

Objective 13. Apply oxidation-reduction reaction principles to batteries.

We looked at acid-base reactions earlier. These reactions are also called proton transfer reactions. An acid loses/donates protons. A base gains protons. Protons are transferred from the acid to the base. Every acid has a conjugate (partner) base. Every base has a conjugate (partner) acid.

We'll look at oxidation-reduction reactions. These reactions are also called electron transfer reactions. A substance that loses (donates) electrons is being oxidized. A substance that gains (accepts) electrons is being reduced. Electrons are transferred from the substance that loses electrons to the substance that gains electrons.

The substance that is being oxidized (loses electrons) is called the reducing agent because it is reducing another substance (gains electrons).

The substance that is being reduced (gains electrons) is called the oxidizing agent because it is oxidizing another substance (loses electrons).

Every reducing agent has a conjugate (partner) oxidizing agent. Every oxidizing agent has a conjugate (partner) reducing agent.

1. Metal elements lose electrons to form metal cations – metal elements are oxidized and are reducing agents.

Non-metal elements gain electrons to form non-metal anions – non-metal elements are reduced and are oxidizing agents.

In Chem 1A, we looked at the Activity Series of Metals. Some metals lose electrons more easily (more active) than other metals. This list ranks metal elements from most active to least active or strongest reducing agent to weakest reducing agent. If a metal element is a strong reducing agent, its partner metal ion is a weak oxidizing agent.

E.g., Al is a strong reducing agent because it easily loses its electrons. Al^{3+} ion is a weak oxidizing agent because it does not want to gain electrons.

a. Al exists on the Earth's surface as bauxite, Al_2O_3 , because _____. Bauxite has to be _____ to form Al metal. (Note: Al is the most abundant metallic element on the Earth's crust but its production consumes about 5% of electricity generated in the U.S. (<http://www.aluminum.org/industries/production/primary-production>))

b. Gold (Au) is a _____ reducing agent because it _____ loses its electrons. Au^{3+} ion is a _____ oxidizing agent because it _____ gain electrons. Gold exists on the Earth's surface as _____ because _____.

2. See Electrochemistry Lecture Slide 5 – The Activity Series of Metals. Lithium metal is the most active metal. Zinc is the next most active. Copper is not an active metal. This means Li easily loses its electron (oxidized) to form Li^+ ion. Cu does not easily lose its electrons (oxidized) to form Cu^{+2} ion.

See Electrochemistry Lecture Slide 6 - the Standard Reduction Potential Table. This Table is an Activity Series with Numbers – the ability of a metal ion to gain electrons is quantified. This Table shows metal ions gaining electrons (reduced) whereas the Activity Series shows metals losing electrons (oxidized).

$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$ metal has a standard reduction potential of -0.76 V

$\Delta G = -nFE = (2 \text{ moles of electrons})(96,500 \text{ C/mole})(-0.76 \text{ V}) = +146,700 \text{ J}$.

$\Delta G > 0$ so this means this reaction is not spontaneous. This means Zn^{2+} ion does not easily gain electrons (reduced) to form Zn metal. This also means zinc “prefers” to stay as an ion rather than a metal.

Look at the reverse of this reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^-$. $\Delta G = -146,700 \text{ J}$ (change the sign of ΔG).

$\Delta G < 0$ so this means Zn easily loses its electrons (oxidized) to form Zn^{2+} ion. This also means zinc “prefers” to form an ion rather than stay a metal.

a. The standard reduction potential of $\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$ metal is -0.44 V.

(i) Calculate ΔG for this reaction.

(ii) Look at the reverse of this reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^-$. Calculate ΔG for this reaction.

(iii) Explain why Zn is easier to oxidize than Fe.

b. The standard reduction potential of $\text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au}$ metal is 1.50 V.

(i) Calculate ΔG for this reaction.

(ii) Based on your value of ΔG , does gold “prefer” to be an ion or a metal?

(iii) Explain why gold is found on the Earth as a metal and not as a compound.

3. See Electrochemistry Lecture Slide 9. The standard reduction potentials for bleach (as HClO), hydrogen peroxide (H_2O_2), oxygen (O_2), and iodine (I_2) are given.

- a. Rank the following common oxidizing agents in order of strength: bleach (NaClO), hydrogen peroxide (H_2O_2), oxygen (O_2), and iodine (I_2). Give reasons for your ranking.
- b. Calculate ΔG for the strongest oxidizing agent.
- c. Due to its unreactiveness and other properties, gold (Au) is considered a noble metal. What is the standard reduction potential for Au^{3+} to Au ? Calculate ΔG for the oxidation of Au to Au^{3+} ion.
- d. H_2O_2 is the only oxidizing agent of the four that oxidizes Au .
- (i) Write the reduction half reaction for H_2O_2 .

Write the oxidation half reaction of Au .

The same number of electrons is transferred between the oxidizing agent (H_2O_2) and the reducing agent (Au). What factor do you have to multiply each half reaction so the same number of electrons are transferred between the H_2O_2 and the Au ?

Write a balanced chemical equation that shows the reaction of H_2O_2 and Au .

- (ii) Calculate ΔG and E for the reaction of H_2O_2 and Au .

e. Silver is also unreactive. Which oxidizing agent oxidizes Ag ? If more than one oxidizing agent oxidizes Ag , choose one oxidizing agent and write one balanced chemical equation to show your answer.

4. Batteries and thermodynamics.

- a. (i) A battery is a _____ (voltaic or electrolytic) cell. A battery _____ energy, which means the battery reaction is _____ and has a ΔG _____ 0.
- (ii) In a battery, the _____ active metal loses electrons to the _____ active metal.
- (iii) The anode is the electrode at which oxidation occurs – the anode is the more active metal. The cathode is the electrode at which reduction occurs – the cathode is the less active metal.
- b. An aluminum-silver battery produces almost 2.5 V.
- (i) Which metal, Al or Ag , is the anode?
- (ii) Draw cell diagram of the Al-Ag battery. Label the anode and cathode. Write the half reaction that occurs at each electrode.
- (iii) Calculate E_{cell} . (Answer: it should be close to 2.5 V.)
- c. You make an iron-sodium battery. The anode is _____. This battery produces _____ V.
- d. You make a copper-silver battery. The anode is _____. This battery produces _____ V.

5. The electricity just went out in your house and you need 3 V to run your study lamp to study for your “How to Download Music for Free” class. You remember you have a tin (Sn) cup, silver (Ag) spoon, copper (Cu) wire, iron (Fe) nail, and zinc (Zn) rod and the corresponding metal ion solutions.

- a. To make the highest voltage battery, which combination of oxidizing agent and reducing agent would you want to use? Choose one only. Give reasons. Calculate the voltage of this battery.
 - (i) the strongest oxidizing agent and strongest reducing agent
 - (ii) the strongest oxidizing agent and weakest reducing agent
 - (iii) the weakest oxidizing agent and strongest reducing agent
 - (iv) the weakest oxidizing agent and weakest reducing agent.
 - b. To make the lowest voltage battery, which combination of oxidizing agent and reducing agent would you want to use? Choose one only. Give reasons. Calculate the voltage of this battery.
 - c. Which metals would you use to make a 3 V battery? Draw a diagram of this cell. Label the anode and cathode. Write the half reaction at each electrode and the overall cell reaction. Calculate the cell voltage.
 - d. Is K_{eq} for this reaction greater than 1 or less than 1? Give reasons.
- You connect the same metal as the anode and cathode in a battery. What will be the voltage?
Can you use the same metal as the anode and cathode in a battery? Give reasons.

6. As a battery discharges, the voltage drops. When the voltage drops below the minimum voltage needed to run your electronic device, your device does not work and your battery is “dead.”

The Nernst equation allows you to calculate the battery voltage under non-standard state (standard state is 25°C and 1 M solutions) conditions:

$$E = E^\circ - (RT/nF) \ln ([\text{products}]/[\text{reactants}])$$

where R = gas constant = 8.31 J/mole K , T is temperature in K , n = moles of electrons transferred, F = Faraday's constant = $96,500 \text{ C/mole}$.

- a. Your night light in your bathroom needs 1 V to operate. You use a Daniell cell (Cu/Zn) cell to run your night light. Calculate the cell voltage when 50% of the reactants have been consumed. (Answer: between 1.08 and 1.09 V)

b. Calculate the % of reactants that are consumed in the Daniell cell when the cell voltage drops to 1 V. Use the Nernst equation. (Answer: % reactants consumed > 99.9%)

7. A lead acid battery is used in your car. Lead and lead (IV) oxide are the electrodes and sulfuric acid is the electrolyte.

a. Write the chemical reaction for the discharging reaction. Identify the cathode and anode. Write the half reaction that occurs at each electrode and the overall cell reaction. Calculate the cell voltage under standard state (25°C and 1 M solutions) conditions. (Answer: E between 2.0 and 2.06 V)

b. The sulfuric acid in a car battery is 18 M. Calculate the cell voltage under this non-standard state condition. (Answer: E between 2.08 and 2.13 V)

c. You forget to turn off your headlights. Reactants react and products are produced so concentration changes. What equation do you want to use to calculate the battery voltage as it discharges?

d. Write the chemical reaction for the charging reaction. Identify the cathode and anode. Write the half reaction that occurs at each electrode and the overall cell reaction. What voltage is needed to charge a lead acid battery?

e. In theory, a lead acid battery should last forever. Explain why it doesn't.