Principles of Reactivity: Electron Transfer Reactions

What is oxidation?
When a molecule/ion loses electrons (becomes more positive)
Whatever is oxidized is the oxidizing agent

What is reduction?
When a molecule/ion gains electrons (becomes more negative)
Whatever is reduced is the oxidizing agent

How to Assign Oxidation Numbers

- The oxidation state is zero for any element in its free state.
- The oxidation state of a monatomic ion is the electric charge on the ion. All group IA elements form ions with a single positive charge, group IIA elements form 2+ ions and the halogens form −1 ions.
- Fluorine always has an oxidation state of −1 in its compounds. The other halogens have oxidation states of −1 unless they are combined with a more electronegative halogen or oxygen.
Assigning Oxidation Numbers Continued

• Hydrogen has oxidation state of +1 except when it is combined with a less electronegative element
• The oxidation state of oxygen is –2 except when it is bonded to fluorine (where it may be +1 or +2) and in peroxides where it has an oxidation state of –1
• The sum of the oxidation states of all the atoms in a molecule or ion is equal to the overall charge on the species.

Practice Writing Oxidation States
for Each Element in the Following Compounds

K₂S, Cr₂O₇⁻, NH₃, BH₃, BaO₂, MnO₄⁻, Br⁻, ClO₃⁻

Balancing Redox Equations

In redox equations, something will be oxidized and something will be reduced.

Sometimes the number of electrons that was lost in the oxidation process does not equal the number of electrons gained in the reduction process.

Therefore, we have to balance the redox equation
**Rules to Balancing Redox Equations**

1. Separate into two half reactions
2. Balance every element except hydrogen and oxygen
3. Balance the oxygen by adding water to the side that needs oxygens
4. Balance the hydrogens by adding H+ to the side that needs hydrogen
5. Add electrons to the more positive side such to equal to the charge on the other side

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**Balancing Redox Cont’d**

6. Repeat steps 2-5 for the other half reaction
7. Equal the number of electrons of the two half reactions
8. Add the two half reactions
9. If the solution is in basic conditions, add the water equation

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**Test Your Skill**

Balance the following redox equations

\[
\text{Fe(s) + Ag}^+ \rightarrow \text{Ag(s) + Fe}^{2+}
\]

\[
\text{MnO}_4^{-}\text{(aq) + Fe}^{2+} \rightarrow \text{Fe}^{3+}\text{(s) + Mn}^{2+}
\]

\[
\text{H}_2\text{O}_2\text{(aq) + N}_2\text{H}_4\text{(aq) \rightarrow N}_2\text{(g) + H}_2\text{O(l)}
\]

In basic conditions
Chemical Change Leading to an Electric Current

How can we take this chemical energy and convert it to electrical energy?

...With a Galvanic Cell

Anode—negative electrode where oxidation occurs

Cathode—positive electrode where reduction occurs

If this number reads positive, the reaction is spontaneous in the forward direction

Electrons move toward the cathode

Fig 18-14       Pg 877

The copper/zinc electrochemical cell. The voltmeter measures the difference in electrical potentials between the two electrodes.
If the zinc-and copper-containing portions of this redox system are physically separated, electron transfer can occur only through an external wire.

\[
\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(wire)}
\]

\[
\text{Cu}^{2+} + 2e^- \quad \text{(wire)} \rightarrow \text{Cu(s)}
\]

Write the half reactions of the previous voltaic cell.

- Oxidation: \( \text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(wire)} \)
- Reduction: \( \text{Cu}^{2+} + 2e^- \quad \text{(wire)} \rightarrow \text{Cu(s)} \)

Electrodes are passive
Write the two half reactions

\[
\text{Fe}^{3+}(aq) + 1\ e^- \rightarrow \text{Fe}^{2+}(aq)
\]

\[
\text{H}_2(g) + 2\ \text{H}_2\text{O}(l) \rightarrow 2\ \text{H}_3\text{O}^+(aq) + 2e^-
\]

Which one occurs at the anode?

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How do we calculate Standard Redox Potentials?

We must compare the half reactions to a standard

What is that standard?

\[
2\ \text{H}_3\text{O}^+(aq) + 2e^- \rightarrow \text{H}_2(g) + 2\ \text{H}_2\text{O}(l) \quad E^\circ = 0.00\ \text{V}
\]

This is called the standard hydrogen electrode or SHE

Now that we have a standard, we can calculate standard redox potential by using the table of standard redox potentials

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\(E^\circ\) means at standard state...298 K, 1 atm and 1 M of solute
Problem:

Calculate the standard redox potential for the spontaneous reaction of the following two half reactions:

\[ \text{Ag}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Ag(s)} \quad E^° = +0.80 \text{ V} \]

\[ \text{Na}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Na(s)} \quad E^° = -2.714 \text{ V} \]

If you ever have to multiply the half reactions to equal moles of electrons, do not multiply the reduction potential.

Another Problem:

Is the following reaction written spontaneous in the forward direction?

\[ \text{Ni}^2+(\text{aq}) + \text{Cu(s)} \rightarrow \text{Ni(s)} + \text{Cu}^2+(\text{aq}) \]

How does the relate to \( \Delta G \)?

\[ \Delta G^° = -nFE^° \]

Where

- \( \Delta G \) = free energy
- \( n \) = number of moles of electron
- \( F \) = Faraday’s constant \((9.65 \times 10^4 \text{ J/V\text{\textperiodcentered}mol})\)
- \( E^° \) = standard redox potential

If at nonstandard state: \( \Delta G = -nFE \)
Electrochemical Cells at Nonstandard Conditions

As said before, the standard cell potential, $E^\circ$, is measured under standard conditions (298 K, 1 atm, and 1.0 M).

If we are not at standard conditions, we have to solve for $E$ at nonstandard conditions

$$E = E^\circ - \left(\frac{RT}{nF}\right) \ln Q$$

The Nernst Equation

When temperature equals 298 K, the equation can be written:

$$E = E^\circ - \left(\frac{0.0257}{n}\right) \ln Q$$

When we are at equilibrium, $E$ becomes zero

$$E = 0 = E^\circ - \left(\frac{0.0257}{n}\right) \ln K$$

Which rearranges to

$$\frac{nE^\circ}{0.0257} = \ln K$$
Batteries and Fuel Cells

Batteries are classified as two types:

Primary: use oxidation-reduction reactions that cannot be reversed very easily

Secondary: reactions of these batteries can be reversed (rechargeable batteries)

Primary Batteries

The Primary Batteries - Dry Cell Battery
Invented by Georges Leclanché

Anode, oxidation Zn Metal
Zn(s) → Zn^{2+} + 2e⁻

Cathode, reduction Carbon Rod
2NH\textsubscript{4}^{+}(aq) + 2e⁻ → 2NH\textsubscript{3}(g) + H\textsubscript{2}(g)

Two gases are produced that must be taken care of

That is why there is MnO\textsubscript{2}
2MnO₂(s)  +  H₂  →  Mn₂O₃(s)  +  H₂O(l)

And the ammonia gas is taken up by the Zn²⁺ that was formed from the oxidation of zinc metal:

Zn²⁺(aq)  +  2NH₃  +  2Cl⁻(aq)  →  Zn(NH₃)₂Cl₂(s)

Zinc chloride battery very similar to dry cell, but the electrolyte at the cathode is mainly ZnCl₂.

Three More Types of Primary Batteries

Alkaline Batteries:

Anode, oxidation
Zn(s)  +  2OH⁻(aq)  →  Zn(OH)₂(s)  +  2e⁻

Cathode, reduction
2MnO₂(s)  +  H₂O(l)  +  2e⁻  →  Mn₂O₃(g)  +  2OH⁻(aq)

Anode - Zn(s) and 2OH⁻
Cathode MnO₂(s) and Carbon

Increase storage density--Longer Life
**Mercury Batteries:**

- **Anode, oxidation**  
  \[ \text{Zn(s)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2e^- \]

- **Cathode, reduction**  
  \[ \text{HgO(s)} + \text{H}_2\text{O(l)} + 2e^- \rightarrow \text{Hg(l)} + 2\text{OH}^-(\text{aq}) \]

**Lithium Batteries:**

- **Anode**  
  Li(s) and 2OH^-

- **Cathode**  
  2MnO_2(s)

**Secondary Batteries**

The primary batteries no longer produce a current when the chemicals inside have reached equilibrium conditions. Secondary batteries can be recharged.

**How?**

The original reactant concentration can be restored by reversing the net cell reaction using an external source of electric energy.
Lead Storage Batteries:
The battery is recharged by current from the car’s alternator

Anode:
\[ \text{Pb}(s) + \text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{PbSO}_4(s) + \text{H}_3\text{O}^+ + 2e^- \]

Cathode:
\[ \text{PbO}_2(s) + 3\text{H}_3\text{O}^+ + 2\text{HSO}_4^- + 2e^- \rightarrow \text{PbSO}_4(s) + 5\text{H}_2\text{O}(l) \]

Nickel-Cadmium Batteries
Have the advantage that the oxidizing and reducing agent can be regenerated easily

Anode: \[ \text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd(OH)}_2(s) + 2e^- \]

Cathode: \[ \text{NiO(OH)}(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^-(aq) \]

Lithium Ion Batteries

Anode – ultrapure graphite (carbon)

Cathode – lithium cobalt oxide, nickel oxide or manganese oxide prepared with millions of tiny pores

Lithium forms a complex with the metal oxide

Requires liquid electrolytes – lithium salt in solution
Lithium Polymer Batteries

Refinement of the lithium ion battery
Integrates the electrolyte into a polymer plastic separator

Electrolysis

Use of electric current to bring about chemical change

The reaction can be driven in the opposite direction by an external potential of opposite sign and greater than 2.05 V.
Whether a cell operates galvanically or electrolytically, the electrode where oxidation occurs is always called the anode.

Fig 18-26  Pg 901

The electropolating of silver.

Pg 901

Courtesy International Silver Plating, Inc.
Electrolysis of Water

Anode: \[6\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+_3\text{O}^+(aq) + 4e^-\]

Cathode: \[4\text{H}^+_3\text{O}^+(aq) + 4e^- \rightarrow 2\text{H}_2(g) + 4\text{H}_2\text{O}(l)\]

Overall: \[2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)\]

Box 18-2B  Chemistry and Technology: Fuel Cells

Fuel serves as the electron source and the electrodes are catalysts.