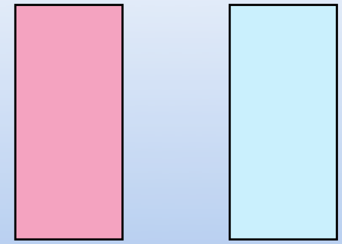
Today

Electrochemistry
electrons moving about
equilibrium with a control knob

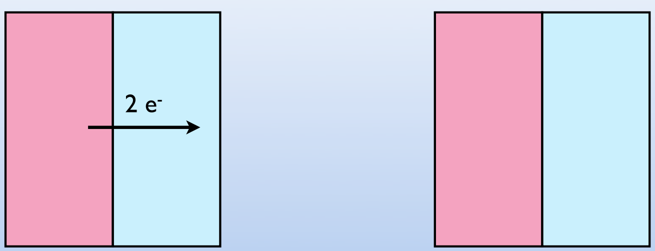
Batteries
what is going on (the simple view)



Cd
on one side

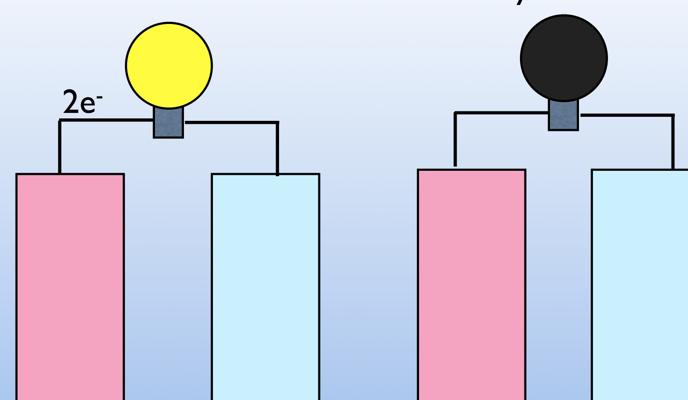
Ni^{3+}
on the
other side

Electrons have a lower free energy
in Ni^{2+} than Cd^{2+} (and Cd)



Cd Ni^{3+} Cd^{2+} $2Ni^{2+}$

To make a battery you need the
electrons to flow "externally"



Cd Ni^{3+} Cd^{2+} $2Ni^{2+}$

what is really happening

$$2NiO(OH) + Cd + H_2O \longrightarrow 2Ni(OH)_2 + Cd(OH)_2$$

How can we understand this?

We need to know about Redox numbers
Think in terms of half reactions

First some language for the quiz

Redox

Short hand for chemistry that involves
Oxidation and Reduction

Oxidation when an element loses electrons

$$Mn \longrightarrow Mn^{2+}\ 2e^-$$

Reduction when an element gains electrons

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

Keep it straight

OIL RIG
Oxidation Is Loss
Reduction Is Gain

LEO says GER
Lose Electrons Oxidation
Gain Electrons Reduction

JREMIT GROL
Just REMember IT Gain Reduction
Oxidation Loss

Oxidation numbers
CHAPTER 4!!!

Keeping track of charge

Easy in ions
"Book keeping" in molecules

for molecules oxidation numbers are a convention
in which we imagine what the
charge would be if it broke up into pieces
(we can't really assign electrons to different elements)

MgO

If we imagine this breaking up it would make

Mg^{2+} and O^{2-}

So the "oxidation state" of Mg is 2+
the "oxidation state" of O is 2-

How will we ever figure it out?

There are rules.

TABLE 4.3 Rules for Assigning Oxidation States

1. The oxidation state of an atom in an element is 0. For example, the oxidation state of each atom in the substances Na(*s*), $O_2(g)$, $O_3(g)$, and Hg(*l*) is 0.
2. The oxidation state of a monatomic ion is the same as its charge. For example, the oxidation state of the Na^+ ion is +1.
3. In its covalent compounds with nonmetals, hydrogen is assigned an oxidation state of +1. For example, in the compounds HCl, NH_3, H_2O, and CH_4, hydrogen is assigned an oxidation state of +1.
4. Oxygen is assigned an oxidation state of −2 in its covalent compounds, such as CO, CO_2, SO_2, and SO_3. The exception to this rule occurs in peroxides (compounds containing the O_2^{2-} group), where each oxygen is assigned an oxidation state of −1. The best-known example of a peroxide is hydrogen peroxide (H_2O_2).
5. In binary compounds the element with the greater attraction for the electrons in the bond is assigned a negative oxidation state equal to its charge in its ionic compounds. For example, fluorine is always assigned an oxidation state of −1. That is, for purposes of counting electrons, fluorine is assumed to be F^-. Nitrogen is usually assigned −3. For example, in NH_3, nitrogen is assigned an oxidation state of −3; in H_2S, sulfur is assigned an oxidation state of −2; in HI, iodine is assigned an oxidation state of −1; and so on.
6. The sum of the oxidation states must be zero for an electrically neutral compound and must be equal to the overall charge for an ionic species. For example, the sum of the oxidation states for the hydrogen and oxygen atoms in water is 0; the sum of the oxidation states for the carbon and oxygen atoms in CO_3^{2-} is −2; and the sum of oxidation states for the nitrogen and hydrogen atoms in NH_4^+ is +1.

Rule 6

The sum of all oxidation numbers in a compound is equal to its charge

H_2O
2 x oxidation number for H + oxidation number for O = 0

Rule 1

The oxidation state of an atom in an element is 0

Example: $O_2(g)$, $H_2(g)$, C(s), Na(s), Hg(l)

why?
monatomic have no charge
If diatomic break up they will end up as neutral atoms

Rule 2

the oxidation state of a monatomic ion is the same as its charge

Example: Na^{+} is 1+
Fe^{3+} is 3+
Fe^{2+} is 2+

Rule 3

In a compound with no metals H is assign to +1

H_2O H is 1+
HCl H is 1+
note: H_2 is not a compound

What is oxidation state of O in H_2O?

A. 0
B. +1
C. +2
D. -1
E. -2

Since H is +1, O must be -2

Rule 4

Oxygen is -2

Rule 4b
except in peroxides O_2^{-}
compound with O-O bonds

Rule 5

Most electronegative element is assigned its charge in an ion

Example HCl
H is +1
Cl is -1

$MgBr_2$
Br is -1
Mg is +2

What is oxidation state of Fe in Fe_2O_3?

A. -3

B. +1

C. +2

D. +3

E. -2

Since O is -2, Fe must be +3

Let's look at a reaction

$$Fe_2O_3(s) + 3CO(g) \longleftrightarrow 2Fe(s) + 3CO_2(g)$$

What is happening to the oxidation number of iron in this reaction?

In Fe_2O_3 it is +3
in Fe it is 0

Iron is being REDUCED

Let's look at a reaction

$$Fe_2O_3(s) + 3CO(g) \longleftrightarrow 2Fe(s) + 3CO_2(g)$$

What is happening to the oxidation number of carbon in this reaction?

In CO it is +2
in CO_2 it is +4

Carbon is being Oxidized

Let's look at a reaction

$$Fe_2O_3(s) + 3CO(g) \longleftrightarrow 2Fe(s) + 3CO_2(g)$$

CO is reducing the Fe_2O_3 to Fe
CO is the "reducing agent"
it is doing the reducing

Fe_2O_3 is oxidizing the CO to CO_2
Fe_2O_3 is the "oxidizng agent"
it is doing the oxidizing

In the following reaction what is the oxidizing agent?

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

A. Fe

B. O_2 ← Fe goes from 0 to +3 it is oxidized by the O_2

C. Fe_2O_3

D. there is no oxidizing agent (oxidizer)

Writing Half Reactions

$$H_2O_2 + I^- \longleftrightarrow I_2 + H_2O$$

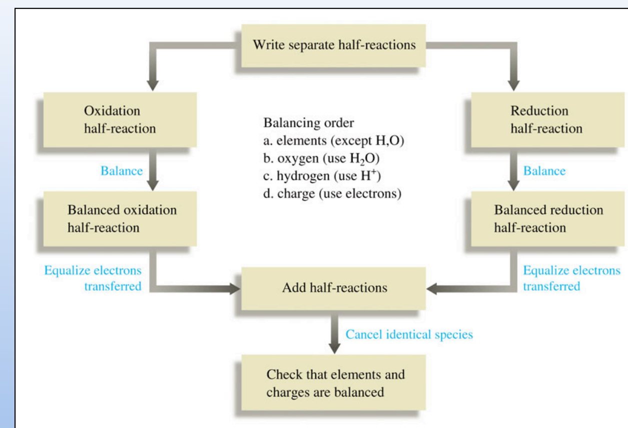
One reaction for oxidation
I goes from -1 to 0

$$I^- \longrightarrow I_2$$

One reaction for reduction
O goes from -1 to -2

$$H_2O_2 \longrightarrow H_2O$$

Balancing Redox Reactions



One reaction for oxidation

I goes from -1 to 0

$$I^- \longrightarrow I_2$$

$$2I^- \longrightarrow I_2$$

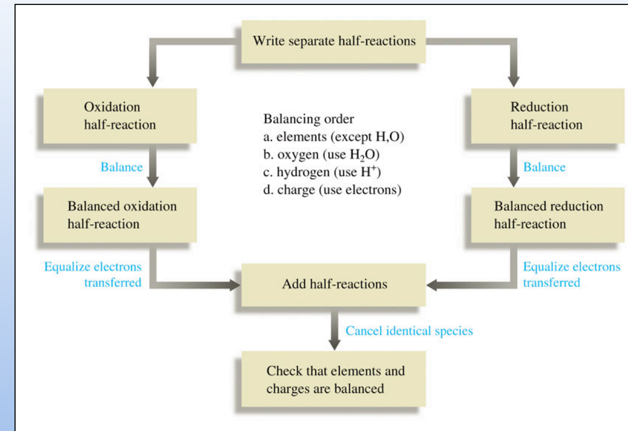
$$2I^- \longrightarrow I_2 \quad +2e^-$$

One reaction for reduction

O goes from -1 to -2

$$H_2O_2 \longrightarrow H_2O$$

Balancing Redox Reactions



One reaction for reduction

O goes from -1 to -2

$$H_2O_2 \longrightarrow H_2O$$

$H_2O_2 \longrightarrow 2H_2O$ add H_2O to balance O

$2H^+ + H_2O_2 \longrightarrow 2H_2O$ add H^+ to balance H

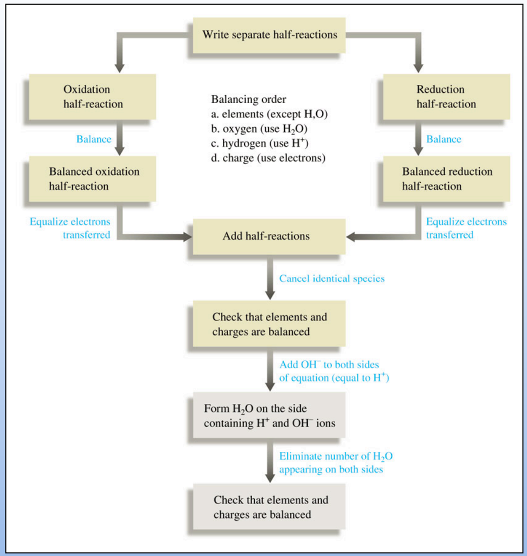
$2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$ add e^- to balance charge

$$2I^- \longrightarrow I_2 \quad +2e^-$$

$$+$$

$$2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$$

$$2I^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O + I_2$$


Write separate half-reactions
Oxidation half-reaction
Reduction half-reaction
Balancing order
a. elements (except H$_2$O)
b. oxygen (use H$_2$O)
c. hydrogen (use H$^+$)
d. charge (use electrons)
Balance
Balance
Balanced oxidation half-reaction
Balanced reduction half-reaction
Equalize electrons transferred
Equalize electrons transferred
Add half-reactions
Cancel identical species
Check that elements and charges are balanced
Add OH$^-$ to both sides of equation (equal to H$^+$)
Form H$_2$O on the side containing H$^+$ and OH$^-$ ions
Eliminate number of H$_2$O appearing on both sides
Check that elements and charges are balanced