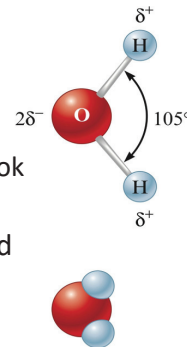


## Chapter 4

# Types of Chemical Reactions and Solution Stoichiometry

## Water

- One of the most important substances on Earth.
- One of the most abundant substances on Earth.
- Can dissolve many different substances.
  - It's not that it is super versatile.
  - It's just that it is everywhere, in every nook and cranny of the Earth
- It is absolutely essential to life directly and indirectly (in some surprising ways)
- A polar molecule because of its unequal (asymmetric, lopsided) charge distribution.



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Water has been the natural choice of solvent to conduct solution chemistry because it is:

- easy to find, almost free, and cheap to purify
- easy to work with
- hugely important in the chemistry of the planet

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If a solid is soluble in water, it means water molecules are able to provide favorable (attractive) interactions, competitive with the attractive interactions within the solid.

Remarkably, water molecules can often compete with the strong attractions present between the cations and anions of an ionic solid.

➤ When it does, that solid is soluble in water.

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## Aqueous Solutions

- **Solvent**  
liquid water
- **Solute**  
substance being dissolved
- **Electrolyte**  
substance that, when dissolved in a polar solvent like water, produces a solution that can conduct electricity  
(because it produces ions, which are charged)

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## Electrolytes

### Strong electrolyte:

When dissolved in water, dissociates almost completely into ions

- Highly water-soluble ionic compounds (e.g. NaCl, K<sub>2</sub>SO<sub>4</sub>)
- Strong acids (e.g. HCl, H<sub>2</sub>SO<sub>4</sub>)
- Strong bases (e.g. KOH)

In this course, **we will assume that all ionic compounds dissolve as separated cations and anions**

### Weak electrolyte:

When dissolved in water, only some of it produces ions

- Weak acids (e.g. HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)
- Weak bases (e.g. NH<sub>3</sub>)

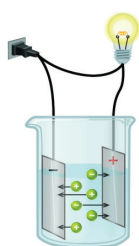
### Non-electrolyte:

Does not dissociate into ions at all (e.g. sugars, alcohols, oils)

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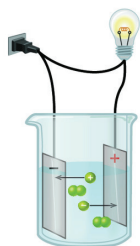
## Electrolyte solutions conduct electricity

ions can carry the electric charge through the solution



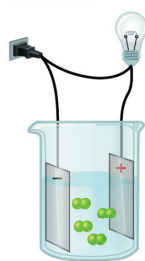
**KCl**  
High conductivity

**Strong Electrolytes** conduct current efficiently (bulb shines brightly at high concentration)



**Acetic Acid**  
Low conductivity

**Weak Electrolytes** conduct only a small current (bulb glows dimly even at high concentration)



**Sugar**  
No conductivity

**Nonelectrolytes** conduct no current (bulb remains unlit).

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## Be aware:

The terms “strong electrolyte” or “weak electrolyte” refers to the **substance** dissolved (i.e. solute)

- A concentrated solution of a strong electrolyte is a good conductor and can make the bulb glow bright.

## But ...

- A dilute solution of a strong electrolyte won't conduct much electricity, and the bulb will not glow bright.
  - Even if the dissolved “strong electrolyte” fully dissociated, if there isn't much of it, it will still have low conductivity

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On the other hand,

Even a concentrated solution of a weak electrolyte is not a good conductor and will not make the bulb glow bright.

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A molecular substance like hydrogen chloride (HCl), which is not ionic, but fully dissociates into ions when dissolved in water, is also a strong electrolyte.

- Because it's a strong acid, fully dissociating into  $\text{H}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  ions

*Note: Acids produce  $\text{H}^+$  ions in water, along with an anion*

Strong acids are strong electrolytes

-- fully ionize in water

Weak acids are weak electrolytes

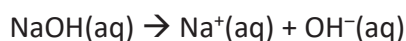
-- only partially ionize in water

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Almost all the bases we see in this course are **metal hydroxides** like NaOH or KOH, and are strong electrolytes (because they are ionic compounds).

- Remember: we will assume that all ionic compounds fully dissociate into their ions when dissolved

*Note: Bases produce  $\text{OH}^-$  ions in water, along with a cation*



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One **weak base** we encounter is ammonia:  $\text{NH}_3$

- A **molecular compound** (as opposed to the usual metal hydroxide like NaOH)
  - no guarantee it will fully ionize
  - indeed it doesn't
- A small portion reacts with water to form  $\text{NH}_4^+$  and  $\text{OH}^-$  ← Produced by reacting with water
- Not fully converted to ions
  - so it is a **weak electrolyte**

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## Chemical Reactions in Solutions

To do anything useful, we must know:

- The nature of the reaction.
- The amounts of chemicals present in the solutions.

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## Concentration of Solutions: Molarity

Molarity ( $M$ ) = moles of solute per 1 liter of solution

$$M = \text{Molarity} = \frac{\text{moles of solute}}{\text{volume of solution (in L)}} = \frac{n}{V}$$

Unit of Molarity: “Molar” ( $M$ )

Slightly confusing:  
Unit symbol  $M$  is the same as  
the symbol for the concept

If 2.0 liters of a solution contains 6.0 moles of solute, its concentration is:

$$\frac{6.0 \text{ mol}}{2.0 \text{ L}} = 3.0 \text{ molar or } 3.0 M$$

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Concentration of Solutions: Molarity

### Example

A 500.0-g sample of potassium phosphate is dissolved in enough water to make 1.50 L of solution. What is the molarity of the solution?

Steps:

1. Convert mass to moles, using molar mass
2. Use formula for molarity

Molar mass of  $K_3PO_4 = (3)(39.10) + (1)(30.97) + (4)(16.00) = 212.27 \text{ g/mol (m.m.)}$

$$\text{Number of moles} = n = 500.0 \text{ g} \times \frac{1 \text{ mol}}{212.27 \text{ g}} = 2.36 \text{ mol}$$

$$\text{Molarity} = M = \frac{n}{V} = \frac{2.36 \text{ mol}}{1.50 \text{ L}} = 1.57 M \text{ (molar)}$$

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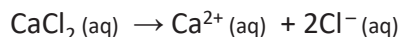
Concentration of Solutions: Molarity

### Concentration of Ions

-- given the concentration of an ionic compound

- Multiply the concentration of the compound by the number of ions in the formula.
- Applies to cations, anions, i.e. all ions

For a 0.25  $M$   $CaCl_2$  solution:



Molarities of  $Ca^{2+}$  and  $Cl^{-}$ :

$$M_{Ca^{2+}} = 1 \times 0.25 M = 0.25 M$$

$$M_{Cl^{-}} = 2 \times 0.25 M = 0.50 M$$

$$M_{ions} = (1+2) \times 0.25 M = 0.75 M$$

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Concentration of Solutions: Molarity

### Example

Which of the following solutions has the greatest number of ions?

a) 400.0 mL of 0.10  $M$   $NaCl$

$$M_{ions} = (1+1)(0.10 M) = 0.20 M$$

$$n_{ions} = M_{ions} V = (0.20) (400.0 \times 10^{-3}) = 0.080 \text{ mol}$$

b) 300.0 mL of 0.10  $M$   $CaCl_2$

$$M_{ions} = (1+2)(0.10 M) = 0.30 M$$

$$n_{ions} = M_{ions} V = (0.30) (300.0 \times 10^{-3}) = 0.090 \text{ mol}$$

c) 200.0 mL of 0.10  $M$   $FeCl_3$

$$M_{ions} = (1+3)(0.10 M) = 0.40 M$$

$$n_{ions} = M_{ions} V = (0.40) (200.0 \times 10^{-3}) = 0.080 \text{ mol}$$

d) 800.0 mL of 0.10  $M$  sucrose

$$M_{ions} = 0 \text{ mol} \quad \text{Not an electrolyte!}$$

Note that finding the greatest number of **moles** is sufficient.

Multiplying each mol by  $6.022 \times 10^{23}$  wouldn't affect the ranking

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Concentration of Solutions: Molarity

Number of moles of solute is the product of molarity ( $M$ ) and volume ( $V$ )

$$n = M \cdot V$$

↑  
Moles of solute

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## Dilution

The process of adding solvent to a concentrated solution to achieve the molarity desired for a particular solution.

- Dilution with water does not alter the numbers of moles of solute present.

$$\text{Moles of solute before dilution} = n_1 = M_1 \cdot V_1$$

$$\text{Moles of solute after dilution} = n_2 = M_2 \cdot V_2$$

$$n_1 = n_2 \implies M_1 \cdot V_1 = M_2 \cdot V_2$$

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## Concept Practice

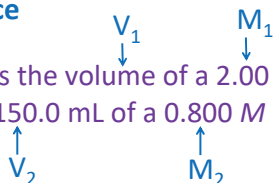
A 0.50 M solution of sodium chloride in an open beaker sits on a lab bench. Which of the following would **decrease** the concentration of the salt solution?

- Pour some of the solution down the sink drain.
- Add more sodium chloride to the solution.
- Let the solution sit in open air for a couple of days.
- Add water to the solution.
- At least two of the above would decrease the concentration of the salt solution.

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## Practice

What is the volume of a 2.00 M NaOH solution needed to make 150.0 mL of a 0.800 M NaOH solution?



$$M_1 V_1 = M_2 V_2$$

If in mL units, then  $V_1$  will also be in mL

$$(2.00 \text{ M}) V_1 = (0.800 \text{ M}) (150.0 \text{ mL})$$

$$V_1 = \frac{(0.800 \text{ M}) (150.0 \text{ mL})}{(2.00 \text{ M})} = 60.0 \text{ mL}$$

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## Types of Chemical Reactions

- Precipitation
  - Acid–Base
- Double-displacement reactions*  
Also called:  
*Double-replacement*  
*Exchange*  
*Methathesis*
- Oxidation–Reduction  
*A wide variety of reactions, including single-replacement reactions*
  - Decomposition
  - Combination (Synthesis)

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## Precipitation Reactions

A **double displacement** reaction in which a solid forms and separates from the solution.

Precipitate (*verb*): to drop out of solution

Precipitate (*noun*): the solid that forms

We will consider precipitation of ionic compounds

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Remember: When ionic compounds dissolve in water, the resulting solution contains the **separated ions**.

If ions from **two soluble ionic compounds**

**cation** from one, **anion** from the other

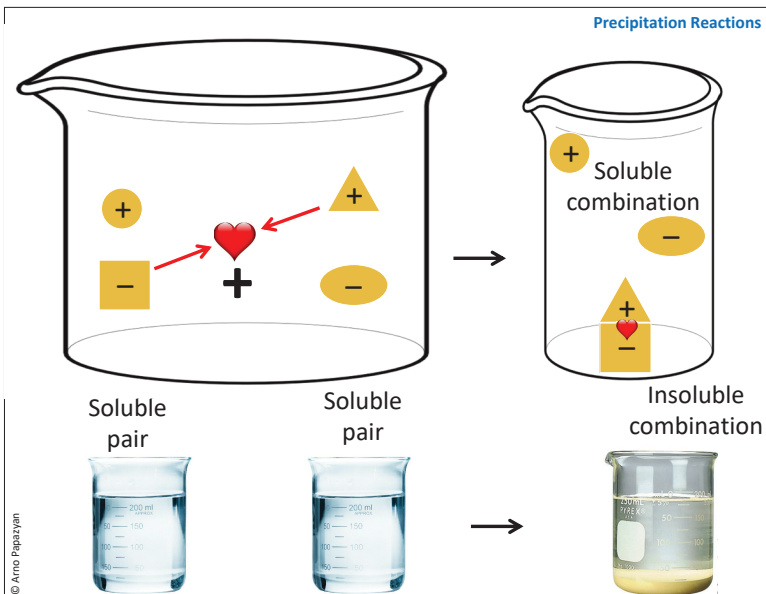
correspond to an **insoluble** compound

**they combine and precipitate**

if they are in the same solution

- it doesn't matter if there are soluble combinations
- insoluble combination wins**
  - Because these ions are "happier" together in solid form
  - That's why that combination is insoluble

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### Terms related to precipitation

- **Soluble:** solid dissolves in solution; (aq) is used in the reaction equation.
- **Insoluble:** solid does not dissolve in solution; (s) is used in reaction equation.
- **Insoluble** and **slightly soluble** are often used interchangeably. We will do that too.
  - What's called "soluble" or "insoluble" may differ slightly, depending on the industry, discipline, or preferences of an instructor
- **Marginally soluble:** considered "soluble", but barely
  - cannot have concentrated solutions

### Solubility Rules for cation-anion pairs

Before you get scared by a bunch of rules to memorize, observe that the solubility rules are ordered in decreasing solubility:

Always soluble

Always **soluble** cations (with any anion!)

➤ They never precipitate!

Always **soluble** anions (with any cation!)

➤ They never precipitate!

Less soluble as we go down the list of rules

Generally **soluble** anions  
-- with exceptions

Generally **insoluble** anions  
-- with exceptions

"Always" **insoluble**

"Others": **insoluble** anions  
-- except with "always soluble" cations

### Solubility Rules for cation-anion pairs

1. Alkali metal (**Group 1**) cations and  $\text{NH}_4^+$  are always soluble
2. **Nitrate** (& **perchlorate**, **chlorate**, **acetate**) salts are always soluble.
3. Most  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  salts are soluble (except with  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ).  
*halides*
4. Most **sulfates** are soluble (except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$ ; and  $\text{Ag}_2\text{SO}_4$  is only "marginally soluble").
5. Most **hydroxides** are insoluble or only slightly soluble.  
Exceptions: see Rule 1, and  
 $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  are somewhat soluble
6. Salts of "**other**"\* anions ( $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$  etc. we see in General Chemistry\*\*) are insoluble (exceptions: see Rule 1)

\* anions not mentioned explicitly in the rules

\*\* **not literally** all other anions known to humankind!

### Additional observations about alkaline earth ionic compound solubilities

For Group 2 metals, hydroxide & sulfate solubility trends are opposite of each other

$\text{Mg}(\text{OH})_2$  not soluble

$\text{MgSO}_4$  soluble

decreasing  
solubility of  
hydroxides

increasing  
solubility of  
sulfates

$\text{Ba}(\text{OH})_2$  soluble

$\text{BaSO}_4$  not soluble

12	<b>Mg</b>
	Magnesium
24.305	
20	<b>Ca</b>
	Calcium
40.078	
38	<b>Sr</b>
	Strontium
87.62	
56	<b>Ba</b>
	Barium
137.33	
99	

### On sulfides:

- Sulfide ion,  $\text{S}^{2-}$ , is generally **insoluble** (except, as always, with alkali metals and ammonium)
- Sulfides of Group 2 metals (alkaline earth) **are** soluble.

But:

- Sulfide ion in water is unstable in the long term.
- It slowly reacts with water to produce  $\text{H}_2\text{S}$  gas.

Because its solutions are unstable, I don't include sulfide in the "normal" rules of solubility.

### A silly way to remember the Solubility Rules

- mnemonics are about the exceptions
- exceptions are insoluble in rules 3 & 4, and soluble in later rules

### Some silly mnemonics for the Solubility Rules

- Group I and amonia "**I am**" always soluble
- perchlorate, chlorate, acetate, nitrate "**pecan**" always soluble
- Halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) generally **soluble**
  - except with  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$
  - "He lost his halo at the Silver Hog Pub"
- Sulfate ( $\text{SO}_4^{2-}$ ) generally **soluble**
  - except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$
  - "So 4 his fun, Sr. (Señor) Baca goes to the Silver Hog Pub"
- Hydroxide ( $\text{OH}^-$ ) generally **insoluble**
  - except with  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$
  - "Oh, except for Sr. Baca!"
- Compounds of other anions are **insoluble** (exception: Rule 1)  
Others are powders, except where I am

Which of the following ions forms a compound with  $\text{Pb}^{2+}$  that is **soluble** in water?

- $\text{S}^{2-}$
- $\text{Cl}^-$
- $\text{NO}_3^-$
- $\text{SO}_4^{2-}$
- $\text{Na}^+$

Precipitation reactions can be represented in three different forms:

- Molecular** equation
- Complete ionic** equation
- Net ionic** equation

### "Molecular" Equation

A better term would have been "Formula Equation" since there are no molecules around.

➤ All ions or ionic compounds

- Reactants and products shown as compounds
  - instead of the dissociated ions
- Use solubility rules to determine which compounds are aqueous and which compounds are solids.

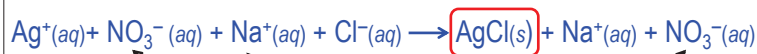


$\text{Ag}^+$  and  $\text{Cl}^-$  are not soluble together

### Complete Ionic Equation

All **soluble** substances that are ionized in aqueous solution are represented as ions.

**Only the precipitate is written as a compound**



Precipitate is not written as separate ions!

Spectator ion

Spectator ion

Spectator ions don't participate in the reaction. They appear on both sides of the reaction in the same state.



## Net Ionic Equation

- Includes only the ions that do something.  
i.e. the ions that precipitated



- No spectator ions

$\text{Na}^+$  and  $\text{NO}_3^-$  are spectator ions. They remain in solution. So they don't show up in the net ionic equation

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## Concept Practice

Write the correct “molecular” equation, complete ionic equation, and net ionic equation for the reaction between cobalt(II) chloride and sodium hydroxide.

Formula (Molecular) Equation:



Complete Ionic Equation:



Net Ionic Equation:



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## Solving Stoichiometry Problems for Reactions in Solution

- Identify the species present in the combined solution, and determine what reaction occurs.
- Write the balanced equation (net ionic or “molecular”, depending on which seems more convenient) for the reaction.
- Calculate the moles of reactants.
- Determine which reactant is limiting.
- Calculate the moles of product(s), as required.
- Convert to grams or other units, as required.

**Not really different from general stoichiometry questions!**

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## Practice

10.0 mL of a 0.30 M sodium phosphate solution reacts with 20.0 mL of a 0.20 M lead(II) nitrate solution (assume volumes add up perfectly). Will there be a reaction? If so, what is the product?

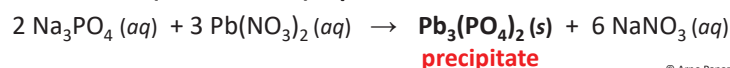
- Two solutions of ionic compounds**, typically we think of a double-displacement reaction of the “**precipitation**” kind.
- Will there be a precipitate? **If not**, the ions would still be floating around just as before the two solutions were mixed, and there would be **no reaction**.

sodium phosphate:  $\text{Na}_3\text{PO}_4(aq)$  exists as  $3\text{Na}^+(aq) + \text{PO}_4^{3-}(aq)$

**insoluble together**

lead (II) nitrate:  $\text{Pb}(\text{NO}_3)_2(aq)$  exists as  $\text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq)$

“Molecular” (or “formula”) equation:



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## Practice (continuing the same question)

10.0 mL of a 0.30 M sodium phosphate solution reacts with 20.0 mL of a 0.20 M lead(II) nitrate solution (assume volumes add up perfectly). “What mass of precipitate will form?”

$2\text{Na}_3\text{PO}_4(aq) + 3\text{Pb}(\text{NO}_3)_2(aq) \rightarrow \text{Pb}_3(\text{PO}_4)_2(s) + 6\text{NaNO}_3(aq)$   
 (0.30)(10.0x10<sup>-3</sup>) (0.20)(20.0x10<sup>-3</sup>)  
 M V M V  
 3.0x10<sup>-3</sup> mol 4.0x10<sup>-3</sup> mol  
 ↓ ÷ 2 ↓ ÷ 3  
 1.5x10<sup>-3</sup> > 1.3x10<sup>-3</sup>  
**Smaller; limiting**

Calculate number of moles from:  $n = M \cdot V$

**To find the limiting reactant:**  
Divide reactant moles by their coefficients in the equation

$4.0 \times 10^{-3} \text{ mol Pb}(\text{NO}_3)_2 \times \frac{1 \text{ mol Pb}_3(\text{PO}_4)_2}{3 \text{ mol Pb}(\text{NO}_3)_2} \times \frac{811.54 \text{ g Pb}_3(\text{PO}_4)_2}{1 \text{ mol Pb}_3(\text{PO}_4)_2} = 1.1 \text{ g Pb}_3(\text{PO}_4)_2$   
 3 mol Pb(NO<sub>3</sub>)<sub>2</sub> gives 1 mol Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

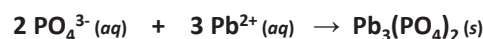
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## Practice (continuing the same question)

Initial amounts:

What is the concentration of **phosphate ions remaining** in solution, after precipitation?”

For a reacting ion, it's better to use the net ionic equation, with moles of ions



We calculated earlier the moles of reactant compounds

$$n_{\text{Na}_3\text{PO}_4} = 3.0 \times 10^{-3} \text{ mol before reaction}$$

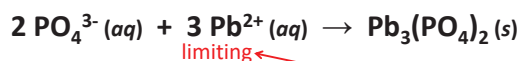
$$n_{\text{Pb}(\text{NO}_3)_2} = 4.0 \times 10^{-3} \text{ mol before reaction}$$

$$n_{\text{PO}_4^{3-}} = \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol Na}_3\text{PO}_4} \cdot 3.0 \times 10^{-3} \text{ mol Na}_3\text{PO}_4 = 3.0 \times 10^{-3} \text{ mol PO}_4^{3-}$$

$$n_{\text{Pb}^{2+}} = \frac{1 \text{ mol Pb}^{2+}}{1 \text{ mol Pb}(\text{NO}_3)_2} \cdot 4.0 \times 10^{-3} \text{ mol Pb}(\text{NO}_3)_2 = 4.0 \times 10^{-3} \text{ mol Pb}^{2+}$$

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Remaining amount = (Initial amount) – (Consumed amount)



Initial:	3.00x10 <sup>-3</sup> mol	4.0x10 <sup>-3</sup> mol
Consumed:	2.67x10 <sup>-3</sup> mol	4.0x10 <sup>-3</sup> mol
Remaining:	3.3x10 <sup>-4</sup> mol	0 mol

$$\text{mol PO}_4^{3-} \text{ consumed} = 4.0 \times 10^{-3} \text{ mol Pb}^{2+} \times \frac{2 \text{ mol PO}_4^{3-}}{3 \text{ mol Pb}^{2+}} = 2.67 \times 10^{-3} \text{ mol PO}_4^{3-} \text{ consumed}$$

[ 3 mol Pb<sup>2+</sup> consumes 2 mol PO<sub>4</sub><sup>3-</sup> ]

$$\text{mol PO}_4^{3-} \text{ remaining} = 3.00 \times 10^{-3} \text{ mol} - 2.67 \times 10^{-3} \text{ mol} = 3.3 \times 10^{-4} \text{ mol PO}_4^{3-} \text{ remaining}$$

$$V_{\text{total}} = 10.0 \text{ mL} + 20.0 \text{ mL} = 30.0 \times 10^{-3} \text{ L}$$

$$M_{\text{PO}_4^{3-}} = \frac{3.3 \times 10^{-4} \text{ mol}}{30.0 \times 10^{-3} \text{ L}} = 0.01 \text{ M}$$

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### Practice (continuing the same question)

What is the **concentration of nitrate ions remaining in solution** after the reaction is complete?

- NO<sub>3</sub><sup>-</sup> is a spectator ion.
- It remains in solution.
- So, as far as NO<sub>3</sub><sup>-</sup> is concerned, it's a **dilution** problem.
- The other solution didn't have any nitrate, so the nitrate got diluted when the two solutions combined.

We find the moles of NO<sub>3</sub><sup>-</sup> was brought in by 4.0 × 10<sup>-3</sup> mol Pb(NO<sub>3</sub>)<sub>2</sub>

$$n_{\text{NO}_3^-} = 4.0 \times 10^{-3} \text{ mol Pb(NO}_3)_2 \times \frac{2 \text{ mol NO}_3^-}{1 \text{ mol Pb(NO}_3)_2} = 8.0 \times 10^{-3} \text{ mol NO}_3^-$$

*before and after reaction*

$$M_{\text{NO}_3^-} = \frac{8.0 \times 10^{-3} \text{ mol}}{30.0 \times 10^{-3} \text{ L}} = 0.27 \text{ M}$$

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### Practice (continuing the same question)

We could also use

$$M_1 V_1 = M_2 V_2$$

if we start with the initial concentration of NO<sub>3</sub><sup>-</sup> instead of the moles of NO<sub>3</sub><sup>-</sup>

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## Acids, Bases, and Their Reactions

Acid-base “neutralization” reactions are also “double-displacement”

We touched on acids and bases earlier

- When we discussed inorganic nomenclature
- And earlier in this chapter when we considered electrolytes

We will now look at them at more depth

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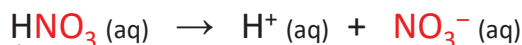
## Acids & bases as defined by Arrhenius

- Oldest acid-base concept
- Applies in aqueous solutions
- **Acids provide H<sup>+</sup> in aqueous solution**
- **Bases provide OH<sup>-</sup> in aqueous solution**
- When an acid and a base “neutralize” each other
  - H<sup>+</sup> and OH<sup>-</sup> combine to form H<sub>2</sub>O
  - Remaining parts of the acid and the base form a “salt”

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## Acids as defined by Arrhenius (“Arrhenius Acids”)

**Acid: provides H<sup>+</sup>**



“Acidic” hydrogens are attached to an anion

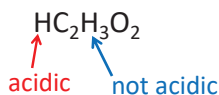
H<sup>+</sup>(aq) produced actually attaches to a water molecule, forming H<sub>3</sub>O<sup>+</sup>

H<sub>3</sub>O<sup>+</sup> (aq) is called “hydronium”

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- In the formula of an Arrhenius acid, the acidic hydrogen is written first.
- Any other hydrogens later in the formula are not acidic.



- An acid with one acidic hydrogen is “monoprotic”



- An acid with two acidic hydrogens is “diprotic”

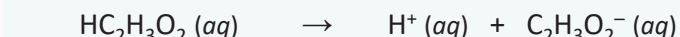


- An acid with three acidic hydrogens is “triprotic”



### Weak acids:

Only some of the weak acid molecules dissociate into ions



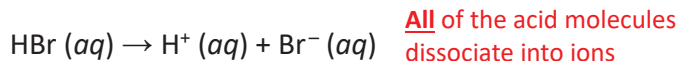
Most acetic acid molecules remain undissociated

Only some of the molecules dissociate into ions

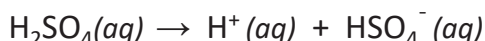
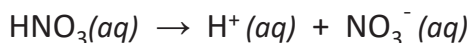
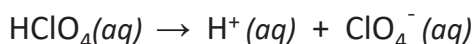
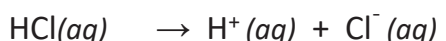
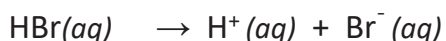
The format of a reaction equation gives the impression that all reactions are always complete. That's not true

### Strong acids:

Practically all of the strong acid molecules dissociate into  $\text{H}^+$  and the anion of the acid.



### List of “Strong Acids” we need to know:

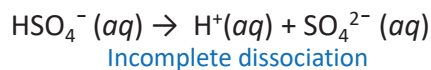


Even for a strong acid like  $\text{H}_2\text{SO}_4$ , if there is more than one acidic H, only the 1<sup>st</sup> dissociation is complete. The 2<sup>nd</sup> H doesn't dissociate easily.

Binary hydrogen compounds of halogens, except  $\text{HF} (aq)$

### “Weak Acids” we need to know:

- Any acid not listed among the “strong”
  - Some may be fairly strong, but just don't dissociate fully
- Organic acids such as acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ )
- $\text{HF} (aq)$
- $\text{H}_3\text{PO}_4$
- The anion produced after diprotic or triprotic acids, even if they are strong in releasing their first acidic H



Extracurricular knowledge, if you enjoy obscure info



### The strange case of Hydrogen Fluoride (HF)

- HF is normally regarded as a weak acid.
- In dilute aqueous solution, after HF dissociates fully,  $\text{F}^-$  forms a tight ion pair with the  $\text{H}_3\text{O}^+$  just created
  - makes  $\text{H}_3\text{O}^+$  unavailable to function as free  $\text{H}^+ (aq)$
- Actually when there isn't much water around, HF is a stronger acid than our usual “strong” acids like  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , etc.

### Nevertheless:

In the world of General Chemistry where aqueous (and not very concentrated) solutions rule, we will regard HF as a “weak acid”

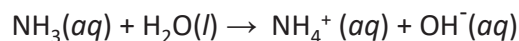
### Bases as defined by Arrhenius (“Arrhenius bases”)

#### Base: provides $\text{OH}^-$



- Bases in the Arrhenius definition act by producing  $\text{OH}^-$  ions
- Most inorganic bases are metal hydroxides, such as  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ .
- In General Chemistry it's common to assume all metal hydroxides to be strong bases.
- Ammonia ( $\text{NH}_3$ ) is the only weak base we will need to know in this course.

$\text{NH}_3$ , a molecular compound and a weak base, creates the hydroxide ion by reacting with water:

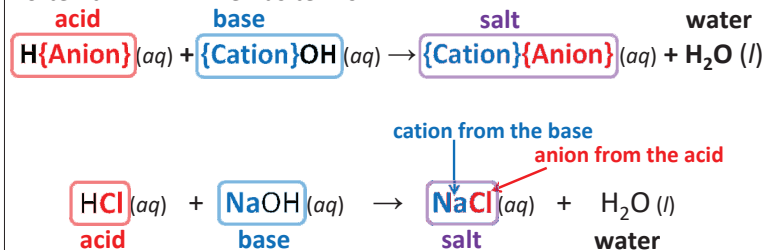


Since it is a weak base, the reaction is not complete, and most of the ammonia molecules dissolved in water remain as  $\text{NH}_3$  molecules.

When you see a reagent bottle labeled " $\text{NH}_4\text{OH}$ " or "ammonium hydroxide", it is mostly dissolved ammonia rather than the "compound"  $\text{NH}_4\text{OH}$ .

### Arrhenius acid-base reactions (Neutralization)

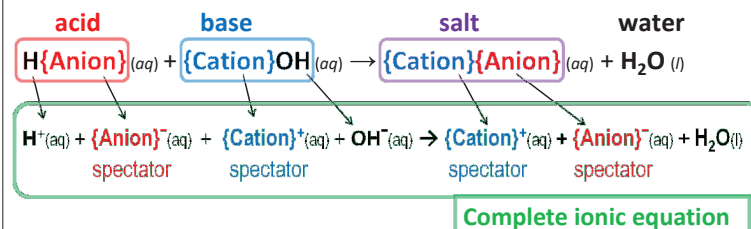
When we think about acid-base neutralization reactions, we often think in Arrhenius terms



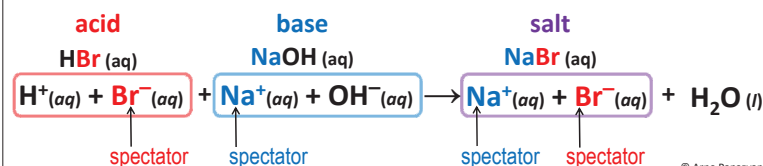
- Ions are shown only as part of compounds above.
- So it is the "molecular equation" representation of an acid-base reaction.

### Complete ionic equation for Arrhenius acid-base reactions

Acid, base, and the produced salt written as ions

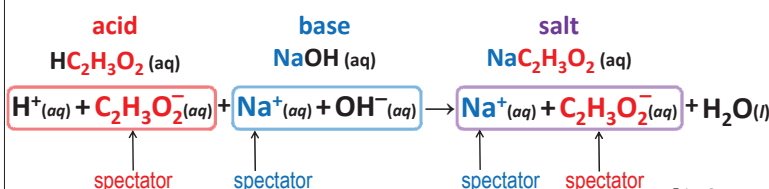


#### Example:



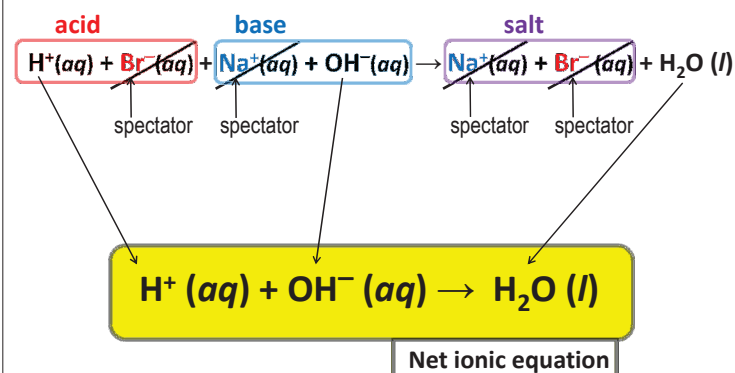
**Complete ionic equation** for an Arrhenius acid-base reaction is written the same way even if we have a weak acid and/or weak base.

- Partial dissociation of a weak acid or base into ions only applies when the acid or base is alone in solution
- In an acid/base reaction, even weak acids and bases are consumed completely (if they are limiting)



### Net ionic equation for an Arrhenius acid-base reaction

Obtained when we eliminate spectator ions from the complete ionic equation



## Performing Calculations for Acid–Base Reactions

- No different from other reactions, really.
- Often we do “titrations”
- In a titration there is no limiting reactant, by definition
- Balancing is easy because  $\text{H}^+$  and  $\text{OH}^-$  must come in equal moles
  - we can even do the stoichiometry without writing the reaction
  - but don't feel you must be able to

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## Acid–Base Titrations

**Titration:** delivery of a measured volume of a solution of known concentration (the titrant) into a solution containing the substance being analyzed (the analyte).

**Equivalence point:** exactly enough titrant added to react completely with the analyte.

➤ The ideal we try to achieve at the end of titration

**Endpoint:** the indicator changes color so you can tell the equivalence point has been reached. It's an experimental approximation of the equivalence point.

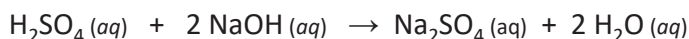
➤ What we can achieve in practice, with our indicator

**There is no limiting or excess reactant in titrations  
-- by design**

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## Practice

For the titration of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with sodium hydroxide ( $\text{NaOH}$ ), how many mL of 0.1054 M sodium hydroxide would be required to react with 1.00 L of 0.500 M sulfuric acid to reach the endpoint?



$$n_{\text{H}_2\text{SO}_4} = M_{\text{H}_2\text{SO}_4} V_{\text{H}_2\text{SO}_4} = (0.500)(1.00) = 0.500 \text{ mol H}_2\text{SO}_4$$

$$n_{\text{NaOH}} = 0.500 \text{ mol H}_2\text{SO}_4 \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} = 1.00 \text{ mol NaOH}$$

$$n_{\text{NaOH}} = M_{\text{NaOH}} V_{\text{NaOH}}$$

$$1.00 \text{ mol} = (0.1054 \text{ mol/L}) V_{\text{NaOH}}$$

$$\Rightarrow V_{\text{NaOH}} = 9.49 \text{ L} = 9.49 \times 10^3 \text{ mL}$$

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When the acid and base are used in stoichiometric amounts, such as during titrations, you can use the following formula:

$$\underbrace{\alpha M_{\text{acid}} V_{\text{acid}}}_{\text{Moles of H}^+ \text{ from acid}} = \underbrace{\beta M_{\text{base}} V_{\text{base}}}_{\text{Moles of OH}^- \text{ from base}}$$

Where  $\alpha$  = number of acidic H's in the acid formula  
 $\beta$  = number of OH's in the base formula

$\alpha = 1$  for HCl

$\alpha = 2$  for  $\text{H}_2\text{SO}_4$

$\alpha = 3$  for  $\text{H}_3\text{PO}_4$

$\beta = 1$  for KOH

$\beta = 2$  for  $\text{Ca}(\text{OH})_2$

$\beta = 3$  for  $\text{Al}(\text{OH})_3$

**Don't confuse it with the dilution formula!**

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Then the previous example:

For the titration of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) with sodium hydroxide ( $\text{NaOH}$ ), how many mL of 0.1054 M sodium hydroxide would be required to react with 1.00 L of 0.500 M sulfuric acid to reach the endpoint?

could be solved this way:

$$\alpha M_{\text{acid}} V_{\text{acid}} = \beta M_{\text{base}} V_{\text{base}}$$

$$(2) (0.500) (1.00) = (1) (0.1054) V_{\text{NaOH}}$$

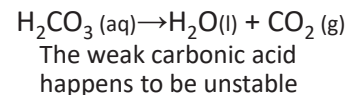
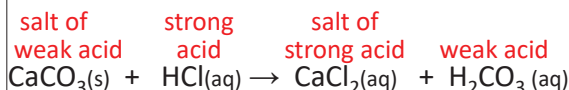
$$V_{\text{NaOH}} = 9.49 \text{ L} = 9.49 \times 10^3 \text{ mL}$$

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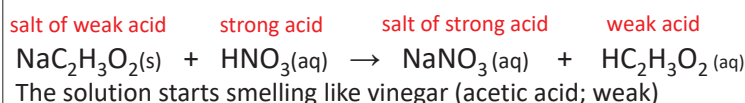
A common ingredient in “antacids” that neutralize the “stomach acid” ( $\text{HCl}(aq)$ ) is  $\text{CaCO}_3$ , a “salt”. How come?

$\text{CaCO}_3$  is a “salt”, and not a “base” in the Arrhenius sense. How does it neutralize an acid?

**Strong acids can “push” weak acids out of their salts, to form their own salt instead.**



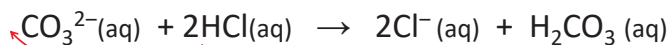
Another example:



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“Strong acids pushing weak acids out of their salts” can be understood as an acid/base reaction under a more general definition: “Bronsted-Lowry” definition of acids and bases

The anion (e.g.  $\text{CO}_3^{2-}$ ) of a weak acid (e.g.  $\text{H}_2\text{CO}_3$ ) “accepting” an  $\text{H}^+$  from a stronger acid (e.g.  $\text{HCl}$ ) is acting as a “Bronsted-Lowry” base.



We will study the more general “Bronsted-Lowry” definition of acids and bases in a later chapter.

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## Redox Reactions

### Oxidation-Reduction reactions

- One or more electrons are transferred.
- Electrons are not created or destroyed in chemical reactions:

number of **electrons gained** = number of **electrons lost**

#### Reduction

(yes, it's confusing, but there is a reason for the name)

#### Oxidation

Remember by:

Oxidation Is Loss of  $e^-$

Reduction Is Gain of  $e^-$

**OIL RIG**

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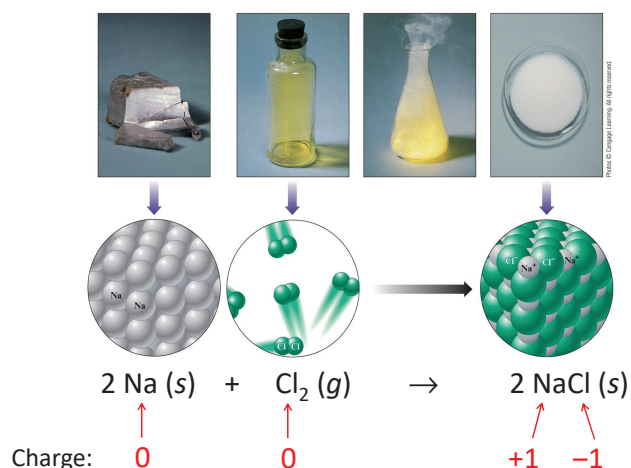
Originally “oxidation” referred literally to combining with oxygen

- The more oxygens combined with an atom, the more “oxidized” it was
- Oxygen was thought of as “oxide” in its compounds (with its  $-2$  charge)
- So, the more oxygens bonded to an atom, the more positive it was
  - To have a neutral compound
- Oxidation was then generalized to mean an increase in “charge” (and not necessarily bonding to oxygen)
- And charge itself was generalized to the more abstract “oxidation state” (which is often not an actual charge)

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## A simple redox reaction:

### Reaction of Sodium and Chlorine



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## We keep track of electron gain and loss using Oxidation numbers (Oxidation states)

- They are like charges, but not exactly
- Oxidation numbers are the charges that would exist if the atoms always formed ionic bonds, with the electron ending up on the atom that likes them more.
  - e.g. oxygen likes electrons more than hydrogen
- Oxidation numbers are often not actual charges
  - when the bonds the atom makes is not ionic
  - But charges on ions are real
- Even when they are not actual charges, the net change in oxidation states does determine the net number of electrons transferred

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## Hierarchy of Rules for Assigning Oxidation States

- The oxidation state of an atom in a free element is 0.
- The oxidation state of a monoatomic ion is equal to its charge.
- The sum of the oxidation states of all atoms in
  - a neutral molecule or formula unit is 0
  - a polyatomic ion is equal to the charge of the ion

**Sum of oxidation states in an entity = net charge**

- In their compounds,
  - Group I metals have an oxidation state of **+1**
  - Group II metals have an oxidation state of **+2**

- In their compounds, nonmetals are assigned oxidation states according to a hierarchical table. **Elements higher in the table have priority over lower entries.**

“Oxygen is  $-2$ ” can be overridden by a “higher” rule like “Fluorine is  $-1$ ”

Fluorine	$-1$
Hydrogen	$+1$
Oxygen	$-2$
Group 7A	$-1$
Group 6A	$-2$
Group 5A	$-3$

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## Examples on monatomic species

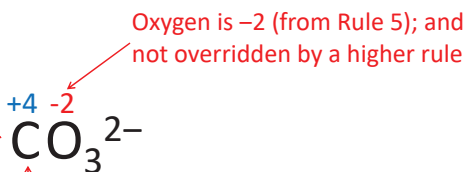
Cu(s)	Oxidation state = 0
H <sub>2</sub> (g)	Oxidation state = 0
H <sub>2</sub> (l)	Oxidation state = 0
H (g)	Oxidation state = 0
H <sup>+</sup> (aq)	Oxidation state = +1
S <sub>8</sub> (s)	Oxidation state = 0
S <sup>2-</sup> (s)	Oxidation state = -2
Fe <sup>3+</sup> (aq)	Oxidation state = +3

## Finding the oxidation states of elements in a compound or polyatomic ion

1. If you recognize a polyatomic ion, treat it separately first
2. Find the lowest priority element in compound or ion
  - Deal with it last
  - Its oxidation state will be determined by higher-priority rules
3. Assign other elements their preferred oxidation states
4. Determine the oxidation state of the last (lowest priority) element using the oxidation states of other elements and Rule 3
  - It might not agree with its "default" oxidation state (e.g. oxygen might end up with -1 or +2 instead of the "default" -2). That's completely ok.

Find the **oxidation states** for each of the elements in:

Lowest priority  
(doesn't even  
have a preferred  
oxidation state)



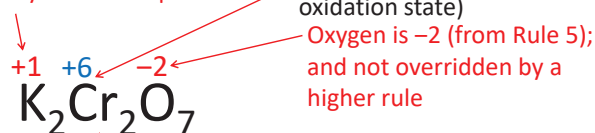
No specific rule; determined from oxygen's, using the rule "sum of oxidation numbers equals the charge of the ion"

$$(1)x + 3(-2) = -2 \implies x = +4$$

Find the **oxidation states** for each of the elements in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  
Suppose we didn't recognize the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> part as the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion and we looked at the entire formula

The oxidation state of a monatomic ion is equal to its charge (Rule 2); Group 1A metals are always +1 in compounds

Lowest priority (doesn't even have a preferred oxidation state)



No specific rule; determined from others, using the rule "sum of oxidation numbers in a compound equals zero"

$$(2)(+1) + (2)x + 7(-2) = 0 \implies x = +6$$

We got lucky because K has a high-priority oxidation state

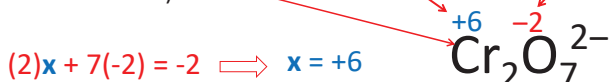
Find the **oxidation states** for each of the elements in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

Suppose we recognized the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> part as the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion

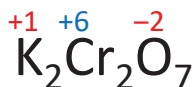
Lowest priority  
(doesn't even  
have a preferred  
oxidation state)

determined from oxygen and "sum of oxidation numbers in an ion equals ion charge"

Oxygen is -2 (from Rule 5); and not overridden by a higher rule



Then we would have determined the oxidation state of the metal as we always did. Its charge needs to neutralize the anion(s) in the formula. But we already know K is always +1.



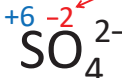
Find the **oxidation states** for each of the elements in CuSO<sub>4</sub>

Here we must recognize SO<sub>4</sub> as SO<sub>4</sub><sup>2-</sup>. Otherwise we either can't determine both Cu and S, or worse, we assign -2 to S as "higher priority" than Cu (since there is a rule for S, but there isn't one for Cu), and end up assigning +10 to Cu!

"sum of oxidation numbers in an ion equals ion charge"

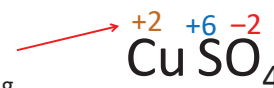
$$(2)x + 7(-2) = -2 \implies x = +6$$

Oxygen = -2 as highest priority element here

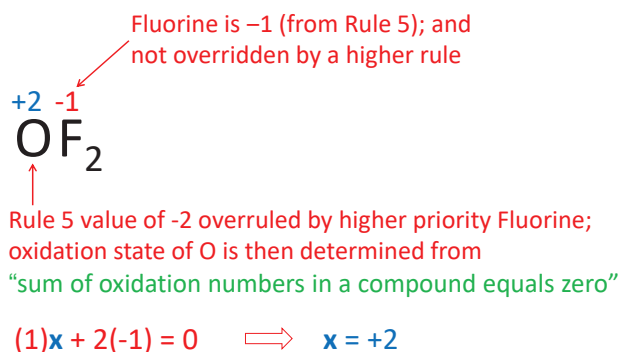


Because it needs to neutralize the 2- charge of the sulfate.

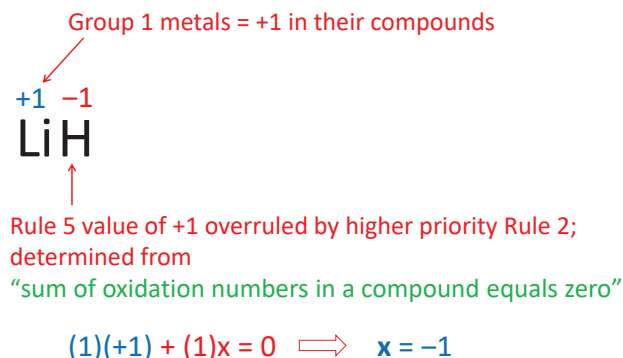
We could do this before learning about oxidation numbers!



Find the **oxidation states** for each of the elements in:



Find the **oxidation states** for each of the elements in:



### Re-stating "oxidation" and "reduction" in terms of oxidation state (instead of electrons)

**Oxidation:** increase in oxidation state (loss of electrons)

**Reduction:** decrease in oxidation state (gain of electrons)

### Oxidation and reduction are coupled

- Electrons lost by one atom must be gained by another.
- Electrons are not lost; they are transferred

Number of electrons lost = Number of electrons gained

- If there is an atom getting oxidized, there must be at least one other atom getting reduced
- If there is an atom getting reduced, there must be at least one other atom getting oxidized

### Oxidation and reduction are coupled

**Oxidized substance:** reducing agent

- If something is **oxidized**, it must be **reducing** something else

**Reduced substance:** oxidizing agent

- If something is **reduced**, it must be **oxidizing** something else

**And remember:**

- "oxidizing agent" and "reducing agent" are always **on the reactant side!**
- They **cannot be products!**

In a redox reaction:

- What we said about electrons applies equally to oxidation states.
- An increase in the oxidation state of an atom is coupled with a decrease in the oxidation state of another atom



### It's a redox reaction if ...

#### The oxidation state of any element changes in the reaction

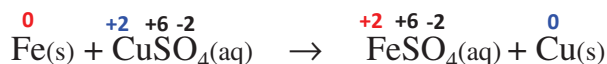
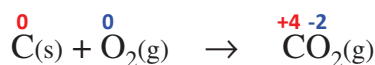
Remember: If there is an element that changed its oxidation state, there must be another that also changed in the opposite direction

It's probably a redox reaction if there is an elemental substance such as  $O_2(g)$ ,  $Cu(s)$ , etc., anywhere in the reaction

Oxidation state is zero for an elemental substance

In a compound atoms normally have nonzero oxidation states.

If the elemental substance like  $O_2(g)$ ,  $H_2(g)$ ,  $S_8(s)$ ,  $Fe(s)$  appears on either side of a reaction, it must occur in a compound on the other side of the reaction.



There are exceptions to:

*"It's probably a redox reaction if there is an elemental substance such as  $O_2(g)$ ,  $Cu(s)$ , etc., anywhere in the reaction"*

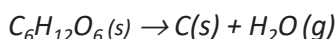
#### Exception:

When the element is in an "elemental state" on both sides of the reaction. For example, there is no redox here:



#### Exception:

When the element happens to have an average of zero oxidation state in a compound. For example, there is no redox here:

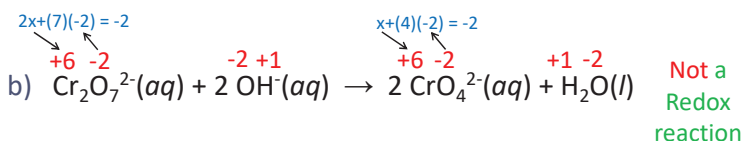
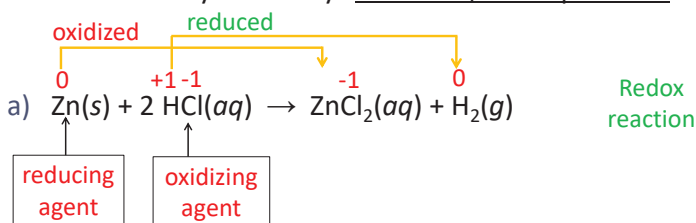


### Example

Which of the following are oxidation-reduction reactions?

Identify the oxidizing agent and the reducing agent.

Remember: they are always reactants, never products



### Single-displacement reactions

Type of redox reactions where:

- the more "active" element (metal or hydrogen) replaces the less active one.

The **more active element gets oxidized** into a cation

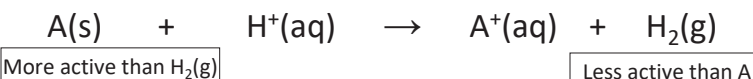
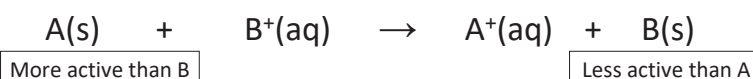
- Reduces the cation of the less active element

The **less active element gets reduced** out of its cation form into its elemental form

In a single-displacement reaction:

The **more active element gets oxidized** into a cation

The **less active element gets reduced** out of its cation form into its elemental form



A Partial Activity Series of the Elements			
Oxidation Reaction			
Strongly reducing ↑	Li → Li <sup>+</sup> + e <sup>-</sup>	These elements react rapidly with aqueous H <sup>+</sup> ions (acid) or with liquid H <sub>2</sub> O to release H <sub>2</sub> gas.	Doesn't need an acid to produce H <sub>2</sub> (g)
	K → K <sup>+</sup> + e <sup>-</sup>		
	Ba → Ba <sup>2+</sup> + 2 e <sup>-</sup>		
	Ca → Ca <sup>2+</sup> + 2 e <sup>-</sup>		
	Na → Na <sup>+</sup> + e <sup>-</sup>		
	Mg → Mg <sup>2+</sup> + 2 e <sup>-</sup>	These elements react with aqueous H <sup>+</sup> ions or with steam to release H <sub>2</sub> gas.	Needs acidic solution or steam to produce H <sub>2</sub> (g)
	Al → Al <sup>3+</sup> + 3 e <sup>-</sup>		
	Mn → Mn <sup>2+</sup> + 2 e <sup>-</sup>		
	Zn → Zn <sup>2+</sup> + 2 e <sup>-</sup>		
	Cr → Cr <sup>3+</sup> + 3 e <sup>-</sup>		
Weakly reducing ↓	Fe → Fe <sup>2+</sup> + 2 e <sup>-</sup>	These elements react with aqueous H <sup>+</sup> ions to release H <sub>2</sub> gas.	Needs acidic solution to produce H <sub>2</sub> (g)
	Co → Co <sup>2+</sup> + 2 e <sup>-</sup>		
	Ni → Ni <sup>2+</sup> + 2 e <sup>-</sup>		
	Sn → Sn <sup>2+</sup> + 2 e <sup>-</sup>		
	H <sub>2</sub> → 2 H <sup>+</sup> + 2 e <sup>-</sup>		
	Cu → Cu <sup>2+</sup> + 2 e <sup>-</sup>	These elements do not react with aqueous H <sup>+</sup> ions to release H <sub>2</sub> .	Cannot reduce H in any form to produce H <sub>2</sub> (g)
	Ag → Ag <sup>+</sup> + e <sup>-</sup>		
	Hg → Hg <sup>2+</sup> + 2 e <sup>-</sup>		
	Pt → Pt <sup>2+</sup> + 2 e <sup>-</sup>		
	Au → Au <sup>3+</sup> + 3 e <sup>-</sup>		

Need to remember only the "noble metals" that don't react with acids

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A Partial Activity Series of the Elements			
Oxidation Reaction			
Strongly reducing ↑	Li → Li <sup>+</sup> + e <sup>-</sup>		• Metals tend to lose electrons
	K → K <sup>+</sup> + e <sup>-</sup>		
	Ba → Ba <sup>2+</sup> + 2 e <sup>-</sup>		
	Ca → Ca <sup>2+</sup> + 2 e <sup>-</sup>		
	Na → Na <sup>+</sup> + e <sup>-</sup>		
	Mg → Mg <sup>2+</sup> + 2 e <sup>-</sup>		• The stronger the tendency, the more reactive the metal
	Al → Al <sup>3+</sup> + 3 e <sup>-</sup>		
	Mn → Mn <sup>2+</sup> + 2 e <sup>-</sup>		
	Zn → Zn <sup>2+</sup> + 2 e <sup>-</sup>		
	Cr → Cr <sup>3+</sup> + 3 e <sup>-</sup>		
Weakly reducing ↓	Fe → Fe <sup>2+</sup> + 2 e <sup>-</sup>		• The more active metals are more readily oxidized (stronger reducing agents)
	Co → Co <sup>2+</sup> + 2 e <sup>-</sup>		
	Ni → Ni <sup>2+</sup> + 2 e <sup>-</sup>		
	Sn → Sn <sup>2+</sup> + 2 e <sup>-</sup>		
	H <sub>2</sub> → 2 H <sup>+</sup> + 2 e <sup>-</sup>		
	Cu → Cu <sup>2+</sup> + 2 e <sup>-</sup>		• More active metal reduces the less active metal
	Ag → Ag <sup>+</sup> + e <sup>-</sup>		
	Hg → Hg <sup>2+</sup> + 2 e <sup>-</sup>		
	Pt → Pt <sup>2+</sup> + 2 e <sup>-</sup>		
	Au → Au <sup>3+</sup> + 3 e <sup>-</sup>		

More reactive (strongly reducing) element will replace the less reactive element in a compound:

$$\text{Fe(s)} + \text{CuSO}_4\text{(aq)} \rightarrow \text{Cu(s)} + \text{FeSO}_4\text{(aq)}$$

more active                      less active

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### Predicting single-replacement reactions from the activity series

You don't need to "memorize" the activity series, other than the listed "noble metals" (less active than H<sub>2</sub>(g))

If you know "noble metals" Cu, Ag, Hg, Pt, Au, you can predict:

- Noble metals don't replace H<sup>+</sup>(aq) to produce H<sub>2</sub>(g)
  - No reaction with acids
- Non-noble metals replace H<sup>+</sup>(aq) to produce H<sub>2</sub>(g)
- Non-noble metals replace noble metals from compounds by reducing them to elemental form

Consult the activity series table to predict the "competition" between noble metals or between non-noble metals

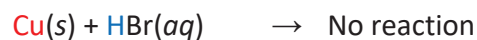
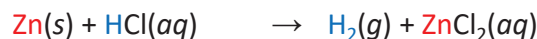
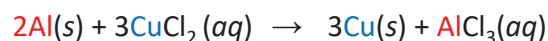
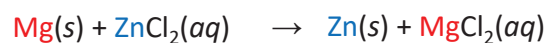
For example, Cu(s) **can** reduce Ag<sup>+</sup> ion to Ag(s)  
 Ag(s) **cannot** reduce Cu<sup>+</sup> ion to Cu(s)  
 Zn(s) **can** reduce Fe<sup>2+</sup> to Fe(s)  
 Fe(s) **cannot** reduce Zn<sup>2+</sup> to Zn(s)

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- Activity series includes Hydrogen, H<sub>2</sub>(g), because its cation is what acids produce.
- If a metal is more active than hydrogen, it "displaces" H<sup>+</sup>(aq) by reducing it to hydrogen molecules H<sub>2</sub>(g).
- Metals that are higher than hydrogen in the activity series react with (and are corroded by) acids.
  - While we "feel" that the acid is attacking the metal, actually it is the metal attacking the acid and displacing hydrogen
- "Noble metals" such as Cu, Hg, Ag, Au, Pt are less active than hydrogen, do not displace H<sup>+</sup>(aq), and are resistant to corrosion by acids.

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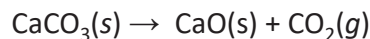
### Practice



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### Decomposition Reactions

- A compound breaks down into other compounds or elements
- It may involve oxidation-reduction, but not necessarily
- **One reactant, more than one product**



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## Synthesis (Combination) Reactions

- Opposite of Decomposition
- More than one substance (compounds or elements) combine to give one product
- It may involve oxidation-reduction, but not necessarily
- **More than one reactant, one product**

