

# Solubility of precipitations

**Precipitation** is the process of a compound coming out of solution. It is the opposite of dissolution or solvation. In dissolution, the solute particles separate from each other and are surrounded by solvent molecules. In precipitation, the solute particles find each other and form a solid together. This solid is called the precipitate or sometimes abbreviated "ppt".

### Solubility Equilibria

Precipitation and dissolution are a great example of a dynamic equilibrium. Any time there is a solution with a little bit of solid solute in it, both processes will be happening at once. Some molecules or ions will leave the solid and become solvated, and some solvated solute particles will bump into the solid and get stuck there. The rates of the 2 processes determine the overall effect: if precipitation happens faster, then a lot of solid can come out of the solution very quickly. If dissolution happens faster, then the solid will dissolve. As the solution becomes more concentrated, the rate of precipitation will increase and the rate of dissolution will decrease, so that eventually the concentration will stop changing, and this is equilibrium. When equilibrium is reached, the solution is **saturated**, and that concentration defines the **solubility** of the solute. Solubility is the maximum possible concentration, and it is given in M, g/L, or other units. Solubility changes with temperature, so if you look up solubility data it will specify the temperature.

#### **Precipitation Reactions**

Precipitation can happen for various reasons, such as that you cooled a solution, or removed some solvent by evaporation, or both. (This is often used as a way to purify a compound.) You can also have a precipitation reaction, when you mix two solutions together and a new combination of ions is **super-saturated** in the combined solution. For example, maybe you mixed a solution of silver(I) nitrate and sodium chloride. Silver(I) chloride is very insoluble, so it will precipitate, leaving soluble sodium nitrate in solution. Precipitation reactions can be a good way to prepare a salt you want from some other salts with the right anion and cation. Precipitation reactions can also be used to detect the presence of particular ions in solution. For instance, you might test for chloride, iodide and bromide in an unknown solution by adding silver(I) ions and looking for precipitation.

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Figure (1) precipitation stages

(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution.

(b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid.

(c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature.

(d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

# Solubility Rules and Identifying a Precipitate

- 1. Alkali metal (Group IA) compounds are soluble.
- 2. Ammonium (NH<sub>4</sub><sup>+</sup>) compounds are soluble.
- 3. Nitrates ( $NO_{3^{-}}$ ), chlorates ( $ClO_{3^{-}}$ ), and perchlorates ( $ClO_{4^{-}}$ ) are soluble.
- 4. Most hydroxides (OH<sup>-</sup>) are insoluble. The exceptions are the alkali metal hydroxides and Ba(OH)<sub>2</sub>. Ca(OH)<sub>2</sub> is slightly soluble.



- 5. Most chlorides (Cl<sup>-</sup>), bromides (Br<sup>-</sup>) or iodides (I<sup>-</sup>) are soluble. The exceptions are those containing Ag<sup>+</sup>, Hg<sup>+2</sup>, and Pb<sup>+2</sup>.
- 6. Carbonates ( $CO_3^{-2}$ ), phosphates ( $PO_4^{-3}$ ) and sulfides ( $S^{-2}$ ) are insoluble. The exceptions are the alkali metals and the ammonium ion.
- 7. Most sulfates (SO4<sup>-2</sup>) are soluble. CaSO4 and Ag2SO4 are slightly soluble. BaSO4, HgSO4 and PbSO4 are insoluble.

## Writing Equations for Precipitation Reactions

Chemists may write equations in different ways to emphasize the important parts. For instance, we might write an equation like this, which describes mixing 2 solutions of different soluble salts and getting a precipitate:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

Alternately, we might write the same reaction just focusing on the part that forms the precipitate, and leaving out the **spectator ions** that don't really do anything, just stay in solution:

$$Ag^+(aq)+Cl^-(aq)
ightarrow AgCl(s)$$

#### What Determines Solubility?

**Solubility**: The amount of a substance that will dissolve in a given amount of a solvent to give a saturated solution under specified conditions.

Solubility depends on the relative stability of the solid and solvated states for a particular compound. For instance, if it has very strong interactions between molecules or ions in the solid state, then it won't be very soluble unless the solvation interactions are also very strong. (Ionic salts are a good example: usually they have strong interactions in the solid and solvated states.) If the interactions in the solid are weak, the compound can still be insoluble in polar solvents if the interactions with the solvent are weaker than the Coulomb interactions of the



solvent molecules with other solvent molecules. (This is why wax is insoluble in water: it is non-polar, so the wax-wax interactions are weak, but the wax-water interactions are weaker than the water-water interactions.) We can't explain what makes these interactions strong or weak well until after we study chemical bonding, but in general ionic compounds with larger charges on the ions and smaller ions are less soluble, because they can have stronger Coulomb interactions in the solid.

### **Factors Affecting Solubility**

1. Solid Solubility and Temperature: Solubility often depends on temperature; the solubility of many substances increases with increasing temperature. For many solids dissolved in liquid water, the solubility increases with temperature.

The increase in kinetic energy that comes with higher temperatures allows the solvent molecules to more effectively break apart the solute molecules that are held together by intermolecular attractions. The increased vibration (kinetic energy) of the solute molecules causes them to dissolve more readily because they are less able to hold together.

• **Kinetic energy:** The energy possessed by an object because of its motion, equal to one half the mass of the body times the square of its velocity.

2. Gas Solubility and Temperature: Solubility of a gas in water tends to decrease with increasing temperature, and solubility of a gas in an organic solvent tends to increase with increasing temperature. Gases dissolved in water become less soluble with increasing temperature. Gases dissolved in organic solvents become more soluble with increasing temperature. Dissolved oxygen in water is important to the survival of fish, so increasing temperature (and therefore less dissolved oxygen in water) can cause problems for fish.

## 3. Gas Solubility in Organic Solvents

The trend that gas solubility decreases with increasing temperature does not hold in all cases. While it is in general true for gases dissolved in water, gases dissolved in organic solvents tend to become more soluble with increasing temperature. There are several molecular reasons for the change in solubility of gases with increasing temperature, which is why there is no one trend independent of gas and solvent for whether gases will become more or less soluble with increasing temperature.

#### 4. Solubility and Pressure

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Increasing pressure will increase the solubility of a gas in a solvent.