

Solubility, K_{sp} (the solubility product)

- You've done lots of equilibrium problems, K_a problems, and K_b problems. Solubility (precipitation reactions) are just another example of reactions in water in which we use an equilibrium relationship (K_{sp} = K solubility product).
- Remember a little bit about the basics of solvation: you know "like dissolves like." We expect polar solvents (water) to dissolve ions and polar molecules, whereas nonpolar solvents (CCl_4) work better for nonpolar solutes. So, you've got a little intuition with which to look at solubility, but it's not enough and you have to remember the solubility rules (ugh!).

Soluble

- All nitrates (NO_3^-) are soluble
- All chlorides (Cl^-) are soluble except $AgCl$, Hg_2Cl_2 , $PbCl_2$
- All bromides (Br^-) are soluble except $AgBr$, Hg_2Br_2
- All iodides (I^-) are soluble except AgI , Hg_2I_2 , PbI_2 , HgI_2
- All sulfates (SO_4^{2-}) are soluble except $BaSO_4$, $PbSO_4$, $SrSO_4$
- All Group IA salts are soluble
- Most acetates (CH_3COO^-) and ammonium (NH_4^+) salts are soluble

Insoluble

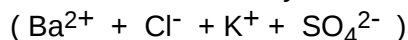
- All carbonates (CO_3^{2-}) are insoluble except those of the Group IA elements and $(NH_4)_2CO_3$
- All sulfites (SO_3^{2-}) are insoluble except those of the Group IA elements and $(NH_4)_2SO_3$
- All phosphates (PO_4^{3-}) are insoluble except those of the Group IA elements and $(NH_4)_3PO_4$
- All sulfides (S^{2-}) are insoluble except those of the Group IA and IIA elements and $(NH_4)_2S$
- All hydroxides (OH^-) are insoluble except those of the Group IA elements and $Ba(OH)_2$ and NH_4OH

- * Some things can be considered to be slightly soluble and I didn't include them in either of the above tables.

You use solubility rules to predict if a precipitate will form when you mix two solutions (precipitation reactions). If any combination of cation and anion forms an insoluble species, you will have precipitation.

For example: Mix together aqueous solutions of barium chloride ($BaCl_2$) and potassium sulfate (K_2SO_4).

Both of these are soluble in water, so before you mix them together what you've really got is:

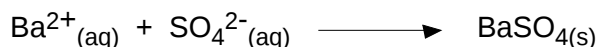


To check and see if a precipitate will form, switch ions and check the solubility rules:

$BaSO_4$ is insoluble and that's a big yes to a precipitate (ppt).

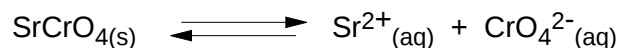
KCl is soluble, so no ppt.

When you write out the overall rxn, make sure you write out the net ionic equation (only include ions that do something, spectator ions algebraically cancel out). For the example, the net ionic equation would be:



Now, equilibrium is this idea of reversibility in chemical reactions. It might seem kind of oxymoronic to talk about equilibrium for insoluble species, but we can talk about equilibrium of insoluble molecules because, to some small extent, all insoluble products dissolve in solution and reach an equilibrium. Everything dissolves in everything and there's a little bit of everything, everywhere. A little bit can be a very little bit though. The **equilibrium constant for the dissolution of insoluble/slightly soluble molecules** is called **the solubility product, K_{sp}** .

For example: put some strontium chromate into water



$$K_{sp} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}]$$

Always leave the solid out of the equilibrium expression. (This usually winds up making the algebra easy also.) Also, K_{sp} is constant for a particular temperature, but it will change with changing temperature.

You'll use K_{sp} to solve the following types of problems:

Type 1. Calculate the concentration of an ion or both ions in solution as follows:

Pb^{2+} and Cl^- solutions are mixed and a ppt forms. If $[\text{Cl}^-] = .1\text{M}$, what is the concentration of Pb^{2+} ?

$$\begin{aligned} \text{for PbCl}_2: \quad K_{sp} &= 1.7 \times 10^{-5} = [.1]^2[x] \\ 1.7 \times 10^{-5} &= [x] = \text{molar concentration of Pb}^{2+} \end{aligned}$$

Type 2. You can be asked to tell whether or not a ppt will form when two solutions are mixed.

—► use a Q_{sp} and compare it to K_{sp} :

$$\begin{aligned} Q_{sp} &> K_{sp} \text{ ppt forms} \\ Q_{sp} &< K_{sp} \text{ no ppt} \\ Q_{sp} &= K_{sp} \text{ is saturated to the point of precipitation, anything more will produce the first ppt.} \end{aligned}$$

For example: Will a ppt form when 75 ml of 0.02 M Ag_2SO_4 is mixed with 50 ml of 0.005M K_2CO_3 ?

$$\text{The } K_{sp} \text{ of } \text{Ag}_2\text{CO}_3 = 8 \times 10^{-12}$$



Okay, the trickiest thing is to remember to add the individual solution volumes and calculate a molarity for each ion in the mixture.

$$\text{Total Volume} = .075\text{L} + .05\text{L} = .125\text{L}$$

$$\text{moles Ag}^{+} = 2 \cdot (.02\text{M})(.075\text{L}) = .003 \text{ moles}$$

$$[\text{Ag}^{+}] = .003\text{moles}/.125\text{L} = .024 \text{ M}$$

$$\text{moles CO}_3^{2-} = (.005\text{M})(.05\text{L}) = .00025 \text{ moles}$$

$$[\text{Ag}^{+}] = .00025\text{moles}/.125\text{L} = .002 \text{ M}$$

$$Q_{sp} = [\text{CO}_3^{2-}][\text{Ag}^{+}]^2 = (.002\text{M})(.024)^2 = 1.2 \times 10^{-6} > K_{sp} \quad \text{yes it will precipitate}$$

Type 3. In some problems you'll have to pay attention to the effect of "common ions." Just remember to do careful bookkeeping on the concentration of any ions in the K_{sp} expression.

There's another reaction that can occur in water that involves the formation of complex ions. Complex ions occur when a metal atom is joined by a coordinate covalent bond to neutral molecules and/or negative ions. This comes into play because it's a way of making insoluble compounds dissolve in solution. It happens like this:

1.

- put AgCl into H_2O
- It's insoluble so it just sits as a ppt.

2.

• Add some ammonia and complex ions will form

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{N} : \text{Ag} : \text{N}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \quad ^+$$

3.

- Now look at the equilibrium of the complex ion
- The name of the equilibrium constant for this is the formation constant, K_f .

$$\text{Ag}^+ + 2 \text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]}$$

4.

- The ppt is gone because the Ag from the AgCl became $\text{Ag}(\text{NH}_3)_2^+$ which is soluble.

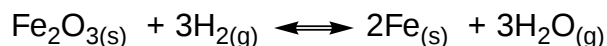
- $K_f = 1.7 \times 10^7$, so the formation of the complex ion is highly favorable

Here are some formation constants for complex ions

Cations		Anions	
Complex ion	K_f	Complex ion	K_f
$\text{Cd}(\text{NH}_3)_6^{2+}$	2.8×10^7	AgCl_2^-	1.8×10^5
$\text{Co}(\text{NH}_3)_6^{2+}$	1.0×10^5	CuCl_2^-	1.8×10^5
$\text{Co}(\text{NH}_3)_6^{3+}$	1.0×10^{23}	PtCl_4^{2-}	1.8×10^{16}
$\text{Co}(\text{NH}_3)_5^{2+}$	2.0×10^{28}	$\text{Cd}(\text{CN})_2^{2-}$	1.8×10^{18}
$\text{Cu}(\text{NH}_3)_4^{2+}$	2.0×10^{12}	$\text{Fe}(\text{CN})_6^{3-}$	1.8×10^{52}
$\text{Ni}(\text{NH}_3)_6^{2+}$	9.0×10^8	$\text{Fe}(\text{CN})_6^{4-}$	1.8×10^{45}
$\text{Zn}(\text{NH}_3)_4^{2+}$	3.6×10^8	$\text{Hg}(\text{CN})_4^{2-}$	1.8×10^{41}
		$\text{Zn}(\text{CN})_4^{2-}$	1.8×10^{16}
		$\text{Al}(\text{OH})_4^-$	1.8×10^{33}
		$\text{Cd}(\text{OH})_4^{2-}$	1.8×10^9
		$\text{Zn}(\text{OH})_4^{2-}$	1.8×10^{14}

Student Packet: 5.3: Solubility: AssessMe questions

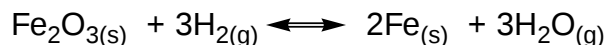
- 1) If the volume of the reaction vessel is decreased, what happens to the following equilibrium?



$\Delta H = 15 \text{ kJ}$

- A) Shift left
 B) Shift right
 C) No change
 D) Not possible to predict
 E) I'm clueless

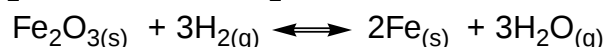
- 2) If $\text{Fe}_2\text{O}_{3(s)}$ is added to the following reaction, what happens to the equilibrium?



$\Delta H = 15 \text{ kJ}$

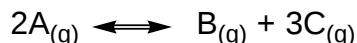
- A) Shift left
 B) Shift right
 C) No change
 D) Not possible to predict
 E) I'm clueless

- 3) For the following reaction, the equilibrium concentrations under certain conditions were found to be $[\text{H}_2\text{O}] = 1.0 \text{ M}$ $[\text{H}_2] = 2.5 \text{ M}$ What is the value for K?



- A) 0.40
 B) 0.064
 C) 15.6
 D) Insufficient information to calculate.
 E) I'm clueless

- 4) Calculate the equilibrium constant for the following reaction:



given that a 1.0 L vessel was initially filled with 5.0 atm of pure A and the partial pressure of gas A was found to be 3.5 atm at equilibrium.

- A) 11.1 atm²
 B) 0.70 atm²
 C) 3.8 atm²
 D) None of these
 E) I'm clueless

- 5) $8.9 \times 10^{-5} \text{ g}$ of silver chloride will dissolve in 100 ml of water at room temperature. What is the approximate molality of a saturated solution?

- A) $1.78 \times 10^{-4} \text{ m}$
 B) $1.78 \times 10^{-3} \text{ m}$
 C) $1.24 \times 10^{-5} \text{ m}$
 D) $6.21 \times 10^{-6} \text{ m}$
 E) I'm clueless

- 6) The correct definition of the solubility product for silver chloride is:

- A) $K_{sp} = [\text{Ag}^+][\text{Cl}^-]/[\text{AgCl}]$
 B) $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
 C) $K_{sp} = 1/([\text{Ag}^+][\text{Cl}^-])$
 D) $K_{sp} = [\text{AgCl}]/([\text{Ag}^+][\text{Cl}^-])$
 E) I'm clueless

Student Packet: 5.3: Solubility: ShowMe questions

- 1) Write the equation for the solubility product, K_{sp} , of each of the following salts:



- 2) Calculate the value of K_{sp} for lead chloride (PbCl_2), which has a solubility of $1.59 \times 10^{-2} \text{ M}$ at 25°C .
- 3) The solubility product of silver phosphate is 1.8×10^{-18} at 25°C . What is the solubility of silver phosphate and what are the equilibrium concentrations of dissolved species in a saturated solution of silver phosphate at 25°C ?
- 4) The solubility product of nickel (II) carbonate is 1.4×10^{-7} . What is the solubility of $\text{NiCO}_{3(s)}$ in pure water? What is its solubility in $0.100 \text{ M Na}_2\text{CO}_3$?

Student Packet: 5.3: Solubility: TestMe questions

1) Which of the following is the correct expression for the solubility product of barium hydroxide?

A) $K_{sp} = [\text{Ba}^{2+}]^2[\text{OH}^-]$ B) $K_{sp} = \frac{[\text{Ba}^{2+}][\text{OH}^-]^2}{[\text{Ba}(\text{OH})_2]}$

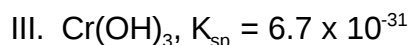
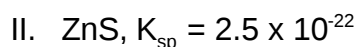
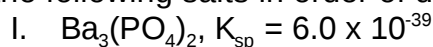
C) $K_{sp} = \frac{[\text{Ba}^{2+}]^2[\text{OH}^-]}{[\text{Ba}(\text{OH})_2]}$ D) $K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2$

E) $K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]$

2) Calculate the solubility of silver chloride at 25°C.
(K_{sp} of AgCl = 1.6×10^{-10})

- A) 1.3×10^{-5} M
B) 1.6×10^{-5} M
C) 1.6×10^{-10} M
D) 3.2×10^{-5} M
E) 3.6×10^{-5} M

3) Arrange the following salts in order of decreasing solubility in pure water:



- A) I > II > III B) I > III > II C) II > I > III D) II > III > I E) III > I > II

4) The solubility of Ag_2S in 0.050 M AgNO_3 is 6.4×10^{-47} M. What is the solubility product, K_{sp} , of Ag_2S ?

- A) 1.6×10^{-49} B) 3.2×10^{-48} C) 2.0×10^{-94} D) 1.0×10^{-95} E) 3.4×10^{-36}

5) The solubility product of $\text{Mg}(\text{OH})_2$ at 25°C is 8.9×10^{-12} . Rank the following solvents in terms of increasing solubility of $\text{Mg}(\text{OH})_2$:

I. Pure water

II. 0.100 M NaOH

III. 0.100 M $\text{Mg}(\text{NO}_3)_2$

- A) I > II > III B) I > III > II C) II > I > III D) I > III > II E) III > I > II