Solubility Equilibrium

Section 7.6

Homework

Precipitation
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Common Ion Effect
Pg. 470 #1-3
Pg. 471 #1-11

The story so far…

- Dissolution and Precipitation are opposite processes, which occur simultaneously in an aqueous solution.
- Only SATURATED solutions are in a state of solubility equilibrium, where $rate_{dissolution} = rate_{precipitation}$.
  - Unsaturated solutions are NOT at equilibrium
  - Adding more solute to a saturated solution will cause $rate_{precipitation}$ to ↑; solid precipitate will form.
- For a dissolution process, the equilibrium constant is called the solubility product constant, K_{sp}.
  - $K_{sp} = [\text{ion 1}]^m [\text{ion 2}]^n$

(from last class' example) $MgF_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\,F^-_{(aq)}$

$K_{sp} = [Mg^{2+}]\,[F^-]^2 = (2.76 \times 10^{-4})\,(5.52 \times 10^{-4})^2$

Concentrations at equilibrium

$K_{sp} = 8.35 \times 10^{-11}$

If the solution was UNSATURATED,

$[Mg^{2+}] < 2.76 \times 10^{-4}$ mol/L

$[F^-] < 5.52 \times 10^{-4}$ mol/L

$Q = [Mg^{2+}]\,[F^-]^2 < 8.35 \times 10^{-11}$

Reaction quotient – that value you calculate to TEST whether the system is at equilibrium

For solubility equilibria, the reaction quotient (Q) is called the **trial ion product**.

It can be used to predict whether a precipitate will form.

$Q < K_{sp}$ System is unsaturated. It could hold more solute ions.

$Q = K_{sp}$ System is at equilibrium. It is exactly saturated. No precipitate will form.

$Q > K_{sp}$ System is saturated. There are higher concentrations of ions than can be dissolved. **A solid precipitate will form.**

Practice. Will a precipitate of $PbSO_{4\,(s)}$ form?
At the temperature in question, K_{sp} for $PbSO_{4\,(s)}$ is 1.8×10^{-8}.

$[Pb^{2+}_{(aq)}]$	$[SO_4^{2-}{}_{(aq)}]$	$Q = [Pb^{2+}]\,[SO_4^{2-}]$	Precipitate?
5.74×10^{-5}	1.48×10^{-4}	8.46×10^{-9}	
6.22×10^{-4}	3.89×10^{-3}	2.42×10^{-6}	
2.87×10^{-4}	6.27×10^{-5}	1.8×10^{-8}	

Example 1. *Using Q to predict precipitation.*

If **100 mL of 0.100 mol/L $CaCl_{2\,(aq)}$** and **100 mL of 0.0400 mol/L $Na_2SO_{4\,(aq)}$** are mixed at 20°C, determine whether a precipitate will form. For $CaSO_4$ (aq) at 20°C, K_{sp} is 3.6×10^{-5}.

Means: Will a double displacement reaction happen when these solutions are mixed? If so, will $CaSO_4$ (s) precipitate?

Strategy
1. Write the balanced equation for this reaction. Use solubility rules to determine products' states. (pg. 465)
2. Find [IONS] before mixing.
3. Use dilution formula to find [IONS] after mixing. ($C_2 = \frac{C_1 V_1}{V_2}$)
4. Calculate Q. Compare to K_{sp}. Interpret!

GIVENS
$[CaCl_2]$ = 0.100 M
v_{CaCl2} = 100 mL

$[Na_2SO_4]$ = 0.0400 M
v_{Na2SO4} = 100 mL

For $CaSO_4$, **K_{sp} is 3.6 ×10^{-5}**

❶ **$CaCl_{2\,(aq)} + Na_2SO_{4\,(aq)} \rightarrow CaSO_{4\,(s)} + NaCl_{\,(aq)}$**

According to Table 3 (p. 465), $CaSO_4$ has LOW solubility
∴ possibility of precipitation!
…but are $[Ca^{2+}]$ and $[SO_4^{2-}]$ high enough?

❷ **BEFORE MIXING,**

$[Ca^{2+}] = [CaCl_2] = 0.100$ mol/L

$[SO_4^{2-}] = [Na_2SO_4] = 0.0400$ mol/L

❸ **AFTER MIXING,**

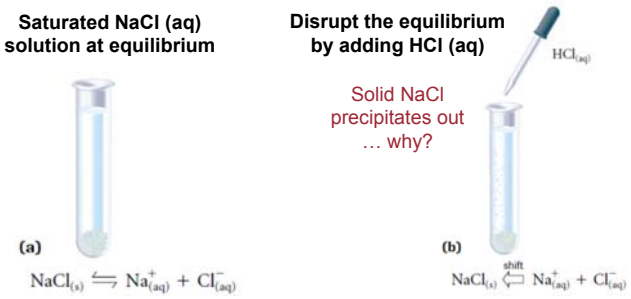
$[Ca^{2+}] = \frac{(0.100\text{ mol/L})(100\text{ mL})}{(200\text{ mL})} = 0.0500$ mol/L

$[SO_4^{2-}] = \frac{(0.0400\text{ mol/L})(100\text{ mL})}{(200\text{ mL})} = 0.0200$ mol/L

❹ For the dissolution equilibrium $CaSO_{4\,(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$,

$Q = [Ca^{2+}][SO_4^{2-}] = (0.0500)(0.0200) = 1.000 \times 10^{-3}$

$Q > K_{sp}$
∴ precipitate WILL form



Learning Checkpoint

Homework
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- Comparing Q to K_{sp} allows you to determine:
  - is a solution saturated? ($Q = K_{sp}$)
  - if not, will a precipitate form? ($Q > K_{sp}$)

The **common ion effect** is a reduction in the solubility of a salt, caused by the presence of another salt having the same ion.

Example.

- At 25°C, the molar solubility of $PbCl_{2\,(s)}$ in pure water is 0.0162 mol/L.
- If you try to dissolve $PbCl_2$ in a solution of $NaCl_{\,(aq)}$, its solubility will be reduced.
  - Cl^- is the common ion
  - At saturation, you will have LESS than 0.0162 mol/L of $PbCl_2$.

Example 2. Solubility calculations with a common ion

What is the molar solubility of $PbCl_{2\,(s)}$ in a 0.2 mol/L NaCl (aq) solution at 25°C? The K_{sp} of $PbCl_2$ is 1.7 x 10^{-5} at 25°C.

❶ For the initial solution of NaCl (aq),
We know that there is a 1:1:1 ratio of $NaCl_{\,(aq)} : Na^+{}_{(aq)} : Cl^-{}_{(aq)}$
∴ $[Cl^-]_0 = [NaCl]_0 = 0.2$ mol/L

	$PbCl_{2\,(s)}$ ⇌	$Pb^{2+}{}_{(aq)}$	2 $Cl^-{}_{(aq)}$
I	--	0	**0.2**
C	--	+ x	+ 2x
E	--	x	0.2 + 2x

This is the concentration of Cl^- already present due to the $NaCl_{\,(aq)}$

x represents the mol/L of Pb^{2+} from the dissolving of $PbCl_2$; In other words, the molar solubility of $PbCl_2$

$K_{sp} = 1.7 \times 10^{-5}$

	$PbCl_{2\,(s)}$ ⇌	$Pb^{2+}{}_{(aq)}$	2 $Cl^-{}_{(aq)}$
E	--	x	0.2 + 2x

❷ $K_{sp} = [Pb^{2+}][Cl^-]^2$ *sub in* ⟹ $1.7 \times 10^{-5} = x\,(0.2 + 2x)^2$

$1.7 \times 10^{-5} \cong x\,(0.2)^2$

$x \cong \frac{1.7 \times 10^{-5}}{(0.2)^2}$

$x \cong 4.2 \times 10^{-4}$ mol/L

HUNDRED RULE

$\frac{0.2}{K} = \frac{0.2}{1.7\times10^{-7}} \gg 100$

CHECK

$\frac{2x}{0.2} = \frac{2(4.2 \times 10^{-4})}{0.2}$

=0. 42%

∴ Simplifying assumption was valid

Practice!

Calculate the molar solubility of $PbI_{2\,(s)}$ in a 0.10 mol/L solution of $NaI_{\,(aq)}$ at 25°C.

Ans: 8.5×10^{-7} mol/L

Use Appendix B4 (pg. 725) to find the K_{sp} of PbI_2.

Learning Checkpoint

- The solubility of an ionic compound may decrease when a common ion is added to the equilibrium system.

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