Solubility Product Principle

Dealing with the equilibrium of sparsely soluble solids

How do we deal with solids?

- The solids are <u>only slightly soluble</u> (very little dissolves in water).
- What does dissolve behaves as a <u>strong electrolyte</u> (100% dissociation).
- Solutions become <u>saturated</u> and solid may remain at bottom of container.
- Can solubility be manipulated?

Let's consider silver chloride

$$AgCl\ (s) = Ag^+ + Cl^-$$
s s s

- What is the equilibrium constant?

  $K_{sp} = (Ag^+)(Cl^-) = s^2$
- Now what about the value of the K_{sp}?

  $K_{sp} = 1.6 \times 10^{-10}$
- Can we calculate the solubility, s?

  $s = (K_{sp})^{1/2} = 1.3 \times 10^{-5}$ M

Write the dissociation of the solids and the K_{sp} expressions

- $AgBr\ (s) = Ag^+ + Br^-$ $K_{sp} = (Ag^+)(Br^-)$
- $CaF_2\ (s) = Ca^{++} + 2F^-$ $K_{sp} = (Ca^{++})(F^-)^2$
- $Fe(OH)_3\ (s) = Fe^{+3} + 3OH^-$

  $K_{sp} = (Fe^{+3})(OH^-)^3$

What is the pH of a bottle of Milk of Magnesia, a common antacid?

Milk of Magnesia is $Mg(OH)_2$ with $K_{sp} = 8.9 \times 10^{-12}$

$$Mg(OH)_2\ (s) = Mg^{++} + 2OH^-$$
s s 2s

$K_{sp} = (Mg^{++})(OH^-)^2 = s(2s)^2 = 4s^3$

$s = (K_{sp}/4)^{1/3} = 1.3 \times 10^{-4}$ M

$(OH^-) = 2s = 2.6\ 10^{-4}$ M pOH = 3.58 pH = 10.42

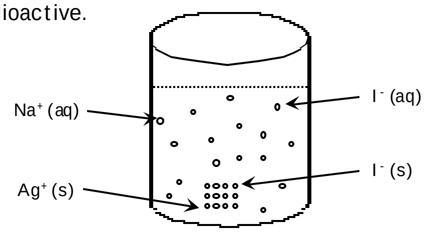
Would the solubility of AgI be the same or different in a solution of NaI? If different, how?

To address this you need to write a reaction and consider Le Chatelier's principle-

$$AgI(s) = Ag^+ + I^-$$

The addition of the NaI causes the reaction to shift to the left. Hence the solubility decreases!

A beaker with NaI, where the aqueous I^- is radioactive, and a crystal of AgI is placed in the beaker, where the I^- in the solid is non-radioactive.



The beaker is allowed to sit for a period of time.

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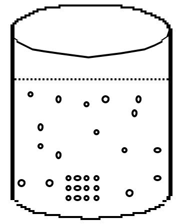
After a period of time, what do you notice about the distribution of the radioactive I^-?



Explain the observation.

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What happened in the beaker?

$AgI\ (s) = Ag^+ + I^-$

dissolves to saturate the aqueous NaI solution with AgI

However, after time passes, the radioactive I^- is found in the solid AgI.

The process is dynamic, as AgI is constantly dissolving and crystallizing.

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What influences the solubility?

- What would happen if we added HCl to the AgCl solution? Decreases solubility
- What would happen if we added NH_3 to the AgCl solution?

The addition of ammonia adds a new twist! As the Ag^+ reacts to form a complex ion as shown below:

$Ag^+ + 2NH_3 = Ag(NH_3)_2^+ \quad K = ?$

Free silver ion — Complexed silver ion

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The formation of complex ions

Ammonia will react with silver (I) ion:

Reactant or product favored?

$Ag^+ + NH_3 = \cancel{Ag(NH_3)^+} \quad K_1 = 2.1 \times 10^3$

$\cancel{Ag(NH_3)^+} + NH_3 = Ag(NH_3)_2^+ \quad K_2 = 8.2 \times 10^3$

$Ag^+ + 2NH_3 = Ag(NH_3)_2^+ \quad K_f = K_1K_2 = 1.7 \times 10^7$

Thiosulfate, used in photography, is an even stronger complexing agent. Why?

$Ag^+ + 2S_2O_3^{-2} = Ag(S_2O_3)_2^{-3} \quad K_f = 2.9 \times 10^{13}$

Formation constant

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Let's examine some reactions:

$AgCl\ (s) = \cancel{Ag^+} + Cl^- \quad K_{sp}$

Add these two reactions

$\cancel{Ag^+} + 2NH_3 = Ag(NH_3)_2^+ \quad K_f$

$AgCl\ (s) + 2NH_3 = Ag(NH_3)_2^+ + Cl^- \quad K_{sp}K_f$

How is the solubility of AgCl (s) influenced?

According to Le Chatelier's principle- the solubility of AgCl (s) increases as the (NH_3) is increased.

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