The Solubility of Salts
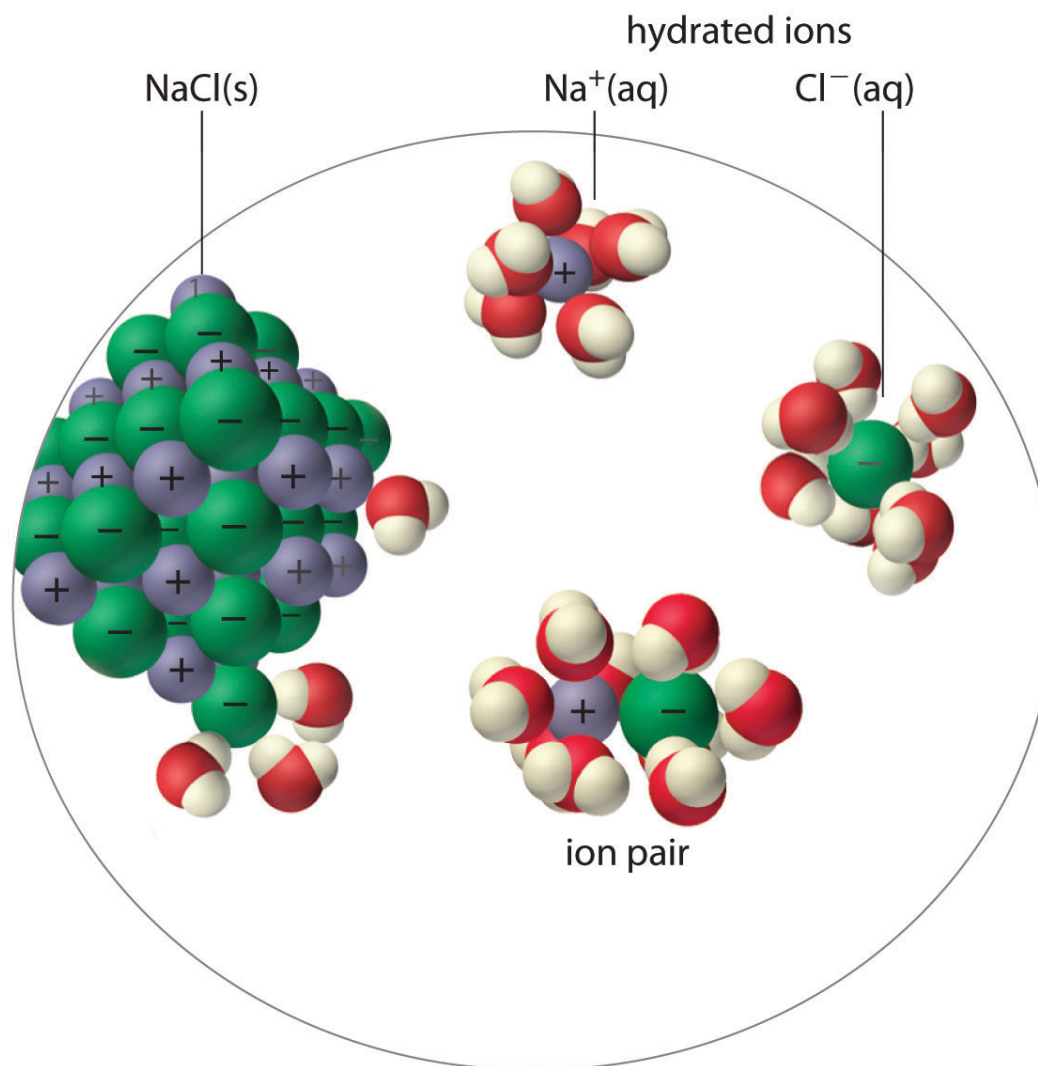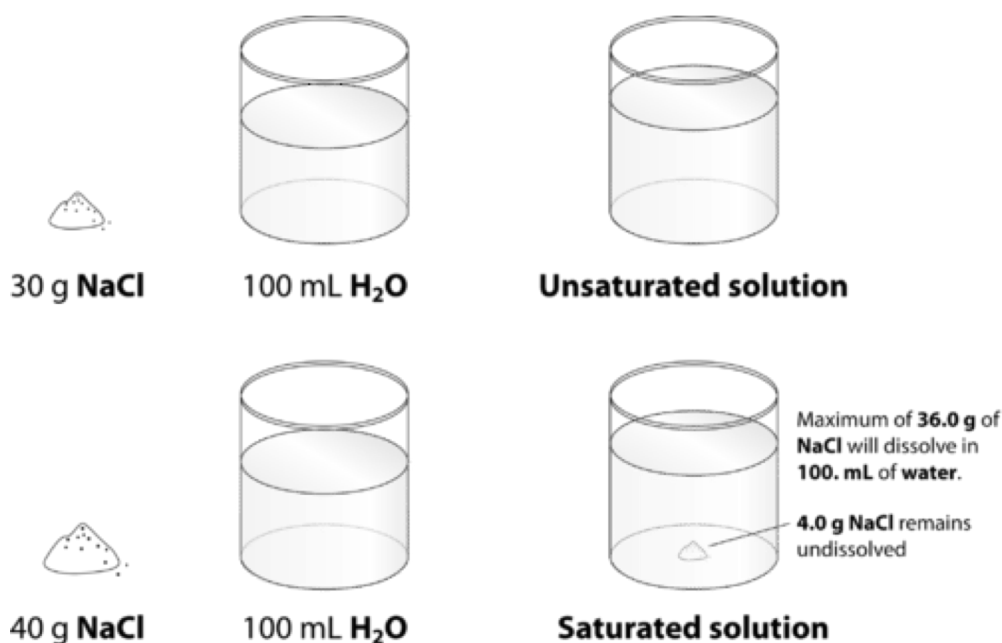
✓ When a soluble salt dissolves in water, it dissociates completely into separate **hydrated** (or solvated or aquated) cations and anions that move apart from each other.

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

✓ Suppose that you have a beaker of water to which you add some soluble salt, stirring until it dissolves. You add more and that dissolves. You keep adding more and more salt, eventually reaching a point that no more of the salt will dissolve no matter how long or how vigorously you stir it. When this point is reached and no more solute will dissolve, the solution is said to be **saturated**, and the undissolved solute precipitates to the bottom.

30 g **NaCl**   100 mL **H₂O**   **Unsaturated solution**

Maximum of **36.0 g** of
NaCl will dissolve in
100. mL of **water**.

4.0 g NaCl remains
undissolved

40 g **NaCl**   100 mL **H₂O**   **Saturated solution**

✓ At this point, the rate at which the ions dissociate into separate cations and anions and the rate at which the separate cations and anions combine to re-form the solid (the reverse of the dissociation reaction) become equal to each other and an equilibrium between the undissolved solid and the dissociated ions in the aqueous solution is established.

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

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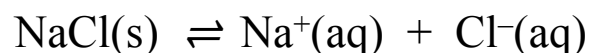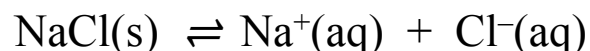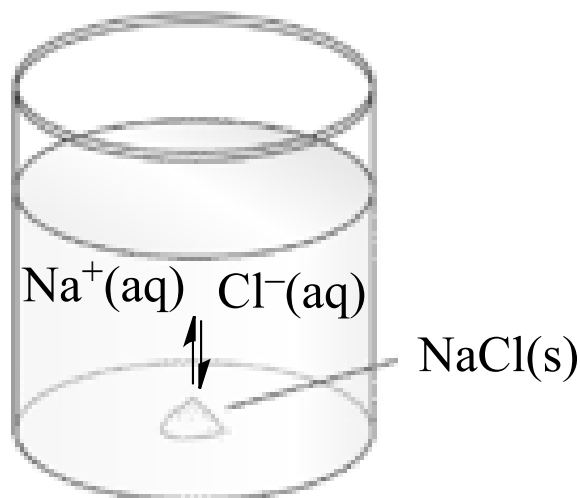
$$K = [Na^+][Cl^-]$$

✓ Unfortunately, this simple type of equilibrium expression cannot be used because the saturated solution for a soluble salt is not an ideal solution. The high concentrations of the ions in the saturated solution can form ion-pairs and larger clusters, so that the aqueous solution is far from ideal.

✓ Therefore, we restrict our attention to insoluble salts (or slightly soluble, sparingly soluble, or marginally soluble salts) for which concentrations of the solvated ions are so low that the interactions among solvated ions are negligible.

The Solubility Product

✓ The sparingly soluble salt AgCl(s) establishes the following equilibrium when placed in water.
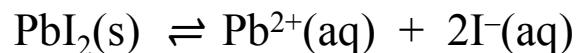

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
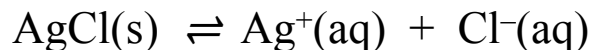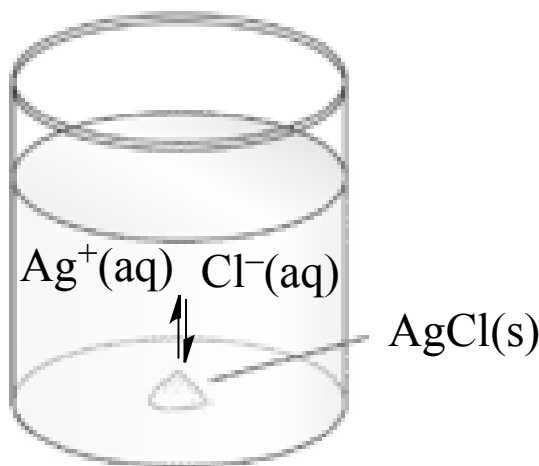
$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10} \text{ M}^2 \text{ at 25 °C and } 2.2 \times 10^{-8} \text{ M}^2 \text{ at 100 °C}$$
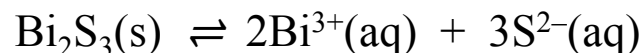
(units are usually omitted)

✓ K_{sp} is called the **solubility product constant**.

✓ Note that [AgCl] is not included in the equilibrium expression because it is a pure solid.

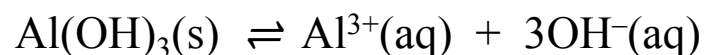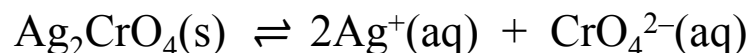✓ If no solid is present, the equilibrium expression is not valid.

✓   Other examples:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$$

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3 = 1.0 \times 10^{-15}$$

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$

$$K_{sp} = [Al^{3+}][OH^-]^3 = 1.3 \times 10^{-33}$$

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4{}^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}] = 9.0 \times 10^{-12}$$

✓   The K_{sp} values at 25 °C for many common ionic solids are listed in the following table.

✓   Notice that K_{sp} values are all very small values because the solids are insoluble or sparingly soluble salts.

✓   One way to identify insoluble/sparingly soluble/marginally soluble/slightly soluble salts is from their K_{sp} values. Another way is by using the **solubility rules**.

Some Values for Solubility Product Constants (K_{sp}) at 25 °C

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$	1.3×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.1×10^{-9}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	2.8×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$	5.3×10^{-9}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	9.1×10^{-6}
Calcium oxalate	$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$	2.7×10^{-9}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,OH^-(aq)$	6.3×10^{-31}
Copper(II) sulfide	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	8.7×10^{-36}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$	4×10^{-38}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$	1.6×10^{-5}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.8×10^{-13}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$	7.1×10^{-9}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
Magnesium fluoride	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$	3.7×10^{-8}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$	1.8×10^{-11}
Magnesium phosphate	$Mg_3(PO_4)_2(s) \rightleftharpoons 3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq)$	1×10^{-25}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)$	1.3×10^{-18}
Mercury(II) sulfide	$HgS(s) \rightleftharpoons Hg^{2+}(aq) + S^{2-}(aq)$	2×10^{-53}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.5×10^{-17}

General Rules for the Solubility of Ionic Substances in Water

1. Nearly all salts of nitrates (NO_3^-) and acetates ($C_2H_3O_2^-$ or $CH_3CO_2^-$) are soluble.

2. All salts of chlorides (Cl^-) are soluble, except salts of Ag^+ ions, Hg_2^{2+} ions and Pb^{2+} ions. All salts of bromides (Br^-) are soluble, except salts of Ag^+ ions, Hg_2^{2+} ions and Pb^{2+} ions. All salts of iodides (I^-) are soluble, except salts of Ag^+ ions, Hg_2^{2+} ions and Pb^{2+} ions.

3. All salts of sulfates (SO_4^{2-}) are soluble, except salts of Ba^{2+}, Sr^{2+}, and Pb^{2+}. Salts of Ca^{2+} ions, Hg_2^{2+} ions, and Ag^+ ions are only slightly soluble.

4. All salts of group I metal ions and ammonium (NH_4^+) ions are soluble.

5. All salts of hydroxides (OH^-) are insoluble, except for group I metal ions and ammonium (NH_4^+) ions. Salts of Ba^{2+} ions, Sr^{2+} ions, and Ca^{2+} ions are marginally soluble.

6. All salts of sulfides (S^{2-}) are insoluble except those of group I metal ions, ammonium (NH_4^+) ions, Ca^{2+} ions, Sr^{2+} ions, and Ba^{2+} ions.

7. All salts of phosphates (PO_4^{3-}) and carbonates (CO_3^{2-}) are insoluble except those of group I metal ions and ammonium (NH_4^+) ions.

8. Most salts of chromates (CrO_4^{2-}) are only slightly soluble except those of group I metal ions and ammonium (NH_4^+) ions.

Solubility and K_{sp}

✓ The **solubility** of a solute is the quantity of the solute that dissolves in a certain amount of solvent. The **molar solubility** is the solubility in units of moles per liter ($mol \cdot L^{-1}$).

✓ The molar solubility of an insoluble/sparingly salt can be calculated from K_{sp}.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$

(I) Initial concentrations (M):   –   0   0

(C) Change in concentrations (M): $-x$ ➡ $+x$ $+x$

(E) Equilibrium concentrations (M):   – x x

$$K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = (x)(x) = x^2$$

$$x = 1.3 \times 10^{-5}\ M$$

✓ The amount x represents the concentration of AgCl(s) that dissolved (which is the molar solubility).

Molar solubility of AgCl in water $= 1.3 \times 10^{-5}\ M$

Sample Exercise 18.4   Calculating Molar Solubility from K_{sp}

The K_{sp} of CaF_2 is 3.9×10^{-11}. Calculate the concentrations of Ca^{2+} and F^- ions and the molar solubility of $CaF_2(s)$ in pure water.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = 3.9 \times 10^{-11}$$

	$CaF_2(s)$		$Ca^{2+}(aq)$	$+ 2F^-(aq)$
(I) Initial concentrations (M):	$-$		0	0
(C) Change in concentrations (M):	$-x$	$\longrightarrow$	$+x$	$+2x$
(E) Equilibrium concentrations (M):	$-$		x	$2x$

$$K_{sp} = 3.9 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = 2.1 \times 10^{-4}\ M$$

$$[Ca^{2+}] = x = 2.1 \times 10^{-4}\ M$$

$$[F^-] = 2x = 4.2 \times 10^{-4}\ M$$

$$\text{Molar solubility of } CaF_2(s) = x = 2.1 \times 10^{-4}\ M$$

Practice Exercise: The K_{sp} value of $Al(OH)_3(s)$ is 5.0×10^{-33} at 25 °C. Calculate its molar solubility in pure water at 25 °C. (Answer: $3.7 \times 10^{-9}\ M$)

Sample Exercise 18.5   Calculating K_{sp} from Molar Solubility

Silver chromate, $Ag_2CrO_4(s)$, is a red solid that dissolves in water to the extent of 8.7×10^{-5} mol·L^{-1}. Calculate its K_{sp}.

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

	$Ag_2CrO_4(s)$		$2Ag^+(aq)$	$CrO_4^{2-}(aq)$	
(I) Initial concentrations (M):	–		0	0	
(C) Change in concentrations (M):	$-x$	→	$+2x$	$+x$	
(E) Equilibrium concentrations (M):	–		$2x$	x	($x = 8.7 \times 10^{-5}$ M)

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}] = (2x)^2(x) = 4x^3 = 4(8.7 \times 10^{-5})^3 = 2.6 \times 10^{-12}$$

Practice Exercise: Calculate the K_{sp} value for bismuth sulfide, $Bi_2S_3(s)$, which has a solubility of 1.0×10^{-15} in pure water at 25 °C. (Answer: 1.1×10^{-73})