The reduction half-reaction requires 6 e⁻, while the oxidation half-reaction produces 2 e⁻.

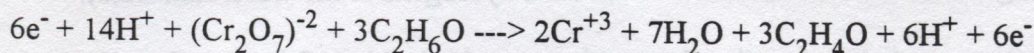
- The sixth step involves multiplying each half-reaction by the smallest whole number that is required to equalize the number of electrons gained by reduction with the number of electrons produced by oxidation. Using this guideline, the oxidation half reaction must be multiplied by "3" to give the 6 electrons required by the reduction half-reaction.



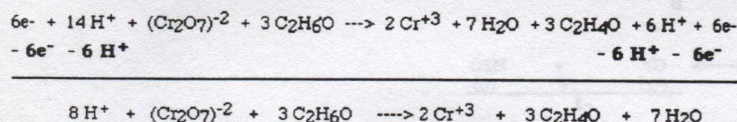
- The seventh and last step involves adding the two half reactions and reducing to the smallest whole number by cancelling species which on both sides of the arrow.



adding the two half-reactions above gives the following:



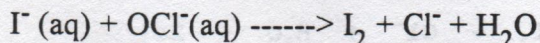
Note that the above equation can be further simplified by subtracting out 6 e⁻ and 6 H⁺ ions from both sides of the equation to give the final equation.



Note: the equation above is completely balanced in terms of having an **equal number of atoms as well as charges**.

Example 2 - Balancing Redox Reactions in Basic Solutions

The active ingredient in bleach is the hypochlorite (OCl⁻) ion. This ion is a powerful oxidizing agent which oxidizes many substances under basic conditions. A typical reaction is its behavior with iodide (I⁻) ions as shown below in net ionic form.

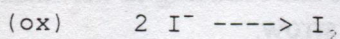


Balancing redox equations in basic solutions is identical to that of acidic solutions except for the last few steps as shown below.

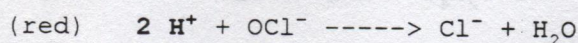
- First, divide the equation into two halves; an oxidation half-reaction and reduction-reaction by grouping appropriate species.



- Second, if needed, balance both equations, by inspection ignoring any oxygen and hydrogen atoms. (The non-hydrogen and non-oxygen atoms are already balanced, hence skip this step)
- Third, balance the oxygen atoms using water molecules. (The hydrogen and oxygen atoms are already balanced; hence, skip this step also.)
- Fourth, balance any hydrogen atoms by using an (H⁺) for each hydrogen atom

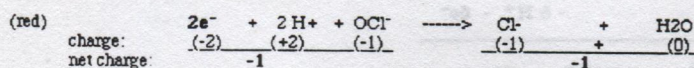
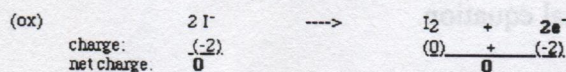


(as no hydrogens are present, skip this step for this half-reaction)

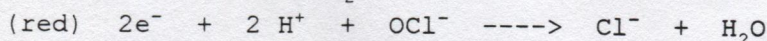


(two hydrogen ions must be added to balance the hydrogens in the water molecule).

- Fifth, use electrons (e⁻) to equalize the net charge on both sides of the equation. Note; each electron (e⁻) represents a charge of (-1).

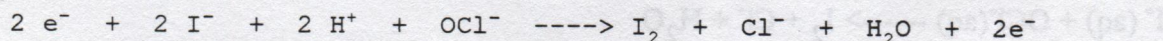


- Sixth, equalize the number of electrons lost with the number of electrons gained by multiplying by an appropriate small whole number.

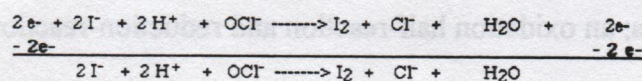


(as the number of electrons lost equals the number of electrons gained, skip this step)

- Add the two equations, as shown below.



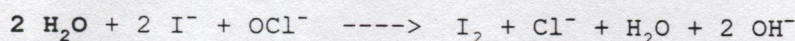
and subtract "like" terms from both sides of the equation. Subtracting "2e⁻" from both sides of the equation gives the net equation:



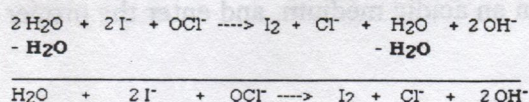
8. To indicate the fact that the reaction takes place in a basic solution, one must now add one (OH⁻) unit for every (H⁺) present in the equation. The OH⁻ ions **must be added to both sides of the equation** as shown below.



9. Then, on that side of the equation which contains both (OH⁻) and (H⁺) ions, combine them to form H₂O. Note, combining the 2 OH⁻ with the 2 H⁺ ions above gives 2 HOH or 2 H₂O molecules as written below.



10. Simplify the equation by subtracting out water molecules, to obtain the final, balanced equation.



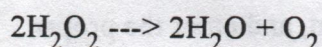
Note that both the atoms and charges are equal on both sides of the equation, and the presence of hydroxide ions (OH⁻) indicates that the reaction occurs in basic solution.

Basic Applications

EXERCISE 8 Disproportionation Reactions

Disproportionation reaction are those in which a single element is simultaneously oxidized and reduced.

- (1) For the following reaction



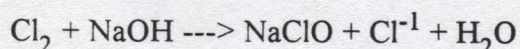
List the symbol of the element that undergoes disproportionation:

What is the total number of electrons lost in the oxidation half-reaction?

What is the total number of electrons lost in the reduction half-reaction?

[Check Answer](#)

- (2) For the following reaction,



List the symbol of the element that undergoes disproportionation:

What is the total number of electrons lost in the oxidation half-reaction?

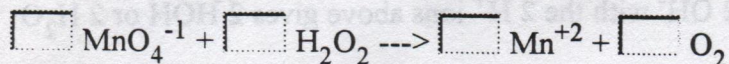
What is the total number of electrons lost in the reduction half-reaction?

[Check Answer](#)

Basic Applications

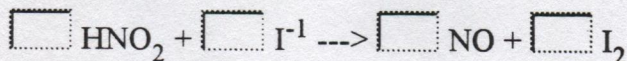
EXERCISE 9 Balancing Redox Equations

(1) Balance the following reaction assuming it occurs in an acidic medium, and enter the proper coefficients in the blank spaces.



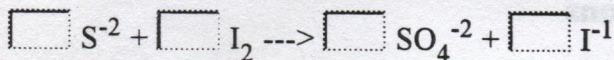
Check Answer

(2) Balance the following reaction assuming it occurs in an acidic medium, and enter the proper coefficients in the blank spaces.



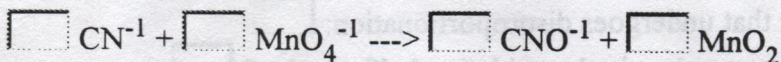
Check Answer

(3) Balance the following reaction assuming it occurs in a basic medium, and enter the proper coefficients in the blank spaces.

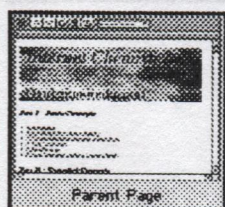


Check Answer

(4) Balance the following reaction assuming it occurs in a basic medium, and enter the proper coefficients in the blank spaces.

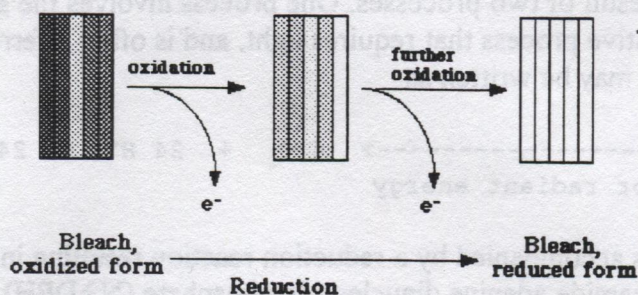


Check Answer



Bleaching Agents

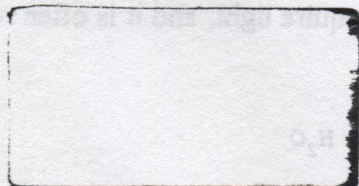
Bleaching agents are compounds which are used to remove color from substances such as textiles. In earlier times textiles were bleached by exposure to the sun and air. Today most commercial bleaches are oxidizing agents, such as sodium hypochlorite (NaOCl) or hydrogen peroxide (H_2O_2) which are quite effective in "decolorizing" substances via oxidation. The action of these bleaches can be illustrated in the following simplified way:



Recall that an oxidizing agent is any substance which causes another substance to lose one or more electrons. The decolorizing action of bleaches is due in part to their ability to remove these electrons which are activated by visible light to produce the various colors. The hypochlorite ion (OCl^-), found in many commercial preparations, is reduced to chloride ions and hydroxide ions forming a basic solution as it accepts electrons from the colored material as shown below.

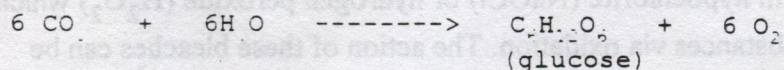


Bleaches are often combined with "optical brighteners". These compounds are quite different from bleaches. They are capable of absorbing wavelengths of ultraviolet light invisible to the human eye, and converting these wavelengths to blue or blue-green light. The blue or blue-green light is then reflected by the substance making the fabric appear much "whiter and brighter" as more visible light is seen by the eye.

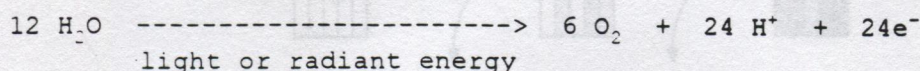


Photosynthesis

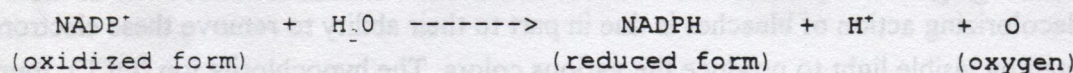
An example of naturally-occurring biological oxidation-reduction reactions is the process of photosynthesis. It is a very complex process carried out by green plants, blue-green algae, and certain bacteria. These organisms are able to harness the energy contained in sunlight, and via a series of oxidation-reduction reactions, produce oxygen and sugar, as well as other compounds which may be utilized for energy as well as the synthesis of other compounds. The overall equation for the photosynthetic process may be expressed as:



The equation is the net result of two processes. One process involves the splitting of water. This process is really an oxidative process that requires light, and is often referred to as the "**light reaction**". This reaction may be written as:



The oxidation of water is accompanied by a reduction reaction resulting in the formation of a compound, called nicotinamide adenine dinucleotide phosphate (NADPH). This reaction is illustrated below:



This reaction is linked or coupled to yet another reaction resulting in the formation of a highly energetic compound, called adenosine triphosphate, (ATP). As this reaction involves the addition of a phosphate group (labeled, as P_i) to a compound called, adenosine diphosphate (ADP) during the **light reaction**, it is called **photophosphorylation**.



Think of the **light reaction**, as a process by which organisms "capture and store" radiant energy as they produce oxygen gas. This energy is stored in the form of chemical bonds of compounds such as NADPH and ATP.

The energy contained in both NADPH and ATP is then used to reduce carbon dioxide to glucose, a type of sugar ($\text{C}_6\text{H}_{12}\text{O}_6$). This reaction, shown below, does not require light, and it is often referred to as the "**dark reaction**".



The chemical bonds present in glucose also contain a considerable amount of potential energy. This stored energy is released whenever glucose is catabolized (broken down) to drive cellular processes. The carbon skeleton in glucose also serves as a source of carbon for the synthesis of other important biochemical compounds such as, lipids, amino acids, and nucleic acids.

In simplest terms, the process of photosynthesis can be viewed as one-half of the carbon cycle. In this half, energy from the sun is captured and transformed into nutrients which can be utilized by higher organisms in the food chain. The release of this energy during the metabolic re-conversion of glucose to water and carbon dioxide represents the second half of the carbon cycle and it may be referred to as catabolism or "oxidative processes".

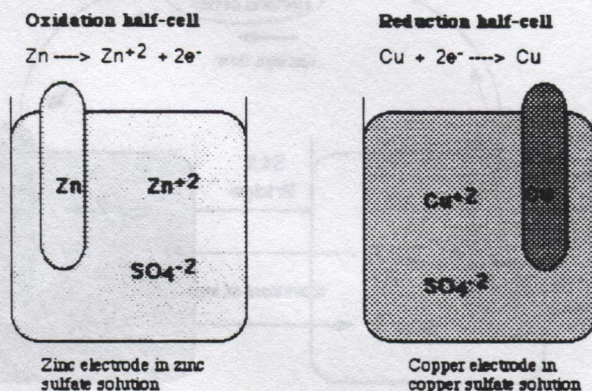
Electrochemical Cells

Many oxidation-reduction reactions occur spontaneously, giving off energy. An example involves the spontaneous reaction that occurs when zinc metal is placed in a solution of copper ions as described by the net ionic equation shown below.

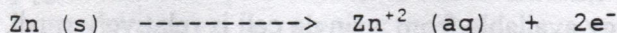


The zinc metal slowly "dissolves" as its oxidation produces zinc ions which enter into solution. At the same time, the copper ions gain electrons and are converted into copper atoms which coats the zinc metal or sediments to the bottom of the container. The energy produced in this reaction is quickly dissipated as heat, but it can be made to do useful work by a device called, an **electrochemical cell**. This is done in the following way.

An electrochemical cell is composed to two compartments or **half-cells**, each composed of an electrode dipped in a solution of electrolyte. These half-cells are designed to contain the oxidation half-reaction and reduction half-reaction separately as shown below.



The half-cell, called the **anode**, is the site at which the **oxidation** of zinc occurs as shown below.



During the oxidation of zinc, the zinc electrode will slowly dissolve to produce zinc ions (Zn²⁺), which enter into the solution containing Zn²⁺ (aq) and SO₄²⁻ (aq) ions.

The half-cell, called the **cathode**, is the site at which **reduction** of copper occurs as shown below.



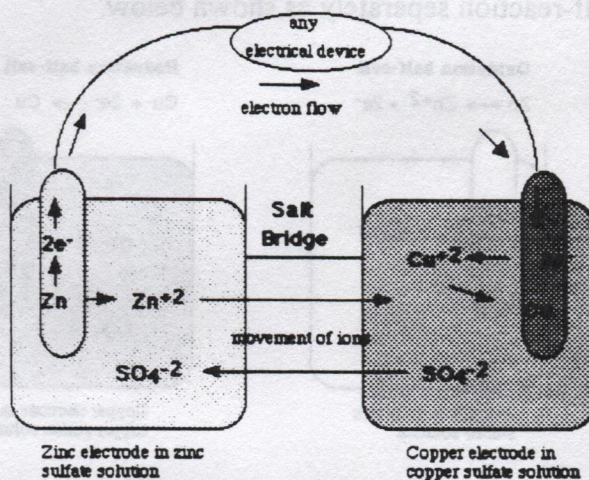
When the reduction of copper ions (Cu²⁺) occurs, copper atoms accumulate on the surface of the solid copper electrode.

The reaction in each half-cell does **not** occur unless the two half cells are connected to each other.

Recall that in order for oxidation to occur, there must be a corresponding reduction reaction that is

linked or "coupled" with it. Moreover, in an isolated oxidation or reduction half-cell, an imbalance of electrical charge would occur, the anode would become more positive as zinc cations are produced, and the cathode would become more negative as copper cations are removed from solution. This problem can be solved by using a "salt bridge" connecting the two cells as shown in the diagram below. A "salt bridge" is a porous barrier which prevents the spontaneous mixing of the aqueous solutions in each compartment, but allows the migration of ions in both directions to maintain electrical neutrality. As the oxidation-reduction reaction occurs, cations (Zn^{+2}) from the anode migrate via the salt bridge to the cathode, while the anion, $(\text{SO}_4)^{-2}$, migrates in the opposite direction to maintain electrical neutrality.

The two half-cells are also connected externally. In this arrangement, electrons provided by the oxidation reaction are forced to travel via an external circuit to the site of the reduction reaction. The fact that the reaction occurs spontaneously once these half cells are connected indicates that there is a difference in potential energy. This difference in potential energy is called an **electromotive force (emf)** and is measured in terms of **volts**. The zinc/copper cell has an **emf** of about 1.1 volts under standard conditions.



Any electrical device can be "spliced" into the external circuit to utilize this potential energy produced by the cell for useful work. Although the energy available from a single cell is relatively small, electrochemical cells can be linked in series to boost their energy output. A common and useful application of this characteristic is the "**battery**". An example is the lead-acid battery used in automobiles. In the lead-acid battery, each cell has a lead metal anode and lead (IV) oxide (lead dioxide) cathode both of which are immersed in a solution of sulfuric acid. This single electrochemical cell produces about 2 volts. Linking 6 of these cells in series produces the **12-volt battery** found in most cars today. One disadvantage of these "wet cells" such as the lead-acid battery is that it is very heavy and bulky. However, like many other "wet cells", the oxidation-reduction reaction which occurs can be readily reversed via an external current such as that provided by an automobile's alternator. This prolongs the lifetime and usefulness of such devices as an energy source.

Spontaneity of REDOX Systems

Voltaic Cells are spontaneous in that they will generate electrical current simply by connecting the half cells together. Electrolytic Cells, on the other hand, are non-spontaneous. In order for you to deposit chemical substances at the electrodes electrical energy from some battery or power source must force the reactions to happen. How can we predict whether a REDOX system is spontaneous? We use the same indicator for predicting spontaneity as we did for any Chemical reaction. The change in Free Energy must be negative for any Chemical system to be spontaneous.

Relationship Between Delta G and Cell Potential

There is a relationship between Delta G and the cell potential:

$$\Delta G^0 = - n F E_{\text{cell}}^0$$

where:

n = electron exchange (after balancing)

F = Faraday's Constant = 96,500 Coulombs / equivalent

$$E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0$$

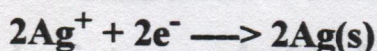
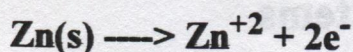
According to this equation Delta G can only be negative if the cell potential is positive. If the cell potential were negative then the two negatives would be replaced with a positive making the system non-spontaneous.

Let's take an example:

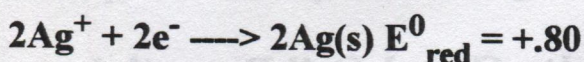
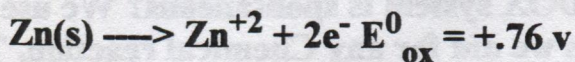
In the following reaction: $\text{Zn(s)} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag(s)}$

1. Determine the Standard Cell Potential
2. Determine the Delta G at standard conditions
3. Will this reaction occur spontaneously as written

1. Identify the two half cells



2. Look up the standard reduction potential of the Silver and the standard Oxidation potential of the Zinc



3. Determine the standard cell potential by adding the two potentials together

$$E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0 = .76 + .80 = 1.56 \text{ volts}$$

4. Determine the Delta G

$$\Delta G^0 = - n F E_{\text{cell}}^0$$

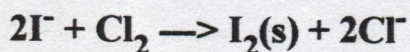
$$\Delta G^0 = - (2)(96,500) (1.56 \text{ v}) = -301,056 \text{ Joules}$$

5. Will this REDOX equation occur spontaneously as written?

Since Delta G is negative then the sytem is spontaneous and would make a good voltaic cell.

Here is one for you to try:

For the following REDOX system:



1. Calculate the Standard Cell Potential
2. Calculate the standard Delta G
3. Will this reaction occur as written?

When you have the answers to the above problem, **you might check for the correct**

solution

If these cells are at Standard Conditions then one could conceivably determine the Delta G using Free Energies of Formation, and then determine the standard cell potential using the same relationship.

Relationship Between Standard Cell Potential and Equilibrium Constant

Electrochemical cells can attain a state of Equilibrium. We know from a previous lesson that:

$$\Delta G^0 = -2.303 R T \log K_{eq}$$

We found in this lesson that:

$$\Delta G^0 = -nFE_{cell}^0$$

Since the right hand side of these two expressions are equal to Delta G they must be equal to each other:

$$-2.303 R T \log K_{eq} = -nFE_{cell}^0$$

or

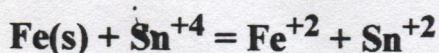
$$E_{cell}^0 = 2.303 R T \log K_{eq} / nF$$

If we combine all the constants in the expression 2.303, R, T, and F we get a value of .0592

$$E_{cell}^0 = (.0592 / n) \log K_{eq}$$

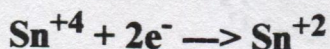
Let's take an example:

Given the following electrochemical cell:

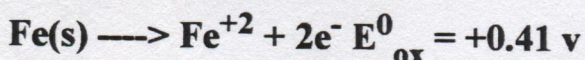


1. Calculate the standard cell potential
2. Calculate the equilibrium constant, K_{eq}

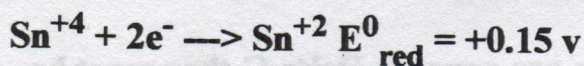
Separate the net reaction into the two half cell reactions.



Look up the reduction potential of Iron II and reverse the sign for the oxidation potential of the oxidation half cell reaction.



Look up the standard reduction potential of the Reduction half cell.



calculate the standard cell potential by adding the half cell potentials

$$E_{cell}^0 = E_{ox}^0 + E_{red}^0 = 0.41 + 0.15 = 0.56 \text{ v}$$

Determine the K_{eq} .

$$E_{cell}^0 = (0.0592 / n) \log K_{eq}$$

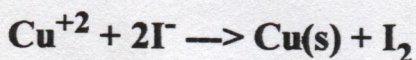
$$0.56 = (0.0592 / 2) \log K_{eq}$$

$$0.56 / .0295 = \log K_{eq} = 18.98$$

$$\text{Antilog}(\log K_{eq} = K_{eq} = \text{Antilog}(18.98)$$

$$K_{eq} = 9.62 \times 10^{18}$$

Here is one for you to try:



ELECTROCHEMISTRY

1. Stoichiometric relationships in electrolysis –

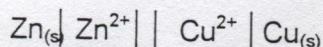
- ♦ \mathcal{F} = faraday = the charge on one mole of electrons = 96,500 coulombs
- ♦ 1 C = 1 ampere x 1 second
- ♦ 1 joule = 1 volt x 1 coulomb "JVC"
- ♦ 1 watt = 1 joule/1 second

Problem 1: How many grams of copper are deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through a solution of CuSO_4 for a period of 20.0 min.? (ans. 0.791 g)

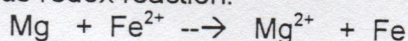
Problem 2: Electroplating is an important application of electrolysis. How much time would it take in minutes to deposit 0.500 g of metallic nickel on a metal object using a current of 3.00 A? The nickel is reduced from the +2 oxidation state. (ans. 9.11 min).

Problem 3: What current is needed to deposit 0.500 g of chromium metal from a solution of Cr^{+3} in a period of 1.00 hr? (ans. 0.773 A)

2. Cell Notation: As a matter of convenience, chemists have devised a shorthand way of describing the makeup of a galvanic cell. The anode half-cell is specified on the left, with the anode electrode given first the vertical bar represents a phase boundary. The set of double vertical bars represents the salt bridge, which separates the two half cells. On the right the cathode half-cell is shown, the the cathode electrode given last.

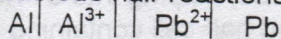


Problem: 4 Sketch and label a galvanic cell that makes use of the following spontaneous redox reaction:



Write the half-reactions for the anode and cathode. Give the abbreviated cell notation.

Problem 5. Write the anode and cathode half-reactions for the following galvanic cell.



3. Cell potentials and thermodynamics: ΔG for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction. In an electrical system, work is supplied by the electric current that is pushed along by the potential of the cell.

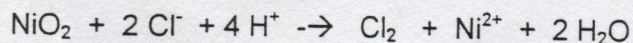
$$\text{Maximum work} = n\mathcal{F}E_{\text{cell}}$$

And - $\Delta G = \text{maximum work} = n\mathcal{F}E$

If we are dealing with the standard cell potential, we can calculate the standard free energy change.

$$\Delta G^\circ = -n\mathcal{F}E^\circ$$

Problem 6: Calculate the standard free energy change for the following reaction, given that its standard cell potential is 0.320 V at 25°C .



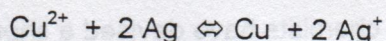
(ans. -61.8 kJ)

4. Determining equilibrium constants. One of the useful applications of electrochemistry is in the determination of equilibrium constants.

$$E^\circ = \frac{0.0592 \text{ V} \log K_c}{n}$$

Problem 7: Calculate K_c for the reaction in problem 6. (ans. 6×10^{10})

Problem 8. The calculated standard cell potential for the reaction

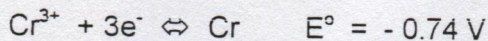
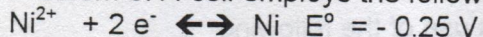


$E^\circ_{\text{cell}} = -0.46 \text{ V}$. Calculate K_c . Does the reaction proceed very far toward completion?

5. Calculating the effect of concentration on E°_{cell}

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V} \log Q}{n}$$

Problem 9. A cell employs the following half-reactions.



Calculate the potential if $[\text{Ni}^{2+}] = 1.0 \times 10^{-4} \text{ M}$ and $[\text{Cr}^{3+}] = 2.0 \times 10^{-3} \text{ M}$.

(ans. 0.42 V)

Problem 10. A chemist wanted to measure the concentration of Cu^{2+} in samples of water in which the copper ion concentration was expected to be very small. The apparatus consisted of a silver electrode, dipping into a 1.00 M solution of AgNO_3 , connected by a salt bridge to a second half-cell containing a copper electrode that was able to be dipped into each water sample. In the analysis of one of the samples, the cell potential was measured to be 0.62 V , with the copper electrode serving as the anode. What was the concentration of copper ion? (ans. $4 \times 10^{-6} \text{ M}$).