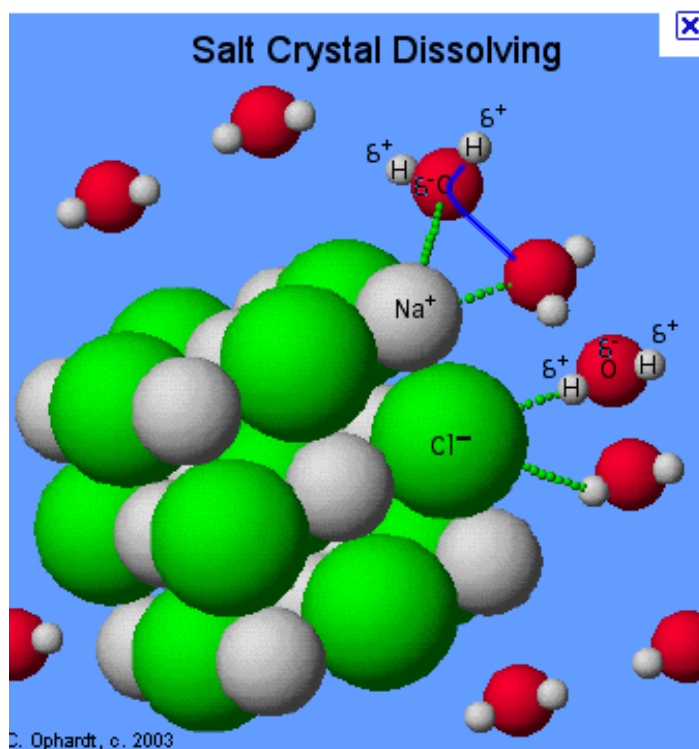
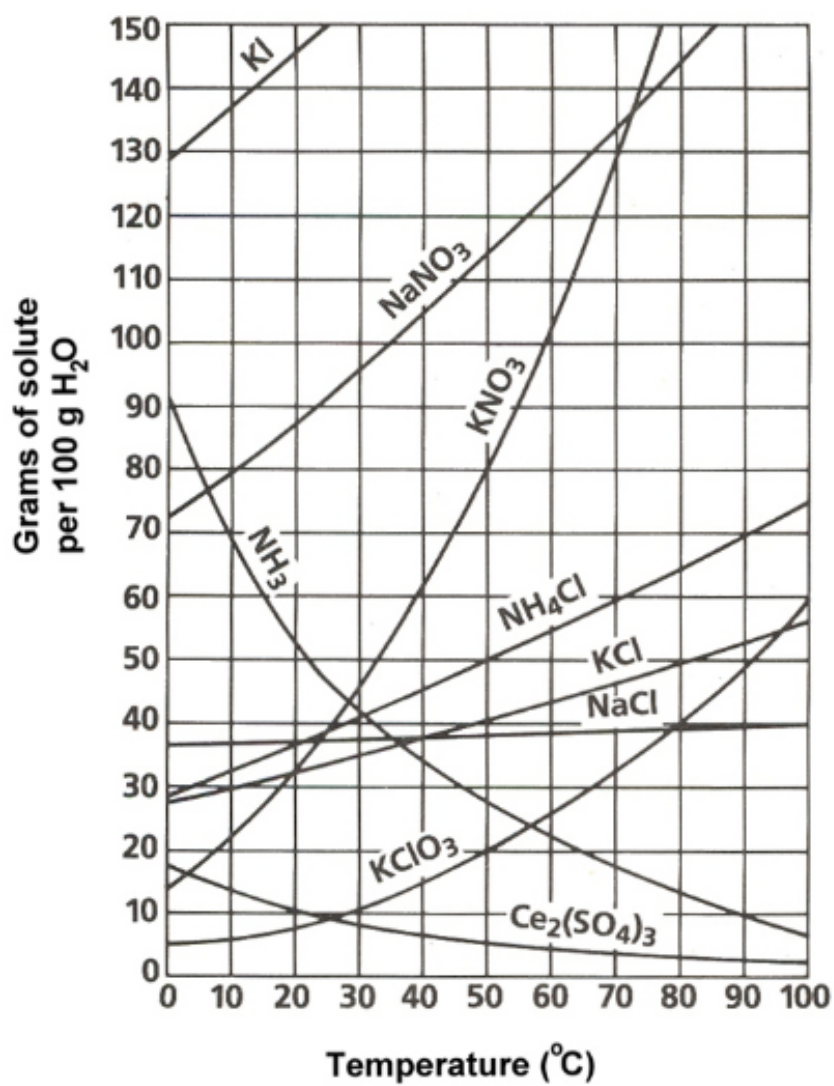


Solutions

Solutions and Solubility



Solutions play a very important role in many biological, laboratory, and industrial applications of chemistry. Of particular importance are solutions involving substances dissolved in water, or aqueous solutions. Solutions represent equilibrium systems, and the lessons learned in our last unit will be of particular importance again. Quantitative measurements of solutions are another key component of this unit.



Introduction to Solutions

1.1 Terms to Know

1.2 General Guidelines Concerning Solubility

Dissolution of NaCl in Water



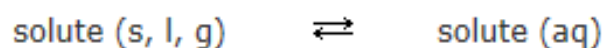
1.3 Factors Affecting Solubility

Imagine pouring a bunch of salt into a glass of water. Eventually you'll reach the point where no more salt will dissolve, and any more you add will simply sit on the bottom. Whenever a solute is dissolved in a liquid, a point is reached in which no more solute will dissolve.

This is the point of **saturation**.

Saturation is an **equilibrium system**,

which you'll remember is a dynamic state in which both the forward and reverse reactions continue but at equal rates.



The Effect of Temperature on Solubility

Generally, increasing the temperature will increase solubility of solids and liquids.

But increasing temperature will lower the solubility of gases

(the gas will escape from solution, going back to the gas phase).

The Effect of Pressure on the Solubility of Gases

The solubility of gases increases when the pressure above the gas is increased.

In other words, more gas will dissolve when pressure is increased.



2.1 Dilute & Concentrated Solutions

- A **dilute** solution is one in which there is a relatively small amount of solute dissolved in the solution.
- A **concentrated** solution contains a relatively large amount of solute.

2.2 Molarity

$$\text{Molarity} = \frac{\text{moles solute}}{\text{litre solution}}$$

Symbol for Molarity = **M**

Recall:

$$VM = \text{moles} \quad V = \text{moles}/M \quad M = \text{moles}/V$$

$$V_1M_1 = V_2M_2$$

CAUTION

Be sure to note that molarity is calculated as the total volume of the entire solution, not just volume of solvent! The solute contributes to total volume.

Here are some sample calculations.

1. Antifreeze is a solution of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$ in water. If 4.50 L of antifreeze contains 27.5 g of ethylene glycol, what is the concentration of the solution?

Pull

Pull

2. What mass of sodium carbonate, Na_2CO_3 is present in 50.00 mL of a 0.750 M solution?

Pull

3. What volume of 1.50 mol/L HCl solution contains 10.0 g of hydrogen chloride?

Full



2.3 Other Measures of Concentration

Parts per million (PPM)

A sample of water contains 25 ppm of lead ions, Pb^{2+} . Convert this concentration to molarity, $\text{mol}\cdot\text{L}^{-1}$.

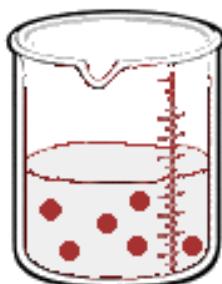
Pull

2.4 Dilutions of Standard Solutions

Imagine we have a salt water solution with a certain concentration.

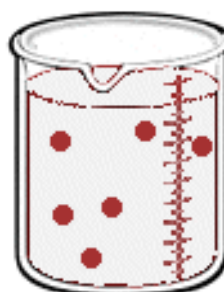
Next we'll dilute this solution - we do that by adding more water, not more salt:

Before Dilution



Solution₁

After Dilution



Solution₂

$$M_1 = \frac{\text{moles}_1}{\text{litre}_1}$$

$$M_2 = \frac{\text{moles}_2}{\text{litre}_2}$$

$$M_1 V_1 = M_2 V_2$$

where

M_1 and M_2 are the concentrations of the original and diluted solutions

and

V_1 and V_2 are the volumes of the two solutions

Example:

What volume of concentrated sulfuric acid, 18.0 M,
is required to prepare 5.00 L of 0.150 M solution by dilution with water?

Pull

Standard Solutions

It is often necessary to have a solution whose concentration is very precisely known.

Solutions containing a precise mass of solute in a precise volume of solution are called **standard solutions**.

Example:

Describe how you would prepare 500.0 mL of a 0.100 M standard solution of KNO_3

Pull

Pull

2.5 The Concentration of Ions in Solution

The solutions we work with in chemistry often involve ionic compounds and acids. Both of these produce electrolytic solutions, meaning they conduct an electrical current due to the production of ions in solution.

It will often be important for us to be able to determine the concentration of these ions

To begin, it will be important for you to be able to write balanced reactions that show how these substances break down into ions.

you will need to be able to determine:

- which ions are produced and
- in what mole ratio.

For example, sodium carbonate, Na_2CO_3 dissociates into ions as:



Notice that two mole of Na^+ ions are produced for every one mole of Na_2CO_3 .

If we have a 0.20 M solution of Na_2CO_3 ,
what will be the concentration of our two ions, Na^+ and CO_3^{2-} ?

This can easily be determined from the coefficients
in our balanced equation:

$$[\text{Na}^+] = 2 \times [\text{Na}_2\text{CO}_3] = 2 \times 0.20 \text{ M} = 0.40 \text{ M}$$

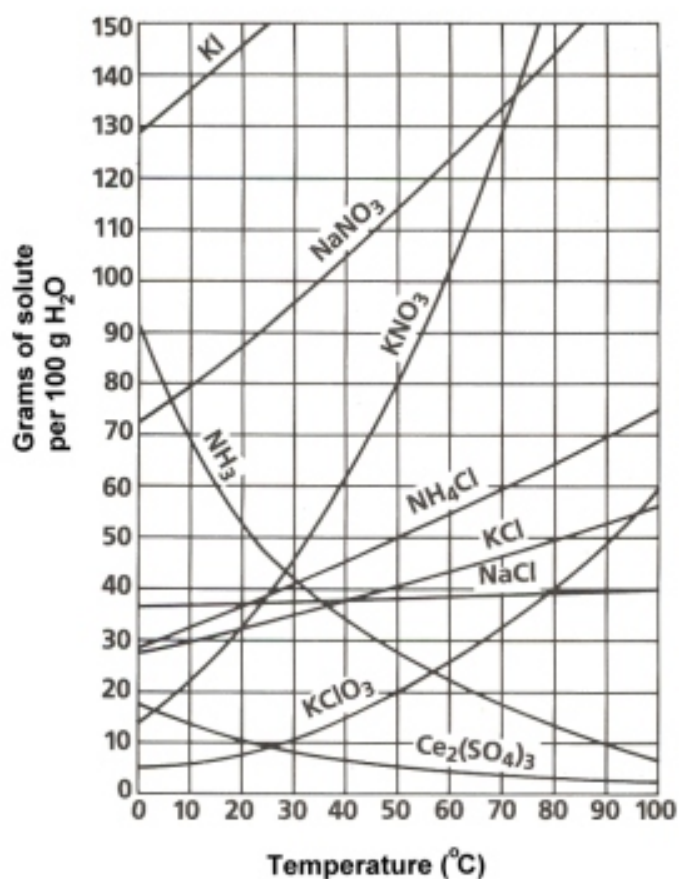
$$[\text{CO}_3^{2-}] = 1 \times [\text{Na}_2\text{CO}_3] = 1 \times 0.20 \text{ M} = 0.20 \text{ M}$$



1. Write balanced reaction equation that show which ions are produced when the following substances are dissolved in water.
 - a. lithium hydroxide
 - b. potassium phosphate
 - c. strontium chloride
 - d. chromium(III) sulfate
2. Iron(III) nitrate has a solubility of 0.15 M. Find concentration of the ions in solution.
3. Calculate ion concentrations in a 2.00 L solution containing 17.1 g aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$

3.1 Solubility Curves

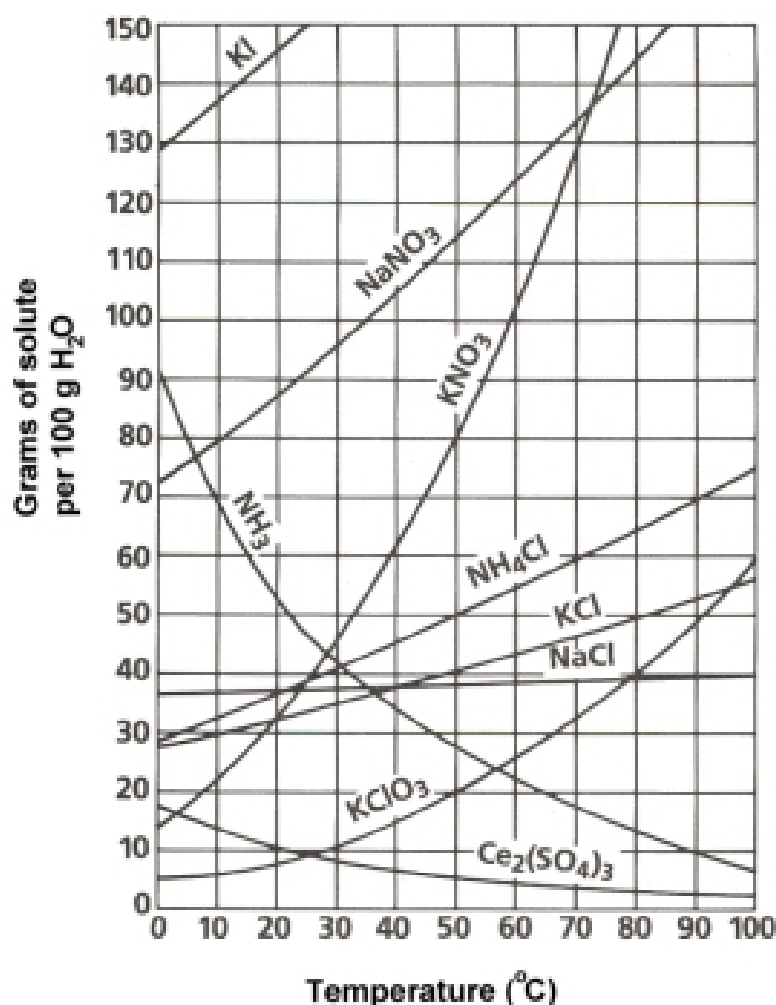
There are charts and tables available that we can use to get an idea of how soluble a certain solute is in a certain solvent.



Solubility curves, like the one shown here, tell us what mass of solute will dissolve in 100g of water over a range of temperatures.

You'll notice that for most substances, solubility increases as temperature increases.

Here's an example of reading the chart. Find the curve for KClO_3 .



At 30°C approximately 10g of KClO_3 will dissolve in 100g of water.

If the temperature is increased to 80°C,
approximately 40g of the substance will dissolve in 100g (or 100mL) of water.

note: 1 g = 1 ml

Here are some for you to try.

1. KNO_3 at 70°C
2. NaCl at 100°C
3. NH_4Cl at 90°C

Pull

Also determine which of the three substances is most soluble in water at 15°C .

On a solubility curve, the lines indicate the concentration of a **saturated solution**
- the maximum amount of solute that will dissolve at that specific temperature.

The molar concentration of the substance can be calculated,

Determine the molarity of a saturated NaCl solution at 25°C .

Pull

Values on the graph below a curve represent unsaturated solutions - more solute could be dissolved at that temperature.

Values above a curve represent supersaturated solutions, a solution which holds more solute than can normally dissolve in that volume of solvent.

Some examples:

What term - saturated, unsaturated, or supersaturated - best describes:

- a solution that contains 70g of NaNO_3 per 100 mL H_2O at 30°C
- a solution that contains 60g of dissolved KCl per 100 mL H_2O at 80°C

3.2 Solubility Tables & the Solubility of Ionic Compounds

Important Data Table			
HTM	PDF	RTF	WORD



Solubility tables allow us to predict whether a certain ionic compound will dissolve in water at 25°C. While this is not as much information as we could gain from a solubility curve, we will use a solubility table for much of what we want to cover in the remainder of this unit. There are different versions of solubility tables, but we will be working with a very basic one.

SOLUBILITY OF COMMON COMPOUNDS IN WATER

Negative Ions (Anions)	Positive Ions (Cations)	Compounds
essentially all	alkali ions	soluble
essentially all	hydrogen ion, H^+	soluble
essentially all	ammonium ion, NH_4^+	soluble
nitrate, NO_3^-	essentially all	soluble
acetate, CH_3COO^-	essentially all	soluble
chloride, Cl^-	Ag^+ , Pb^{2+} , Hg_2^{2+} , Cu^+	low solubility
bromide, Br^-	all others	soluble
iodide, I^-	all others	soluble
sulfate, SO_4^{2-}	Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Ra^{2+} , Ag^+ , Hg^{2+}	low solubility
	all others	soluble
sulfide, S^{2-}	alkali ions ⁺ , H^+ , NH_4^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ra^{2+}	soluble
	all others	low solubility
hydroxide, OH^-	alkali ions ⁺ , H^+ , NH_4^+ , Sr^{2+} , Ba^{2+} , Ra^{2+}	soluble
	all others	low solubility
phosphate, PO_4^{3-}	alkali ions ⁺ , H^+ , NH_4^+	soluble
carbonate, CO_3^{2-}	all others	low solubility
sulfite, SO_3^{2-}		

⁺ Alkali ions = Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+

Reading the table is not difficult. Have a look at the first row of data in the table. It tells us that all negative ions (anions) when combined with any alkali ion (the positive cations from the first column of the periodic table - Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+) form a compound that is soluble in water. Some examples:

- Sodium chloride, NaCl , will be a soluble compound because Na^+ is an alkali ion.
- K_3PO_4 will also be soluble because the cation (K^+) is an alkali ion.

Similarly, the second and third rows tell us that any ionic compound containing the hydrogen ion, H^+ , or ammonium, NH_4^+ , will also be soluble in water.

- Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, will be soluble in water.

Two negative anions - nitrate, NO_3^- , and acetate, CH_3COO^- - will also always form soluble solutions.

- $\text{Cu}(\text{NO}_3)_2$ is soluble
- $\text{Pb}(\text{CH}_3\text{COO})_2$ is soluble



3.3 The Solubility Product Constant, K_{sp}

Recall that for any general reaction:



an equilibrium constant expression can be defined as:

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Since saturated solutions are equilibrium systems, we can apply this mathematical relationship to solutions. We will refer to our equilibrium constant as K_{sp} , where "sp" stands for "solubility product"

For our silver sulfate saturated solution,



we can write our solubility product constant expression as

$$K_{sp} = \frac{[\text{Ag}^+]^2[\text{SO}_4^{2-}]}{[\text{Ag}_2\text{SO}_4]}$$

But remember from our earlier introduction to the equilibrium constant expression that the concentrations of solids and liquids are **NOT** included in the expression because while their *amounts* will change during a reaction, their *concentrations* will remain constant.

Therefore, we will write our solubility product constant expression for our saturated silver sulfate solution as:

$$K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$$

Please note that it is **VERY IMPORTANT** to include the ion charges when writing this equation.

Try this example:

Write the expression for the solubility product constant, K_{sp} , for $\text{Ca}_3(\text{PO}_4)_2$.

Step 1: Begin by writing the balanced equation for the reaction. Remember that polyatomic ions remain together as a unit and do not break apart into separate elements.

Step 2: Write the expression for K_{sp} :

Pull

Solubility Product Tables that give K_{sp} values for various ionic compounds are available (print this out and keep it handy). Because temperature affects solubility, values are given for specific temperatures (usually 25°C).



Recall what we learned about K_{eq}

- If K_{eq} is very large, the concentration of the products must be much greater than the concentration of the reactants. The reaction essentially "goes to completion", which all - or most of - the reactants being used up to form the products.
- If K_{eq} is very small, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent - most of the reactants remain unchanged, and there are few products produced.
- When K_{eq} is not very large or very small, then roughly equal amounts of reactants and products are present at equilibrium.

K_{sp} , which again is just a special case of K_{eq} , provides us with the same useful information:

- A low value of K_{sp} indicates a substance that has a low solubility (it is generally insoluble); for ionic compounds this means that there will be few ions in solution.

Iron(II) sulfide, FeS, is an example of a low K_{sp} : $K_{sp} = 4 \times 10^{-19}$

In a saturated solution of FeS there would be few Fe^{2+} or S^{2-} ions.

- A large value of K_{sp} indicates a soluble substance; for ionic compounds it tells us that there will be many ions in solution.

An example of a relatively large K_{sp} would be for lead(II) chloride, $PbCl_2$ which has a K_{sp} of 1.8×10^{-4}

A saturated solution of $PbCl_2$ would have a relatively high concentration of Pb^{2+} and Cl^{-} ions.

Calculations involving K_{sp}

There are several types of problems we can solve:

1. Calculating K_{sp} when concentration of a saturated solution is known.

Example The concentration of a saturated solution of BaSO_4 is $3.90 \times 10^{-5}\text{M}$. Calculate K_{sp} for barium sulfate at 25°C

Pull

Example The concentration of lead ions in a saturated solution of PbI_2 at 25°C is $1.3 \times 10^{-3} \text{ M}$. What is its K_{sp} ?

Pull

2. Calculating ion concentrations when K_{sp} is known.

Example K_{sp} for $MgCO_3$ at $25^\circ C$ is 2.0×10^{-8} . What are the ion concentrations in a saturated solution at this temperature?

Pull

Example K_{sp} for silver chromate, Ag_2CrO_4 , is 1.1×10^{-12} . Calculate the molar concentration of silver chromate in a saturated solution.

This is a much more difficult example due to the math involved.
Consider it **optional** - you will not be asked to find cube roots on an exam.

Pull



3.4 Precipitation Reactions

SOLUBILITY OF COMMON COMPOUNDS IN WATER

Negative Ions (Anions)	Positive Ions (Cations)	Compounds
essentially all	alkali ions	soluble
essentially all	hydrogen ion, H^+	soluble
essentially all	ammonium ion, NH_4^+	soluble
nitrate, NO_3^-	essentially all	soluble
acetate, CH_3COO^-	essentially all	soluble
chloride, Cl^-	Ag^+ , Pb^{2+} , Hg_2^{2+} , Cu^+	low solubility
bromide, Br^-	all others	soluble
iodide, I^-		
sulfate, SO_4^{2-}	Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Ra^{2+} , Ag^+ , Hg^{2+}	low solubility
	all others	soluble
sulfide, S^{2-}	alkali ions ⁺ , H^+ , NH_4^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ra^{2+}	soluble
	all others	low solubility
hydroxide, OH^-	alkali ions ⁺ , H^+ , NH_4^+ , Sr^{2+} , Ba^{2+} , Ra^{2+}	soluble
	all others	low solubility
phosphate, PO_4^{3-}	alkali ions ⁺ , H^+ , NH_4^+	soluble
carbonate, CO_3^{2-}	all others	low solubility
sulfite, SO_3^{2-}		

⁺Alkali ions = Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+

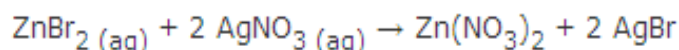
Sometimes when two aqueous solutions are mixed together a solid is produced. This solid is called a **precipitate**, and the reaction is known as a **precipitation reaction**.

Before we can predict whether or not a precipitation reaction will occur, it is useful to review a category of chemical reactions called **double displacement** (or **double replacement**) reactions. In this type of chemical reaction, we will predict what happens when solutions of two ionic compounds are mixed. If any reaction occurs, the two positive cations will exchange places.

For example:



When writing double replacement reactions it is very important that you write down the correct chemical formula for each product before balancing the entire equation.



$\text{ZnBr}_2 (\text{aq})$ is really a short-hand form for writing $\text{Zn}^{2+} (\text{aq}) + 2 \text{Br}^- (\text{aq})$

$\text{AgNO}_3 (\text{aq})$ is really short-hand for $\text{Ag}^+ (\text{aq}) + \text{NO}_3^- (\text{aq})$

It is possible that when these two solutions are mixed together every ion simply remains in solution, as separate ions. If that is the case, then no reaction actually occurs - now we just have one solution with four separate ions present.

But if we look at our [solubility table](#), we see that Ag^+ and Br^- forms an insoluble compound. These two ions will "find each other" in the solution and form an insoluble precipitate, a solid.

This occurs because the attraction between the Ag^+ and Br^- ions is stronger than the attraction between the separate ions and the polar water molecules of the solvent. **This is essentially what insoluble means.**

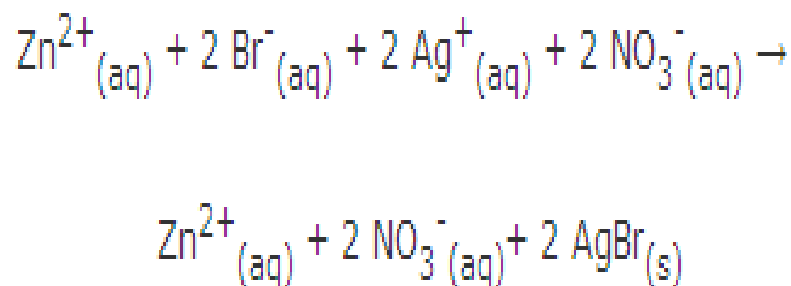
On the other hand, we see in our solubility table that Zn^{2+} and NO_3^- form a soluble compound. Thus these two ions will remain in solution, not really forming a compound at all. The attraction between the polar water molecules and the Zn^{2+} and NO_3^- ions is stronger than the attraction between Zn^{2+} and NO_3^- . **This is what soluble means.**

We now need to return to our double displacement reaction and add the physical states to the two products:



To get a clearer view of what really occurs during this reaction, we will write our solutions out in long form, rather than the short-cut form. Remember - anything that is (aq) is really present as separate ions. This, however, ONLY applies to aqueous states.

Thus we can rewrite our equation as:



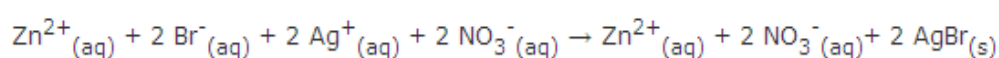
Notice that some ions are the same on both the reactant and product side of the equation, indicating that they did not undergo any change during the reaction. They were present, but did not precipitate.

Ions that are present in a reaction but do not participate are called **spectator ions**.

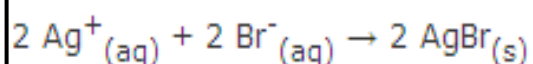
Sometimes we remove spectator ions from an equation in order to highlight what changes actually occurred during a reaction.

Reactions in which the spectator ions have been removed are called **net ionic equations**.

Therefore, for the overall equation:



The **net ionic equation** is:



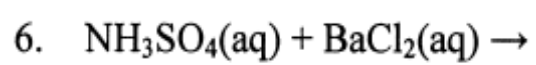
(we usually arrange items so the positive cations are listed before the negative anions.)

Write chemical, complete ionic, and net ionic equations for the following reactions that may produce precipitates. Use NR to indicate that no reaction occurs.

1. Aqueous solutions of potassium iodide and silver nitrate are mixed.

2. Aqueous solutions of ammonium phosphate and sodium sulfate are mixed.

Pull



selective precipitation

We have a solution that contains the following cations:



Of course, it isn't possible to have a beaker full of just cations - each has to be associated with a negative anion. For the sake a argument, let's say each of these cations is associated with nitrate ions, NO_3^- .

Nitrate ions are useful to use since compounds containing nitrate are ALWAYS soluble. So we really have a mixture of AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2$. The nitrate ions will remain spectator ions, so we will not need to consider them further.

We wish to isolate each ion by causing one at a time to precipitate out of solution. Once a solid precipitate forms, we can filter the solid precipitate out, leaving the other ions still in solution.

We are given the following solutions to use:



As with nitrate, you should begin to recognize that sodium ions, Na^+ , also always form soluble compounds. So Na^+ will remain as a spectator ion and we can ignore it. Thus, we are really given solutions of the following anions:



We will be adding these one at a time to our cation mixture. We need to determine the order that we add these solutions so that we have ONE AND ONLY ONE precipitate occur with the first addition. This will remove one of the cations from the solution. We then continue until all cations are isolated from each other.

To help us analyze our situation, we'll prepare a chart, with the cations we need to separate along one axis and anions along the other axis:

	Ag^+	Cu^{2+}	Mg^{2+}
S^{2-}			
Cl^-			
OH^-			

Precipitate #1 --

Precipitate #2 --

Precipitate #3 --

Pull

To summarize our solution:

1. First add NaCl to remove Ag^+ , forming the precipitate $\text{AgCl}_{(s)}$
2. Second, add Na_2S to remove Cu^{2+} , forming $\text{CuS}_{(s)}$
3. Last add NaOH to remove Mg^{2+} , forming $\text{Mg}(\text{OH})_{2(s)}$



