Electrochemistry

Name: ___________________________

AP Chemistry Lecture Outline

Video
2003
(7:16)

Introduction to Electrochemistry

During oxidation-reduction (redox) reactions,
the oxidation states of two substances change.

oxidation =

reduction =

Rules for Assigning Oxidation Numbers

1. Atoms in their elemental form have an oxidation number of zero.
2. For a monatomic ion, the oxidation number is the charge on the ion.
3. Nonmetals can have variable oxidation numbers.
   a. Oxygen is usually 2–, but in the peroxide ion (O_2^{2-}) it is 1–.
   b. Hydrogen is 1+ when bonded to nonmetals, 1– when bonded to metals.
      **
   c. Fluorine is 1–. Other halogens are usually 1–, but are + when combined ^{w}/oxygen.
4. The sum of the oxidation numbers in a neutral compound is zero.

EX. Determine the oxidation number of nitrogen in each of the following.

N_2O_4 NH_3 N_2 KNO_3

Video
2006
(9:38)

Redox Reactions

oxidizing agent (oxidant): is reduced (or has a component that is reduced)

reducing agent (reductant): is oxidized (or has a component that is oxidized)

e.g., $Zn(s) + 2\,H^{+}(aq) \rightarrow$

It goes without saying that...

From this point on, we will omit...
anything with a charge...

EX. Identify the oxidant and the reductant. $2\ H_2O + Al + MnO_4^- \rightarrow Al(OH)_4^- + MnO_2$

NOTE: A substance is <u>oxidized</u>/reduced if...

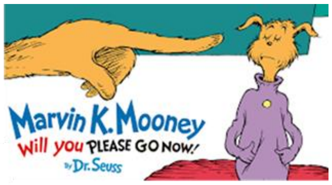
Strong oxidizers are good at being...

i.e., they are greedy for...

The strongest oxidizer is…

Other strong oxidizers (besides ___) are…

and oxyanions in which the central atom has a large ___ charge, e.g.,



Strong reducers are good at being...

i.e., they would rather that at least one of their e⁻s would...

The strongest reducing agent is…

Other strong reductants are...

Video
2009
(9:42)

Introduction to Half-Reactions

<u>Balancing Oxidation-Reduction Reactions</u>

-- We must conserve mass AND conserve charge.

<u>half-reaction</u>:

EX. Write half-reactions for… $Sn^{2+} + 2\ Fe^{3+} \rightarrow Sn^{4+} + 2\ Fe^{2+}$

In an electrochemical setup, one half-cell contains the ‘before’ and ‘after’ varieties of the oxidized substance and the OTHER half-cell contains the ‘before’ and ‘after’ varieties of the reduced substance.

In line notation, the oxidation half-cell is on the left and the reduction half-cell is on the right. The typical pattern includes these various species... ***oxidation*** half-cell REDUCTION half-cell

There are several variations on line notation, but what NEVER changes is that...

EX. The simplest line notation for the last problem... $Sn^{2+} + 2\ Fe^{3+} \rightarrow Sn^{4+} + 2\ Fe^{2+}$...would be:

EX. Write the simplest line notation for the reaction between magnesium and hydrochloric acid.

Video
2012
(9:31)

Steps in Balancing Equations by the Method of Half-Reactions

1. Break overall equation into <u>two</u> half-reactions.
2. a. Balance everything but H and O.
   b. Balance O by adding H_2O as needed.
   c. Balance H by adding H^+ as needed (assuming acidic solution).
   d. Add e^- as needed.
   e. Multiply each half-reaction by integers to cancel e^-.
3. Add the two half-reactions and simplify.

*4. <u>IF IN BASIC SOLN</u>: Now, add enough OH^- to cancel any H^+. Simplify again.

EX. Balance this reaction, which takes place in acidic solution.

$$Cr_2O_7^{2-} + Cl^- \rightarrow Cr^{3+} + Cl_2$$

Video
2015
(9:07)

EX. Balance this reaction, which takes place in basic solution.

$$CN^{-} + MnO_4^{-} \rightarrow CNO^{-} + MnO_2$$

Video
2018
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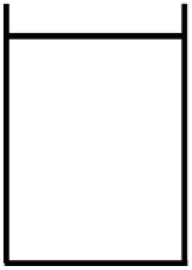
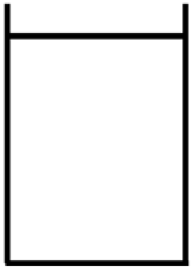
Introduction to Electrochemical Cells

Suppose we place a bar of zinc in a soln of $CuSO_4$. Over time, we observe that a redox reaction occurs...





Net reaction:

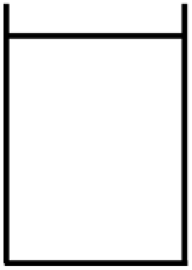
No useful work/energy can be harnessed here because...

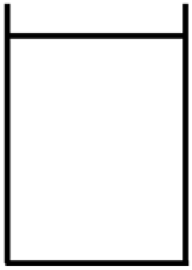
In line notation, we would write:

The above reaction takes place spontaneously; i.e., we set it up and...

From previous studies of thermodynamics, you recall that the SIGN of the change in the Gibbs free energy for such thermodynamically favorable processes is...

If, instead of zinc, we placed a bar of silver in a soln of $CuSO_4$...





For THIS case, ΔG is...

So...If an electrochemical process is spontaneous, can we somehow...

And if it ISN’T, is it possible for us to...

On both counts, the answer is...

We obtain useful work from spont. electrochemical reactions by setting up...

We force NONspontaneous electrochemical reactions to ‘go’ by setting up...

Video
2021
(10:59)

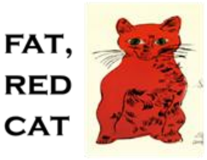
Setting Up a Useful Electrochemical Cell

Each half-reaction of any electrochemical cell (whether galvanic or electrolytic) needs an electrode: a solid (usually metal) surface that acts as a means of getting e^- into and out of the reacting species.

anode: the electrode where __________ takes place, e.g.,

Assuming it isn’t an inert electrode,

the mass of the anode ___________ over time.



cathode: the electrode where __________ takes place, e.g.,

Typically, mass of cathode ___________ over time.

We are concerned with two types of conduction in setting up any electrochemical cell.

metallic conduction: involves electrons flowing through a metal, e.g.,

--

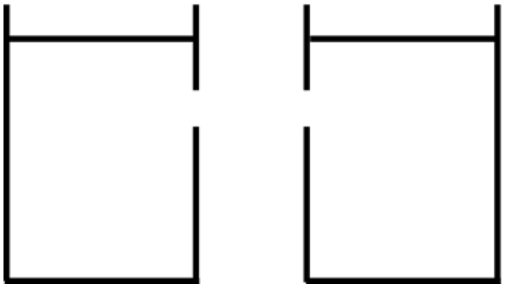
--

ionic conduction: involves motion of ions flowing in a salt soln or molten liquid

A Spontaneous Electrochemical Cell

If ‘D’ has very low resistance, it is...

If ‘D’ has a higher resistance, it is...



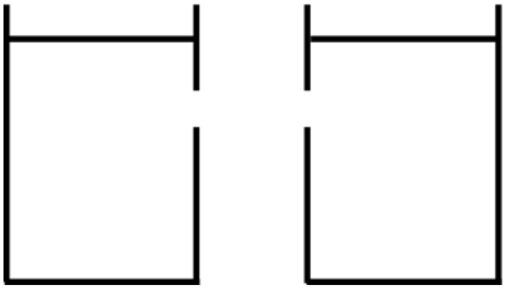
In a galvanic/voltaic cell, we definitely need the anode and cathode compartments to be separated.

-- We want the e$^-$s to have...

A <u>salt bridge</u> or <u>porous disk</u>...

A NONspontaneous Electrochemical Cell

Here, ‘D’ is an external power supply, which...



In an electrolytic cell, it is NOT as essential to physically separate the anode and cathode compartments because we often don’t care WHAT mixes with WHAT, as long as we accomplish what we want, i.e.,

Video
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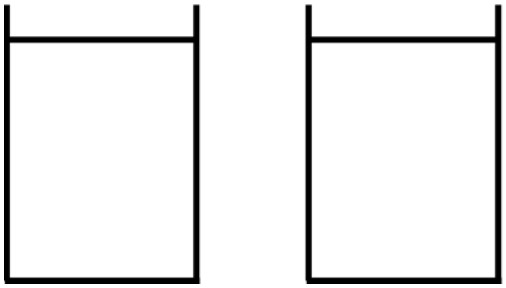
Galvanic/Voltaic Cells: What’s the Use?

‘Oxidized thing’ and ‘reduced thing’ are NOT in direct contact, so we use wires to connect them and then...



‘D’ never...

Electrodes are connected by ______, solns by ____________.

The most familiar galvanic/voltaic cells are ________.

We can think of the $PE_{\text{anode's } e^-}$ $PE_{\text{cathode's } e^-}$.

Video
2027
(8:57)

Electrolytic Cells: What's the Use?

Electrolytic cells (and its process, electrolysis) have many practical uses.

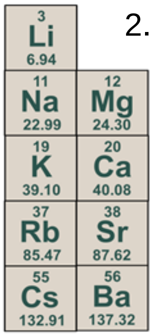
1. electrorefining of metals

An impure anode (of, say, Cu or Zn) with an ultrapure cathode of...

Typically, only the desired metal plates out because...

Soluble impurities...

Insoluble impurities...

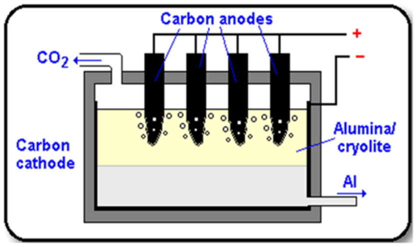


3 Li 6.94	
11 Na 22.99	12 Mg 24.30
19 K 39.10	20 Ca 40.08
37 Rb 85.47	38 Sr 87.62
55 Cs 132.91	56 Ba 137.32

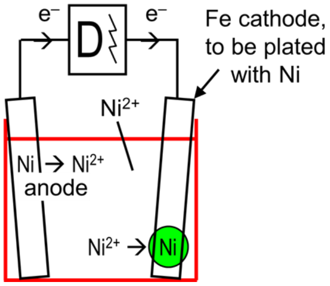
2. reducing the active metals

Less-active metals (e.g., _____) can be reduced via cheaper chemical reduction.

Isolating the active metals requires electrolytic reduction because...



Hall-Heroult process for purifying Al from Al_2O_3 and Na_3AlF_6 (1886)



3. electroplating of metals

In electroplating, we deposit a neutral metal onto the cathode by reducing metal ions from a soln, i.e.,

Video
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(7:22)

The Stoichiometry of Electrolysis

In his work with electrolysis, Michael Faraday found that the mass of metal reduced was:

1. directly proportional to the current that flows through the liquid

1791–1867

2. directly proportional to time
3. directly proportional to molar mass
4. inversely proportional to the metal ion's oxidation #

To solve electrolysis problems...

EX. For how long must a 50.0 A current be passed through molten $BaBr_2$ in order to produce 500. g of barium?

EX. Using a current of 31.2 A for 1.92 h will plate out on the cathode 38.7 g of a metal. If the ions have a valence of 3+, what is the metal?

Video
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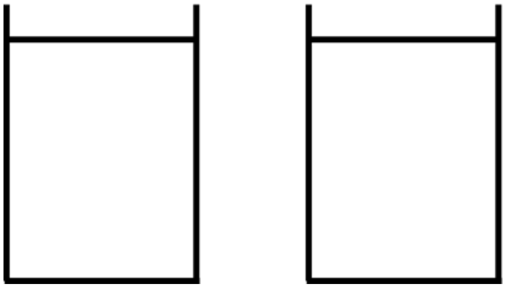
The Standard Hydrogen Electrode

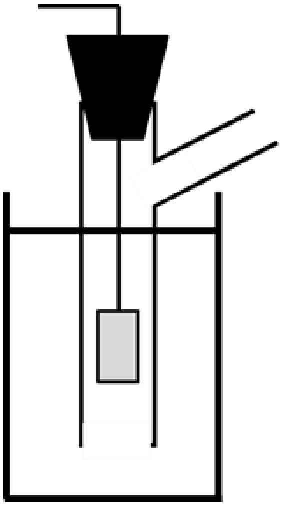
Suppose we set up an electrochemical cell with a Zn electrode in a 1 M $ZnSO_4$ soln and a Cu electrode in a 1 M $CuSO_4$ soln.



We observe that current flows spontaneously, that Zn is the anode, and Cu the cathode, i.e.,

We also find that if we connect a voltmeter to the electrodes, it reads a potential of 1.10 V.

It's reasonable to surmise that the 1.10 V value is due partially to what's happening to the Zn (________) and partially to what's happening to the Cu (________).



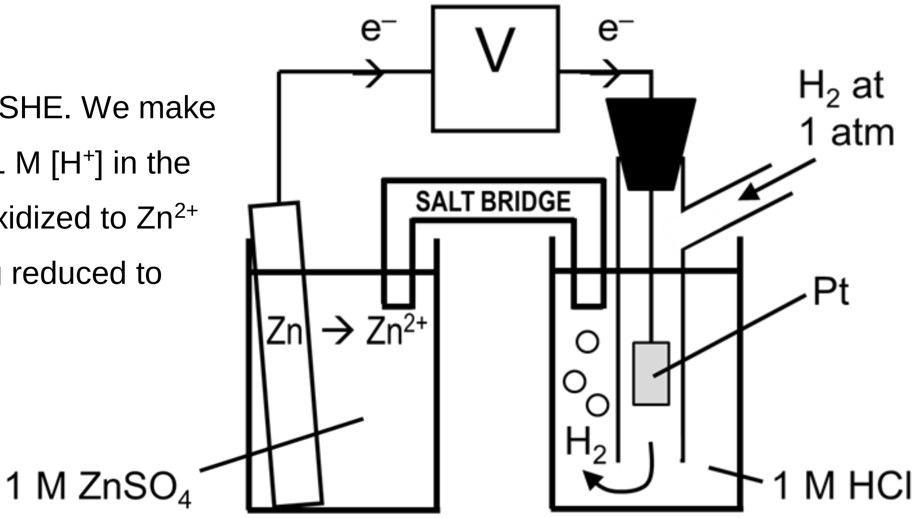
We can't know, because...

Enter the standard hydrogen electrode (SHE)...

By international agreement, the potential for the SHE – by itself – is...

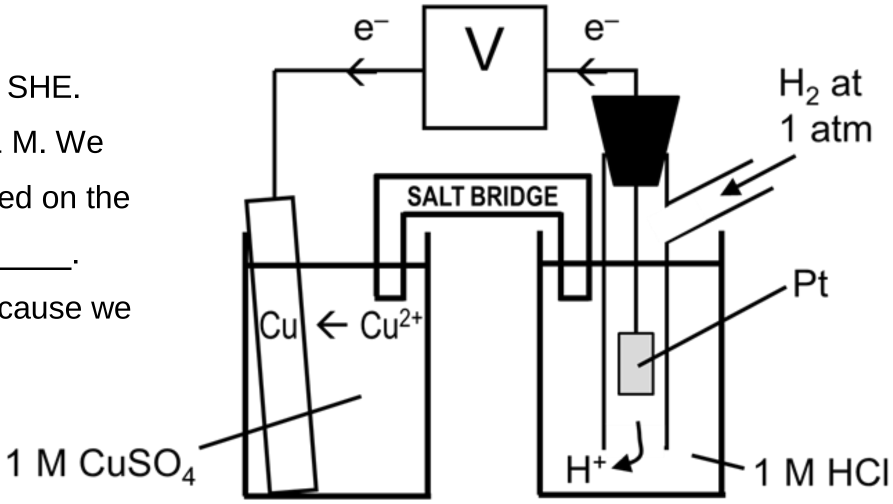
So let's hook up our Zn half-cell to the SHE. We make the [Zn^{2+}] in the soln 1 M, just like the 1 M [H^+] in the other half-cell. We observe Zn being oxidized to Zn^{2+} (   ) and H^+ being reduced to H_2 gas, because we notice...

The voltmeter reads...



Now we hook up our Cu half-cell to the SHE. Again, we make the [Cu^{2+}] in the soln 1 M. We observe that Cu^{2+} ions are being reduced on the Cu electrode, so that must be the ________. The H_2 gas must be being oxidized, because we notice that...

The voltmeter reads...



Voltmeter readings for half-cells paired up with a SHE are standard potentials, E^o.

Here, 'standard' means:
1.
2.
3.

We measured: $Zn \rightarrow Zn^{2+} + 2e^-$ E^o =

$Cu^{2+} + 2e^- \rightarrow Cu$ E^o =

By convention, all E^o values are written as reductions: $Zn^{2+} + 2e^- \rightarrow Zn$ E^o_{red} =

$Cu^{2+} + 2e^- \rightarrow Cu$ E^o_{red} =

All half-cell rxns have been tested relative to a SHE, and their standard reduction potentials tabulated.

Video
2036
(6:28)

The Standard Reduction Potentials Table

The standard reduction potentials can be found in a table. Let's examine the structure of this table...

Top:

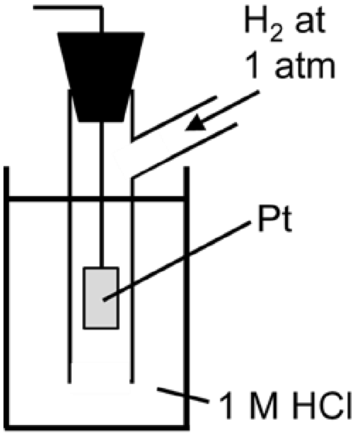
On the left: $F_2 + 2e^- \rightarrow 2F^-$ +2.87 V **On the right:**

$Li^+ + e^- \rightarrow Li$ –3.05 V

Bottom:

As mentioned previously, the reference point for reduction potentials is the standard hydrogen electrode (SHE):

$2H^+ + 2e^- \rightarrow H_2$



Multiples of coefficients DON'T affect E^o_{red}.

e.g.,

We use the standard reduction potentials when finding the cell potential for a given cell, i.e., the potential of the two connected half-cells in an electrochemical setup.

The simplest cell potential is the standard cell potential, which is the potential (i.e., the 'voltage') when all substances are in their standard states, i.e.,

1. any [soln] =
2. any reacting gas =
3. temperature =

The standard cell potential depends on the two half-cells that are involved.
ONE of the half-rxns will be an oxidation and will thus have...

Video
2039
(10:52)

Calculating Standard Cell Potentials

EX. Determine the standard cell potential for the cell given by the equation:

$$Cr + Cu^{2+} \rightarrow Cr^{2+} + Cu$$

The relevant equations from the table are:

(a) $Cu^{2+} + 2\,e^- \rightarrow Cu$

(b) $Cr^{2+} + 2\,e^- \rightarrow Cr$

From the given overall equation, we see that (a)...

Thus, (b)...

You then...

So E^o_{cell} =

EX. Determine the standard cell potential for the cell given by the equation:

$$3\,Fe + 2\,Cr^{3+} \rightarrow 3\,Fe^{2+} + 2\,Cr$$

The relevant equations from the table are:

(a) $Fe^{2+} + 2\,e^- \rightarrow Fe$

(b) $Cr^{3+} + 3\,e^- \rightarrow Cr$

From the given overall equation, we see that (a)...

Thus, (b)...

So E^o_{cell} =

EX. A voltaic cell has the half-rxns:

(a) $Al^{3+} + 3\,e^- \rightarrow Al$ $E^o_{red} = -1.66$ V

(b) $Ba^{2+} + 2\,e^- \rightarrow Ba$ $E^o_{red} = -2.90$ V

Calculate E^o_{cell} and write the balanced equation.

EX. In acidic solution, will Fe^{3+} spontaneously oxidize NO to NO_3^-, or will NO_3^- oxidize Fe^{2+} to Fe^{3+}? Also, determine E^o_{cell}.

The relevant equations from the table are:

(a) $Fe^{3+} + e^- \rightarrow Fe^{2+}$

(b) $NO_3^- + 4\,H^+ + 3\,e^- \rightarrow NO + 2\,H_2O$

Video
2042
(7:31)

Cell Potential and Free Energy

Previously, we introduced Faraday's constant:

Because $1\ \text{V} = \frac{1\ \text{J}}{1\ \text{C}}$, we can write...

...and thus also represent Faraday's constant as...

If we multiply this by the # of moles of e^- moved (n) and also by the cell potential (E, which is in the unit __), we will obtain the unit __, i.e., we get a quantity of...

For a known cell potential E and a known reaction (i.e., we know the number of moles of e^- transferred), we can thus easily determine the...

And since we know... thermodynamically favorable: ...the general equation
NOT thermodynamically favorable: is:

This is an easy way to...

NOTE: This equation applies at both standard and non-standard conditions,
i.e., it could be used as either...

EX. Determine the # of moles of e^- transferred and the standard change in Gibbs free energy for the rxn... $5\ Fe^{2+} + MnO_4^- + 8\ H^+ \rightarrow 5\ Fe^{3+} + Mn^{2+} + 4\ H_2O$

The relevant equations from the table are: $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o_{red} = +0.77\ V$

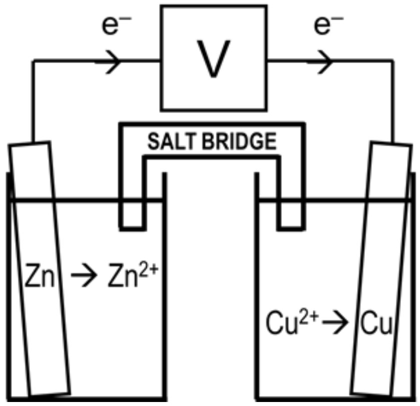
$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$ $E^o_{red} = +1.51\ V$

Video
2045
(9:32)

The Nernst Equation

Dependence of E on Concentration

Standard potentials (E^o) occur under standard conditions: 1 M solns, 1 atm pres., and 25°C. Let's consider conceptually how E will be affected by [ ]s other than 1 M. Here we have:



1 M	1 M
0.01 M	5 M
5 M	0.01 M

Derivation of the Nernst Equation

Walther Nernst
(1864–1941)

While we can tell conceptually how a cell potential E will be affected by nonstandard [ ]s, the Nernst equation allows us to determine E under ANY nonstandard conditions, whether they be [ ]s, temps, or gas pressures.

In units on thermodynamics, the change in the Gibbs free energy under nonstandard conditions was found using...

We've previously learned that...

Substituting yields...

Dividing through by –nF produces the Nernst equation:

where R = 8.314 J/mol-K
T = absolute temp. n = # of mol of e^-
F = 96,485 J/V-mol e^- Q = rxn. quotient

Consider again the Zn/Cu cells above, at 25°C:

When $[Zn^{2+}]$ = 1 M and $[Cu^{2+}]$ = 1 M...
When $[Zn^{2+}]$ = 0.01 M and $[Cu^{2+}]$ = 5 M...

When $[Zn^{2+}]$ = 5 M and $[Cu^{2+}]$ = 0.01 M...

Video
2048
(5:04)

EX. $Fe + Cd^{2+} \rightarrow Cd + Fe^{2+}$ Find the cell potential at 55°C when $[Cd^{2+}]$ = 2.0 M and $[Fe^{2+}]$ = 0.030 M.

The relevant equations from the reduction table are:

$Fe^{2+} + 2e^- \rightarrow Fe$
$Cd^{2+} + 2e^- \rightarrow Cd$

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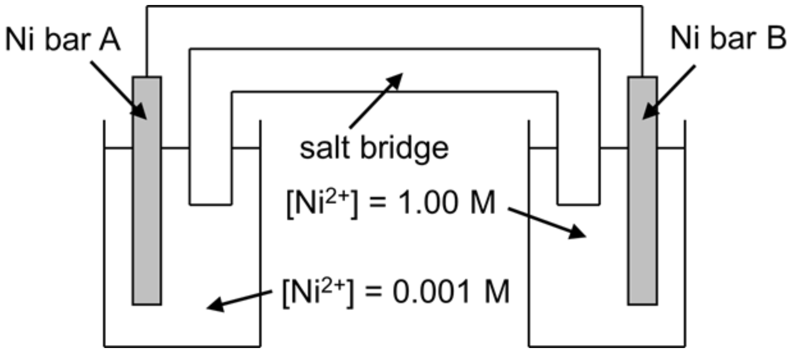
Concentration Cells



concentration cell:

-- E^o for a [ ] cell =

-- Charge flows until...

-- In the above example, cell will act to equalize $[Ni^{2+}]$s, so… Bar A:

Bar B:

Add...

Thus, in general…

At equilibrium…

EX. A [ ] cell has Cell A with $[Fe^{3+}] = 2.35$ M and Cell B with $[Fe^{3+}] = 2.25 \times 10^{-3}$ M. Identify the anode and cathode, and calculate the emf, at 37°C.

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ΔG^o, E^o, and the Equilibrium Constant K

In this unit, we have already used the equation $\Delta G = \Delta G^o + RT \ln Q$ (with help from $\Delta G^{(o)} = -nFE^{(o)}$) to derive the Nernst equation:

In units on thermodynamics, it is often shown that,
at equilibrium (where $\Delta G = 0$ and $Q = K$) the same
equation ($\Delta G = \Delta G^o + RT \ln Q$) will yield the results:

These are two versions of a single equation that relates the standard change in Gibbs free energy to the value of the equilibrium constant. We now add to this...

Using once again the fact that $\Delta G^o = -nFE^o$, we now turn $\Delta G^o = -RT \ln K$ into...

and finally into...

Similarly, we change

into...

Armed with these equations, if we know any ONE of ΔG^o, E^o, or K...

EX. Determine the value of the equilibrium constant at 25°C for the reaction:

$$2\ Ag^+ + Fe \rightarrow Fe^{2+} + 2\ Ag$$

The relevant equations from the table are:

$Fe^{2+} + 2\ e^- \rightarrow Fe$ $E^o_{red} = -0.44$ V

$Ag^+ + e^- \rightarrow Ag$ $E^o_{red} = +0.80$ V

Video
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(4:47)

Basics of Corrosion

Most metals oxidize rather easily in air.

-- There are some exceptions, e.g.,

$Au^{3+} + 3\ e^- \rightarrow Au$ $E^o_{red} = +1.50$ V

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ $E^o_{red} = +1.23$ V

<u>corrosion</u>: spontaneous redox rxns in which metals react w/something in the environment to form...

e.g, Ag_2S

Galvanic corrosion can occur when two different metals are in contact.

Within a given metal, corrosion is initiated most readily at points of strain.

--

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(9:57)

Protecting Against Corrosion

"How do we try to protect metals from corrosion?"

1. painting

2. plate with a thin layer of less-easily-oxidized metal

e.g., ____ and ____ form durable oxide coatings when plated onto steel

Many "tin" cans are actually Sn-coated steel.

** When/if the less-easily-oxidized metal is breached, corrosion occurs...

3. <u>galvanizing</u>: coating with more-active Zn

--

** Once Zn has corroded away...

4. Some metals (e.g., Al and Mg) naturally form a protective metal-oxide coating.

-- Coating is thin and thus transparent, but it is very tough and...

The oxide coating is sometimes called a <u>passive film</u>, and the formation of the film is termed...

5. Some <u>alloys</u> have corrosion-resistance.

-- Stainless steels contain ___ and ___, which form passive oxide films on the surface.

-- We can also produce corrosion-resistant <u>surface alloys</u> over top of...

The ultimate goal is passivation, using...

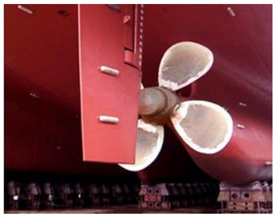
6. <u>cathodic protection</u>: protecting a metal by connecting it to a more active metal; the more active metal corrodes...

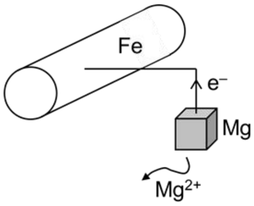
-- The protected metal becomes the cathode.

-- The more active metal is oxidized and is called the ____________________.

-- Metals often sacrificed:

examples of cathodic protection:





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Primary Cells

Strictly speaking, a battery consists of _________ electrochemical cells arranged together to provide a source of direct current, but the term is also commonly used to denote...

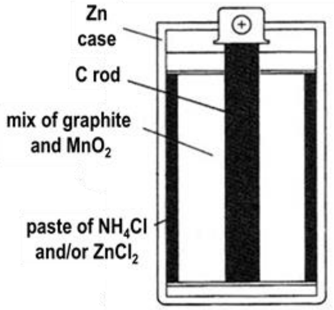
Examples of batteries-in-the-strict-sense:

<u>Primary cells</u>...

D-cells AAs AAAs 12-V battery 9-V battery

Once the reactants in a primary cell have been altered in the reaction, further chemical action is impossible, and their properties are such that...

Types of Primary Cells



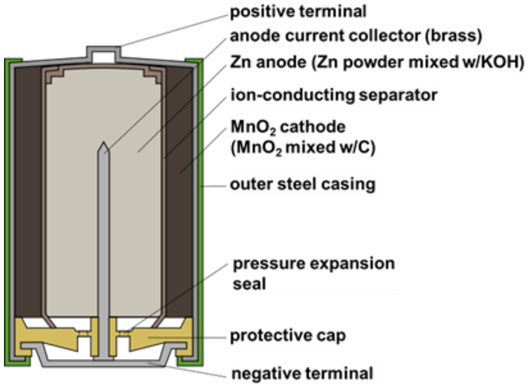
Zinc-carbon cells were the first commercial cells to be developed.

-- The outer casing of Zn is the anode, so the Zn is...

-- A rod of carbon in the center is the cathode, but the reduction half-reaction actually involves...

If the paste is primarily $ZnCl_2$, the cells are marketed as ____________.

--



Alkaline cells are so-named because they contain the basic substance KOH instead of the acidic NH_4Cl found in Zn-C cells. They also have a...

Compared to “heavy-duty” Zn-C cells, alkaline cells have a service life that is about...

They also have...

All single Zn-C cells and alkaline cells have a potential of about _____ because the same basic chemicals (namely, ____ and ______) are used. We say ‘about’ because there can be...

--

For a battery (i.e., several single cells in series), we simply…

-- A 9-volt battery is...

Video
2063
(10:09)

Secondary Cells

<u>Secondary cells</u>...

-- The orig. reactants can be regenerated by forcibly passing direct current...

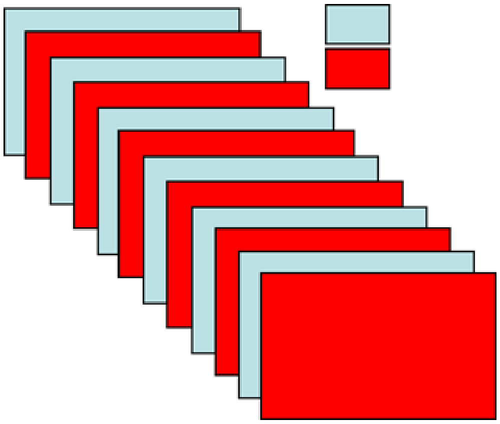
Let’s go into some detail about the lead-acid battery, or lead storage battery.

Gaston Planté
1834 – 1889

-- first rechargeable cell

-- well-known today for their use in...

Lead-acid batteries in cars consist of alternating plates of ___ and _____, usually divided into six cells. The anode is the ___; the cathode the _____. Thus, electrons depart the battery from the ___, flow through the external circuit, and re-enter at the _____.



Each of the six separate cells is bathed in...

Each cell yields a potential of about ____, so the battery (i.e., the six cells wired in series) yields a total potential of ____.

The oxidation and reduction half-reactions are, respectively:

$$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2\,e^-$$

$$PbO_2 + HSO_4^- + 3\,H^+ + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$$

The overall rxn eq is thus:

When a car is running, its ________ applies a potential in the opposite direction, forcing the rxn...

We see that in the reverse reaction, $PbSO_4$ acts as a necessary reactant. The problem is that the $PbSO_4$ has to be...

And after many charge/discharge cycles and physical jarring from bumpy roads...

Then the $[HSO_4^-]$ ___, and the battery...

We can gauge the remaining useful life of a lead-acid battery by measuring the _______ of the acid in each cell.