18.3 Solubility Equilibrium

Connecting to Your World

Barium sulfate is ingested by a patient before X-ray images of the digestive tract are taken. Barium sulfate absorbs the X-rays, thereby producing light areas on the developed X-ray film. However, barium salts are usually toxic. You will learn why patients can ingest this poisonous substance without harm.

What is a solution?

- A solution is a mixture in which a solid has been dissolved into a liquid, usually water
- It is expressed as (aq) for its state of matter
- Ionic compounds are solids at room temperature
- In order for the ions to interact with one another, they need to be dissolved in water, forming a solution

Solubility

- Dissolving and precipitating
  - Ex. Tooth decay from acids
  - Precipitation of salts in the kidneys which forms stones
  - Dissolved salts in rainwater
- A **saturated** solution is one where no more solute can dissolve in solution
- Solubility equations look like net ionic equations
  - $BaSO_{4(s)} \leftrightarrow Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Equilibrium Expressions and Solubility

- **Equilibrium** expresses the degree to which the solid is soluble in water
- $BaSO_{4(s)} \leftrightarrow Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$
  - This equation indicates that at equilibrium there is a presence of all three entities
  - However, ***we are only concerned with the concentration of ions in the solution,*** although we accept that there is some undissolved ionic compound present ($BaSO_{4(s)}$)

- The equilibrium reaction would be as follows:

Ionic Compound(s) ↔ $Cation^{+}$(aq) + $Anion^{-}$(aq)

$AgCl_{(s)} \leftrightarrow Ag^{1+}{}_{(aq)} + Cl^{1-}{}_{(aq)}$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

You can write an equilibrium expression for this process.

$$K_{eq} = \frac{[Ag^+] \times [Cl^-]}{[AgCl]}$$

$$K_{eq} \times [AgCl] = [Ag^+] \times [Cl^-] = K_{sp}$$

e.g. Write the Ksp expression for:

(i) AgCl (ii) $BaSO_4$ (iii) $PbCl_2$

(i) Ionization Equation: $AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

$K_{sp} = [Ag^{+}_{(aq)}] [Cl^{-}_{(aq)}]$

(ii) Ionization Equation: $BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$K_{sp} = [Ba^{2+}_{(aq)}] [SO_4^{2-}{}_{(aq)}]$

(iii) Ionization Equation: $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\ Cl^{-}_{(aq)}$

$K_{sp} = [Pb^{2+}_{(aq)}] [Cl^{-}_{(aq)}]^2$

The Solubility Product Constant

- Solubility varies from one ionic compound to the next
- Some ionic compounds can dissolve quite significantly in water where others cannot
  - They are either **soluble** or **insoluble**
- Table 18.1, p. 561 highlights some of the solubilities of various ionic compounds
  - **Water is always the solvent**

Table 18.1

Solubilities of Ionic Compounds in Water		
Compounds	**Solubility**	**Exceptions**
Salts of Group 1A metals and ammonia	Soluble	Some lithium compounds
Ethanoates, nitrates, chlorates, and perchlorates	Soluble	Few exceptions
Sulfates	Soluble	Compounds of Pb, Ag, Hg, Ba, Sr, and Ca
Chlorides, bromides, and iodides	Soluble	Compounds of Ag and some compounds of Hg and Pb
Sulfides and hydroxides	Most are insoluble	Alkali metal sulfides and hydroxides are soluble. Compounds of Ba, Sr, and Ca are slightly soluble.
Carbonates, phosphates, and sulfites	Insoluble	Compounds of the alkali metals and of ammonium ions

- **Although an ionic compound may be considered insoluble, a small amount does actually dissolve**
- The equilibrium reaction would be as follows:

Ionic Compound(s) ↔ Cation^{+}(aq) + Anion^{-}(aq)

$AgCl_{(s)} \leftrightarrow Ag^{1+}_{(aq)} + Cl^{1-}_{(aq)}$

The **solubility product constant (K_{sp})**, equals the product of the concentrations of the ions, each raised to a power equal to the coefficient of the ion in the dissociation equation.

$$K_{sp} = [Ag^+] \times [Cl^-]$$
$$K_{sp} = 1.8 \times 10^{-10}$$

The smaller the numerical value of the solubility product constant, the lower the solubility of the compound.

Scale, formed by the precipitation of slightly soluble salts, builds up around faucets.

Why are insoluble substances hard to remove?

They do NOT dissolve in a solvent such as water.

Review

Any ionic solid placed in water establishes an equilibrium between its dissociated ions in solution and the solid that is undissolved

The solubility product constant is an equilibrium constant that describes the equilibrium between a solid and its ions in solution

Table 18.2, p. 562 – examine for high/low solubilities

Table 18.2

Solubility Product Constants (K_{sp}) at 25°C

Salt	K_{sp}	Salt	K_{sp}	Salt	K_{sp}
Halides		**Sulfates**		**Hydroxides**	
AgCl	1.8×10^{-10}	$PbSO_4$	6.3×10^{-7}	$Al(OH)_3$	3.0×10^{-34}
AgBr	5.0×10^{-13}	$BaSO_4$	1.1×10^{-10}	$Zn(OH)_2$	3.0×10^{-16}
AgI	8.3×10^{-17}	$CaSO_4$	2.4×10^{-5}	$Ca(OH)_2$	6.5×10^{-6}
$PbCl_2$	1.7×10^{-5}	**Sulfides**		$Mg(OH)_2$	7.1×10^{-12}
$PbBr_2$	2.1×10^{-6}	NiS	4.0×10^{-20}	$Fe(OH)_2$	7.9×10^{-16}
PbI_2	7.9×10^{-9}	CuS	8.0×10^{-37}	**Carbonates**	
PbF_2	3.6×10^{-8}	Ag_2S	8.0×10^{-51}	$CaCO_3$	4.5×10^{-9}
CaF_2	3.9×10^{-11}	ZnS	3.0×10^{-23}	$SrCO_3$	9.3×10^{-10}
Chromates		FeS	8.0×10^{-19}	$ZnCO_3$	1.0×10^{-10}
$PbCrO_4$	1.8×10^{-14}	CdS	1.0×10^{-27}	Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	1.2×10^{-12}	PbS	3.0×10^{-28}	$BaCO_3$	5.0×10^{-9}

SAMPLE PROBLEM 18.3

Finding the Ion Concentrations in a Saturated Solution

What is the concentration of lead ions and chromate ions in a saturated lead chromate solution at 25°C? ($K_{sp} = 1.8 \times 10^{-14}$)

Analyze ***List the knowns and the unknowns.***

Knowns

- $K_{sp} = 1.8 \times 10^{-14}$
- $K_{sp} = [Pb^{2+}] \times [CrO_4^{2-}]$
- $PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$

Unknowns

- $[Pb^{2+}] = ?\ M$
- $[CrO_4^{2-}] = ?\ M$

For each Pb^{2+} ion formed, one CrO_4^{2-} ion is formed.

Calculate ***Solve for the unknowns.***

$$K_{sp} = [Pb^{2+}] \times [CrO_4^{2-}] = 1.8 \times 10^{-14}$$

At equilibrium $[Pb^{2+}] = [CrO_4^{2-}]$. Substitute $[Pb^{2+}]$ for $[CrO_4^{2-}]$ in the expression for K_{sp} to get an equation with one unknown.

$$K_{sp} = [Pb^{2+}] \times [Pb^{2+}] = [Pb^{2+}]^2 = 1.8 \times 10^{-14}$$

Solve for $[Pb^{2+}]$.

$$[Pb^{2+}] = [CrO_4^{2-}] = \sqrt{1.8 \times 10^{-14}} = 1.3 \times 10^{-7}M$$

Finding the Ion Concentrations in a Saturated Solution

What is the concentration of lead ions and chromate ions in a saturated lead chromate solution at 25°C? ($K_{sp} = 1.8 \times 10^{-14}$)

① $PbCrO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_{4(aq)}^{2-}$

② $K_{sp} = 1.8 \times 10^{-14}$

③ $1.8 \times 10^{-14} = [Pb^{2+}_{(aq)}][CrO_{4(aq)}^{2-}]$

$= X \cdot X$

$\sqrt{1.8 \times 10^{-14}} = \sqrt{X^2}$

$1.3 \times 10^{-7} = X$

$[Pb^{2+}_{(aq)}] = [CrO_{4(aq)}^{2-}] = 1.3 \times 10^{-7} M$

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Extra question

What is the concentation of barium and sulfate ions in a saturated barium sulfate solution at 25°C?

$K_{sp} = 1.1 \times 10^{-10}$

Example

① $PbCrO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_{4(aq)}^{2-}$

② $K_{sp} = 1.8 \times 10^{-14}$

③ $1.8 \times 10^{-14} = [Pb^{2+}_{(aq)}][CrO_{4(aq)}^{2-}]$

$= X \cdot X$

$\sqrt{1.8 \times 10^{-14}} = \sqrt{X^2}$

$1.3 \times 10^{-7} = X$

17. Lead(II) sulfide (PbS) has a K_{sp} of 3.0×10^{-28}. What is the concentration of lead(II) ions in a saturated solution of PbS?

$$PbS_{(s)} \rightleftharpoons Pb^{2+}_{(aq)} + S^{2-}_{(aq)}$$

$$K_{sp} = [Pb^{2+}_{aq}][S^{2-}_{aq}]$$

$$3.0 \times 10^{-28} = (x)(x)$$

$$\sqrt{3.0 \times 10^{-28}} = \sqrt{x^2}$$

$$x = 1.7 \times 10^{-14}\ M$$

$$[Pb^{2+}] = 1.7 \times 10^{-14}\ M$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{3(aq)}^{2-}$$

$$K_{sp} = [Ca^{2+}_{(aq)}][CO_{3(aq)}^{2-}]$$

$$4.5\times10^{-9} = (x)(x)$$

$$\sqrt{4.5\times10^{-9}} = \sqrt{x^2} \quad ((Ca^{2+})^2$$

$$6.7\times10^{-5} = x$$

What is the concentation of barium and sulfate ions in a saturated barium sulfate solution at 25°C?

Ksp = 1.1×10^{-10}

$BaSO_4 \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Ksp = [Ba^{2+}_{aq}][$SO_4^{2-}{}_{aq}$]

$1.10 \times 10^{-10} = x * x$

$\sqrt{1.10\ 10^{-10}} = \sqrt{x^2}$

(Ba^{2+}) [SO_4^{2-}] = x = 1.0×10^{-5} m

The Common Ion Effect

- When an ionic compound has reached **saturation**, another ionic compound can be added to increase the concentration of one of the ions
- Le Chatelier's principle says that when a stress is applied to an equilibrium, it re-establishes itself by adjusting its equilibrium position
- The reaction will shift to the left, resulting in more reactant (ionic compound(s)) forming

Common Ion Effect – continued…

- As long as another compound, containing either a cation or anion from the original compound, is being added, the equilibrium position will adjust itself so that Ksp does not change

Original – Ksp = $[Pb^{2+}]\ [CrO_4^{2-}] = 1.8 \times 10^{-14}$

- Adding $Pb(NO_3)_2$

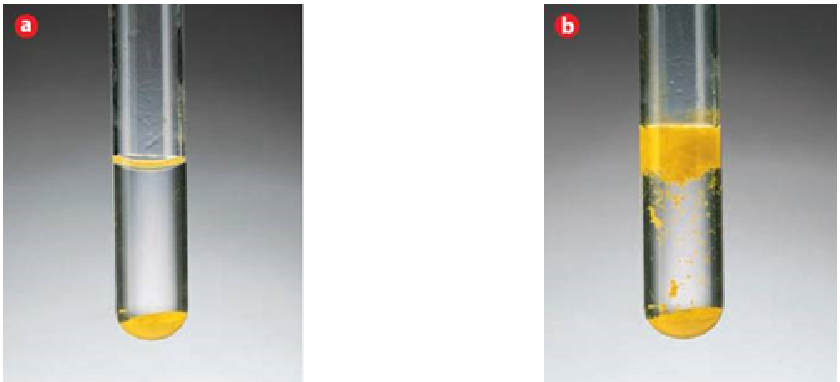
Revised – Ksp = $\mathbf{[Pb^{2+}]}[CrO_4^{2-}] = 1.8 \times 10^{-14}$

Definitions

- A **common ion** is the cation or anion that is found in both ionic compounds (salts) in a solution
- **Common ion effect** is the lowering of the solubility of an ionic compound as a result of the addition of a common ion
- **Spectator ions** are those that do not participate in the reaction. They stay in solution and do not precipitate

Common ion and common ion effect

Example: adding lead (II) nitrate to an existing saturated solution of lead (II) chromate



A saturated solution of lead(II) chromate is pale yellow.

When a few drops of lead nitrate are added to the solution, more lead(II) chromate precipitates.

Precipitates

- K_{sp} can be used to determine whether a precipitate will form when solutions are mixed

If the product of the concentration of two ions (Q_{sp}) in the mixture is greater than the K_{sp} of the compound formed from the ions, a precipitate will form

Precipitation

- If we compare the reaction quotient, Q, for the current solution concentrations to the value of K_{sp}, we can determine whether precipitation will occur.
  - $Q = K_{sp}$: the solution is saturated; no precipitation
  - $Q < K_{sp}$: the solution is unsaturated; no precipitation
  - $Q > K_{sp}$: the solution is above saturation; the salt above saturation will precipitate

SAMPLE PROBLEM 18.4

Finding Equilibrium Ion Concentrations in the Presence of a Common Ion

Photographic film is covered with a light-sensitive emulsion containing silver bromide. The K_{sp} of silver bromide is 5.0×10^{-13}. What is the bromide-ion concentration of a 1.00-L saturated solution of AgBr to which 0.020 mol of $AgNO_3$ is added?

Analyze ***List the knowns and the unknown.***

Knowns
- $K_{sp} = 5.0 \times 10^{-13}$
- moles of $AgNO_3$ added = 0.020 mol
- volume of solution = 1 L
- $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$
- $K_{sp} = [Ag^+] \times [Br^-]$

Unknown
- $[Br^-] = ?\ M$

Express the concentrations of the two ions in one unknown. Let the equilibrium concentration of bromide ion from the dissociation be x. Then the equilibrium concentration of silver ion is $x + 0.020$.

Calculate ***Solve for the unknown.***

Because of the small value of K_{sp}, you can make a simplifying assumption: x will be negligibly small compared to 0.020. Thus the $[Ag^+]$ at equilibrium is approximately equal to $0.020M$. Solve for x and substitute these values into the K_{sp} expression.

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

$$x = \frac{K_{sp}}{[Ag^+]} = \frac{(5.0 \times 10^{-13})}{[Ag^+]}$$

$$= \frac{(5.0 \times 10^{-13})}{0.020}$$

y $$= [Br^-] = 2.5 \times 10^{-11} M$$

The equilibrium concentration of bromide ion is $2.5 \times 10^{-11} M$.

19. What is the concentration of sulfide ion in a 1.0-L solution of iron(II) sulfide to which 0.04 mol of iron(II) nitrate is added? The K_{sp} of FeS is 8×10^{-19}.

Ksp = 8×10^{-19}

mols of $FeNO_3$ added = 0.04 mol

volume = 1L

$FeS \rightleftharpoons Fe^{2+}_{(aq)} + S^{2-}_{(aq)}$

Ksp = $[Fe^{2+}][S^{2-}]$

$Ksp = [Fe^{2+}][S^{2-}]$

$\frac{8.0 \times 10^{-19}}{0.04} = \frac{(0.04)[S^{2-}]}{0.04}$

$2 \times 10^{-17} M = [S^{2-}]$

Will a precipitate form when 0.500L of 0.002M $Ba(NO_3)_2$ reacts with 0.500L of 0.008M Na_2SO_4? [K_{sp} ($BaSO_4$) = 1.1×10^{-10}]

knowns

$Ba(NO_3)_2$ K_{sp}= 1.1×10^{-10}

initial moles of $Ba(NO_3)_2$ = 0.002 M

initial moles of Na_2SO_4 = 0.008 M

volume of solution = 0.50L + 0.50L =1.0 L

To predict if a precipitate will form the concentration after dilution needs to be calculated, if it exceeds the Ksp of $Ba(NO_3)_2$, a precipitate will form

Each solution was diluted with an equal volume of the other solution, so the concentration of each with be half after mixing:

moles of $Ba(NO_3)_2$ = 0.001 M

moles of Na_2SO_4 = 0.004 M

$[Ba^{2+}] \times [SO_4^{2-}]$ = (0.001M) x (0.004M) = 4×10^{-6}

$Ba(NO_3)_2$ K_{sp}= 1.1×10^{-10}

The trial product is larger therefore a precipitate will form , this will continue until the product of the concentration of the ions remaining in solution equals 1.1×10^{-10}

Finding Equilibrium Ion Concentration Using a Common Ion

Work through Sample Problem 18.4, p. 564.

Questions 19, 20, p. 564

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Section 18.3 Review

SECTION 18.3 SOLUBILITY EQUILIBRIUM

1. Write the solubility product expression for **a.** $Ca(OH)_2$ and **b.** Ag_2CO_3.
2. What is the concentration of silver ions in a saturated solution of silver carbonate? The K_{sp} of Ag_2CO_3 is 8.1×10^{-12}.
3. The equilibrium concentration of hydroxide ions in a saturated solution of iron(II) hydroxide is $1.2 \times 10^{-5} M$ at a certain temperature. Calculate the K_{sp} of $Fe(OH)_2$ at this temperature.
4. Strontium carbonate has a $K_{sp} = 9.3 \times 10^{-10}$ at 25°C. What is the concentration of strontium ions in a saturated solution of $SrCO_3$?
5. What is the equilibrium concentration of silver ions at 25°C in a 1.0-L saturated solution of silver carbonate to which 0.20 mol of Na_2CO_3 has been added? The K_{sp} of Ag_2CO_3 is 8.1×10^{-12} at 25°C.
6. Will a precipitate of $PbSO_4$ form when 400.0 mL of 0.0050M $MgSO_4$ is mixed with 600.0 mL of 0.0020M $Pb(NO_3)_2$? The K_{sp} of $PbSO_4 = 6.3 \times 10^{-7}$.
7. Will precipitation of $CaCO_3$ occur when 500.0 mL of $4.2 \times 10^{-3} M$ $CaCl_2$ is mixed with 500.0 mL of $2.6 \times 10^{-3} M$ Na_2CO_3? The K_{sp} of $CaCO_3$ is 4.5×10^{-9}.
8. Which of these compounds would not decrease the solubility of $Mg(OH)_2$ when added to a saturated solution of the compound?

   NaOH, $MgCl_2$, NaCl, KOH

Example

Ex. Ksp of $BaSO_4 = 1.1 \times 10^{-10}$

$Ba(NO_3)_2$ = 0.50L, 0.002M

Na_2SO_4 = 0.50L, 0.008M

Possible precipitate = $Ba(SO_4)_2$

The product of the ions barium and sulfate has to exceed the Ksp

Because they are mixed, the concentrations are cut in half, so…

Precipitate Example…

$Ba(NO_3)_2$ = 0.001M (mol/L)
Na_2SO_4 = 0.004M (mol/L)

$[Ba^{2+}]$ = 0.001M
$[SO_4^{2-}]$ = 0.004M

$Q_{sp} = [Ba^{2+}] \times [SO_4^{2-}] = (0.001M) \times (0.004M) = 4 \times 10^{-6}$

$K_{sp} = 1.1 \times 10^{-10}$ **Does a precipitate form?**

Finding Equilibrium Ion Concentration Using a Common Ion

Work through Sample Problem 18.4, p. 564.

Questions 19, 20, p. 564

Questions 21 – 28, p. 565

Section 18.3 Review