

## Ionic Equilibria in Aqueous Solution: Solubility Product, $K_{sp}$

Aqueous solution equilibria are important in industrial, analytical and biological processes.

The equilibrium between an undissociated solid solute and its dissolved products in solution is known as solubility equilibria.

Reminder: solubility is a concentration RATE.

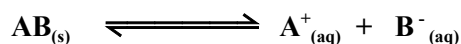
Solubility is defined as **the maximum number of moles of solute that can be dissolved in one liter of solution at a given temperature.**

(NOTE: Mole of solution per liter of solution, units:  $\text{mol L}^{-1}$ ,  $\text{mol dm}^{-3}$ )

When increasing quantities of a sparingly soluble ionic compound AB dissolves in water, a saturated solution is eventually formed, the ions in saturated solution are in equilibrium with the excess undissolved solute.

There is a dynamic equilibrium between undissolved solid and dissolved (aqueous) ions. The rate of dissolving (forward) is equal to the rate of crystallization (precipitation) (reverse).

The equilibrium at saturation can be written as:

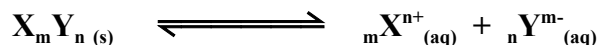


The equilibrium constant for this equation system is called the Solubility Product or  $K_{sp}$ .

$K_{sp}$  is the product of the concentrations of the ions in solution when the system is at saturation, (i.e. equilibrium).

In the case above:  $K_{sp} = [\text{A}^+][\text{B}^-]$

In general, where a compound  $\text{X}_m\text{Y}_n$  reaches equilibrium with its aqueous solution as follows:



The solubility product ( $K_{sp}$ ) is written as:

$$K_{sp} = [\text{X}^{n+}]^m [\text{Y}^{m-}]^n$$

The solubility product constant,  $K_{sp}$ , like other equilibrium constants is temperature dependent. Hence the temperature at which a solubility product is measured should always be stated.

The solubility product of a salt is usually obtained from its solubility.

The Table on page 6 gives some solubility product,  $K_{sp}$ , values at  $25^\circ\text{C}$ .

### Assignment

Write the dissociation equation and the corresponding  $K_{sp}$  expression for the following:

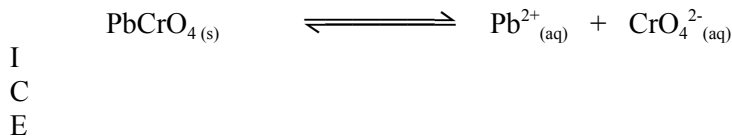
1. Silver bromide, AgBr
2. Silver bromate, AgBrO<sub>3</sub>
3. Lead (II) sulphate, PbSO<sub>4</sub>
4. Iron (III) hydroxide
5. silver carbonate
6. Aluminium Sulphide

## Calculations using solubility product, $K_{sp}$

There are two types, using  $K_{sp}$  and finding  $K_{sp}$

### I. Calculating Solubility given Solubility Product, $K_{sp}$ : Use of $K_{sp}$ to predict solubility

**Sample Problems 1:** the  $K_{sp}$  of lead (II) chromate,  $PbCrO_{4(s)}$ , at  $25\text{ }^{\circ}\text{C}$  is  $2.0 \times 10^{-16}$



$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.0 \times 10^{-16}$$

$$\text{Therefore: } [Pb^{2+}] = [CrO_4^{2-}] = \sqrt{2.0 \times 10^{-16}} = 1.414 \times 10^{-8} \text{ mol/L}$$

This means that lead (II) chromate is insoluble. If one tries to dissolve lead (II) chromate, the maximum amount that can be dissolved will be  $1.4 \times 10^{-8}$  moles. in one liter. Small numbers like these mean that the compound is insoluble.

The solubility product,  $K_{sp}$ , is the product of the MAXIMUM AMOUNT of solute ions that can be dissolved at that temperature.

The  $K_{sp}$  values are indicators of the solubility of compounds.

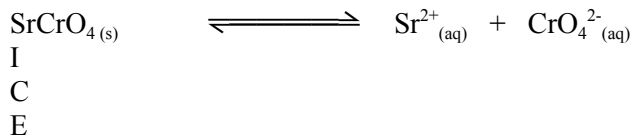
Generally speaking, small  $K_{sp}$  values mean low solubility (insoluble).

((Strictly speaking, ALL ionic compounds or polar covalent compounds are soluble to some extent.))

[An arbitrary value is used for high school chemistry: Below a solubility value of  $0.1 \text{ mol L}^{-1}$ , compounds are taken to be insoluble.]

Obviously, an “insoluble” lead or mercury or organometallic compound with a solubility of (say)  $0.0001 \text{ mol/L}$  would be hazardous to health if ingested.

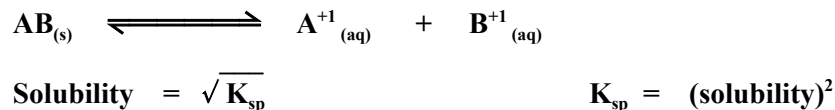
**Example 2:** The  $K_{sp}$  for Strontium chromate,  $SrCrO_4$  is  $3.60 \times 10^{-5}$ . Calculate the solubility of  $SrCrO_4$  at  $25^{\circ}\text{C}$ .



$$\begin{array}{l} \text{i.e. } K_{sp} = [Sr^{2+}][CrO_4^{2-}] = 3.6 \times 10^{-5} \\ K_{sp} = x^2 \\ = 36 \times 10^{-6} \\ \text{Therefore: } “x” = 6.0 \times 10^{-3} \text{ mol L}^{-1} \end{array}$$

This is the solubility of  $SrCrO_4$ . This calculation tells us that at  $25^{\circ}\text{C}$  one cannot have higher concentration of  $SrCrO_4$ ; i.e. Strontium chromate is insoluble for all practical purposes.

Generally, for simple **AB** compound, the solubility is the SQUARE ROOT of the  $K_{sp}$  and conversely, the  $K_{sp}$  is the SQUARE of the solubility.



(NOTE: only for AB compounds, not  $A_2B$ ,  $AB_2$ ,  $A_2B_3$  etc.)

**Assignment:**

- $K_{sp}(\text{AgBrO}_3) = 3.39 \times 10^{-5}$  at  $16^\circ\text{C}$ , what is its solubility?
- $K_{sp}(\text{NiS}) = 4.0 \times 10^{-21}$  at  $20^\circ\text{C}$ , what is its solubility?

**Calculation for compound with the formula: “ $A_2B$ ” type**

Example 1: The  $K_{sp}$  for silver carbonate,  $\text{Ag}_2\text{CO}_3$  is  $6.2 \times 10^{-12}$ . Calculate the solubility for silver carbonate.

Let the solubility of  $\text{Ag}_2\text{CO}_3$  be “x” moles  $\text{L}^{-1}$ , i.e. the maximum that dissolves is the x moles/liter.

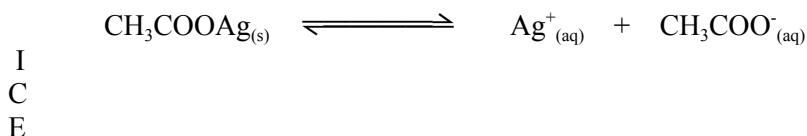


$$\begin{aligned}
 K_{sp} &= [\text{Ag}^{+1}]^2[\text{CO}_3^{-2}] \\
 &= (2x)^2(x) \\
 &= 4x^3 \\
 \therefore 6.2 \times 10^{-12} &= 4x^3 \\
 1.55 \times 10^{-12} &= x^3 \\
 \therefore x &= 1.16 \times 10^{-4} \text{ mol L}^{-1}
 \end{aligned}$$

The solubility of  $\text{Ag}_2\text{CO}_3$  is  $1.16 \times 10^{-4} \text{ mol L}^{-1}$ .

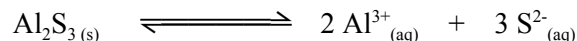
**II. Calculating Solubility Product,  $K_{sp}$  given Solubility**

Example 1: A saturated solution of silver acetate,  $\text{CH}_3\text{COOAg}$  has a concentration of  $0.05 \text{ mol/L}$ . What is the  $K_{sp}$ ? [Note: “AB” Type]



i.e.  $K_{sp} = [\text{Ag}^{+}] = [\text{CH}_3\text{COO}^{-}] = 5.0 \times 10^{-2} \text{ mol L}^{-1}$   
 $K_{sp} = [\text{Ag}^{+}][\text{CH}_3\text{COO}^{-}] = (5.2 \times 10^{-2})^2 \rightarrow \underline{2.5 \times 10^{-3}}$

**Example 2:** The solubility of aluminum sulfide,  $\text{Al}_2\text{S}_3$  is  $2.0 \times 10^{-7} \text{ mol L}^{-1}$ . Calculate the  $K_{\text{sp}}$  for aluminum sulfide.



A concentration of  $2.0 \times 10^{-7} \text{ mol L}^{-1}$  produces an IONIC CONCENTRATION as follows:

$$[\text{Al}^{3+}] = 4.0 \times 10^{-7} \text{ and } [\text{S}^{2-}] = 6.0 \times 10^{-7} \text{ mol L}^{-1}$$

The solubility product is:  $K_{\text{sp}} = [\text{Al}^{3+}]^2 [\text{S}^{2-}]^3$   
 i.e.  $K_{\text{sp}} = (4.0 \times 10^{-7})^2 (6.0 \times 10^{-7})^3$   
 $= 3.5 \times 10^{-32}$

**Assignment:**

1. The solubility of silver carbonate,  $\text{Ag}_2\text{CO}_3(\text{s})$  is  $1.25 \times 10^{-4} \text{ mol L}^{-1}$  at  $20^\circ\text{C}$ , what is its  $K_{\text{sp}}$  ?
2. The solubility of lead (II) iodide,  $\text{PbI}_2(\text{s})$  is  $2.1 \times 10^{-3}$  at  $25^\circ\text{C}$ , what is its  $K_{\text{sp}}$  ?

Limitations to the solubility product concept

The solubility product concept is valid only for saturated solutions in which the total concentration of ions is not more than  $0.01 \text{ mol L}^{-1}$ . For concentrations greater than this, the value of  $K_{\text{sp}}$  is no longer constant, hence can not be used for soluble substances such as  $\text{AgNO}_3$ ,  $\text{NaCl}$ , etc.

Use of  $K_{\text{sp}}$  to predict precipitation

An important application of solubility product is that they can be used to predict the maximum concentrations of ions in solution. Hence, to predict whether or not precipitation will occur.

To check whether a precipitate will form when solutions are mixed, one calculates the ion product, ( i.e. the trial product) for ions in question in solution.

**If the trial product, Q, is LESS THAN the  $K_{\text{sp}}$ , there will be no precipitate.**

(The compound is soluble.)

**If the trial product, Q, is GREATER THAN the  $K_{\text{sp}}$  there will be a precipitate.**

(The ion concentrations are beyond solubility.)

**Example 1:** Given the  $K_{\text{sp}}$  for calcium sulfate so  $2.4 \times 10^{-5}$  at  $25^\circ\text{C}$ . If a 1.0 litre of  $0.02 \text{ mol L}^{-1}$  solution of  $\text{CaCl}_2(\text{aq})$  is mixed with 1.0 litre of  $0.0004 \text{ mol L}^{-1}$  solution of  $\text{Na}_2\text{SO}_4(\text{aq})$ . Will a precipitate form? (A precipitate of  $\text{CaSO}_4$ )

**Solution:**

Since the volume is doubled, the concentration of the reacting ions will be halved. [Divide concentration by 2 and use  $C_1V_1 = C_2V_2$  to calculate the final concentration.]

Therefore:  $[\text{Ca}^{2+}] = 0.01 = 1.0 \times 10^{-2} \text{ mol L}^{-1}$   
 and  $[\text{SO}_4^{2-}] = 0.0002 = 2.0 \times 10^{-4} \text{ mol L}^{-1}$

$$\text{Trial product, Q} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$\text{Trial product, Q} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (1.0 \times 10^{-2})(2.0 \times 10^{-4})$$

$$= 2.0 \times 10^{-6}$$

This is less than the  $K_{\text{sp}}$  for calcium sulphate given in the question as  $2.4 \times 10^{-5}$   
 Therefore, precipitate will NOT occur.

**Example 2:** Mix 1.0 litre of 0.08 mol/L CaCl<sub>2</sub> with 1.0 litre of 0.02 mol/L Na<sub>2</sub>SO<sub>4</sub>.  
Will a precipitate of calcium sulphate, CaSO<sub>4</sub>, form?

**Solution:**

Since the volume is doubled, the concentration of the reacting ions will be halved. [Divide concentration by 2 and use  $C_1V_1 = C_2V_2$  to calculate the final concentration.]

$$\begin{aligned} \text{Trial product, } Q &= [\text{Ca}^{2+}][\text{SO}_4^{2-}] \\ [\text{Ca}^{2+}] &= 4.0 \times 10^{-2} \text{ mol/L} \\ \text{and} \quad [\text{SO}_4^{2-}] &= 1.0 \times 10^{-2} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} \text{Trial product, } Q &= [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (4.0 \times 10^{-2})(1.0 \times 10^{-2}) \\ &= 4.0 \times 10^{-4} \end{aligned}$$

This is more than  $K_{sp}$  for calcium sulphate of  $2.4 \times 10^{-5}$ , therefore a precipitate will occur, until the excess ions are all precipitated. (Excess above solubility)

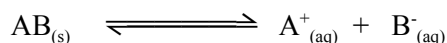
On the following pages are lists of common ions and a table of solubility.

**Precipitation of solids in Nature:**

1. Stalagmites and stalactites: these precipitate from a saturated solution of calcium carbonate; they precipitate slowly from water in which the concentrations of  $\text{Ca}^{+2}_{(aq)}$  and  $\text{CO}_3^{-2}_{(aq)}$  have an ionic product greater than the solubility product of calcium carbonate.
2. Coral reefs grow when the concentrations of  $\text{Ca}^{+2}_{(aq)}$  and  $\text{CO}_3^{-2}_{(aq)}$  ions around the coral must be large enough to precipitate calcium carbonate from the surrounding water.
3. Oyster: the concentrations of  $\text{Ca}^{+2}_{(aq)}$  and  $\text{CO}_3^{-2}_{(aq)}$  must be large enough to precipitate calcium carbonate from sea water from its shell.

**The common ion effect**

In general the solubility of a salt is reduced, i.e. suppressed in the presence of a common ion.



In the presence of either  $\text{A}^{+1}$  or  $\text{B}^{-1}$  from another source, the solubility of the salt AB is reduced.

Example:

Calculate the solubility of  $\text{BaSO}_4_{(s)}$ , given  $K_{sp}(\text{BaSO}_4) = 1.0 \times 10^{-10}$  in:

(a) water:

(b)  $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4_{(aq)}$

## K<sub>sp</sub> Values

Ionic products and K<sub>sp</sub> values for some substances at 25°C

SALT	IONIC PRODUCT	K <sub>sp</sub>
AgC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	[Ag <sup>+</sup> ][C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> ]	2.5 x 10 <sup>-3</sup>
AgBr	[Ag <sup>+</sup> ][Br <sup>-</sup> ]	4.8 x 10 <sup>-13</sup>
Ag <sub>2</sub> CO <sub>3</sub>	[Ag <sup>+</sup> ] <sup>2</sup> [CO <sub>3</sub> <sup>=</sup> ]	8.2 x 10 <sup>-12</sup>
AgCl	[Ag <sup>+</sup> ][Cl <sup>-</sup> ]	1.2 x 10 <sup>-10</sup>
AgI	[Ag <sup>+</sup> ][I <sup>-</sup> ]	1.5 x 10 <sup>-16</sup>
Ag <sub>2</sub> S	[Ag <sup>+</sup> ] <sup>2</sup> [S <sup>=</sup> ]	1.6 x 10 <sup>-49</sup>
Al(OH) <sub>3</sub>	[Al <sup>3+</sup> ][OH <sup>-</sup> ] <sup>3</sup>	5.0 x 10 <sup>-33</sup>
BaCO <sub>3</sub>	[Ba <sup>++</sup> ][CO <sub>3</sub> <sup>=</sup> ]	4.9 x 10 <sup>-9</sup>
BaSO <sub>4</sub>	[Ba <sup>++</sup> ][SO <sub>4</sub> <sup>=</sup> ]	1.1 x 10 <sup>-10</sup>
CdS	[Cd <sup>++</sup> ][S <sup>=</sup> ]	1.0 x 10 <sup>-28</sup>
CaCO <sub>3</sub>	[Ca <sup>++</sup> ][CO <sub>3</sub> <sup>=</sup> ]	4.8 x 10 <sup>-9</sup>
CaF <sub>2</sub>	[Ca <sup>++</sup> ][F <sup>-</sup> ] <sup>2</sup>	4.2 x 10 <sup>-11</sup>
Ca(OH) <sub>2</sub>	[Ca <sup>++</sup> ][OH <sup>-</sup> ] <sup>2</sup>	1.3 x 10 <sup>-6</sup>
CaSO <sub>4</sub>	[Ca <sup>++</sup> ][SO <sub>4</sub> <sup>=</sup> ]	6.1 x 10 <sup>-5</sup>
CuCl	[Cu <sup>+</sup> ][Cl <sup>-</sup> ]	3.2 x 10 <sup>-7</sup>
Cu <sub>2</sub> S	[Cu <sup>+</sup> ] <sup>2</sup> [S <sup>=</sup> ]	1.6 x 10 <sup>-48</sup>
CuS	[Cu <sup>++</sup> ][S <sup>=</sup> ]	8.5 x 10 <sup>-45</sup>
FeS	[Fe <sup>++</sup> ][S <sup>=</sup> ]	3.7 x 10 <sup>-19</sup>
Fe(OH) <sub>3</sub>	[Fe <sup>3+</sup> ][OH <sup>-</sup> ] <sup>3</sup>	1.5 x 10 <sup>-36</sup>
HgS	[Hg <sup>++</sup> ][S <sup>=</sup> ]	3.0 x 10 <sup>-53</sup>
MgCO <sub>3</sub>	[Mg <sup>++</sup> ][CO <sub>3</sub> <sup>=</sup> ]	2.5 x 10 <sup>-5</sup>
Mg(OH) <sub>2</sub>	[Mg <sup>++</sup> ][OH <sup>-</sup> ] <sup>2</sup>	5.9 x 10 <sup>-12</sup>
MnS	[Mn <sup>++</sup> ][S <sup>=</sup> ]	1.4 x 10 <sup>-15</sup>
NiS	[Ni <sup>++</sup> ][S <sup>=</sup> ]	1.8 x 10 <sup>-21</sup>
PbCl <sub>2</sub>	[Pb <sup>++</sup> ][Cl <sup>-</sup> ] <sup>2</sup>	1.0 x 10 <sup>-4</sup>
PbCrO <sub>4</sub>	[Pb <sup>++</sup> ][CrO <sub>4</sub> <sup>=</sup> ]	1.8 x 10 <sup>-14</sup>
PbSO <sub>4</sub>	[Pb <sup>++</sup> ][SO <sub>4</sub> <sup>=</sup> ]	1.9 x 10 <sup>-8</sup>
PbS	[Pb <sup>++</sup> ][S <sup>=</sup> ]	8.4 x 10 <sup>-28</sup>
SrSO <sub>4</sub>	[Sr <sup>++</sup> ][SO <sub>4</sub> <sup>=</sup> ]	2.8 x 10 <sup>-7</sup>
ZnS	[Zn <sup>++</sup> ][S <sup>=</sup> ]	4.5 x 10 <sup>-24</sup>

**Solubility of Common Inorganic Compounds in Water**  
(Low solubility = “insoluble”)

Negative Ions (anions)	+	Positive Ions (cations)	–	Compounds with the solubility
Essentially <b>all</b>		<b>Alkali ions</b> (Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , Fr <sup>+</sup> )		Soluble
Essentially <b>all</b>		<b>Hydrogen ions</b> [H <sup>+</sup> <sub>(aq)</sub> ]		Soluble (ACIDS)
Essentially <b>all</b>		<b>Ammonium ions</b> (NH <sub>4</sub> <sup>+</sup> )		Soluble
<b>Nitrate</b> , NO <sub>3</sub> <sup>-</sup>		<b>Essentially all</b>		Soluble
<b>Acetate</b> , CH <sub>3</sub> COO <sup>-</sup>		<b>Essentially all</b>		Soluble
Chloride, Cl <sup>-</sup> Bromide, Br <sup>-</sup> Iodide, I <sup>-</sup>		Ag <sup>+</sup> , Pb <sup>+</sup> , Hg <sup>2+</sup> , Cu <sup>+</sup> , Ti <sup>+</sup>		Low solubility
		All others		Soluble
Sulfate, SO <sub>4</sub> <sup>2-</sup>		Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Pb <sup>2+</sup> , Ra <sup>2+</sup>		Low solubility
		All others		Soluble
Sulfide, S <sub>2</sub> <sup>-</sup>		Alkali ions, H <sup>+</sup> <sub>(aq)</sub> , NH <sub>4</sub> <sup>+</sup> , Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Ra <sup>2+</sup>		Soluble
		All others		Low solubility
Hydroxide, OH <sup>-</sup>		Alkali ions, H <sup>+</sup> <sub>(aq)</sub> , NH <sub>4</sub> <sup>+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Ra <sup>2+</sup> , Ti <sup>+</sup>		Soluble
		All others		Low solubility
Phosphate, PO <sub>4</sub> <sup>3-</sup> Carbonate, CO <sub>3</sub> <sup>2-</sup>		Alkali ions, H <sup>+</sup> <sub>(aq)</sub> , NH <sub>4</sub> <sup>+</sup>		Soluble
Sulfite, SO <sub>3</sub> <sup>2-</sup>		All others		Low solubility