Types of Aqueous Reactions

Recognizing types of Reactions
It is possible to predict the possible products of a reaction based on the reactants.
Many of these predictions are easy to make if you understand a few basic things about molecules/atoms.
You, too, can learn to predict reaction products!

A Question
(NH₄)₂SO₄ + FeCl₃ →
What happens when you mix ammonium sulfate and ferric chloride?
A better question is: what COULD happen?
What kind of molecules are these?
Ionic!
In solution, what form do ionic compounds take?
Ions!

Are these the same?
(NH₄)₂SO₄ + FeCl₃ → Fe₂(SO₄)₃ + NH₄Cl
(NH₄)₂SO₄ (aq) + FeCl₃ (aq) → Fe₂(SO₄)₃ (aq) + NH₄Cl (aq)
Kind of depends on what you mean by the same…
The “state of matter” is important. What if they were all solids?

The bottom 2 are definitely different from each other. And only one of them makes any sense!
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\[(\text{NH}_4)_2\text{SO}_4 + \text{FeCl}_3 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{NH}_4\text{Cl}\]

In solution, what form do ionic compounds take?
- \(\text{NH}_4^+\)
- \(\text{SO}_4^{2-}\)
- \(\text{Fe}^{3+}\)
- \(\text{Cl}^-\)

What about the products?
- \(\text{Fe}_2(\text{SO}_4)_3\)
- \(\text{NH}_4\text{Cl}\)

In solution...
- \(\text{Fe}^{3+}\)
- \(\text{SO}_4^{2-}\)
- \(\text{NH}_4^+\)
- \(\text{Cl}^-\)

NO DIFFERENCE! NO REACTION!

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**What are the possible products?**

- \((\text{NH}_4)_2\text{SO}_4 (\text{aq}) + \text{FeCl}_3 (\text{aq}) \rightarrow \)
- \(\text{Fe}_2(\text{SO}_4)_3 + \text{NH}_4\text{Cl}\)
- **Why?**
- Because + ions can only associate with negative ions and – ions can only associate with positive ions

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**What are the possible products?**

- \((\text{NH}_4)_2\text{SO}_4 (\text{aq}) + \text{FeCl}_3 (\text{aq}) \rightarrow \)
- \(\text{NH}_4^+ + \text{SO}_4^{2-} + \text{Fe}^{3+} + \text{Cl}^-\)
- \(\text{Fe}_2(\text{SO}_4)_3 + \text{NH}_4\text{Cl}\)
- **Are these products solids, liquids, gases, or aqueous?**
- **Depends!** They are ionic, so they could be solids. But, they could also be water soluble (sols). Which is it? (The reactants are in water already)
- **Does it make a difference?**
- **You bet it!**
Possible Reactions

\[(\text{NH}_4\text{H}_2\text{SO}_4 \text{ (aq)} + \text{FeCl}_3 \text{ (aq)} \rightarrow \text{Fe}_2(\text{SO}_4)_3 \text{ (aq)} + \text{NH}_4\text{Cl} \text{ (aq)})\]

\[(\text{NH}_4\text{H}_2\text{SO}_4 \text{ (aq)} + \text{FeCl}_3 \rightarrow \text{Fe}_2\text{SO}_4 \text{ (s)} + \text{NH}_4\text{Cl} \text{ (s)})\]

The top one...?

No Reaction – just a bunch of ions in water!

These are all DIFFERENT reactions.

How would you know which happens?

You need to know the solubility of the products.

Predicting Solubilities

Solubility is very complicated, but there are a few simple rules that help with a large number of compounds:

1. Group 1A salts are all soluble.
2. All salts containing nitrates, ammonium, chlorate, perchlorate, and acetate are soluble.
3. All Cl, Br, I salts are soluble EXCEPT for Ag, Pb, and Hg salts.
4. All sulfates are soluble EXCEPT for Pb, Ca, Ag, Sr, Hg, and Ba salts.
5. Metal hydroxides are INSOLUBLE except for those of Group 1A and Ca, Sr, and Ba salts.
6. All salts containing phosphate, carbonate, sulfite, and sulfide are insoluble EXCEPT for those of Group 1A and NH$_4$.
Based on those rules...

(NH₄)₂SO₄ (aq) + FeCl₃ (aq) → Fe₂(SO₄)₃ (aq) + NH₄Cl(aq)
(NH₄)₂SO₄ (aq) + FeCl₃ (aq) → No Reaction

Precipitation Reactions

This is an example of a “double-replacement reaction” – swapping cations between anions.

This is also an example of a “precipitation reaction” – forming a solid from a reaction performed in aqueous solution. (Although no precipitation reaction occurred in this instance due to solubility of the products.)
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**Another Example**

\[ \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + \text{Ca(NO}_3)_2(\text{aq}) \rightarrow ??? \]

What’s the first thing to consider?

What is the nature of the reactants?

They are ionic!

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**Another Example**

\[ \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + \text{Ca(NO}_3)_2(\text{aq}) \rightarrow ??? \]

What’s the first thing to consider?

What is the nature of the reactants?

They are ionic!

\[ \text{Fe}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) \rightarrow ??? \]

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**Possible Reactions**

\[ \text{Fe}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) \rightarrow ??? \]

Double Replacement!

\[ \text{Fe}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) \rightarrow \text{Fe(NO}_3)_3(\text{aq}) + \text{CaSO}_4(\text{aq}) \]

Next thing to consider…?

Soluble or insoluble?
Possible Products

Fe³⁺(aq) + SO₄²⁻(aq) + Ca²⁺(aq) + NO₃⁻(aq) → Fe(NO₃)₃ + CaSO₄

Soluble! (All salts containing nitrates, ammonium, chloride, perchlorate, and acetate are soluble.)

CaSO₄???

Insoluble! (All sulfates are soluble EXCEPT Pb, Ca, Sr, Hg²⁺ and Ba)

Actual Reaction…

Fe₂(SO₄)₃(aq) + Ca(NO₃)²(aq) → Fe(NO₃)₃(aq) + CaSO₄(s)

• This is a precipitation reaction and a double-replacement reaction!

Fe₂(SO₄)₃(aq) + 3 Ca(NO₃)²(aq) → 2 Fe(NO₃)₃(aq) + 3 CaSO₄(s)

Net Ionic Equation

Sometimes, to simplify the expression down to its most important elements, rather than write the full chemical equation it is distilled down to a net ionic equation

We ignore spectator ions (dissolved ions that don’t change in the reaction) and write only the species that change.
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Writing the Net Ionic Equation

\[ \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 3 \text{Ca(NO}_3)_2(\text{aq}) \rightarrow 2 \text{Fe(NO}_3)_3(\text{aq}) + 3 \text{CaSO}_4(\text{s}) \]

Rewrite with aqueous ionic species as ions:

\[ 2 \text{Fe}^{3+}(\text{aq}) + 3 \text{SO}_4^{2-}(\text{aq}) + 3 \text{Ca}^{2+}(\text{aq}) \rightarrow 2 \text{Fe}^{3+}(\text{aq}) + 6 \text{NO}_3^-(\text{aq}) + 3 \text{CaSO}_4(\text{s}) \]

Cancel things that appear on both sides!

\[ 3 \text{SO}_4^{2-}(\text{aq}) + 3 \text{Ca}^{2+}(\text{aq}) \rightarrow 3 \text{CaSO}_4(\text{s}) \]

Advantages of the Net Ionic Equation:

1. It is complete – all changes are spelled out.
2. It is concise – only things that actually change in the reaction are shown.
3. It is the simplified recipe – if I want to make CaSO\textsubscript{4}, does it matter what I use as the source of SO\textsubscript{4}\textsuperscript{2-}?

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\[ 3 \text{SO}_4^{2-}(\text{aq}) + 3 \text{Ca}^{2+}(\text{aq}) \rightarrow 3 \text{CaSO}_4(\text{s}) \]

Precipitation Reactions

It should be possible for you to recognize the possibility of a precipitation reaction:

1. Recognize the reactants are ionic
2. The ionic species are aqueous
3. Double replacement products are, therefore, possible
4. One or more of the possible products is insoluble.
Clicker Question #2
Write the correct balanced equation for the following reaction:
\[ \text{K}_2\text{SO}_4 (aq) + \text{Pb(NO}_3\text{)}_2 (aq) \rightarrow \]
A. \[ \text{K}_2\text{SO}_4 (aq) + 2 \text{Pb(NO}_3\text{)}_2 (aq) \rightarrow 2 \text{PbSO}_4 (s) + 2 \text{KNO}_3 (s) \]
B. \[ \text{K}_2\text{SO}_4 (aq) + \text{NO}_3^- (aq) \rightarrow \text{KNO}_3 (s) \]
C. \[ \text{K}_2\text{SO}_4 (aq) + 2 \text{Pb(NO}_3\text{)}_2 (aq) \rightarrow \text{PbSO}_4 (s) + 2 \text{KNO}_3 (s) \]
D. \[ \text{Pb}^{2+} (aq) + \text{SO}_4^{2-} (aq) \rightarrow \text{PbSO}_4 (s) \]
E. No Reaction

Predicting Solubilities
Solubility is very complicated, but there are a few simple rules that help with a large number of compounds:
1. Group 1A salts are all soluble.
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5. Metal hydroxides are INSOLUBLE except for those of Group 1A and Ca, Sr, and Ba.
6. All salts containing phosphates, carbonates, sulfites, and sulfides are insoluble EXCEPT for those of Group 1A and NH\(_4\).+.

Acid-base reactions
Another type of aqueous chemical reaction is an acid/base reaction – the reaction between an acid and a base.

There are different types of acids and bases. We rely on the Bronsted-Lowry definition:
- Bronsted-Lowry acid – proton (H\(^+\)) donor
- Bronsted-Lowry base - proton (H\(^+\)) acceptor
Recognizing acids and bases

Acids are easiest to recognize in this system.
- Bronsted-Lowry acid - proton donor

If you are going to donate a proton, what must be true?
You must have a proton!!!

Which of these compounds is an acid?

HCl – yep, it has a proton
Fe₂(SO₄)₃ – nopes, it has no proton
NaOH – nopes, it has no proton! (This is the trick question, hydroxide is a unit, there isn’t a separate proton there)
NaNO₃ – nopes, it has no proton
H₂SO₄ – yep, it has a proton – two, in fact.
Recognizing acids and bases

- Bronsted-Lowry base - proton acceptor

If you are going to accept a proton, what must be true?

You must have available electrons – H⁺ is a cation, it needs electrons.

Strong vs. weak

Electrolytes (soluble ionic species) in general, and acids and bases in particular, are considered to come in two types: strong and weak.

This is not what it sounds like! It has nothing to do with how powerful the solutions is.

A strong electrolyte is one that completely dissociates into its ions in water. A weak electrolyte is one that only partially dissociates into its ions in water.

Aqueous Acids & Bases

The key to the aqueous chemistry of acids and bases is WATER! (Huge surprise, I know! 😊)

Water, among its many interesting properties, is also amphiprotic. Water is both an acid and a base!

H₂O⁻ – It has a proton and it has excess electrons on the oxygen.
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**General Acid/Base Reaction**

\[ H-A + X-B \rightarrow H-B + X-A \]

(where X and A are any chemical species, H is the proton, and B is any basic species)

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**Products of Acid/Base reactions**

All acid/base reactions have the same two net products: water & a salt!

- \( HCl + NaOH \rightarrow H_2O + NaCl \)
- \( H_2SO_4 + LiOH \rightarrow H_2O + LiHSO_4 \)
- \( HCl + NH_3 \rightarrow Cl^- + NH_4^+ \) Where’s the water?

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**The role of water**

NH₃ is a weak base – ammonia.

Any weak base in water will accept a proton from water.

\( \text{NH}_3(aq) + H_2O(l) \rightarrow \text{NH}_4^+(aq) + OH^-(aq) \)
\( \text{NH}_3(aq) + H_2O(l) \rightarrow \text{NH}_4OH(aq) \)

Ammonia and ammonium hydroxide are used interchangeable.
The role of water

\[ \text{HCl} + \text{NH}_3 \rightarrow \text{Cl}^- + \text{NH}_4^+ \]
\[ \text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_3\text{OH}(aq) \]
\[ \text{HCl} + \text{NH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{NH}_4\text{Cl} \]

This is the reason for the old Earth Science myth that all bases have OH\(^-\).
They DO, as long as they are in water!

Gas Evolution Reactions

Just what it sounds like: reactions that create a gas as a product.

These reactions can be difficult to identify. A couple guidelines:
1. Sulfides tend to create gas products: \( \text{H}_2\text{S}(g) \)
2. Carbonates and bicarbonates (\( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \)) form compounds that break down into gases: \( \text{H}_2\text{CO}_3(aq) \) breaks down into \( \text{H}_2\text{O}(l) \) and \( \text{CO}_2(g) \).
3. Sulfates and bisulfites (\( \text{SO}_4^{2-} \) and \( \text{HSO}_3^- \)) form compounds that break down into gases: \( \text{H}_2\text{SO}_3(aq) \) breaks down into \( \text{H}_2\text{O}(l) \) and \( \text{SO}_2(g) \).
4. Ammonium compounds (\( \text{NH}_4^+ \)) can form compounds that break down into \( \text{NH}_3(g) \): \( \text{NH}_4\text{OH}(aq) \) breaks down into \( \text{H}_2\text{O}(l) \) and \( \text{NH}_3(g) \).

Gas Evolution Reaction - Examples

\[ 2 \text{HCl}(aq) + \text{K}_2\text{S}(aq) \rightarrow \]

The key here is to see the sulfide. In solution, both of these compounds are ionic and break down into ions:

\[ 2 \text{H}^+(aq) + 2 \text{Cl}^-(aq) + 2 \text{K}^+(aq) + \text{S}^{2-}(aq) \rightarrow \]

So, it is still a double replacement reaction:

\[ 2\text{H}^+(aq) + 2\text{Cl}^-(aq) + 2 \text{K}^+(aq) + \text{S}^{2-}(aq) \rightarrow \text{H}_2\text{S} + 2\text{KCl} \]
Gas Evolution Reaction - Examples

2 HCl(aq) + K₂S(aq) → H₂S(g) + 2KCl(aq)

But, like with the precipitation reactions, we need to determine what kind of compound the products are.

KCl?

Ionic, so it dissociates!

H₂S?

Actually, it is Jumping Jack Flash!

It's a Gas! Gas! Gas!

Gas Evolution Reaction - Examples

2 HCl(aq) + K₂S(aq) → H₂S (g) + 2KCl(aq)

Or, if you want to write it as a net ionic equation:

2H⁺(aq) + 2Cl⁻(aq) + 2K⁺(aq) + S²⁻(aq) → H₂S(g) + 2K⁺(aq) + 2Cl⁻(aq)

Cancel the "spectators"

2H⁺(aq) + S²⁻(aq) → H₂S(g)

This really shows you a whole class of gas evolution reactions. Take any acid (source of H⁺) and any soluble sulfide (source of S²⁻) and you get H₂S (g)!
So, in 10 seconds or less!

HCl(aq) + Li₂S(aq) \rightarrow H₂S(g) + LiCl(aq)
H₂SO₄(aq) + FeS(aq) \rightarrow H₂S(g) + FeSO₄(aq)

How to make a bomb!

http://www.youtube.com/watch?v=0fdbzEpm4D

http://www.youtube.com/watch?v=4N0m9SPEx

http://www.youtube.com/watch?v=4N0m9SPEx
Another tricky type of reaction:

Oxidation-reduction reactions ("redox reactions") are barely chemical reactions at all.

What is a chemical reaction?
A process in which bonds are broken and made so that atoms change partners.

Consider 2 molecules

FeO and Fe_2O_3

Are they different?

Yes.

What’s the difference?

Iron (II) oxide vs. Iron (III) oxide The Oxidation State is different.

What is an “oxidation state”?

The simplest way to think about an “oxidation state” is that it is the charge the atom has or could have if you separated it from the atoms it is bonded to.
Are you stuck with your oxidation state?

Asked a different way: If you are iron in FeO, are you stuck being Fe$^{2+}$ forever?

In fact, you can change oxidation states as often is you like. But, there's a catch...

How do you change oxidation states?

Add or subtract electrons. Fe$^{2+}$ has 1 more electron than Fe$^{3+}$.

What does this reaction look like?

Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ + 1 e$^-$

Is this a “real” reaction?

Depends on what you mean by “real” and by reaction. Something changed, but no atoms were rearranged so it isn’t like the other reactions we’ve seen before. And, you might ask, what happens to the electron?

This is an “electrochemical” reaction

Fe$^{2+}$ $\rightarrow$ Fe$^{3+}$ + 1 e$^-$

It’s a special kind of process, part electrical and part (barely) chemical. The atom changes oxidation state and creates an electron. The electron can do useful work (power your Ipod) or chemical work (change the oxidation state of something else).
Electrons come, electrons go

Fe^{2+} \rightarrow Fe^{3+} + 1 e^{-}
Mn^{5+} + 3 e^{-} \rightarrow Mn^{2+}

When electrons “go”, it is called an “oxidation”. When electrons “come”, it is called a “reduction”.

[It’s easiest to remember that a “reduction” reduces the charge on the ion (oxidation state).]

Like acids and bases...

Oxidation and Reduction always happens simultaneously:

Oxidation half-reaction: Fe^{2+} \rightarrow Fe^{3+} + 1 e^{-}
Reduction half-reaction: Mn^{5+} + 3 e^{-} \rightarrow Mn^{2+}
Full reaction: 3 Fe^{2+} + Mn^{5+} \rightarrow 3 Fe^{3+} + Mn^{2+}
WTFDYGT????????????

Chemical reactions don’t have electrons

Oxidation and Reduction half-reactions balance so that no NET electrons remain.

Oxidation gives you 1 e⁻: Fe^{2+} \rightarrow Fe^{3+} + 1 e⁻
Reduction needs 3: Mn^{5+} + 3 e⁻ \rightarrow Mn^{2+}

3 x (Fe^{2+} \rightarrow Fe^{3+} + 1 e⁻) + Mn^{5+} + 3 e⁻ \rightarrow Mn^{2+}
3 Fe^{2+} + Mn^{5+} + 3e⁻ \rightarrow 3 Fe^{3+} + Mn^{2+} + 3e⁻
3 Fe^{2+} + Mn^{5+} \rightarrow 3 Fe^{3+} + Mn^{2+}
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Is it always that easy?

Of course NOT!

We’ll talk about these reactions in much greater detail later. For now, we just want to recognize one when we see it. We’ll figure out how to balance them after the snow melts.

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Determining oxidation states

1. Free elements are always 0 (Cu, Fe, H2)
2. The oxidation state of a monoatomic ion is just its charge (Cu2+, Fe3+, S2-)
3. The sum of the oxidation of all atoms in a compound or ion is the charge of the compound or ion (H2O, NH4+)
4. Metals are always positive. Group 1A metals are ALWAYS +1. Group 2A metals are ALWAYS +2. (NaCl, Ca(OH)2)
5. Halogens (Group VIIA) are 95% of the time -1.
6. Chalcogenides (Group VIA) are 95% of the time -2.

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Ionic compounds

For an ion or an ionic compound, the oxidation state is easy: it’s the charge on the ion.

FeCl3 – Fe must be +3 because there are 3 Cl- ions stuck to it.

MnO2 – Mn must be +4 because there are 2 O2- ions stuck to it.
Covalent compounds

Here is where it is a little tricky. The atoms in a covalent compound don’t have a real charge on them. BUT, they do have a potential charge if you pulled them all apart and the electrons they share get split up.

\[ \text{CO} \rightarrow \text{carbon must be } +2 \text{ since O wants to be } -2 \]
\[ \text{CO}_2 \rightarrow \text{carbon must be } +4 \text{ since there are 2 O that want to be } -2 \text{ each} \]

What’s the oxidation state of the atoms?

\[ \text{SrBr}_2 \]
Br is a halogen – it must be -1 when bonded to a metal
Sr must be +2

\[ \text{SO}_3 \]
O is usually -2, which means S must be +6
What's the oxidation state of the atoms?

CO$_3^{2-}$
O is usually -2, which means C must be +4 since the entire molecule is -2

NO$_3^-$
O is usually -2, which means N must be +5 since the entire molecule is -1

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What's the oxidation state of K?
A. +1
B. -1
C. +2
D. -2
E. Cannot be determined.

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K is a Group IA metal. It is +1 ALWAYS!
I is, therefore, -1 (as it usually is for halogens) because the whole molecule must add up to ZERO.
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**MnO**

What is the oxidation state of Mn?

A. +2  
B. +4  
C. +1  
D. -1  
E. -2 

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**MnO**

Mn is not in one of our 1st two columns. So we can’t know its oxidation state directly.

HOWEVER, oxygen is Group VIA and is almost always -2.

So, if O is -2, Mn must be +2 for the whole molecule to be neutral.

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2 CuO + 2 FeO → Fe₂O₃ + Cu₂O

Redox reaction? You bet!

How can you tell? Two things are changing oxidation state. (There must always be an oxidation and a reduction.)

What are the oxidation states?
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2 CuO + 2 FeO → Fe₂O₃ + Cu₂O

CuO - Copper is +2
  How do you know?
  Because O is -2

Cu₂O - Copper is ...
  +1
  How do you know?
  Because O is -2

2 CuO + 2 FeO → Fe₂O₃ + Cu₂O

CuO - Copper is +2
  How do you know?
  Because O is -2

Cu₂O - Copper is ...
  +1
  How do you know?
  Because O is -2

As soon as you see one thing changing oxidation state...
...there is another! (Yoda 1980)

There has to be an oxidation and a reduction.

2 CuO + 2 FeO → Fe₂O₃ + Cu₂O

FeO - Fe is +2 (because O is -2)

Fe₂O₃ - Fe is +3 (because O is -2)

2 CuO + 2 FeO → Fe₂O₃ + Cu₂O

Cu goes from +2 (CuO) to +1 (Cu₂O) while Fe goes from +2 (FeO) to +3 (Fe₂O₃)

So Fe is giving up an electron (going from +2 to +3) while Cu is gaining an electron (going from +2 to +1).
Clicker Question

Which of the following is a redox reaction:

A. Li(s) + O_2(g) → Li_2O(s)
B. Pb(NO_3)_2(s) + Na_2SO_4(s) → PbSO_4(s) + 2 NaNO_3(s)
C. Mg(s) + Br_2(l) → MgBr_2(s)
D. A and C
E. A, B, and C.