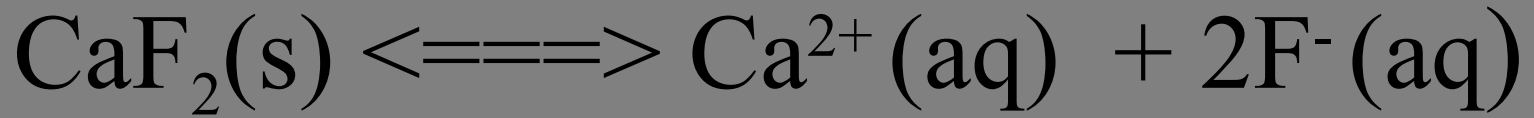# Solubility Product

Application of Equilibrium concepts

Introduction

- In even the most insoluble compounds, a few ions at the least dissolve.

- We can treat dissolving as a mini reaction in which the cation(s) and anion(s) separate and are hydrated or solvated by water consider

- $CaF_2(s) <===> Ca^{2+}(aq) + 2F^-(aq)$

$$CaF_2(s) \Longleftrightarrow Ca^{2+}(aq) + 2F^-(aq)$$

- How could you apply equilibrium concepts to determine how much Ca^{2+} is present at equilibrium.

- Try a Keq !!! :)

- [products]
  reactants

- $\dfrac{[Ca^{2+}][F\text{-}]^2}{[CaF_2]}$

What's wrong with our approach?

- Recall that pure solids and pure liquids are excluded from Keq calculations.

- K= $[Ca^{2+}][F-]^2$

- This is usually referred to as Ksp or the solubility product constant.

High values for Ksp

- The higher the value of Ksp, the more soluble the substance.

- Most chlorides, nitrates, acetates and many sulfates

Low values for Ksp

- The lower the value of Ksp, the less soluble the material. Some materials are very insoluble.

- Most sulfides and oxides

Remember

- Ksp is not solubility. It is Ksp, it is used to calculate molar solubility.

- It is related but not the same

- If you are asked about solubility, be sure to calculate it.

- **X--** the molar solubility!!!

X= molar solubility

The solubility product constant is *related* to the solubility of an ionic solute

$$K_{sp} = [Ag^+][Cl^-]; \text{ solubility given by } [Ag^+]$$

From stoichiometry, the ion ratio is 1:1, so $[Ag^+] = [Cl^-]$, both of which are unknown (x)

$$K_{sp} = x^2 \qquad \text{and } [Ag^+] = (K_{sp})^{1/2}$$

Molar solubilities

- Ksp of cupric iodate is known to be 1.4 x $10^{-7.}$ What is the molarity of Cu^{+2} in a saturated solution?

- Dissolving equation
  - $Cu(IO_3)_2 <==> Cu^{2+} + 2\ IO_3^-$

- Ksp expression
  - $Ksp = [Cu^{2+}]\ [IO_3^-]^2$

Molar solubility cont

- $Cu(IO_3)_2 \Longleftrightarrow Cu^{2+} + 2\ IO_3^-$

- Substitute according to stoichiometry of balanced equation

- $Cu(IO_3)_2 \Longleftrightarrow Cu^{2+} + 2\ IO_3^-$

- Let   x   and   2x

- Substitute and solve

- $Ksp = x\ (2x)^2 = 4x^3$

- $x =\ 3.3\ x\ 10^{-3}\ mol/L$

Calculating Ksp from solubility

- The solubility of Bi_2S_3 at 25°C is 1.0 x 10-15 M. What is the Ksp for bismuth sulfide?

- Bi_2S_3 <==> $2Bi^{3+} + 3S^{2-}$

- Let   2x and 3x

- Then Ksp = $(2x)^2 (3x)^3$

- Ksp = $108x^5$ and x = 1.0×10^{-15}

- Ksp = 1.1×10^{-73} and that is a small number

Common Ion effect

- Solubility will decrease due to LeChatelier's principle

- What is the solubility of Ag_2CrO_4 in a 0.100 M solution of $AgNO_3$? The Ksp of Ag_2CrO_4 is 9.0×10^{-12}

- $Ksp = [Ag^+]^2[CrO_4^{2-}]$

- let $Ag = (0.100 + 2x)^2$

- $CrO_4^{2-} = x$

Common Ksp's

- Ksp's after we have substituted X and multiples of X fall into some very common patterns based on the ratio of cations to anions.

- 1:1 x^2

- 2:1 or 1:2 $4x^3$

- 1:3 or 3:1 $27x^4$

- 2:3 or 3:2 $108x^5$

- Check twice if you don't get one of these

Remember Ksp is small X will be small

- $Ksp = (0.100)^2 \, x$

- because $(0.100 - x \approx 0.100)$

- $x = 9.0 \times 10^{-10} \, M$

Types of problems

- Given X (molar solubility) calculate Ksp
- Given Ksp calculate molar solubility
  - or the concentration of either the cation or the anion
- Common ion effect.
  - Substitute in the common ion in place of x
- Will precipitation occur?
  - Concentrations after precipitation

Will precipitation occur?

- Dissolving reaction of the insoluble product of a double displacement reaction.

- Ksp expression, no numbers yet.

- **New!** There are no unkowns in this type of problem. Find the actual concentrations in the story problem. Plug these values into the Ksp expression (after adjusting for dilution) and call the answer Qip

Does Precipitation Occur?

Q_{ip} is the ion product reaction quotient and is based on initial conditions of the reaction

Precipitation *should* occur if $Q_{ip} > K_{sp}$

Precipitation *cannot* occur if $Q_{ip} < K_{sp}$

A solution is *just saturated* if $Q_{ip} = K_{sp}$

Qip obeys the Ksp law

- We need to see Ksp to tell us how to treat the numbers square, cube etc.

- These problems are unique. We have no unknowns!

- No X's No X's No X's No X's NoX's

- Look up and/or calculate the actual initial concentrations based on what you are mixing together.

Will ppt occur if

- We mix 750.0 mL 4.00×10^{-3} M $Ce(NO_3)_3$ with 300.00 mL 2.00 M KIO_3. Ksp $Ce(IO_3)_3$ = 1.9×10^{-10}

Just follow the steps

- $Ce(IO_3)_3 <==> Ce^{3+} + 3IO^{3-}$

- $Ksp = [Ce^{3+}] [IO^{3-}]^3$

- Find the actual concentration of these species after mixing

- $(750/1050)\ 4.00 \times 10^{-3}$ M Ce^{3+}

- $(300/1050)\ 2.00 \times 10^{-3}$ M IO_3^-

- Qip = [Ce^{3+}][IO3^{-}]^{3}
- (2.86 x 10^{-3})(5.71 x 10^{-3})^{3}
- Qip = 5.32 X 10^{-10}
- How does this compare to the limit of Ksp?
- Qip>Ksp so yes we get precipitation

Er...

Concentrations after ppt

- What are the final (eqm) concentrations of Pb^{2+} and I^- after the mixing of 100 mL of 0.005 M $Pb(NO_3)_2$ and 200 mL of NaI ? The Ksp of PbI_2 is 1.9 x 10^{-10}

- Key concept: check to see if ppt occurs, if not concentrations do not change. Problem is a paper tiger.

Does ppt occur

- Need to find whether Qip is greater than Ksp
- 1) Dissolving equation
  - PbI2 <==> Pb^{2+} + $2I^-$
- 2) Ksp expression for the above
  - $[Pb^{2+}][I^-]^2$
- 3) Calculate the initial concentrations after mixing the solutions

Calculating concentration after mixing

- $[Pb^{2+}]$ = (100mL/300mL) x 0.0500 M
- = 1.67 x 10^{-2} M
- I = (200mL/300mL) x 0.100 M
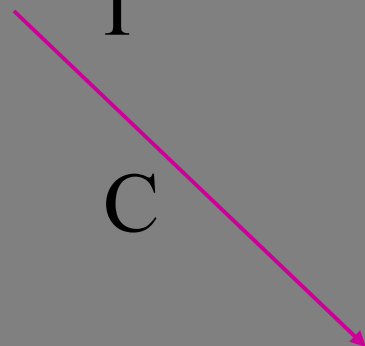- = 6.67 x 10^{-2} M

Substitute initial concentrations

- $Ksp = [Pb^{2+}][I^-]^2$

- $Qip = (1.67 \times 10^{-2})(6.67 \times 10^{-2})^2$

- $\quad = 7.43 \times 10^{-5} >> 1.4 \times 10^{-8}$

- Yes we have a ppt. But you suspected that didn't you !!! ;)

Now stoichiometry!!

- The formation of the insoluble PbI_2 will go all the way until we run out of $Pb2^+$ or I^-

- ICE it !

Goes to completion

	Pb2+	2I-	PbI2
I	.005 mol	.020 mol	0
C	.005-x	0.20-2x	x
E	0		--
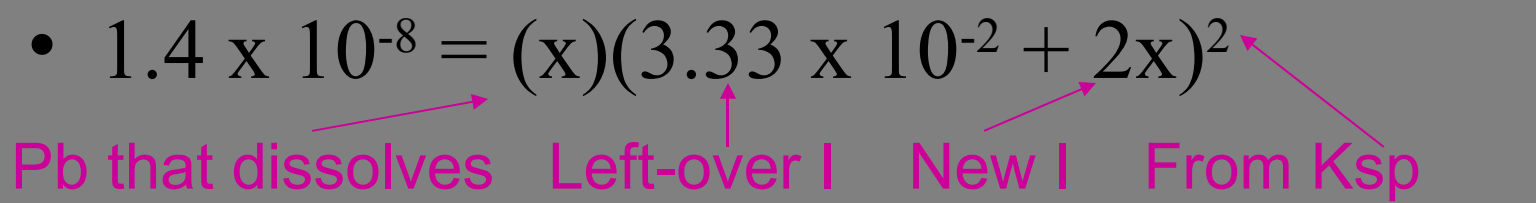
Finish ICE table

	Pb2+	2I-	PbI2
I	0.005 mol	0.020 mol	0
C	0.005-x	0.020-2x	x
E	0	0.010	--

Calculate Eqm concentrations

- I- at eqm* we have <u>0.01 moles</u> | 1000mL
-                        300mL | 1L
- 3.33×10^{-2} M
- Pb begins to dissolve because it can't stay 0 according to the Ksp. x of it is formed
- $Pb^{2+} = x$ and I- = $3.33 \times 10^{-2} + 2x$

Substitute Into Ksp and done

- $K_{sp} = [Pb^{2+}][I^-]^2$
- $1.4 \times 10^{-8} = (x)(3.33 \times 10^{-2} + 2x)^2$

Pb that dissolves   Left-over I   New I   From Ksp

- This simplifies (thankfully) to (x is small)
- $1.4 \times 10^{-8} = (x)(3.33 \times 10^{-2})^2$
- So $x = Pb^{2+} = 1.3 \times 10^{-5}$ M
- And I- $= 3.33 \times 10^{-2}$ M Whew!!!