SOLUBILITY EQUILIBRIUM
1: SOLUBILITY CONSTANT

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SOLUBILITY

Ionic salts can be soluble or insoluble in water. We have already learned about the solubility rules which help us determine which salts will be soluble. However, even when a salt is considered insoluble, it might be slightly soluble. How slightly? This is what we learn in this chapter.

- Insoluble salts are soluble in equilibrium in water.
- Solubility constants are just like K_c – except it is called K_{sp}, the solubility product.
- One can use the K_{sp} values to determine the concentrations of ions.
- K_{sp} is also used to calculate the concentration of salts required for precipitation of a salt.

Writing equations for solubility: $MX_{n(s)} \rightleftharpoons M^{n+}_{(aq)} + nX^{-}_{(aq)}$

- For the above reaction: $K_{sp} = [M^{n+}][X^{-}]^{n}$
- The coefficients for the ions are used as powers for the ions.
- As usual, solids and liquids are not included in the expressions.

SOLUBILITY PRODUCT AND EXPRESSION

K_{sp} , the solubility product can be used to determine molar solubility (and solubility). The smaller the K_{sp} value, the lower the solubility of that salt.

For example:

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

$$K_{\text{sp}} = [Al^{3+}][OH^{-}]^{3} \qquad = 1.8 \times 10^{-33}$$

$$Bi_2S_{3\,(s)} \rightleftharpoons 2Bi^{2+}{}_{(aq)} + 3S^{2-}{}_{(aq)}$$

$$K_{\text{sp}} = [Bi^{2+}]^{2}[S^{2-}]^{3} \qquad = 1.6 \times 10^{-72}$$ *less soluble*

Molar solubility can be expressed in two units:

- Molar solubility – mol/L (used to calculate the value of K_{sp}).
- Solubility – g/L.

Usually, this data will be for a solution at 25 ^{o}C because solubility depends on temperature.

EXAMPLE 1: WRITING K_{sp} EXPRESSION

Write the solubility–product expression for the following salts:

a. Hg_2Cl_2

b. $HgCl_2$

Answer:

$$Hg_2Cl_{2\,(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

(Note: Hg_2^{2+} is a polyatomic ion)

$$HgCl_{2\,(s)} \rightleftharpoons Hg^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

$$K_{sp} = [Hg^{2+}][Cl^-]^2$$

EXAMPLE 2: CALCULATING MOLAR SOLUBILITY

Calculate the molar solubility of SnS at 25 °C. K_{sp} = 1.0 × 10^{-26})

Answer:

$$SnS_{(s)} \rightleftharpoons Sn^{2+}_{(aq)} + S^{2-}_{(aq)}$$

		Sn^{2+}	S^{2-}
Initial		0	0
Change		$+s$	$+s$
Eq conc		s	s

$$K_{sp} = [\mathrm{Sn}^{2+}][\mathrm{S}^{2-}] = 1.0 \times 10^{-26}$$

$$1.0 \times 10^{-26} = (s)(s) = s^2$$

$$s = \boxed{1.0 \times 10^{-13}\ M}$$

EXAMPLE 3: CALCULATING SOLUBILITY

Calomel, whose chemical name is mercury(I) chloride, Hg_2Cl_2, was once used in medicine (as a laxative and diuretic). It has a K_{sp} of 1.3×10^{-18}. What is the molar solubility and solubility in grams per liter of Hg_2Cl_2?

Answer:	$Hg_2Cl_{2\,(s)} \rightleftharpoons$	$Hg_2^{2+}{}_{(aq)}$ +	$2Cl^-{}_{(aq)}$
Initial		0	0
Change		$+s$	$+2s$
Eq conc		s	$2s$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$K_{sp} = s(2s)^2 = s(4s^2) = 4s^3$$

$$1.3 \times 10^{-18} = 4s^3$$

$$s^3 = 3.25 \times 10^{-19}$$

$$s = \boxed{6.88 \times 10^{-7}\ \mathrm{M}}$$

The molar solubility is $6.9 \times 10^{-7}\ M$, to calculate solubility in g/L find the molar mass of Hg_2Cl_2.

$$\frac{6.88 \times 10^{-7}\ \mathrm{mol}}{\mathrm{L}} \times \frac{472.086\ \mathrm{g}}{1\ \mathrm{mol}} = \boxed{3.2 \times 10^{-4}\ \mathrm{g/L}}$$

EXAMPLE 4: CALCULATING K_{sp} - 1

Exactly 0.133 mg of AgBr will dissolve in 1.00 L of water. What is the value of K_{sp} for AgBr?

Answer:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

$$K_{sp} = [Ag^+][Br^-]$$

The solubility is given as 0.133 mg/1.00 L, but K_{sp} uses molarity:

$$\frac{0.133 \times 10^{-3}\text{ g}}{1.00\text{ L}} \times \frac{1\text{ mol}}{187.77\text{ g}} = 7.083 \times 10^{-7}\text{ M}$$

$$[Ag^+] = [Cl^-] = s = 7.083 \times 10^{-7}\text{ M}$$

$$K_{sp} = [Ag^+][Cl^-] = (7.083 \times 10^{-7})^2$$

$$\boxed{K_{sp} = 5.02 \times 10^{-13}}$$

EXAMPLE 5: CALCULATING K_{sp} - 2

An experimenter finds that the solubility of barium fluoride is 1.10 g in 1.00 L of water at 25°C. What is the value of K_{sp} for barium fluoride, BaF_2, at this temperature?

Answer:	$BaF_{2\,(s)} \rightleftharpoons$	$Ba^{2+}{}_{(aq)}$ +	$2F^{-}{}_{(aq)}$
Initial		0	0
Change		$+s$	$+2s$
Eq conc		s	$2s$

$$K_{sp} = [Ba^{2+}][F^{-}]^2$$

The solubility is given as 1.1 g/1.00 L, but K_{sp} uses molarity:

$$s = \frac{1.1\ \text{g}}{1.00\ \text{L}} \times \frac{1\ \text{mol}}{175.32\ \text{g}} = 6.27 \times 10^{-3}\ \text{M}$$

$[Ba^{2+}] = s = 6.27 \times 10^{-3}$ M and $[F^{-}] = 2s = 2(6.27 \times 10^{-3}) = 1.25 \times 10^{-2}$ M

$$K_{sp} = [Ba^{2+}]\,[F^{-}]^2 = (6.27 \times 10^{-3})(1.25 \times 10^{-2})^2 = \boxed{9.80 \times 10^{-7}}$$

K_{sp} FOR SOME SALTS

Dissociation of salts can be shown as a generic equation: $A_xB_{y\,(s)} \rightleftharpoons xA_{(aq)} + yB_{(aq)}$

The K_{sp} of some salts are given in the tables below.

Compound	Formula	Ksp
Ammonium hydroxide	$Al(OH)_3$	1.8×10^{-33}
Barium carbonate	$BaCO_3$	8.1×10^{-9}
Barium fluoride	BaF_2	1.7×10^{-6}
Barium sulfateq	$BaSO_4$	1.1×10^{-10}
Bismuth sulfide	Bi_2S_3	1.6×10^{-72}
Cadmium sulfide	CdS	8.0×10^{-28}
Calcium fluoride	CaF_2	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	8.0×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	1.2×10^{-26}
Chromium (III) hydroxide	$Cr(OH)_3$	3.0×10^{-29}
Cobalt (II) sulfide	CoS	4.0×10^{-21}
Copper (I) bromide	$CuBr$	4.2×10^{-8}
Copper (II) hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Copper (II) sulfide	CuS	6.0×10^{-37}
Iron (II) hydroxide	$Fe(OH)_2$	1.6×10^{-14}
Iron (II)sulfide	FeS	6.0×10^{-19}
Iron (III) hydroxide	$Fe(OH)_3$	1.1×10^{-36}
Lead (II) carbonate	$PbCO_3$	3.3×10^{-14}
Lead (II) chloride	$PbCl_2$	2.4×10^{-4}

Compound	Formula	Ksp
Lead (II) chromate	$PbCrO_4$	2.0×10^{-14}
Lead (II) fluoride	PbF_2	4.0×10^{-8}
Lead (II) iodide	PbI_2	1.4×10^{-8}
Lead (II) sulfide	PbS	3.4×10^{-28}
Magnesium carbonate	$MgCO_3$	4.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	1.2×10^{-11}
Manganese (II) sulfide	MnS	3.0×10^{-14}
Mercury (I) chloride	Hg_2Cl_2	3.5×10^{-18}
Mercury (II) sulfide	HgS	4.0×10^{-54}
Nickel (II) sulfide	NiS	1.4×10^{-24}
Silver bromide	$AgBr$	7.7×10^{-13}
Silver carbonate	Ag_2CO_3	8.1×10^{-12}
Silver chloride	$AgCl$	1.6×10^{-10}
Silver iodide	AgI	8.3×10^{-17}
Silver sulfide	Ag_2S	6.0×10^{-51}
Strontium carbonate	$SrCO_3$	1.6×10^{-9}
Tin (II) sulfide	SnS	1.0×10^{-26}
Zinc hydroxide	$Zn(OH)_2$	1.8×10^{-14}
Zinc sulfide	ZnS	3.0×10^{-23}

EXAMPLE 6: CONCEPT CHECK

Lead compounds have been used as paint pigments, but because the lead(II) ion is toxic, the use of lead paints in homes is now prohibited. Which of the following lead(II) compounds would yield the greatest number of lead(II) ions when added to the same quantity of water (assuming that some undissolved solid always remains): $PbCrO_4$, $PbSO_4$, or PbS?

Answer:

We can begin by identifying the value of K_{sp} for each compound:

$PbCrO_4$	1.8×10^{-14}
$PbSO_4$	1.7×10^{-8}
PbS	2.5×10^{-27}

Each salt produces two ions, so each has the same expression for the solubility−product constant: $K_{sp} = s^2$.

The solubility will be largest for $PbSO_4$.

KEY CONCEPTS

- Calculate molar solubility
- Calculate K_{sp}
- Predict relative solubilities