

Slide 1

The End of Equilibrium!  
(well, for us!)

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Slide 2

$K_{sp}$   
What is the solubility of  $\text{FeCO}_3$ ?  
Solubility = MAXIMUM amount of a compound that can dissolve in water.  
This is actually an equilibrium.

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Slide 3

Equilibrium problems involve 3 parts:  
1. Balanced equation  
2. "K-equation"  
3. ICE chart  
What is the balanced equation for dissolving something?

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Slide 4

$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

What is the "K-equation"?

$K = [\text{Fe}^{2+}][\text{CO}_3^{2-}]$

The "K" is the PRODUCT of the SOLUBLE ions.  
Hence, this reaction is called a "solubility product".

$K_{\text{sp}} = [\text{Fe}^{2+}][\text{CO}_3^{2-}]$   
 $K_{\text{sp}}(\text{FeCO}_3) = 3.07 \times 10^{-11}$

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Slide 5

What is the solubility of  $\text{FeCO}_3$ ?

$K_{\text{sp}}(\text{FeCO}_3) = 3.07 \times 10^{-11}$

$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

I	S			
		0	0	
C	-x	+x	+x	
E	0.000000000001	x	x	x

$K_{\text{sp}} = 3.07 \times 10^{-11} = [\text{Fe}^{2+}][\text{CO}_3^{2-}] = x \cdot x$   
 $x = \text{SQRT}(3.07 \times 10^{-11}) = 5.54 \times 10^{-6} \text{ M}$

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Slide 6

**Clicker question**

What is the solubility of  $\text{Ba}_3(\text{PO}_4)_2$  at 298K?

$K_{\text{sp}}(\text{Ba}_3(\text{PO}_4)_2) = 6 \times 10^{-39}$

A.  $8 \times 10^{-20} \text{ M}$   
B.  $2 \times 10^{-9} \text{ M}$   
C.  $3 \times 10^{-9} \text{ M}$   
D.  $9 \times 10^{-9} \text{ M}$   
E.  $3 \times 10^{-20} \text{ M}$

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Slide 7

$$\text{Ba}_3(\text{PO}_4)_2 (\text{s}) \leftrightarrow 3 \text{Ba}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq})$$

I	S	0	0
C	-x	+3x	+2x
E	-	3x	2x

$$K_{sp} = 6 \times 10^{-39} = (3x)^3 (2x)^2 = 27x^3 \cdot 4x^2$$
$$5.56 \times 10^{-41} = x^5$$
$$x = 8.89 \times 10^{-9} \text{ M} = 9 \times 10^{-9} \text{ M}$$

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Slide 8

More common units for solubility...

...are g/L.

If you wanted g/L

$$9 \times 10^{-9} \text{ M} = \frac{9 \times 10^{-9} \text{ mol Ba}_3(\text{PO}_4)_2}{\text{L}} \frac{602 \text{ g}}{\text{mol}} = 5 \times 10^{-6} \text{ g/L}$$

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Slide 9

Precipitation Reaction

The reverse reaction:

Solubility Product:  
$$\text{Ba}_3(\text{PO}_4)_2 (\text{s}) \leftrightarrow 3 \text{Ba}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq})$$

Precipitation:  
$$3 \text{Ba}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq}) \leftrightarrow \text{Ba}_3(\text{PO}_4)_2 (\text{s})$$

It's just K "upside down"

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Slide 10

How do you know if something precipitates?

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$\text{Ba}_3(\text{PO}_4)_2 (\text{s}) \leftrightarrow 3 \text{Ba}^{2+} (\text{aq}) + 2 \text{PO}_4^{3-} (\text{aq})$   
 $K_{\text{sp}} = 6 \times 10^{-39}$

What is the  $K_{\text{sp}}$ ?  
It's the limit on the amount of ions in solution.  
 $K_{\text{sp}} = [\text{Ba}^{2+}]^3 [\text{PO}_4^{3-}]^2$

Remember our old friend "Q"?

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Slide 11

What's Q?

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Q is just the concentrations of products and reactants when you are NOT at equilibrium.

$K_{\text{sp}} = [\text{Ba}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 6 \times 10^{-39}$   
 $Q = [\text{Ba}^{2+}]^3 [\text{PO}_4^{3-}]^2 = \text{any other number}$

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Slide 12

Q is less than K means...

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1. You are NOT at equilibrium.
2. You could dissolve more solid: the products (dissolved ions) are too small.

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Slide 13

Q is more than K means...

1. You are NOT at equilibrium.
2. You have TOO MANY products (dissolved ions). They can't stay dissolved, they need to precipitate out!

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Slide 14

A little precipitation question:

500 mL of 0.100 M  $\text{Fe}(\text{NO}_3)_3$  is mixed with 250 mL of 0.100 M KOH. What, if anything, precipitates from the solution? What mass of precipitate is formed?

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Slide 15

What COULD form...?

$\text{KOH}(s) \rightarrow \text{K}^+(aq) + \text{OH}^-(aq)$   
 $\text{Fe}(\text{NO}_3)_3(s) \rightarrow \text{Fe}^{3+}(aq) + 3 \text{NO}_3^-(aq)$

A beaker of KOH and  $\text{Fe}(\text{NO}_3)_3$  has neither KOH nor  $\text{Fe}(\text{NO}_3)_3$ , it's all ions!

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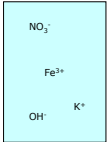
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Slide 16

**The 1<sup>st</sup> Rule of Chemistry...**



Opposites attract!

Positive ions like negative ions.

Negative ions like positive ions.

Positive ions hate positive ions.

Negative ions hate negative ions.

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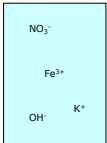
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Slide 17

**Only possible products are...**



KOH or  $\text{KNO}_3$

$\text{Fe(OH)}_3$  or  $\text{Fe(NO}_3)_3$

We know that KOH and  $\text{Fe(NO}_3)_3$  don't form...that's what we started with.

What about  $\text{KNO}_3$  and  $\text{Fe(OH)}_3$ ?

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Slide 18

**How many "Ks" are there in the beaker?**

A. None of the below

B. 3

C. 2

D. 4

E. 5

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Slide 19

What about  $\text{KNO}_3$  and  $\text{Fe}(\text{OH})_3$ ?

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They are both possible products of the reaction. Could they both form? Which one forms first? Do they form together? How would you know?

$K_{sp}$

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Slide 20

When you have 2 possible reactions...

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**BIGGEST K wins!**

Or, in this case, **SMALLEST  $K_{sp}$**

$K_{\text{precipitation}} = 1/K_{sp}$

Small  $K_{sp}$  means big  $K_{\text{precipitation}}$ .

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Slide 21

Precipitation is just the reverse of dissolution.

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$\text{KNO}_3 (\text{s}) \leftrightarrow \text{K}^+ (\text{aq}) + \text{NO}_3^- (\text{aq})$

$K_{sp} (\text{KNO}_3) = \text{HUGE}$  ( $\text{K}^+$  salts are very soluble and nitrates are very soluble)

$\text{Fe}(\text{OH})_3 (\text{s}) \leftrightarrow \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^- (\text{aq})$

$K_{sp} (\text{Fe}(\text{OH})_3) = 2.79 \times 10^{-39}$

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Slide 22

So the only reaction to consider is...

$$\text{Fe(OH)}_3 (\text{s}) \leftrightarrow \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^- (\text{aq})$$

$K_{\text{sp}} (\text{Fe(OH)}_3) = 2.79 \times 10^{-39}$

All equilibrium problems have 3 parts...yada yada yada...

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Slide 23

$K_{\text{sp}} (\text{Fe(OH)}_3) = 2.79 \times 10^{-39}$

$$\text{Fe(OH)}_3 (\text{s}) \leftrightarrow \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^- (\text{aq})$$

I  
C  
E

$K_{\text{sp}} = 2.79 \times 10^{-39} = [\text{Fe}^{3+}][\text{OH}^-]^3$   
What do we know?

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Slide 24

Don't forget the dilution

500 mL of 0.100 M  $\text{Fe(NO}_3)_3$  is mixed with 250 mL of 0.100 M KOH.

So...

Dilution is the solution!

$0.100 \text{ M} \times 0.500 \text{ L} = 0.05 \text{ mol} / 0.750 \text{ L} = 0.0667 \text{ M}$

$0.100 \text{ M} \times 0.250 \text{ L} = 0.025 \text{ mol} / 0.750 \text{ L} = 0.0333 \text{ M}$

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Slide 28

What is product limiting?

$\text{Fe}(\text{OH})_3 (\text{s}) \leftrightarrow \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^{-} (\text{aq})$

I	-	0.067	0.033
C	-	-0.011	-3(0.011)
E	-	0.056	0

$0.067 - x = 0$   
 $x = 0.067$

$0.033 - 3x = 0$   
 $x = 0.011$

The hydroxide runs out first!

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Slide 29

Double your ICE, double your pleasure!

$\text{Fe}(\text{OH})_3 (\text{s}) \leftrightarrow \text{Fe}^{3+} (\text{aq}) + 3 \text{OH}^{-} (\text{aq})$

I	-	0.067	0.033
C	+0.011	-0.011	-3*(0.011)
I	0.011	0.056	0
C	-x	+x	+3x
E	0.011-x	0.056+x	3x

$K_{sp} = 2.79 \times 10^{-39} = [0.056+x][3x]^3$

Look how much simpler that is. Even better, let's try and solve it the easy way!

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Slide 30

Double your ICE, double your pleasure!

$K_{sp} = 2.79 \times 10^{-39} = [0.056+x][3x]^3$

Assume  $x \ll 0.056$

$2.79 \times 10^{-39} = [0.056][3x]^3 = 0.056 * 27x^3$

$1.8452 \times 10^{-39} = x^3$   
 $1.23 \times 10^{-13} = x!$

Pretty good assumption.

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Slide 37

Given the following  $K_{sp}$  values, which salt is LEAST soluble in water?

$$K_{sp}[\text{FeCO}_3] = 3.07 \times 10^{-11}$$
$$K_{sp}[\text{MgCO}_3] = 6.82 \times 10^{-6}$$
$$K_{sp}[\text{KNO}_3] = 1.26 \times 10^2$$

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Slide 38

Be a little careful about stoichiometry...

Imagine the following chloride salts:

$$K_{sp}(\text{XCl}_2) = 12$$
$$K_{sp}(\text{YCl}) = 9$$

Which salt is MORE SOLUBLE?

A.  $\text{XCl}_2$   
B.  $\text{YCl}$   
C. I need more information

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Slide 39

$$K_{sp} = 12 = [\text{X}][\text{Cl}]^2 = (x)(2x)^2$$
$$12 = 4x^3$$
$$x = \sqrt[3]{\frac{12}{4}} = 1.44$$
$$K_{sp} = 9 = [\text{X}][\text{Cl}] = (x)(x)$$
$$9 = x^2$$
$$x = 2\sqrt{9} = 3$$

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Slide 40

I should also be a little careful about concentration...

If the concentrations are very different, even the bigger  $K_{sp}$  may not matter.

It's really a question of Q! ( $Q_{sp}$ )

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Slide 41

The question is when  $Q > K_{sp}$ . But before it can exceed  $K_{sp}$ , Q must equal  $K_{sp}$ , so

$$Q = K_{sp} = 3.07 \times 10^{-11} = [Fe^{2+}][CO_3^{2-}]$$
$$= [2.3 \times 10^{-2}][CO_3^{2-}]$$
$$[CO_3^{2-}] = \frac{3.07 \times 10^{-11}}{2.3 \times 10^{-2}} = 1.33 \times 10^{-9}$$

As soon as my carbonate is 1 tiny bit above that, precipitation starts.

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Slide 42

$$Q = K_{sp} = 6.82 \times 10^{-6} = [Mg^{2+}][CO_3^{2-}]$$
$$= [1.5 \times 10^{-2}][CO_3^{2-}]$$
$$[CO_3^{2-}] = \frac{6.82 \times 10^{-6}}{1.5 \times 10^{-2}} = 4.55 \times 10^{-4}$$

As soon as my carbonate is 1 tiny bit above that, precipitation starts.

But that is waaaaay higher than the carbonate required for the iron to precipitate!

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Slide 43

The effectiveness of the separation...

...depends on how much of the ion is left in solution when the second (or third or fourth) cation starts to precipitate.

Once  $K_{sp}$  is in play, it stays in play...

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Slide 44

Puzzle 1. How much of the first cation is still in solution when the second cation begins to precipitate?

A.  $4.55 \times 10^{-4} M$   
B.  $6.75 \times 10^{-8} M$   
C.  $1.5 \times 10^{-2} M$   
D.  $1.3 \times 10^{-2} M$   
E.  $2.3 \times 10^{-2} M$

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Slide 45

$$Q = K_{sp} = 6.82 \times 10^{-6} = [Mg^{2+}][CO_3^{2-}]$$
$$= [1.5 \times 10^{-2}][CO_3^{2-}]$$
$$[CO_3^{2-}] = \frac{6.82 \times 10^{-6}}{1.5 \times 10^{-2}} = 4.55 \times 10^{-4}$$
$$K_{sp} = 3.07 \times 10^{-11} = [Fe^{2+}][CO_3^{2-}]$$
$$= [Fe^{2+}][4.55 \times 10^{-4} M]$$
$$[Fe^{2+}] = 6.75 \times 10^{-8} M$$

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Slide 49

**Clicker Questions**

What affect would adding acid have on the solubility of  $\text{Ca(OH)}_2$ ?

- A. Increase the solubility
- B. Decrease the solubility
- C. Have no effect on the solubility.

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Slide 50

The solubility of  $\text{FeBr}_2$  in pure water is 1.2 g/100 mL at 298 K. Would you expect the solubility of  $\text{FeBr}_2$  to be \_\_\_\_\_ in 0.100 M  $\text{NaBr}$  at 298 K?

- A. higher
- B. lower
- C. the same

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Slide 51

**LeChatelier's principle**

If you stress an equilibrium, the equilibrium shift to respond to the stress.

$$\text{Ca(OH)}_2 (s) \rightarrow \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq)$$
$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

"Lowering the pH" means increasing  $[\text{H}_3\text{O}^+]$  which will neutralize some of the  $[\text{OH}^-]$ . If you decrease the amount of hydroxide the reaction needs to make more to keep it at equilibrium.

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Slide 52

**REACTIONS ARE STUPID!**

They don't know where the  $\text{Ca}^{2+}$  or the  $\text{OH}^-$  come from.

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Slide 53

**LeChatelier's Principle**

Adding NaBr gives you a second source of  $\text{Br}^-$ . So the reaction needs to make less to get to equilibrium.

$\text{NaBr}(s) \rightarrow \text{Na}^+(aq) + \text{Br}^-(aq)$

$K_{sp} = [\text{Na}^+][\text{Br}^-]$

Still stupid!

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Slide 54

**Sample question**

If you have 500.0 mL of a solution that is 0.022 M in  $\text{Fe}^{2+}$  and 0.014 M in  $\text{Mg}^{2+}$  and add 10.00 mL of 0.100 M  $\text{K}_2\text{CO}_3$ . What is left in solution after the precipitation?

$K_{sp}(\text{FeCO}_3) = 3.07 \times 10^{-11}$

$K_{sp}(\text{MgCO}_3) = 6.82 \times 10^{-6}$

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Slide 55

If you have 500.0 mL of a solution that is 0.022 M in  $\text{Fe}^{2+}$  and 0.014 M in  $\text{Mg}^{2+}$  and add 10.00 mL of 0.100 M  $\text{K}_2\text{CO}_3$ . What is left in solution after the precipitation?

Dilution:

$$0.022 \text{ M} \times \frac{500 \text{ mL}}{510 \text{ mL}} = 0.0216 \text{ M } \text{Fe}^{2+}$$

$$0.014 \text{ M} \times \frac{500 \text{ mL}}{510 \text{ mL}} = 0.0137 \text{ M } \text{Mg}^{2+}$$

$$0.100 \text{ M} \times \frac{10 \text{ mL}}{510 \text{ mL}} = 0.00196 \text{ M } \text{CO}_3$$

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$K_{sp}(\text{FeCO}_3) = 3.07 \times 10^{-11}$   
 $K_{sp}(\text{MgCO}_3) = 6.82 \times 10^{-6}$

I expect the  $\text{FeCO}_3$  to precipitate first

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Slide 57

$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

	0.0216	0.00196
	-x	-x
	0.0216-x	0.00196-x

$3.07 \times 10^{-11} = (0.0216-x)(0.00196-x)$   
 Assume x is LARGE!

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$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

0	0.0216	0.00196
+0.00196	-0.00196	-0.00196
0.00196	0.0196	0
-x	+x	+x
0.00196-x	0.0196+x	x

$3.07 \times 10^{-11} = (0.0196+x)(x)$   
Assume  $x < 0.0196$   
 $3.07 \times 10^{-11} = 0.0196x$   
 $X = 1.56 \times 10^{-9}$

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Slide 59

$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

0	0.0216	0.00196
+0.00196 * M	-0.00196	-0.00196
0.00196 * M	0.0196	0
-1.56x10 <sup>-9</sup>	+1.56x10 <sup>-9</sup>	+1.56x10 <sup>-9</sup>
0.00196 * M	0.0196	1.56x10 <sup>-9</sup>

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Slide 60

**Check  $\text{MgCO}_3$  equilibrium**

After the  $\text{FeCO}_3$  precipitates, the  $\text{CO}_3^{2-}$  concentration is only  $1.56 \times 10^{-9}$

$K_{\text{sp}}(\text{MgCO}_3) = 6.82 \times 10^{-6}$

$Q_{\text{sp}} = (1.56 \times 10^{-9})(0.0137 \text{ M}) = 2.137 \times 10^{-11}$

$Q \ll K$ , so no  $\text{MgCO}_3$  precipitates!

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Slide 61

In terms of the solid...

$$\text{FeCO}_3(\text{s}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$

0	0.0216	0.00196
+0.00196 "M"	-0.00196	-0.00196
0.00196 "M"	0.0196	0
-1.56x10 <sup>-9</sup>	+1.56x10 <sup>-9</sup>	+1.56x10 <sup>-9</sup>
0.00196 "M"	0.0196	1.56x10 <sup>-9</sup>

Effectively "0.00196 M" FeCO<sub>3</sub> precipitated.  
This is not a real concentration – it's not dissolved anymore!

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In terms of the solid:

$$0.00196 \text{ M FeCO}_3 = \frac{0.00196 \text{ mol FeCO}_3}{\text{L solution}} \cdot 0.510 \text{ L}$$
$$= 9.996 \times 10^{-4} \text{ mol} \cdot \frac{115.86 \text{ g}}{\text{mol}} = 0.1158 \text{ g}$$

So 0.1158 g of solid FeCO<sub>3</sub> have precipitated in the beaker!

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Slide 63

Let's take it a little farther.

Suppose we add another 10.00 mL of 0.100 M K<sub>2</sub>CO<sub>3</sub>?

Well, we do the same thing all over again but we are starting with less Fe<sup>2+</sup> and there's some initial CO<sub>3</sub><sup>2-</sup> still floating around.

The reaction starts where the previous one left off!

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Slide 70

**Check  $\text{MgCO}_3$  equilibrium**

After the  $\text{FeCO}_3$  precipitates, the  $\text{CO}_3^{2-}$  concentration is only  $1.56 \times 10^{-9}$

$K_{sp}(\text{MgCO}_3) = 6.82 \times 10^{-6}$

$Q_{sp} = (1.775 \times 10^{-9})(0.01344 \text{ M}) = 2.386 \times 10^{-10}$

$Q \ll K$ , so no  $\text{MgCO}_3$  precipitates!

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Slide 71

**If I compare my two results**

After 1<sup>st</sup> addition:

- 0.1158 g  $\text{FeCO}_3$
- 0.0196 M  $\text{Fe}^{2+}$
- $1.56 \times 10^{-9}$  M  $\text{CO}_3^{2-}$
- 0.0137 M  $\text{Mg}^{2+}$

After 2<sup>nd</sup> addition:

- 0.2317 g  $\text{FeCO}_3$
- 0.01730 M  $\text{Fe}^{2+}$
- $1.775 \times 10^{-9}$  M  $\text{CO}_3^{2-}$
- 0.01344 M  $\text{Mg}^{2+}$

Almost all the  $\text{CO}_3^{2-}$  precipitates each time.

I've doubled the amount of  $\text{FeCO}_3$ .

The  $\text{Fe}^{2+}$  is dropping and the  $\text{CO}_3^{2-}$  is gradually increasing.

The  $\text{Mg}^{2+}$  is being diluted but the actual amount dissolved isn't changing.

You could keep doing this until virtually all the  $\text{FeCO}_3$  is gone EXCEPT there is also  $\text{Mg}^{2+}$  in solution.

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Slide 72

**What happens to the  $\text{Mg}^{2+}$ ?**

The  $\text{CO}_3^{2-}$  is creeping upwards. Eventually, you'll get to the point at which it precipitates!

When...? Check  $K_{sp}$ !!!

(Note: There is a dilution issue, so we'll use the undiluted values to get a ballpark figure.)

$K_{sp}(\text{MgCO}_3) = 6.82 \times 10^{-6} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$

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Slide 76

In terms of amounts:

$$\frac{0.22 \text{ mol Fe}^{2+}}{L} \cdot 0.500L = 0.11 \text{ mol} \frac{55.85 \text{ g}}{\text{mol}} = 6.14 \text{ g Fe}^{2+}$$
$$\frac{6.30 \times 10^{-8} \text{ mol Fe}^{2+}}{L} \cdot 0.500L = 3.15 \times 10^{-8} \text{ mol} \frac{55.85 \text{ g}}{\text{mol}}$$
$$= 1.76 \times 10^{-6} \text{ g Fe}^{2+}$$
$$\frac{1.76 \times 10^{-6} \text{ g Fe}^{2+} \text{ left}}{6.14 \text{ g Fe}^{2+} \text{ initial}} \times 100 = 2.87 \times 10^{-5} \% \text{ left}$$

100% - 2.87 × 10<sup>-5</sup>% left = 99.99997% precipitated!  
Pretty good!

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Slide 77

Once the Mg<sup>2+</sup> starts precipitating...

There is still a wee bit of Fe<sup>2+</sup> left that will co-precipitate with the Mg<sup>2+</sup>.

There ain't a ton, so you are precipitating mostly pure Mg<sup>2+</sup> in this case. But that depends on how different the K<sub>sp</sub> is. If they were closer together, you might have more left.

Only the first compound to precipitate will precipitate in pure form!

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