Today

Redox chemistry

electrons moving switching places

oxidation and reduction

Demonstrations of Redox Chemistry

Silver/Silver ions and Copper/Copper Ions

The electrons are lower in energy in

A. the silver metal

B. the copper metal

C. they are the same

What is happening in these redox reactions?

electrons are moving between different chemical species

$$\overbrace{Ag^{+}(aq) \quad + \quad Cu(s) \quad \longleftrightarrow \quad Ag(s)}^{+1e^-} \quad + \quad Cu^{2+}(aq)$$

$$Ag^{+}(aq) \quad + \quad \underbrace{Cu(s) \quad \longleftrightarrow \quad Ag(s) \quad + \quad Cu^{2+}}_{-2e^-}(aq)$$

electrons are moving from the Cu to the Ag^{+}

Is this reaction balanced?

$$\overbrace{2\,Ag^{+}(aq) + \underbrace{Cu(s) \longleftrightarrow 2\,Ag}_{-2e^-}}^{2\times(+1e^-)}(s) + Cu^{2+}(aq)$$

A. yes

B. no

+1 in Reactant

+2 in Products

When will this reaction stop?

$$2Ag^+ (aq) + Cu(s) \longleftrightarrow 2Ag(s) + Cu^{2+}(aq)$$

A. when the Ag^+ concentration is zero

B. when the Cu solid disappears OR THIS

C. when the system comes to equilibrium

D. it depends on the concentrations of the ions

This will change when we get to equil.

At standard concentration we can compare different metals

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Standard Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Silver

Copper

Hardest to remove an electron

Easiest to remove an electron

Comparing Al/Al^{3+} and Cu/Cu^{2+}

which will form solid metal from ions?

A. Al

B. Cu

C. neither

$Al \rightarrow Al^{3+} + 3e^-$

lower on chart
EASIER to remove e^-!

How many electrons are "moving" in this reaction?

$$\overbrace{2Al\,(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}}^{2x(-3e^-)}(aq) + 3Cu(s)$$

$$3(+2e^-)$$

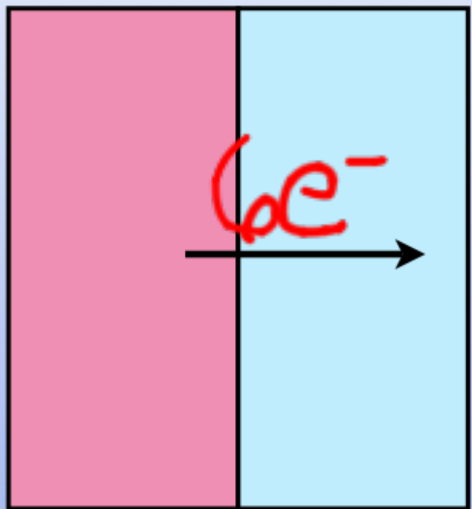
A. 0

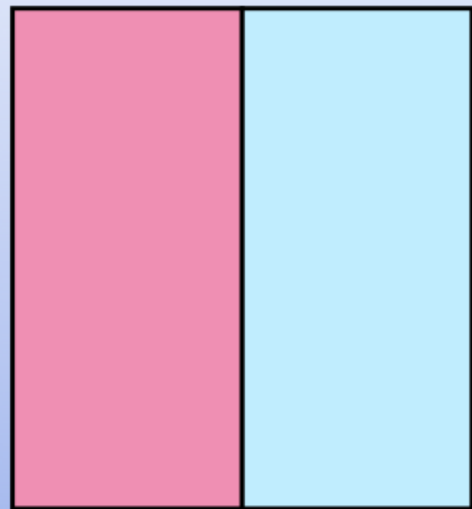
B. 2

C. 3

D. 6

Free energy of $2Al(s) + 3Cu^{2+}(aq)$ is higher than in $2Al^{3+}(aq) + 3Cu(s)$ (assuming the concentrations are high)

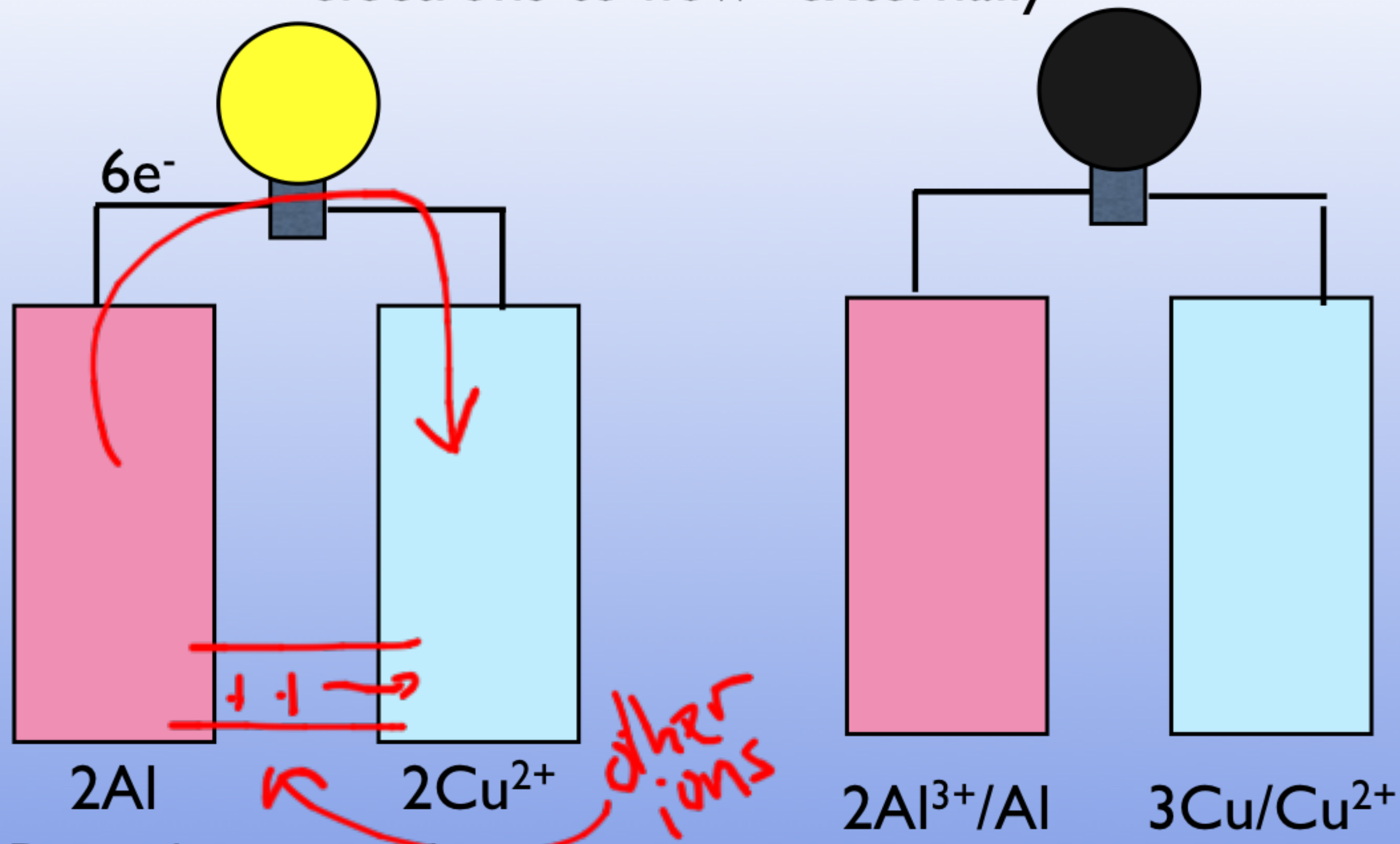




$2Al$ $3Cu^{2+}$ Al / $2Al^{3+}$ $3Cu$ / Cu^{2+}

We can make use of these electrons moving between the two species if we can physically separate the two reactions

To make a battery (or fuel cell) you need the electrons to flow "externally"



During the reaction electrons move and we have a current

Reaction is a equilibrium (“over”) we have no current (dead battery)

We want to not only physically separate the reactions
We want to separate them when we think about them.

Redox Reactions

Divide into two parts oxidation and reduction

Each reaction will be half of the overall reaction

We will have an oxidation half reaction
and a reduction half reaction

First some language

Redox

Short hand for chemistry that involves Oxidation and Reduction

Oxidation   when an element loses electrons

$Al \longrightarrow Al^{3+} + 3e^-$ e^- as product

First some language

Redox

Short hand for chemistry that involves Oxidation and Reduction

Oxidation when an element loses electrons

$Al \longrightarrow Al^{3+}\ 3e^-$

Reduction when an element gains electrons

$Cu^{2+} + 2e^- \longrightarrow Cu$ e^- as react

Keep it straight

OIL RIG
Oxidation Is Loss
Reduction Is Gain

Keep it straight

OIL RIG
Oxidation Is Loss
Reduction Is Gain

LEO says GER
Lose Electrons Oxidation
Gain Electrons Reduction

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

Sometime it is very easy to make the half reactions

$$\overbrace{2Al(s) + 3\underbrace{Cu^{2+}(aq) \longrightarrow 3Cu(s)}_{3(+2e^-)} + 2Al^{3+}(aq)}^{2\times(-3e^-)}$$

Oxidation

$$Al \longrightarrow Al^{3+} + 3e^-$$

Reductions

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

Note to balance the Redox Reaction we must
equal number of electrons
(no electrons lost or gained overall)

Oxidation

$Al \longrightarrow Al^{3+} + 3e^-$ 3 electrons here x 2

Reduction

$Cu^{2+} + 2e^- \longrightarrow Cu$ 2 electrons here x 3

to balance we need equal number of electrons
easiest to stick with whole numbers

Thus we need
oxidation half reaction x 2
reduction half reaction x 3

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 3Cu(s) + 2Al^{3+}(aq)$$

Sometime it is not as easy to “see” the half reactions

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

$-1e^-$ $\quad Na^+ + OH^-$

For this we need to remember oxidation numbers

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 ionic 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 figure it out for other molecules?

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.

Table 4.3 in the book. Read it. Know it

A quick Review

Rule 6 (should be rule zero)

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 a neutral 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

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 the oxidation number for iron in Fe_2O_3?

0 −2

$3(-2) = -6$

A. 0

B. 2+

C. 3+

D. 2-

TOTAL = 0

$2(?) = +6$

+3

What is happening to iron in this reaction?

$$\underbrace{2Fe(s) \quad + \quad 3O_2(g) \longrightarrow 2Fe}_{-3e^-}{}_2O_3(s)$$

$+3$

A. it is oxidized

B. it is reduced

C. it is both oxidized and reduced

D. nothing

Fe starts 0

↓

+3

oxide

What is happening to iron in this reaction?

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

+3

+3e⁻

A. it is oxidized

B. it is reduced

C. it is both oxidized and reduced

D. nothing

monoxide

What is happening to carbon in this reaction?

$$\overset{+2\;-2}{} \qquad \overset{+4\;(-2)\times 2}{}$$

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

A. it is oxidized

B. it is reduced

C. it is both oxidized and reduced

D. nothing

Carbon goes from $+2 \rightarrow +4$

What is reducing the iron? oxide

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

A. CO

B. oxygen

C. Fe_2O_3

D. CO_2

The species that is doing the oxidizing
is the oxidizing agent (it ends up reduced)

The species that is doing the reduction
is the reducing agent (it ends up 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

Balancing redox equations

unbalanced equation

"sodium metal reacts with water to form hydrogen gas under basic conditions"

$$Na + H_2O \longleftrightarrow Na^+ + H_2$$

One reaction for oxidation

Na goes from 0 to +1

$$Na \longrightarrow Na^+$$

One reaction for reduction

H goes from +1 to 0

$$H_2O \longrightarrow H_2$$

How to balance

balance each half reaction separately

1. balance all elements except H & O
2. balance O by adding H_2O
3. balance H by adding H^+
4. balance the charge by adding e^-

add half reactions together to balance electrons

multiply each half reaction by proper factor
to get the same number of electron in each reaction

to convert to reaction in base neutralize H^+ with OH^-

eliminate any H^+, OH^-, or H_2O that appears on both sides of the equation

One reaction for oxidation

Na goes from +1 to 0

$Na \longrightarrow Na^+$ balance elements other than H and O (done)

balance O (none)

balance H (none)

$Na \longrightarrow Na^+ + e^-$ balance the charge (add one electron)

oxidation half-reaction is balanced

One reaction for reduction

H goes from +1 to 0

$$H_2O \longrightarrow H_2$$ balance all but H & O

$$H_2O \longrightarrow H_2 + H_2O$$ add H_2O to balance O

$$2H^+ + H_2O \longrightarrow H_2 + H_2O$$ add H^+ to balance H

$$2H^+ + H_2O + 2e^- \longrightarrow H_2 + H_2O$$ add e^- to balance charge

eliminate any species on both sides of reaction

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

reduction half-reaction is balanced

add half reaction together with equal number of electrons

$$2 \times (Na \longrightarrow Na^{+} + e^{-})$$

$$+$$

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

$$2Na + 2H^{+} \longrightarrow H_2 + 2Na^{+}$$

there should be no more electrons!

This in acidic solution what about base?

to convert to base neutralize the H^+ with OH^-

$$2Na + 2H^+ \longrightarrow H_2 + 2Na^+$$

$$2Na + 2H^+ + 2OH^- \longrightarrow H_2 + 2Na^+ + 2\,OH^-$$

$$2Na + 2H_2O \longrightarrow H_2 + 2Na^+ + 2\,OH^-$$

Reaction balanced in basic conditions