

I. Solubility Rules

First things first, you have to memorize the basic solubility rules in order to (1) know which salts dissociate (break apart) in solution and (2) which ions combine to form precipitates when you mix solutions. The other part of this is that if you are given the name of a compound, you have to know the associated chemical formula. This means that it is assumed that you've memorized most of the standard polyatomic ions. So, here we go with precipitation reactions.

Here are the general rules for things that are **SOLUBLE** (there are exceptions but if you remember these, you'll be able to predict if a salt is soluble most of the time):

1. All salts comprised from alkali metals (Group I), nitrate (NO_3^-), and ammonium (NH_4^+), chlorate (ClO_3^-), and bicarbonate (HCO_3^-) are soluble in water. It doesn't matter what the other anion or cation is in the salt. So get that, you cannot form a precipitate by combining a cation or anion with any of these ions. Repeat the rules to yourself:
 - All Group I metal salts are soluble
 - All nitrates are (NO_3^-) soluble
 - All ammonium (NH_4^+) salts are soluble
 - All chlorates (ClO_3^-) are soluble
 - All bicarbonates (HCO_3^-) are soluble
2. Almost all sulfates (SO_4^{2-}) are soluble, except BaSO_4 , CaSO_4 , PbSO_4 , HgSO_4 , and Ag_2SO_4 .
3. Almost all chlorides, iodides, and bromides are soluble, except precipitates containing mercury(I) (Hg_2^{2+} , not Hg^{2+} !!), Pb^{2+} , or Ag^+ .

Here are the general rules for things that are **INSOLUBLE** (again, there are exceptions but if you remember these, you'll be able to predict if a salt is insoluble most of the time):

1. All salts comprised from Phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), carbonates (CO_3^{2-}), sulfides (S^{2-}) and sulfites (SO_3^{2-}) are insoluble with everything **except the cations listed above** (Group I metals and ammonium). Hydroxides (OH^-) are also insoluble although $\text{Ba}(\text{OH})_2$ is somewhat soluble. Let's do the same drill, repeat these rules to yourself:
 - All Phosphates (PO_4^{3-}) are insoluble except for Group I metal and ammonium salts
 - All chromates (CrO_4^{2-}) are insoluble except for Group I metal and ammonium salts
 - All carbonates (CO_3^{2-}) are insoluble except for Group I metal and ammonium salts
 - All sulfides (S^{2-}) are insoluble except for Group I metal and ammonium salts
 - All sulfites (SO_3^{2-}) are insoluble except for Group I metal and ammonium salts
 - All hydroxides (OH^-) are insoluble except for Group I metal, barium and ammonium salts
2. Ag^+ and Pb^{2+} are insoluble with everything except the anions listed as always soluble (nitrate (NO_3^-), chlorate (ClO_3^-) and bicarbonate (HCO_3^-)).

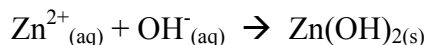
II. The Net Ionic Equation

- A **molecular equation** shows molecules. It shows no dissociation.
- A **complete ionic equation** shows molecules or ions that participate in the reaction including spectator ions.
- A **net ionic equation** shows only molecules or ions that participate in the reaction. **It does not include spectator ions.**

If you are asked to present the **Net Ionic Equation**, remember to **always eliminate spectator ions** (ions that don't take part in the reaction). Precipitation reactions are pretty much based on putting ionically bonded molecules (**salts**) into water, knowing the solubility rules to determine if they dissociate into a solvated cation and anion and then taking a look at what other cations and anions are in solution to see if an insoluble molecule forms when they run into each other. (Try to say that sentence without taking a breath)

For example: Solutions of zinc nitrate and sodium hydroxide are mixed. Write the net ionic equation.

- First, ask yourself if each of these salts is dissociated in solution before mixing.
- In this case, all nitrates are soluble so solution #1 is $(\text{Zn}^{2+}_{(\text{aq})}, \text{NO}_3^{-}_{(\text{aq})})$ and all group I metal salts are soluble so solution #2 is $(\text{Na}^{+}_{(\text{aq})}, \text{OH}^{-}_{(\text{aq})})$.
- Next, take a look at all the cations and anions floating around in solution after you mix them and ask yourself, “is there a pair that will precipitate out when they run into each other?”
- Knowing the solubility rules, you are able to say to yourself “hydroxide salts are insoluble and the zinc cation is not one of the exceptions to that rule” therefore, the net ionic equation is:

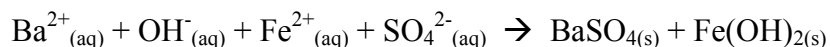


Notice that NO_3^{-} and Na^{+} were not included in the net ionic equation because **they are spectator ions.

Here's another example where you form two precipitates based on mixing solutions containing two soluble salts.

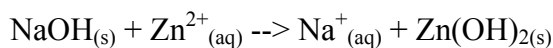
Solutions of barium hydroxide and iron (II) sulfate are mixed. Write the net ionic equation.

- Now, both of these are soluble in solution. Barium hydroxide is one of the exceptions to the general rule that hydroxides are insoluble and all sulfates are soluble except for those made with the cations barium, calcium, lead, mercury (II) and silver.
- Upon mixing these two solutions, two precipitates are formed and there aren't any spectator ions.
- The barium cations run into sulfate and fall out of solution and the iron (II) cations run into hydroxide and fall out of solution. The net ionic equation is therefore:



Two notes for those of you preparing to sit for the AP[®] exam.

1. Be careful to read the phase of what is mixed. A good number of reactions will say something like, “solid sodium hydroxide is put into a solution of zinc nitrate.” Now, you have to recognize that the sodium hydroxide, although soluble in water, is in the solid phase as a reactant. This is how you get something like the sodium cation in a net ionic equation. The net ionic equation in this case would be:



2. You do not have to balance net ionic equations for the reactions part of the exam. You just need to have the correct reactants and products with subscripts for pure phases. You are not required to put an aqueous subscript for ions in these equations because it is implied.

III. Precipitating Agents

Precipitating agents are chemicals that go into solution and in a manner of speaking, indirectly cause a precipitate to form. This happens because the precipitating agent reacts with water to form an anion that then can react with solvated cations to form a precipitate. Know these three:

- **Ammonia, NH₃:** Ammonium reacts with water to form OH⁻ and all hydroxides (OH⁻) are insoluble except for Group I metal, barium and ammonium salts.
- **Hydrogen Sulfide, H₂S:** Hydrogen sulfide is a weak acid. To some small degree it will completely dissociate and introduce sulfide ions, S²⁻, into solution. All sulfides (S²⁻) are insoluble except for Group I metal and ammonium salts. As the sulfide ion is used up for the formation of the precipitate, more will be supplied in order to satisfy the equilibrium for the complete dissociation of hydrogen sulfide (Le Chatelier's Principle).
- **Sulfur Dioxide, SO₂:** in basic solution, sulfur dioxide forms sulfites, SO₃²⁻. All sulfites (SO₃²⁻) are insoluble except for Group I metal and ammonium salts

IV. Complex Ions

As opposed to precipitating agents, there are molecules that cause the solvation of the ions that exist in equilibrium with an insoluble species. Complex ions are formed when a metal cation (typically Cu²⁺, Ag⁺, Zn²⁺, Al³⁺, Cd²⁺, Hg²⁺ and Co²⁺) form what's called a **coordinate covalent bond** with a molecule or ion like OH⁻, NH₃, H₂O or CN⁻. Notice that each of these molecules has at least one lone pair of electrons. For a complex ion, the **metal** is in the center and the species that bonds to it with coordinate covalent bond is called a **ligand**. The atom in the ligand that is bound directly to the metal atom is called the **donor atom** and the **coordination number** is defined as the number of donor atoms bonded to the metal in the complex (this is just a little refresher on complex ions, now back to how this is germane to solubility.) What happens when you introduce a ligand into a solution that contains a metal ion with which it will form a complex ion is that you now have **two competing equilibrium processes**. On the one hand, the complex ion is being formed (the formation constants, K_f, are big numbers--these are very favorable reactions) and since the molecule formed is an ion, it readily dissolves in water (remember like dissolves like: water is polar, it likes ions). The competing process is that the metal ions that are also in equilibrium with the insoluble species. As these metal ions are eaten up by the ligands and solvated in the form a complex ion, some of the precipitate dissolves back into solution—you still need to satisfy the solubility product constant, K_{sp}. Over a period of time, if enough of the ligand is available to essentially keep forcing the concentration of the metal cation to zero, all of the precipitate will break apart and you'll have two solvated species. One is the complex ion and the other is the anion from the original insoluble species.

Here are some common examples:

A. Ammine Complexes

1. Silver Chloride: $\text{AgCl}(s) + 2 \text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+ + 2 \text{Cl}^-$
2. Zinc Hydroxide: $\text{Zn}(\text{OH})_2(s) + 4 \text{NH}_3 \rightarrow \text{Zn}(\text{NH}_3)_4^{2+} + 2 \text{OH}^-$

B. Cyanide Complexes

1. Silver cyanide: $\text{AgCN}(s) + \text{CN}^- \rightarrow \text{Ag}(\text{CN})_2^-$
2. Copper(I) cyanide: $\text{CuCN}(s) + \text{CN}^- \rightarrow \text{Cu}(\text{CN})_2^-$

C. Hydroxide Complexes (mixed with a concentrated base)

1. Aluminum Hydroxide: $\text{Al}(\text{OH})_3(s) + \text{OH}^- \rightarrow \text{Al}(\text{OH})_4^-$
2. Aluminum oxide: $\text{Al}_2\text{O}_3(s) + \text{OH}^- \rightarrow \text{Al}(\text{OH})_4^-$ (not balanced...
water also a reactant)
3. Zinc Hydroxide: $\text{Zn}(\text{OH})_2(s) + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-}$

D. Aqua Complexes

1. Aluminum: $\text{Al}(\text{NO}_3)_3(s) + 6 \text{H}_2\text{O} \rightarrow \text{Al}(\text{H}_2\text{O})_6^{3+} + 3 \text{NO}_3^-$
2. Iron(III): $\text{Fe}(\text{NO}_3)_3(s) + 6 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{H}_2\text{O})_6^{3+} + 3 \text{NO}_3^-$