

### SOLUBILITY EQUILIBRIA (The Solubility-Product Constant, $K_{sp}$ )

We've got good news and we've got bad news... Which do you want first?

The good news: Solubility equilibrium is really simple.

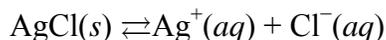
The bad news: You know all those solubility rules that state a substance is *insoluble*? They are actually a little bit soluble after all. Only the future attorneys among you read the fine print. Soluble is often defined as "greater than 3 grams dissolving in 100 mL of water". So, there is a lot of wiggle room for solubility up to 3 grams! This type of equilibria deals with that wiggle room. Apologies for "lying" to you.

If you can actually *see* that a salt is insoluble, usually evidenced by solid "stuff" sitting on the bottom of the container, then the solution is actually *saturated*. Saturated solutions of salts present due to a chemical reaction taking place present yet another type of chemical equilibria.

- Slightly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution. Examine the formation of  $\text{AgCl}(s)$  as a solution of  $\text{AgNO}_3(aq)$  is squirted into a solution of  $\text{NaCl}(aq)$ .

- When the solid is first added to water, no ions are initially present.
- As dissolution proceeds, the concentration of ions increases until equilibrium is established. This occurs when the solution is saturated.
- The equilibrium constant, the  $K_{sp}$ , is no more than the product of the ions in solution. (Remember, solids do not appear in equilibrium expressions.)

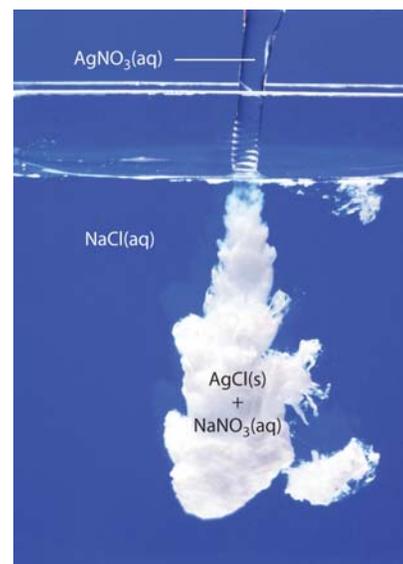
- For a saturated solution of  $\text{AgCl}$ , the equation would be:



- The solubility product expression for the  $\text{AgCl}(s)$  precipitate would be:

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

- The  $\text{AgCl}(s)$  does not appear in the equilibrium expression since solids are left out. Why? *Because*, the concentration of the solid remains relatively constant.

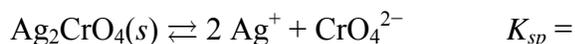


A table of  $K_{sp}$  values follows on the next page.

### Solubility Product Constants, $K_{sp}$ , at 25°C

| Substance            | Formula  | $K_{sp}$              | Substance             | Formula  | $K_{sp}$              |
|----------------------|--|-----------------------|-----------------------|--|-----------------------|
| Aluminum hydroxide   | Al(OH) <sub>3</sub>                              | $4.6 \times 10^{-33}$ | Lead(II) sulfide      | PbS  | $2.5 \times 10^{-27}$ |
| Barium chromate      | BaCrO <sub>4</sub>                               | $1.2 \times 10^{-10}$ | Magnesium arsenate    | Mg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> | $2 \times 10^{-20}$   |
| Barium fluoride      | BaF <sub>2</sub>                                 | $1.0 \times 10^{-6}$  | Magnesium carbonate   | MgCO <sub>3</sub>                                | $1.0 \times 10^{-5}$  |
| Barium sulfate       | BaSO <sub>4</sub>                                | $1.1 \times 10^{-10}$ | Magnesium hydroxide   | Mg(OH) <sub>2</sub>                              | $1.8 \times 10^{-11}$ |
| Cadmium oxalate      | CdC <sub>2</sub> O <sub>4</sub>                  | $1.5 \times 10^{-8}$  | Magnesium oxalate     | MgC <sub>2</sub> O <sub>4</sub>                  | $8.5 \times 10^{-5}$  |
| Cadmium sulfide      | CdS  | $8 \times 10^{-27}$   | Manganese(II) sulfide | MnS  | $2.5 \times 10^{-10}$ |
| Calcium carbonate    | CaCO <sub>3</sub>                                | $3.8 \times 10^{-9}$  | Mercury(I) chloride   | Hg <sub>2</sub> Cl <sub>2</sub>                  | $1.3 \times 10^{-18}$ |
| Calcium fluoride     | CaF <sub>2</sub>                                 | $3.4 \times 10^{-11}$ | Mercury(II) sulfide   | HgS  | $1.6 \times 10^{-52}$ |
| Calcium oxalate      | CaC <sub>2</sub> O <sub>4</sub>                  | $2.3 \times 10^{-9}$  | Nickel(II) hydroxide  | Ni(OH) <sub>2</sub>                              | $2.0 \times 10^{-15}$ |
| Calcium phosphate    | Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>  | $1 \times 10^{-26}$   | Nickel(II) sulfide    | NiS  | $3 \times 10^{-19}$   |
| Calcium sulfate      | CaSO <sub>4</sub>                                | $2.4 \times 10^{-5}$  | Silver acetate        | AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>   | $2.0 \times 10^{-3}$  |
| Cobalt(II) sulfide   | CoS  | $4 \times 10^{-21}$   | Silver bromide        | AgBr   | $5.0 \times 10^{-13}$ |
| Copper(II) hydroxide | Cu(OH) <sub>2</sub>                              | $2.6 \times 10^{-19}$ | Silver chloride       | AgCl   | $1.8 \times 10^{-10}$ |
| Copper(II) sulfide   | CuS  | $6 \times 10^{-36}$   | Silver chromate       | Ag <sub>2</sub> CrO <sub>4</sub>                 | $1.1 \times 10^{-12}$ |
| Iron(II) hydroxide   | Fe(OH) <sub>2</sub>                              | $8 \times 10^{-16}$   | Silver iodide         | AgI  | $8.3 \times 10^{-17}$ |
| Iron(II) sulfide     | FeS  | $6 \times 10^{-18}$   | Silver sulfide        | Ag <sub>2</sub> S                                | $6 \times 10^{-50}$   |
| Iron(III) hydroxide  | Fe(OH) <sub>3</sub>                              | $2.5 \times 10^{-39}$ | Strontium carbonate   | SrCO <sub>3</sub>                                | $9.3 \times 10^{-10}$ |
| Lead(II) arsenate    | Pb <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> | $4 \times 10^{-36}$   | Strontium chromate    | SrCrO <sub>4</sub>                               | $3.5 \times 10^{-5}$  |
| Lead(II) chloride    | PbCl <sub>2</sub>                                | $1.6 \times 10^{-5}$  | Strontium sulfate     | SrSO <sub>4</sub>                                | $2.5 \times 10^{-7}$  |
| Lead(II) chromate    | PbCrO <sub>4</sub>                               | $1.8 \times 10^{-14}$ | Zinc hydroxide        | Zn(OH) <sub>2</sub>                              | $2.1 \times 10^{-16}$ |
| Lead(II) iodide      | PbI <sub>2</sub>                                 | $6.5 \times 10^{-9}$  | Zinc sulfide          | ZnS  | $1.1 \times 10^{-21}$ |
| Lead(II) sulfate     | PbSO <sub>4</sub>                                | $1.7 \times 10^{-8}$  |                       |  |                       |

Write the  $K_{sp}$  expression for each of the following reactions and find its value in the table above.



### ❖ DETERMINING $K_{sp}$ FROM EXPERIMENTAL MEASUREMENTS

- In practice,  $K_{sp}$  values are determined by careful laboratory measurements using various spectroscopic methods.
  - Remember STOICHIOMETRY? Surely, you've made peace with the concept by now...

Example: Lead(II) chloride dissolves to a slight extent in water according to the equation below.



Calculate the  $K_{sp}$  if the lead ion concentration has been found to be  $1.62 \times 10^{-2}M$ .

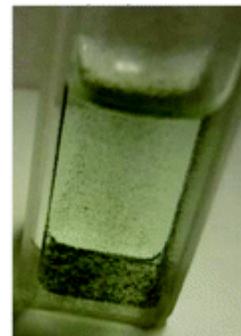
If lead's concentration is  $x$ , then chloride's concentration is  $2x$ . So . . .

$$K_{sp} = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$$

### Exercise 1

### Calculating $K_{sp}$ from Solubility I

Copper(I) bromide has a measured solubility of  $2.0 \times 10^{-4}$  mol/L at  $25^\circ\text{C}$ . Calculate its  $K_{sp}$  value.



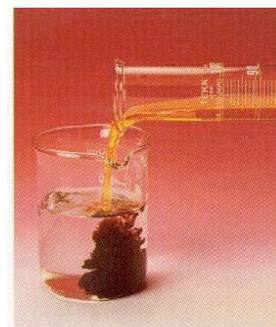
[CuBr]

$$K_{sp} = 4.0 \times 10^{-8}$$

### Exercise 2

### Calculating $K_{sp}$ from Solubility II

Calculate the  $K_{sp}$  value for bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ), which has a solubility of  $1.0 \times 10^{-15}$  mol/L at  $25^\circ\text{C}$ .



Precipitation of bismuth sulfide.

Sulfide is a very basic anion and really exists in water as  $\text{HS}^-$ . We will not consider this complication.

$$K_{sp} = 1.1 \times 10^{-73}$$

## ESTIMATING SALT SOLUBILITY FROM $K_{sp}$

- ❖ Relative solubilities can be deduced by comparing values of  $K_{sp}$  BUT, BE CAREFUL!
- ❖ These comparisons can only be made for salts having the same ION:ION ratio.
- ❖ Please don't forget solubility changes with temperature! Some substances become less soluble in cold water while others increase in solubility! Aragonite is an example.

Example: The  $K_{sp}$  for  $\text{CaCO}_3$  is  $3.8 \times 10^{-9}$  @  $25^\circ\text{C}$ . Calculate the solubility of calcium carbonate in pure water in (a) moles per liter & (b) grams per liter:

### Exercise 3

#### Calculating Solubility from $K_{sp}$

The  $K_{sp}$  value for copper(II) iodate,  $\text{Cu}(\text{IO}_3)_2$ , is  $1.4 \times 10^{-7}$  at  $25^\circ\text{C}$ . Calculate its solubility at  $25^\circ\text{C}$ .

$$= 3.3 \times 10^{-3} \text{ mol/L}$$

### Exercise 4

#### Solubility and Common Ions

Calculate the solubility of solid  $\text{CaF}_2$  ( $K_{sp} = 4.0 \times 10^{-11}$ ) in a  $0.025 \text{ M}$   $\text{NaF}$  solution.

$$= 6.4 \times 10^{-8} \text{ mol/L}$$

## $K_{sp}$ AND THE REACTION QUOTIENT, $Q$

With some knowledge of the reaction quotient, we can decide

- whether a precipitate (ppt) will form AND
- what concentrations of ions are required to begin the precipitation of an insoluble salt.

1.  $Q < K_{sp}$ , the system is not at equil. (*unsaturated*)
2.  $Q = K_{sp}$ , the system is at equil. (*saturated*)
3.  $Q > K_{sp}$ , the system is not at equil. (*supersaturated*)

***Precipitates form when the solution is supersaturated!!!***

### **Precipitation of insoluble salts**

- Metal-bearing ores often contain the metal in the form of an insoluble salt, and, to complicate matters, the ores often contain several such metal salts.
- Dissolve the metal salts to obtain the metal ion, concentrate in some manner, and ppt. selectively only one type of metal ion as an insoluble salt.

#### **Exercise 5**

#### **Determining Precipitation Conditions**

A solution is prepared by adding 750.0 mL of  $4.00 \times 10^{-3} M$   $Ce(NO_3)_3$  to 300.0 mL of  $2.00 \times 10^{-2} M$   $KIO_3$ . Will  $Ce(IO_3)_3$  ( $K_{sp} = 1.9 \times 10^{-10}$ ) precipitate from this solution?

**yes**

## Exercise 6

## Precipitation

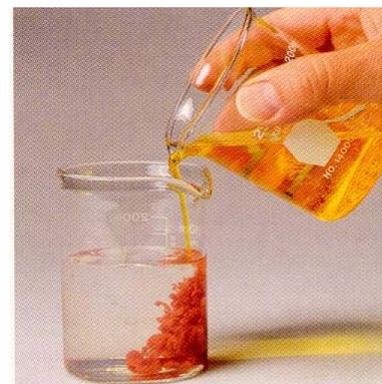
A solution is prepared by mixing 150.0 mL of  $1.00 \times 10^{-2} M$   $Mg(NO_3)_2$  and 250.0 mL of  $1.00 \times 10^{-1} M$  NaF. Calculate the concentrations of  $Mg^{2+}$  and  $F^-$  at equilibrium with solid  $MgF_2$  ( $K_{sp} = 6.4 \times 10^{-9}$ ).



$$\begin{aligned} [Mg^{2+}] &= 2.1 \times 10^{-6} M \\ [F^-] &= 5.50 \times 10^{-2} M \end{aligned}$$

## SOLUBILITY AND THE COMMON ION EFFECT

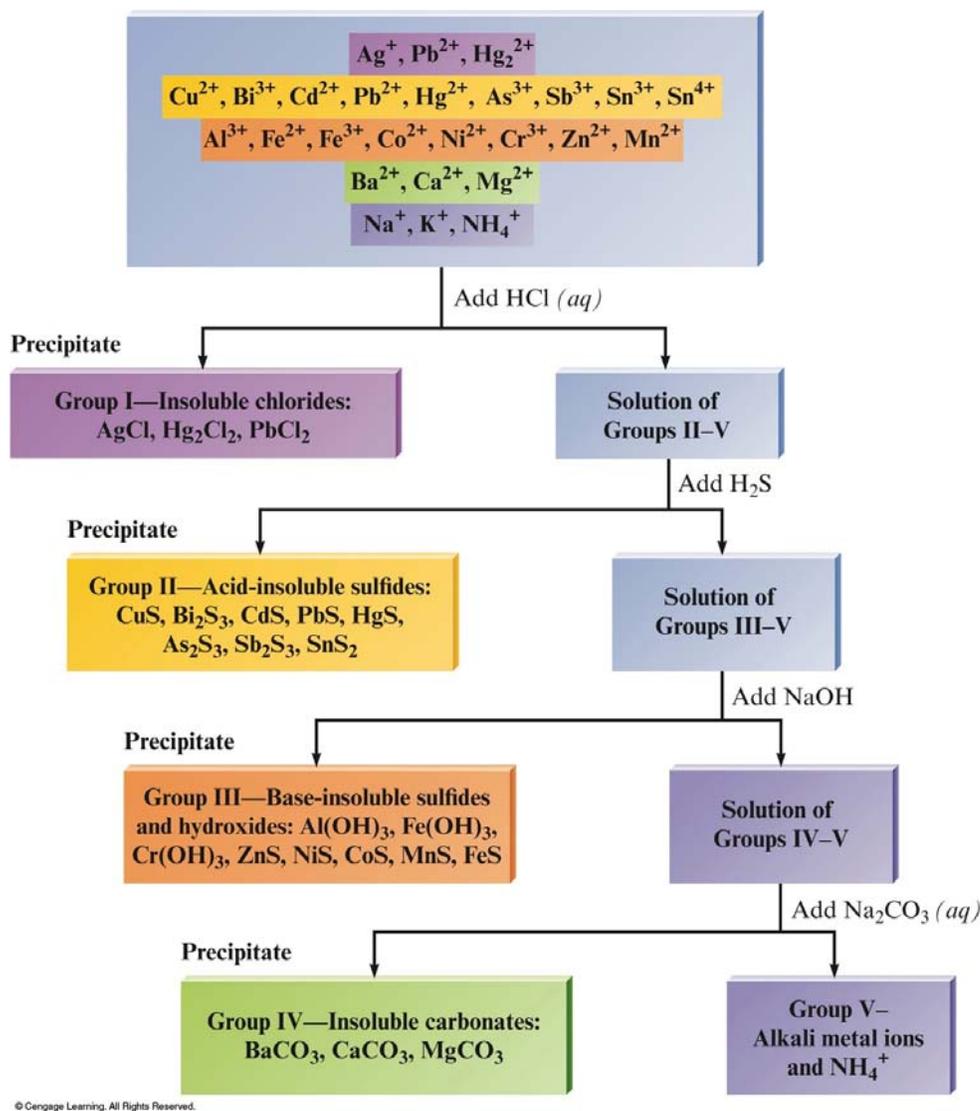
- Experiments show that the solubility of any salt is always less in the presence of a “common ion”.
- Why? LeChâtelier’s Principle, that’s why! Be reasonable and use approximations when you can.
- The pH can also affect solubility. Evaluate the equation to see which species reacts with the addition of acid or base.
- Would magnesium hydroxide be more soluble in an acid or a base? Why?



A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate.

## SOLUBILITY, ION SEPARATIONS, AND QUALITATIVE ANALYSIS

- ❖ This section will introduce you to the basic chemistry of various ions.
- ❖ It also illustrates how principles of chemical equilibria can be applied in the laboratory.
- ❖ **Objective:** Separate the following metal ions from an aqueous sample containing ions of silver, lead(II), cadmium(II) and nickel(II).



- From your knowledge of solubility rules, you know that chlorides of lead and silver will form precipitates while those of nickel and cadmium will not. Adding dilute HCl to sample will ppt. the lead and silver ions while the nickel and cadmium will stay in solution.
- Separate the lead and silver precipitates from the solution by filtration. Heating the solution causes some of the lead chloride to dissolve. Filtering the HOT sample will separate the lead (in the filtrate) from the silver (solid remaining in funnel with filter paper).
- Separating cadmium and nickel ions require precipitation with sulfur. Use the  $K_{sp}$  values to determine which ion will precipitate first as an aqueous solution of sulfide ion is added to the portion of the sample that still contains these ions. Which precipitates first?

### Exercise 7

### Selective Precipitation

A solution contains  $1.0 \times 10^{-4} M \text{Cu}^+$  and  $2.0 \times 10^{-3} M \text{Pb}^{2+}$ . If a source of  $\text{I}^-$  is added gradually to this solution, will  $\text{PbI}_2$  ( $K_{sp} = 1.4 \times 10^{-8}$ ) or  $\text{CuI}$  ( $K_{sp} = 5.3 \times 10^{-12}$ ) precipitate first? Specify the concentration of  $\text{I}^-$  necessary to begin precipitation of each salt.

**CuI will precipitate first**  
**Concentration in excess of  $5.3 \times 10^{-8} M$  required**

### SOLUBILITY AND COMPLEX IONS

- The formation of complex ions can often dissolve otherwise insoluble salts.
- Often as the complex ion forms, the solubility equilibrium shifts to the right (away from the solid) and causes the insoluble salt to become more soluble.

Example: If sufficient aqueous ammonia is added to silver chloride, the latter can be dissolved as  $[\text{Ag}(\text{NH}_3)_2]^+$  forms, which is soluble.

That is a significant improvement with regard to the solubility of  $\text{AgCl}(s)$ .

The equilibrium constant for dissolving silver chloride in ammonia is not large, but, if the concentration of ammonia is sufficiently high, the complex ion and chloride ion must also be high, and silver chloride will dissolve. Of course, this process is quite smelly!



(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form  $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$ .