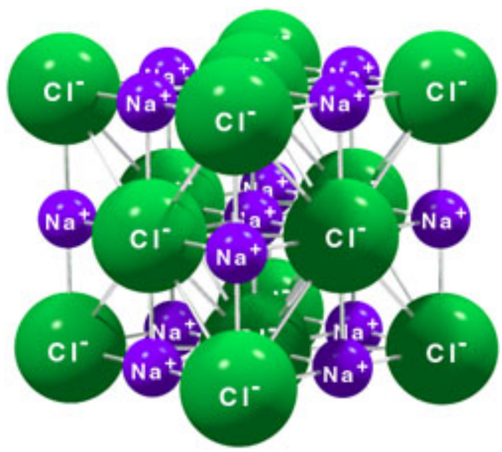
Solubility Equilibria

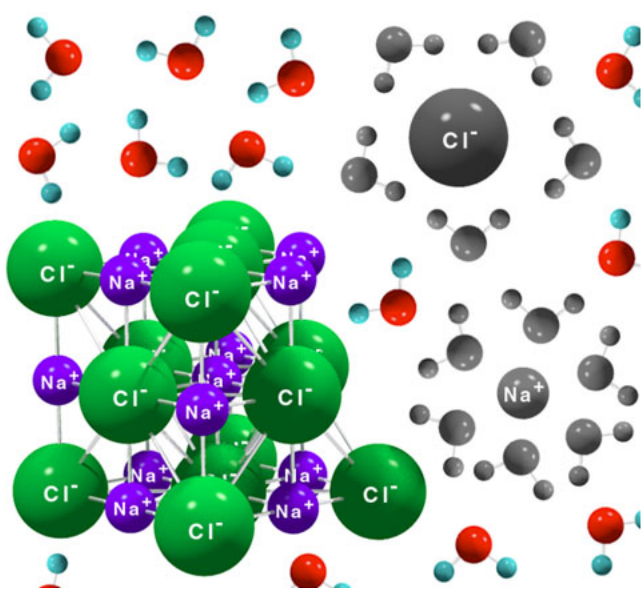
Many solids dissolve in water. The dissolving of ionic solids in water is a very important chemical process. When an ionic compound is placed in water, it forms an aqueous solution with specific and important characteristics.

Dissolution and Precipitation

Ionic substances have characteristic crystal structures made up of ions. Although the ions have positive and negative charges, the overall structure is neutral because the positive charges are exactly balanced by the negative charges.

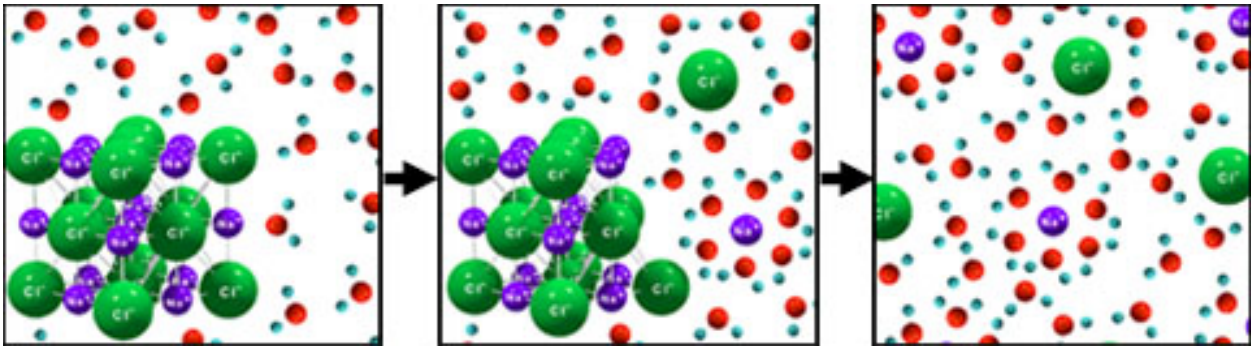


In solution, these ions separate from each other. When an ionic solid, such as $NaCl$ dissolves in water, the positive ends of water molecules are attracted to the Cl^{-} ions, and the negative ends are attracted to the Na^{+} ions. The attraction is strong enough to draw the ions away from the crystal surface and into solution.



The actual separation of ions that occurs when an ionic compound dissolves is called **dissociation**. As ions move into the solution surrounded by a shell of water molecules, other ions are exposed and attracted away from the crystal. In this manner, the crystal continues to dissolve and ions become uniformly distributed in the solution.

The process in which an ionic solid dissolves in a polar liquid is called **dissolution**, and is illustrated below.



The dissolution of $NaCl(s)$ increases the concentrations of both Na^+ and Cl^- ions in solution.

Just as we did with chemical reactions, we can write an equation to show the dissolution of an ionic solid placed in water. The equation for $NaCl(s)$ is shown below.

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

Recall that the symbol (*aq*) denotes an aqueous solution. Only dissociated substances are written as ions in equations. Gases and pure liquids or solids are represented by complete formulas, even when in aqueous solutions.

If a Na^+ ion or a Cl^- ion collides with the surface of $NaCl(s)$, the ion may lose its shell of water molecules and rejoin the solid state. At that spot on the surface of the solid, a small imbalance of electric charge is created. An oppositely charged ion in the solution is then quickly attracted to the spot. When the second ion collides with the solid and sheds its water molecules, electrical neutrality is restored and both ions regenerate part of the solid.

The process in which ions leave a solution and regenerate an ionic solid is called **precipitation**. The solid formed during precipitation is known as the **precipitate**.

Dissolution and precipitation are opposite processes. The precipitation of $NaCl(s)$ lowers the concentration of Na^+ and Cl^- ions in the solution. The equation showing the precipitation of ions from a solution is the reverse of the dissolution equation, and is shown below.

$$NaCl(s) \leftarrow Na^+(aq) + Cl^-(aq)$$

When an ionic solid such as $NaCl(s)$ is placed in pure water, dissolution begins. Over time, the concentrations of Na^{+} and Cl^{-} ions increase as more ions escape from the solid state and enter the solution.

Recall that every substance has its own solubility, which is the maximum quantity of that substance that will dissolve in a given solvent. At some point, no additional $NaCl(s)$ can dissolve because the solution is saturated with ions. Although ions continue to dissolve into solution, other ions begin to precipitate out of solution.

When dissolution and precipitation are occurring at the same rate, $[Na^{+}]$ and $[Cl^{-}]$ have constant values. The solution is said to have attained **solubility equilibrium** because the saturated solution of ions and the remaining solid are in chemical equilibrium.

As with earlier reactions, a solubility equilibrium equation can be written to incorporate both dissolution and precipitation. Two arrows, pointing in opposite directions, are used to indicate a reversible reaction. The solubility equilibrium equation for sodium chloride is

$$NaCl(s) \Leftrightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Example 1
Write the equations for the solubility equilibria established by

a) silver chloride in water.

b) calcium chloride in water.

Notice that these equations must be balanced. When an equation containing ions is balanced, both sides are electrically neutral.

The Solubility Product

Some ionic compounds are more soluble than others. In fact, much of what chemists know about aqueous solutions of ionic substances came from experiments with solids that were believed to be insoluble in water. These experiments proved that even seemingly insoluble solids are actually slightly, or sparingly, soluble in aqueous solutions. Silver chloride, for example, is sparingly soluble as opposed to sodium chloride, which is highly soluble.

Recall the law of mass action, which states that the concentrations of reactants and products at equilibrium are always related to a constant as described by the equilibrium expression. Solubility equilibria can also be described by equilibrium expressions. As an example, consider $AgCl$.

$$AgCl(s) \Leftrightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

The equilibrium expression for this reaction would be

$$K_{sp} = \left[Ag^{+}\right]\left[Cl^{-}\right]$$

Recall that $AgCl(s)$ is not included in the equilibrium expression because it is a pure solid, and the concentrations of pure solids and liquids are considered constant. Also, notice that the subscript of the equilibrium constant has changed. The constant K_{sp} is called the solubility product constant, or simply the **solubility product**.

Example 2
Write the expression for the solubility product for $Fe(OH)_3$.

Worksheet

1. Write the expression for the solubility product for Ag_2CrO_4.
2. Write the expression for the solubility product for PbI_2.
3. Write the expression for the solubility product for $SrSO_4$.
4. Write the expression for the solubility product for $MgCl_2$.
5. Write the expression for the solubility product for $CaSO_4$.
6. Write the expression for the solubility product for $Mg(OH)_2$.
7. Write the expression for the solubility product for $SrCO_3$.
8. Write the expression for the solubility product for $Cu_3(PO_4)_2$.