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: mol L^{-1}, 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:

$$\mathbf{AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}}$$

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: $\mathbf{K_{sp} = [A^{+}][B^{-}]}$

In general, where a compound X_mY_n reaches equilibrium with its aqueous solution as follows:

$$\mathbf{X_mY_{n\ (s)} \rightleftharpoons {}_mX^{n+}_{(aq)} + {}_nY^{m-}_{(aq)}}$$

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

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

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°C.

Assignment

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

1. Silver bromide, AgBr
2. Silver bromate, $AgBrO_3$
3. Lead (II) sulphate, $PbSO_4$
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 °C is 2.0×10^{-16}

$$PbCrO_{4\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

I
C
E

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

Therefore: $[Pb^{2+}] = [CrO_4^{2-}] = \sqrt{2.0 \times 10^{-16}} = 1.414 \times 10^{-8}$ 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 1.4×10^{-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 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 mol/L would be hazardous to health if ingested.

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

$$SrCrO_{4\,(s)} \rightleftharpoons Sr^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

I
C
E

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

This is the solubility of $SrCrO_4$. This calculation tells us that at 25EC one cannot have higher concentration of SrCrO4; 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.

$$\mathbf{AB_{(s)} \rightleftharpoons A^{+1}_{(aq)} + B^{+1}_{(aq)}}$$

$$\textbf{Solubility} = \sqrt{\mathbf{K_{sp}}} \qquad \mathbf{K_{sp}} = \textbf{(solubility)}^2$$

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

Assignment:

1. K_{sp} ($AgBrO_3$) = 3.39×10^{-5} at 16 ^{O}C, what is its solubility?

2. K_{sp} (NiS) = 4.0×10^{-21} at 20 ^{O}C, what is its solubility?

Calculation for compound with the formula: "A_2B" type

Example1: The K_{sp} for silver carbonate, Ag_2CO_3 is 6.2×10^{-12} . Calculate the solubility for silver carbonate.

Let the solubility of Ag_2CO_3 be "x" moles L^{-1}, i.e. the maximum that dissolves is the x moles/liter.

$$Ag_2CO_{3\,(s)} \rightleftharpoons Ag^{+1}_{(aq)} + CO_3^{--2}{}_{(aq)}$$

	$Ag_2CO_{3\,(s)}$	$Ag^{+1}_{(aq)}$	$CO_3^{--2}{}_{(aq)}$
I			
C		2x	x
E			

$$\begin{aligned} K_{sp} &= [Ag^+]^2[CO_3^-] \\ &= (2x)^2 \quad (x) \\ &= 4x^3 \\ .\!:\quad 6.2 \times 10^{-12} &= 4x^3 \\ 1.55 \times 10^{-12} &= x^3 \\ .\!:\quad x &= 1.16 \times 10^{-4} \text{ mol } L^{-1} \end{aligned}$$

The solubility of Ag_2CO_3 is 1.16×10^{-4} mol L^{-1}.

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

Example 1: A saturated solution of silver acetate, CH_3COOAg has a concentration of 0.05 mol/L. What is the K_{sp}? [Note: "AB" Type]

$$CH_3COOAg_{(s)} \rightleftharpoons Ag^+_{(aq)} + CH_3COO^-_{(aq)}$$

	$CH_3COOAg_{(s)}$	$Ag^+_{(aq)}$	$CH_3COO^-_{(aq)}$
I			
C			
E			

i.e. K_{sp} = $[Ag^+]$ = $[CH_3COO^-]$ = 5.0×10^{-2} mol L^{-1}

K_{sp} = $[Ag+][CH_3COO^-]$ = $(5.2 \times 10^{-2})^2 \rightarrow \underline{2.5 \times 10^{-3}}$

Example 2: The solubility of aluminum sulfide, Al_2S_3 is 2.0×10^{-7} mol L^{-1}. Calculate the K_{sp} for aluminum sulfide.

$$Al_2S_{3\,(s)} \rightleftharpoons 2\,Al^{3+}_{(aq)} + 3\,S^{2-}_{(aq)}$$

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

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

The solubility product is: $K_{sp} = [Al^{3+}]^2 [S^{2-}]^3$

i.e. $K_{sp} = (4.0 \times 10^{-7})^2 (6.0 \times 10^{-7})^3$

$= 3.5 \times 10^{-32}$

Assignment:

1. The solubility of silver carbonate, $Ag_2CO_{3\,(s)}$ is 1.25×10^{-4} mol L^{-1} at 20 ^OC, what is its K_{sp} **?**

2. The solubility of lead (II) iodide, $PbI_{2\,(s)}$ is 2.1×10^{-3} at 25 ^OC, what is its K_{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 mol L^{-1}**.** For concentrations greater than this, the value of K_{sp} is no longer constant, hence can not be used for soluble substances such as $AgNO_3$, NaCl, etc.

Use of K_{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 mill 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_{sp}, there will be no precipitate.
(The compound is soluble.)

If the trial product, Q, is GREATER THAN the K_{sp} there will be a precipitate.
(The ion concentrations are beyond solubility.)

Example 1: Given the K_{sp} for calcium sulfate so 2.4×10^{-5} at 25 ^OC. If a 1.0 litre of 0.02 mol L^{-1} solution of $CaCl_{2\,(aq)}$ is mixed with 1.0 litre of 0.0004 mol L^{-1} solution of $Na_2SO_{4\cdot(aq)}$. Will a precipitate form? (A precipitate of $CaSO_4$)

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: $[Ca^{2+}] = 0.01 = 1.0 \times 10^{-2}$ mol L^{-1}

and $[SO_4^{2-}] = 0.0002 = 2.0 \times 10^{-4}$ mol $L.^{-1}$

Trial product, Q = $[Ca^{2+}][SO_4^{2-}]$

Trial product, Q = $[Ca^{2+}][SO_4^{2-}] = (1.0 \times 10^{-2})(2.0 \times 10^{-4})$

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

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

Example 2: Mix 1.0 litre of 0.08 mol/L $CaCl_2$ with 1.0 litre of 0.02 mol/L Na_2SO_4.
Will a precipitate of calcium sulphate, $CaSO_4$, 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.]

Trial product, Q = $[Ca^{2+}][SO_4^{2-}]$
$[Ca^{2+}] = 4.0 \times 10^{-2}$ mol/L
and $[SO_4^{2-}] = 1.0 \times 10^{-2}$ mol/L

Trial product, Q = $[Ca^{2+}][SO_4^{2-}] = (4.0\times10^{-2})(1.0 \times 10^{-2})$
$= 4.0 \times 10^{-4}$

This is more than K_{sp} for calcium sulphate of 2.4×10^{-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 $Ca^{+2}_{(aq)}$ and $CO_3{}^{-2}{}_{(aq)}$ have an ionic product greater than the solubility product of calcium carbonate.
2. Coral reefs grow when the concentrations of $Ca^{+2}_{(aq)}$ and $CO_3{}^{-2}{}_{(aq)}$ ions around the coral must be large enough to precipitate calcium carbonate from the surrounding water.
3. Oyster: the concentrations of $Ca^{+2}_{(aq)}$ and $CO_3{}^{-2}{}_{(aq)}$ 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.

$$AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}$$

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

Example:
Calculate the solubility of $BaSO_{4\,(s)}$, given K_{sp} $(BaSO_4) = 1.0 \times 10^{-10}$ in:
(a) water:

(b) 0.1 mol L^{-1} $Na_2SO_{4\,(aq)}$

K_{sp} Values

Ionic products and K_{sp} values for some substances at 25°C

SALT	IONIC PRODUCT	K_{sp}
$AgC_2H_3O_2$	$[Ag^+][C_2H_3O_2^-]$	2.5×10^{-3}
$AgBr$	$[Ag+][Br^-]$	4.8×10^{-13}
Ag_2CO_3	$[Ag^+]^2[CO_3^=]$	8.2×10^{-12}
$AgCl$	$[Ag^+][Cl^-]$	1.2×10^{-10}
AgI	$[Ag^+][I^-]$	1.5×10^{-16}
Ag	$[Ag^+]^2[S^=]$	1.6×10^{-49}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	5.0×10^{-33}
$BaCO_3$	$[Ba^{++}][CO^=]$	4.9×10^{-9}
$BaSO_4$	$[Ba^{++}][SO_4^=]$	1.1×10^{-10}
CdS	$[Cd^{++}][S^=]$	1.0×10^{-28}
$CaCO_3$	$[Ca^{++}][CO_3^=]$	4.8×10^{-9}
CaF_2	$[Ca^{++}][F^-]^2$	4.2×10^{-11}
$Ca(OH)_2$	$[Ca^{++}]\ [OH^-]^2$	1.3×10^{-6}
$CaSO_4$	$[Ca^{++}][SO_4^=]$	6.1×10^{-5}
$CuCl$	$[Cu^+][Cl^-]$	3.2×10^{-7}
Cu_2S	$[Cu^+]^2[S^=]$	1.6×10^{-48}
CuS	$[Cu^{++}][S^=]$	8.5×10^{-45}
FeS	$[Fe^{++}][S^=]$	3.7×10^{-19}
$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	1.5×10^{-36}
HgS	$[Hg^{++}][S^=]$	3.0×10^{-53}
$MgCO_3$	$[Mg^{++}][CO_3^=]$	2.5×10^{-5}
$Mg(OH)_2$	$[Mg^{++}][OH^-]^2$	5.9×10^{-12}
MnS	$[Mn^{++}][S^=]$	1.4×10^{-15}
NiS	$[Ni^{++}][S^=]$	1.8×10^{-21}
$PbCl_2$	$[Pb^{++}][Cl^-]^2$	1.0×10^{-4}
$PbCrO_4$	$[Pb^{++}][CrO_4^=]$	1.8×10^{-14}
$PbSO_4$	$[Pb^{++}][SO_4^=]$	1.9×10^{-8}
PbS	$[Pb^{++}][S^=]$	8.4×10^{-28}
$SrSO_4$	$[Sr^{++}][SO_4^=]$	2.8×10^{-7}
ZnS	$[Zn^{++}][S^=]$	4.5×10^{-24}

Solubility of Common Inorganic Compounds in Water

(Low solubility = “insoluble”)

Negative Ions (anions)	+	Positive Ions (cations)	_	Compounds with the solubility
Essentially **all**		**Alkali ions** (Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+)		Soluble
Essentially **all**		**Hydrogen ions** [$H^+_{(aq)}$]		Soluble (ACIDS)
Essentially **all**		**Ammonium ions** (NH_4^+)		Soluble
Nitrate, NO_3^-		**Essentially all**		Soluble
Acetate, CH_3COO^-		**Essentially all**		Soluble
Chloride, Cl^- Bromide, Br^- Iodide, I^-		Ag^+, Pb^+, Hg^{2+}, Cu^+, Ti^+		Low solubility
		All others		Soluble
Sulfate, SO_4^{2-}		Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Ra^{2+}		Low solubility
		All others		Soluble
Sulfide, S_2**-**		Alkali ions, $H^+_{(aq)}$, NH_4^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}		Soluble
		All others		Low solubility
Hydroxide, OH^-		Alkali ions, $H^+_{(aq)}$, NH_4^+, Sr^{2+}, Ba^{2+}, Ra^{2+}, Ti^+		Soluble
		All others		Low solubility
Phosphate, PO_4^{3-} Carbonate, CO_3^{2-} Sulfite, SO_3^{2-}		Alkali ions, $H^+_{(aq)}$, NH_4^+		Soluble
		All others		Low solubility