

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

Key ideas: Many important reactions are oxidation-reduction reactions: combustion, photosynthesis, biological reactions. Common oxidizing agents include bleach, hydrogen peroxide.

Oxidation-reduction reactions are also called electron transfer reactions.

Oxidation – loss of electron; reduction – gain of electron

Oxidizing agent oxidizes another substance; the oxidizing agent is reduced (gains electron from another substance – this other substance is a reducing agent). An oxidizing agent has a partner reducing agent (like a base has a partner acid).

Reducing agent reduces another substance (an oxidizing agent); the reducing agent is oxidized (loses electron from another substance – this other substance is an oxidizing agent). A reducing agent has a partner oxidizing agent (like an acid has a partner base).

E.g., hydrogen combustion reaction: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$

Charge 0 0 +1 on H, -2 on O

Oxidized reduced

Reducing agent oxidizing agent

Oxidizing agents and reducing agents are strong or weak (like acids and bases).

Use Table of standard reduction potentials for oxidizing agent or reducing agent strength. (Compare to activity series)

Objective 13b. Electrochemistry – galvanic cell: draw cell diagram (anode, cathode, half reactions, and overall reaction), calculate E_{cell} using Table of electrode potentials.

Key ideas: A battery (galvanic cell) converts chemical energy to electrical energy.

A battery involves a spontaneous chemical reaction ($\Delta G < 0$).

In a battery, two substances, usually metals, with different activity (different ability to lose electrons – see Chem 1A Activity Series) are connected together. Electrons move from the more active metal (anode - oxidation) to the less active metal (cathode - reduction).

Half reactions – oxidation half reaction occurs at anode; reduction half reaction occurs at cathode. Add the two half reactions to get overall reaction.

Need to separate the anode from cathode. Use a salt bridge so ionic current flows through solution.

Use Table of standard reduction potentials for reduction half reactions. Reverse reduction half reaction to get oxidation half reaction. Calculate cell voltage: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.

Cell voltage is related to ΔG by: $\Delta G = -nFE$ where $n = \#$ (or moles) of electrons transferred, $F = \text{Faraday's constant} = 96,500 \text{ C/mole}$.

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.

Practice Problem Solutions:

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 _____.

Answers:

a. Al exists on the Earth's surface as bauxite, Al_2O_3 , because Al is easily oxidized (Al is a strong reducing agent). Bauxite has to be reduced to form Al metal.

b. Gold (Au) is a weak reducing agent because it does not easily/does not want to lose its electrons. Au^{3+} ion is a strong oxidizing agent because it easily gain electrons. Gold exists on the Earth's surface as a metal, not ion because it is a weak reducing agent (difficult to oxidize).

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.

Answers:

a. (i) $\Delta G = -nFE = -(2 \text{ moles of electrons})(96,500 \text{ C/mole})(-0.44 \text{ V}) = +85,000 \text{ J}$. Fe^{2+} does not reduce to Fe.

(ii) $\Delta G = -nFE = -(2 \text{ moles of electrons})(96,500 \text{ C/mole})(+0.44 \text{ V}) = -85,000 \text{ J}$. Fe oxidizes to Fe^{2+} .

(iii) Zn is easier to oxidize than Fe because ΔG for the Zn oxidation is more negative (more spontaneous) than ΔG for Fe oxidation.

b. (i) $\Delta G = -nFE = -(3 \text{ moles of electrons})(96,500 \text{ C/mole})(1.50 \text{ V}) = -434,000 \text{ J}$. Au^{3+} reduces to Au.

(ii) Gold prefers to be a metal.

(iii) Gold is not easily oxidized to gold ion.

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.

Answers:

a. Strongest: hydrogen peroxide (H_2O_2), bleach (as HClO), oxygen (O_2), and iodine (I_2) weakest
Higher E° (reduction potential) means stronger oxidizing agent. Remember, an oxidizing agent oxidizes another substance but the oxidizing agent is reduced.

b. $\Delta G = -nFE = -(2 \text{ moles of electrons})(96,500 \text{ C/mole})(+0.77 \text{ V}) = -342,000 \text{ J}$. H_2O_2 reduces to H_2O spontaneously.

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

$\Delta G = -nFE = -(3 \text{ moles of electrons})(96,500 \text{ C/mole})(1.50 \text{ V}) = -434,000 \text{ J}$. Au^{3+} reduces to Au.

For the oxidation of Au to Au^{3+} ion: $\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$, change the sign of ΔG . So $\Delta G = +434,000 \text{ J}$. Au does not spontaneously oxidize to Au^{3+} .

Or $\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$ has an oxidation potential of -1.50 V (change the sign on the reduction potential of $\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$). So $\Delta G = -nFE = -(3 \text{ moles of electrons})(96,500 \text{ C/mole})(-1.50 \text{ V}) = +434,000 \text{ J}$.

d.

(i) reduction $\frac{1}{2}$ reaction: $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$. 2 electrons are gained by H_2O_2 (the oxidizing agent). Multiply by 3.

oxidation $\frac{1}{2}$ reaction: $\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$. 3 electrons are lost by Au (the reducing agent). Multiply by 2.

Balanced chemical equation: $3\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{Au} \rightarrow 6\text{H}_2\text{O} + 2\text{Au}^{3+}$

Note: 6 electrons are transferred from oxidizing agent to reducing agent (6 electrons gained by H_2O_2 and 6 electrons are lost by Au) – “conservation of charge”.

+6 charge on reactant side = +6 charge on product side – “conservation of charge”.

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

Method 1. Add ΔG for each $\frac{1}{2}$ reaction:

$3(\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O})$ $\Delta G = -nFE = -(6 \text{ moles of electrons})(96,500 \text{ C/mole})(+1.77 \text{ V}) = -1,026,000 \text{ J}$

$2(\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-)$ $\Delta G = -nFE = -(6 \text{ moles of electrons})(96,500 \text{ C/mole})(-1.50 \text{ V}) = +868,000 \text{ J}$.

$3\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{Au} \rightarrow 6\text{H}_2\text{O} + 2\text{Au}^{3+}$ $\Delta G = -1,026,000 \text{ J} + 868,000 \text{ J} = -158,000 \text{ J}$

$\Delta G = -nFE$. Solve for E = $158,000 \text{ J}/(6)(96,500) = 0.27 \text{ V}$

Method 2. Calculate E for $3\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{Au} \rightarrow 6\text{H}_2\text{O} + 2\text{Au}^{3+}$ from each $\frac{1}{2}$ reaction:

$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ $E_{\text{reduction}} = +1.77 \text{ V}$

$\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$ $E_{\text{oxidation}} = -1.50 \text{ V}$

$3\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{Au} \rightarrow 6\text{H}_2\text{O} + 2\text{Au}^{3+}$ $E = E_{\text{reduction}} + E_{\text{oxidation}} = +1.77 \text{ V} + (-1.50 \text{ V}) = 0.27 \text{ V}$

$\Delta G = -nFE = -(6 \text{ moles of electrons})(96,500 \text{ C/mole})(0.27 \text{ V}) = -156,000 \text{ J}$.

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.

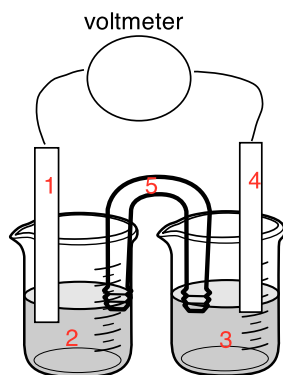
Answers:

a. . (i) A battery is a **voltaic** cell. A battery **produces** energy, which means the battery reaction is **spontaneous** and has a $\Delta G < 0$.

(ii) In a battery, the **more** active metal loses electrons to the **less** active metal.

b. An aluminum-silver battery produces almost 2.5 V.

Cell diagram of the Al-Ag battery.



1 = Al anode, 2 = Al^{3+} (aq) solution, 3 = Ag^+ (aq) solution, 4 = Ag cathode, 5 = salt bridge

Al anode is where oxidation occurs: $\text{Al (s)} \rightarrow \text{Al}^{3+} \text{ (aq)} + 3 \text{ e}^-$

Ag cathode is where reduction occurs: $\text{Ag}^+ \text{ (aq)} + \text{e}^- \rightarrow \text{Ag (s)}$

NOTE: the anode has to be separated from the cathode to make sure the appropriate reaction occurs at each electrode.

See Standard Reduction Potential Table:

$\text{Al}^{3+} \text{ (aq)} + 3 \text{ e}^- \rightarrow \text{Al (s)}$ $E_{\text{reduction}} = -1.66 \text{ V}$

$\text{Ag}^+ \text{ (aq)} + \text{e}^- \rightarrow \text{Ag (s)}$ $E_{\text{reduction}} = +0.80 \text{ V}$

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.80 \text{ V} - (-1.66 \text{ V}) = 2.46 \text{ V}$. In this formula, use the reduction potential of each metal.

Or

Al anode is where oxidation occurs: $\text{Al (s)} \rightarrow \text{Al}^{3+} \text{ (aq)} + 3 \text{ e}^-$ $E_{\text{oxidation}} = +1.66 \text{ V}$ (note sign change from reduction potential to oxidation potential)

Ag cathode is where reduction occurs: $\text{Ag}^+ \text{ (aq)} + \text{e}^- \rightarrow \text{Ag (s)}$ $E_{\text{reduction}} = +0.80 \text{ V}$

$E_{\text{cell}} = E_{\text{reduction}} + E_{\text{oxidation}} = +1.66 \text{ V} + 0.80 \text{ V} = 2.46 \text{ V}$

c. You make an iron-sodium battery. The anode is **sodium**. This battery produces **2.27 V**.

$\text{Fe}^{2+} + 2 \text{ e}^- \rightarrow \text{Fe}$ $E_{\text{reduction}} = -0.44 \text{ V}$. Fe is the cathode.

$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ $E_{\text{reduction}} = -2.71 \text{ V}$. Na is the anode.

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.44 \text{ V} - (-2.71 \text{ V}) = 2.27 \text{ V}$.

d. You make a copper-silver battery. The anode is **copper**. This battery produces **_____ V**.

$\text{Cu}^{2+} + 2 \text{ e}^- \rightarrow \text{Cu}$ $E_{\text{reduction}} = +0.34 \text{ V}$. Cu is the anode.

$\text{Ag}^+ \text{ (aq)} + \text{e}^- \rightarrow \text{Ag (s)}$ $E_{\text{reduction}} = +0.80 \text{ V}$. Ag is the cathode.

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.80 \text{ V} - (+0.34 \text{ V}) = 0.46 \text{ V}$.

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.

Answers:

Use a Standard Reduction Potential Table to rank the 5 metals:

$\text{Zn}^{2+} + 2 \text{ e}^- \rightarrow \text{Zn}$ $E_{\text{reduction}} = -0.76 \text{ V}$. Zn is the strongest reducing agent. Zn^{2+} ion is the weakest oxidizing agent.

$\text{Fe}^{2+} + 2 \text{ e}^- \rightarrow \text{Fe}$ $E_{\text{reduction}} = -0.44 \text{ V}$

$\text{Sn}^{2+} + 2 \text{ e}^- \rightarrow \text{Sn}$ $E_{\text{reduction}} = -0.14 \text{ V}$

$\text{Cu}^{2+} + 2 \text{ e}^- \rightarrow \text{Cu}$ $E_{\text{reduction}} = +0.34 \text{ V}$

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ $E_{\text{reduction}} = +0.80 \text{ V}$. Ag is the weakest reducing agent. Ag^+ ion is the strongest oxidizing agent.

a. (i) the strongest oxidizing agent = **Ag** and strongest reducing agent = **Zn**.

Ag = cathode, Zn = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$.

(ii) the strongest oxidizing agent = **Ag** and weakest reducing agent = **Ag**.

Ag = cathode, Ag = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.80 \text{ V} - (+0.80 \text{ V}) = 0 \text{ V}$.

(iii) the weakest oxidizing agent = **Zn** and strongest reducing agent = **Zn**

Zn = cathode, Zn = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.76 \text{ V} - (-0.76 \text{ V}) = 0 \text{ V}$.

(iv) the weakest oxidizing agent = **Zn** and weakest reducing agent = **Ag**.

Zn = cathode, Ag = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.76 \text{ V} - (+0.80 \text{ V}) = -1.56 \text{ V}$. *Can't use more active metal as the cathode.*

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.

Look for the smallest difference in $E_{\text{reduction}}$ between two metals.

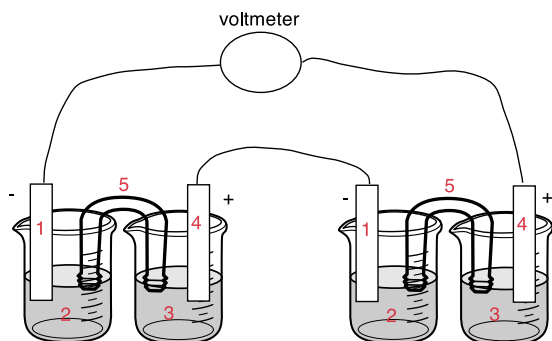
Sn = cathode, Fe = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = -0.14 \text{ V} - (-0.44 \text{ V}) = 0.30 \text{ V}$.

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.

Connect two Zn/Ag batteries in series: $2 \times 1.56 \text{ V} = 3.12 \text{ V}$

Ag = cathode, Zn = anode. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.80 \text{ V} - (-0.76 \text{ V}) = 1.56 \text{ V}$.

1 = Zn anode, 2 = Zn^{2+} (aq) solution, 3 = Ag^+ (aq) solution, 4 = Ag cathode, 5 = salt bridge



d. K_{eq} for this reaction greater than 1. Battery reaction produces a lot of products and is spontaneous ($\Delta G < 0$ based on $\Delta G = -RT \ln K$).

You connect the same metal as the anode and cathode in a battery. What will be the voltage? 0 V

Can you use the same metal as the anode and cathode in a battery? Give reasons. No. The anode and cathode have to have a different activity (ability to lose electrons) for electrons and current to go from one electrode to the other.

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%)

Answers:

a. Standard Reduction Table:



Zn is more active than Cu so Zn is the anode (oxidation) and Cu is the cathode (reduction).

So $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$ under standard state conditions (25°C , 1 M solutions).

Overall reaction: $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$.

Do chemical calculation: initial 1 1

Reacts (50% reacts) 0.5 0.5

Leftover 0.5 1.5

Apply Nernst equation: $E = E^\circ - (RT/nF) \ln ([\text{products}]/[\text{reactants}]) = 1.10 - (8.31)(298)/(2)(96500) \ln (1.5/0.5) = 1.086 \text{ V}$

b. Apply Nernst equation: $1 = 1.10 - (8.31)(298)/(2)(96500) \ln ([\text{products}]/[\text{reactants}])$

solve for $([\text{products}]/[\text{reactants}])$ ($[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$) = 2425.

This means the ratio of $[\text{Zn}^{2+}]$ to $[\text{Cu}^{2+}]$ is 2425 : 1. (This is similar to doing a buffer calculation.)

So the % $[\text{Zn}^{2+}] = 2425/(2425 + 1) = 99.92\%$

And % $[\text{Cu}^{2+}] = 0.08\%$.

So $[\text{Zn}^{2+}] = 1.9992$ and $[\text{Cu}^{2+}] = 0.0008$.

The battery is 99.92% discharged. (and still produces 1 V)

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.

Answers:

a. Standard Reduction Table:



$$E_{\text{oxidation}} = 0.35 \text{ V.}$$



$$E_{\text{reduction}} = 1.69 \text{ V.}$$

Overall reaction as battery discharges:



Standard state conditions = (25°C, 1 M solution of H₂SO₄).

b. Apply Nernst equation:

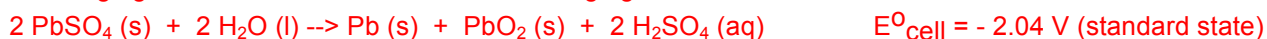
$$E = E^\circ - (RT/nF) \ln ([\text{products}]/[\text{reactants}])$$

$$= 2.04 - (8.31)(298)/(2)(96500) \ln (1/[\text{H}_2\text{SO}_4]^2)$$

$$= 2.04 - (8.31)(298)/(2)(96500) \ln (1/[18]^2) = \mathbf{2.11 \text{ V}}$$

c. Use Nernst equation.

d. Charging reaction is the reverse of the discharging reaction:



2.04 V (standard state) or 2.11 V (18 M H₂SO₄) is required to charge a lead acid battery.

e. Lead acid battery should last forever but it does not because the electrodes deteriorate after many discharging/charging cycles. E.g., the PbSO₄ does not get converted back to Pb and PbO₂ in charging cycle.