

## Introduction to Sparingly Soluble Salts

All ionic compounds dissolve to some extent in water, but the range of solubilities is quite remarkable. (See the table on the right.) Sparingly soluble salts are those which have molar solubilities much less than  $1 \text{ mol L}^{-1}$ .

We wish to investigate the factors that affect solubility, so that we can learn how to:

- (1) dissolve solids that are normally difficult to dissolve
- (2) exploit differences in solubilities to separate the components of mixtures

We shall start by considering a single ionic solid that has a low solubility in water.

When a sparingly soluble ionic solid, such as AgCl, dissolves in water, ions break away from the crystal lattice and enter into the solution and become hydrated. Hydrated ions can also lose their “waters of hydration” and add back onto the surface of the crystal.

At some point, the rate of dissolution will equal the rate of re-crystallization. At that point, the system has reached a state of dynamic equilibrium and the concentrations of ions in the solution stop changing.

The dissolution of AgCl(s) in water is described by the following chemical equation:



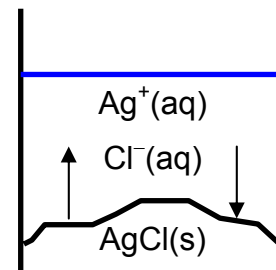
$$K_{\text{sp}} = [\text{Ag}^{\text{+}}]_{\text{eq}} [\text{Cl}^{\text{-}}]_{\text{eq}}$$

The equilibrium constant for this reaction is denoted by  $K_{\text{sp}}$  and is called the solubility product. For a solid such as  $\text{Ag}_3\text{PO}_4$ , we have:



$$K_{\text{sp}} = [\text{Ag}^{\text{+}}]_{\text{eq}}^3 [\text{PO}_4^{3-}]_{\text{eq}}$$

Salt	Molar Solubility
AgClO <sub>4</sub>	27 mol L <sup>-1</sup>
AgF	15 mol L <sup>-1</sup>
NaCl	6 mol L <sup>-1</sup>
NaNO <sub>3</sub>	1 mol L <sup>-1</sup>
PbCl <sub>2</sub>	≈ 10 <sup>-3</sup> mol L <sup>-1</sup>
CaCO <sub>3</sub>	≈ 10 <sup>-4</sup> mol L <sup>-1</sup>
AgCl	≈ 10 <sup>-5</sup> mol L <sup>-1</sup>
CuS	≈ 10 <sup>-12</sup> mol L <sup>-1</sup>



For sparingly soluble salts, the value of  $K_{sp}$  is quite small. We can use the  $K_{sp}$  value for the salt to calculate the molar solubility.

**Example:** Calculate the molar solubility of AgCl in water. Then calculate the molar solubility of  $Ag_3PO_4$  in water.

<b><math>K_{sp}</math> for Some Salts</b> (from Radel & Navidi, 2 <sup>nd</sup> Ed)	
<b>Chromates</b>	
$Ag_2(CrO_4)$	$1.2 \times 10^{-12}$
$Ba(CrO_4)$	$1.2 \times 10^{-10}$
$Sr(CrO_4)$	$3.6 \times 10^{-5}$
<b>Carbonates</b>	
$BaCO_3$	$5.0 \times 10^{-9}$
$CaCO_3$	$4.5 \times 10^{-9}$
$MnCO_3$	$2.2 \times 10^{-11}$
$Li_2CO_3$	$1.7 \times 10^{-3}$
<b>Halides</b>	
$AgCl$	$1.8 \times 10^{-10}$
$AgBr$	$5.0 \times 10^{-13}$
$AgI$	$8.3 \times 10^{-17}$
$PbCl_2$	$1.7 \times 10^{-5}$
$PbBr_2$	$2.1 \times 10^{-6}$
<b>Hydroxides</b>	
$AgOH$	$1.5 \times 10^{-5}$
$Ba(OH)_2$	$5.0 \times 10^{-13}$
$Ca(OH)_2$	$6.5 \times 10^{-6}$
$Fe(OH)_2$	$7.9 \times 10^{-16}$
$Mg(OH)_2$	$7.1 \times 10^{-12}$
$Mn(OH)_2$	$6.0 \times 10^{-14}$
$Sr(OH)_2$	$3.2 \times 10^{-4}$
$Zn(OH)_2$	$4.5 \times 10^{-17}$
$Al(OH)_3$	$1.3 \times 10^{-33}$
$Cr(OH)_3$	$6.3 \times 10^{-31}$
$Fe(OH)_3$	$1.6 \times 10^{-39}$
<b>Phosphates</b>	
$Ag_3(PO_4)$	$1.8 \times 10^{-18}$
$Al(PO_4)$	$9.8 \times 10^{-21}$
$Ca_3(PO_4)_2$	$1.3 \times 10^{-32}$
$Ni_3(PO_4)_2$	$4.7 \times 10^{-32}$
<b>Sulfides</b>	
$Ag_2S$	$1.6 \times 10^{-49}$
$CdS$	$1.0 \times 10^{-27}$
$MnS$	$3.0 \times 10^{-13}$
$ZnS$	$2.5 \times 10^{-21}$

Note carefully!

The solubility depends on the value of  $K_{sp}$  and on the formula of the salt. You cannot predict which salt is more soluble by considering only the  $K_{sp}$  value!!

For a 1:1 salt ....  $S = \sqrt{K_{sp}}$

For a 2:1 salt ...  $S = \sqrt[3]{(K_{sp} / 4)}$

For a 3:1 salt ...  $S = \sqrt[4]{(K_{sp} / 27)}$

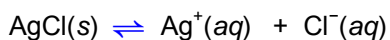
Make sure you can derive these relationships yourself. (Set up the equilibrium summary for each type of salt!)

**Example: (Common Ion Effect)** Calculate the molar solubility of  $\text{AgCl}(s)$  in  $0.10 \text{ mol L}^{-1} \text{ NaCl}(aq)$ .

## Precipitation

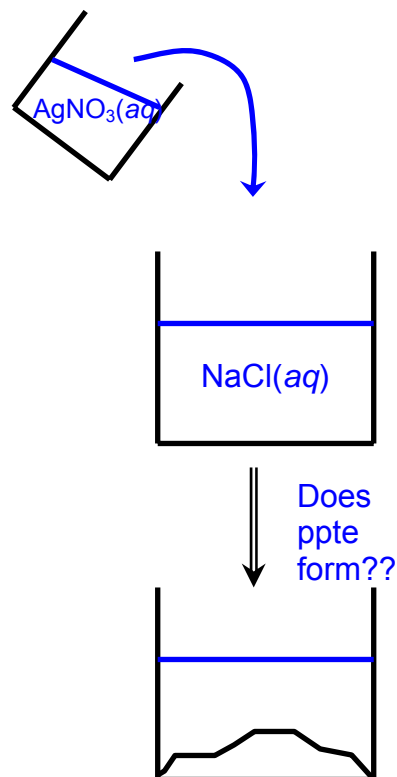
Up to this point, we've focused on the dissolution process (i.e. calculating the equilibrium concentrations of ions in solution when excess solid is in equilibrium with the solution above it.) Now we turn our attention to the precipitation process, in which we mix together different substances with the aim of predicting whether a precipitate will form.

Consider the following equilibrium.



At equilibrium, we must have  $[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}}$ . The solid is in equilibrium with the solution above it. There is no further dissolution of the solid and the solution is **saturated** with respect to  $\text{Ag}^+$  and  $\text{Cl}^-$ .

What if we mix solutions of  $\text{AgNO}_3(a)$  and  $\text{NaCl}(aq)$ ? Will the  $\text{Ag}^+$  and  $\text{Cl}^-$  ions combine to form  $\text{AgCl}(s)$ ? The answer is: It depends!



**Example:** Suppose that 50.0 mL of 0.100 mol L<sup>-1</sup> AgNO<sub>3</sub>(aq) and 60.0 mL of 0.200 mol L<sup>-1</sup> NaCl(aq) are mixed. Does a precipitate form? If so, what are the equilibrium concentrations of Ag<sup>+</sup> and Cl<sup>-</sup>?

### **Selective Precipitation**

Chemists often exploit differences in solubilities to separate ions from a mixture. (This is an important method of quantitative analysis. Practical aspects of quantitative analysis is discussed in CHEM 220/220L.)

**Example:** Finely-divided  $\text{AgNO}_3$ , which is highly soluble in water, is added slowly with stirring to a solution in which  $[\text{Cl}^-] = 0.10 \text{ mol L}^{-1}$  and  $[\text{Br}^-] = 0.10 \text{ mol L}^{-1}$ . Calculate  $[\text{Cl}^-]$  and  $[\text{Br}^-]$  in the solution at the instant the second precipitate just begins to form. In your estimation, is this an effective separation? Would the separation be more or less effective if  $\text{Pb}(\text{NO}_3)_2$  had been used as the precipitating agent?

## Factors Affecting Solubility

Consider the generalized dissolution process below.



Le Chatelier's principle tells us that if we remove  $\text{M}^+$  or  $\text{X}^-$  from solution, then the equilibrium above will shift to the right. Similarly, if we add something to the solution that converts  $\text{M}^+$  or  $\text{X}^-$  into other chemical species, then the equilibrium shifts to the right. Thus, the solubility of MX can be increased dramatically by adding an appropriate substance to the solution.

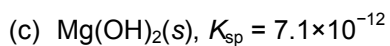
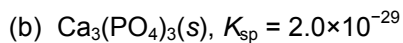
### A. pH effects

If the anion  $\text{X}^-$  is a weak base, then it will bind with protons to form HX. In an acidic environment,  $\text{X}^-$  is readily converted to HX as MX dissolves.

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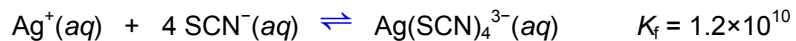
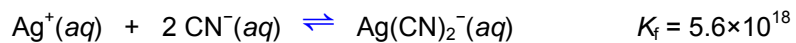
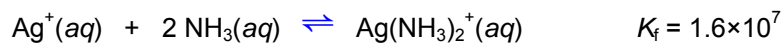
**If the anion of a salt is a strong or weak base, then the salt is much more soluble in acidic solution.**

**Example:** For each of the following salts, state whether the solubility increases, decreases or stays the same when strong acid (e.g.  $\text{HNO}_3$ ) is added to the solution.



## B. Complexing agents

Many metal ions react readily with electron donors to form very stable complexes in solution. For example,  $\text{Ag}^+$  reacts readily with a number of different complexing agents:



When excess complexing agent, such as  $\text{NH}_3$ ,  $\text{NaCN}$ , or  $\text{KSCN}$ , is added to a solution containing  $\text{Ag}^+$  ion, most of the silver ion in solution reacts to form a complex ion and thus  $[\text{Ag}^+]$  is very small. Consequently,  $[\text{Cl}^-]$  can take on a much larger value before precipitation of  $\text{AgCl}$  occurs.



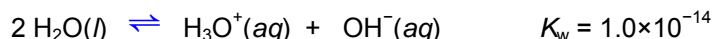
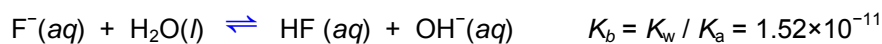
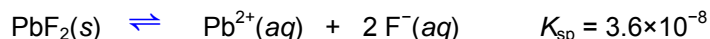
**Example:** A solution is made by dissolving 1.0 mol  $\text{AgNO}_3$  in 0.500 L of  $0.50 \text{ mol L}^{-1} \text{NH}_3(\text{aq})$ . What is the equilibrium concentration of  $[\text{Ag}^+]$ ? How much  $\text{Cl}^-$  can be added to this solution before  $\text{AgCl}(\text{s})$  precipitates? Note:  $K_f = 1.6 \times 10^7$  for  $\text{Ag}(\text{NH}_3)_2^+$  and  $K_{\text{sp}} = 1.8 \times 10^{-10}$  for  $\text{AgCl}$ .

$\text{AgCl}$  has a very low solubility in water but it is much more soluble in aqueous ammonia solution. Have a look at Example 19-13 in the text to see how to calculate the solubility of  $\text{AgCl}$  in  $0.10 \text{ mol L}^{-1} \text{NH}_3(\text{aq})$ .

┌ **Digging Deeper: Solubility equilibria are often a lot more complicated than you might think!**

The simple  $K_{sp}$  calculations we've carried out in previous examples are usually quite inaccurate. This is because the dissolution process is only one of many competing processes that must be considered.

Consider lead (II) fluoride,  $PbF_2$ , which is a salt containing a weakly basic anion,  $F^-$ . To calculate the "true" solubility of  $PbF_2$  in water, we should consider all of the following processes simultaneously.



If we ignore the basic character of  $F^-$ , we calculate the solubility,  $S$ , of  $PbF_2$  directly from the  $K_{sp}$  value:

$$S = [Pb^{2+}] = \sqrt[3]{K_{sp} / 4} = 2.1 \times 10^{-3} \text{ mol L}^{-1}.$$

If wanted to incorporate the basic character of  $F^-$  into our calculations, we'd have to use all of the following equations (5 equations in 5 unknowns):

**Equilibrium constant expressions:**  $K_{sp} = [Pb^{2+}][F^-]^2$      $K_a = [H_3O^+][F^-] / [HF]$      $K_w = [H_3O^+][OH^-]$

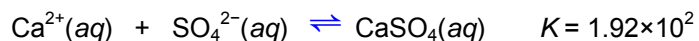
**Material Balance Equation:**  $[F^-] + [HF] = 2 [Pb^{2+}]$

Note: The dissolution of  $PbF_2$  produces twice as much  $F^-$  as  $Pb^{2+}$  but some of the  $F^-$  is converted into HF. Therefore, the  $[F^-] + [HF]$  must be equal to twice the amount of  $PbF_2$  that dissolved.

**Charge Balance Equation:**  $2 [Pb^{2+}] = [F^-] + [OH^-]$

When we solve the system of equations above, we get  $S = [Pb^{2+}] = 2.1 \times 10^{-3} \text{ mol L}^{-1}$ . In this instance, we get the same result as before (i.e., when we neglected the basic character of  $F^-$ ). This is because  $F^-$  is a relatively weak base so the conversion of  $F^-$  to HF is not that important. However, if  $K_b$  for  $F^-$  was  $1.52 \times 10^{-5}$  rather than  $1.52 \times 10^{-11}$ , the calculated solubility would be 4% higher than the value calculated directly from just the  $K_{sp}$  value.

The dissolution process is sometimes further complicated by the fact that the ions don't always separate completely from each other but instead form a stable ion pair in solution. For example, in a saturated solution of  $CaSO_4$ , it has been found experimentally that a significant number of  $CaSO_4$  "molecules" exist in solution. The  $CaSO_4$  "molecule" is really an undissociated ion pair ( $Ca^{2+})(SO_4^{2-})$ . To calculate the "true" solubility of  $CaSO_4(s)$ , one must not only take into account the basic character of  $SO_4^{2-}$  but also the following equilibrium process:



The equilibrium constant for the formation of the  $(Ca^{2+})(SO_4^{2-})$  ion pair is quite large, and thus a significant fraction of the dissolved solid exists in this form. Consequently, the solubility of  $CaSO_4(s)$  in water is actually much greater than one would expect if we neglected the formation of the ion pair!! ┘