

$K_{sp}$

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

Solubility = MAXIMUM amount of a compound that can dissolve in water.

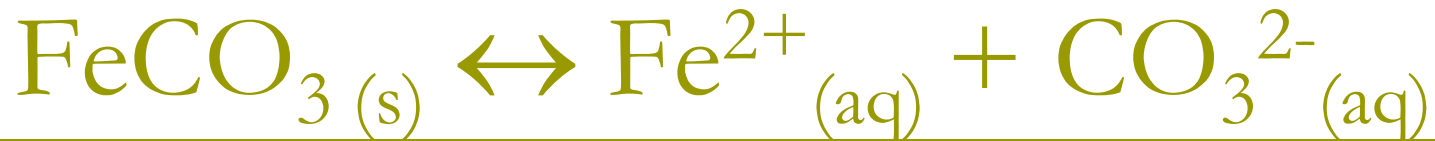
This is actually an equilibrium.

## Equilibrium problems involve 3 parts:

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1. Balanced equation
2. "K-equation"
3. ICE chart

What is the balanced equation for dissolving something?



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”.

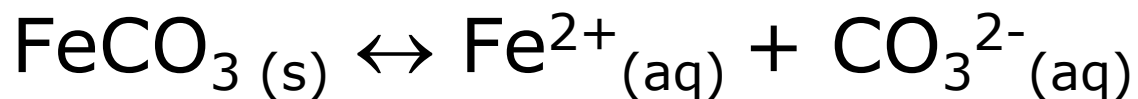
$$K_{sp} = [\text{Fe}^{2+}][\text{CO}_3^{2-}]$$

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

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

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



I S

0

0

C -x

+x

+x

E 0.00000000000001

x

x

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

$$x = \text{SQRT}(3.07 \times 10^{-11}) = 5.54 \times 10^{-6} \text{ M}$$

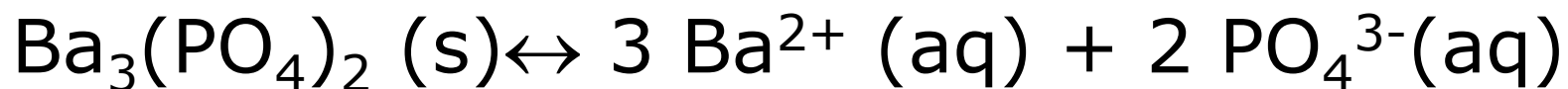
## Clicker question

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



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

$$K_{\text{sp}} = 6 \times 10^{-39} = (3x)^3 (2x)^2 = 27x^3 * 4x^2$$

$$5.56 \times 10^{-41} = x^5$$

$$x = 8.89 \times 10^{-9} \text{ M} = 9 \times 10^{-9} \text{ M}$$

# More common units for solubility...

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...are g/L.

If you wanted g/L

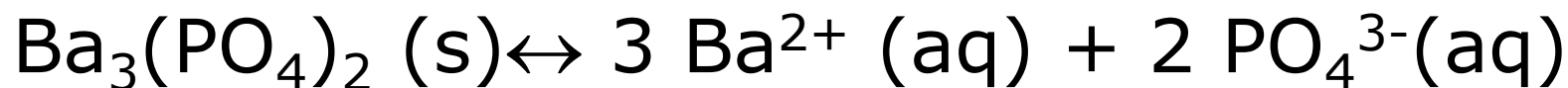
$$9 \times 10^{-9} M = \frac{9 \times 10^{-9} \text{ mol Ba}_3(\text{PO}_4)_2}{L} \frac{602 \text{ g}}{1 \text{ mol}} = 5 \times 10^{-6} \text{ g / L}$$

# Precipitation Reaction

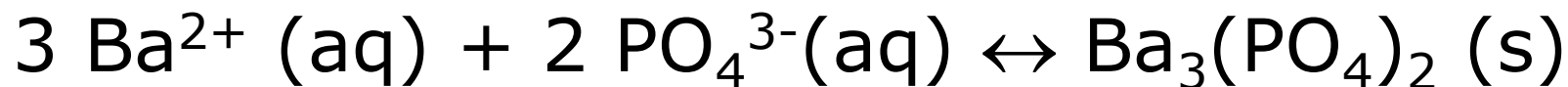
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The reverse reaction:

Solubility Product:



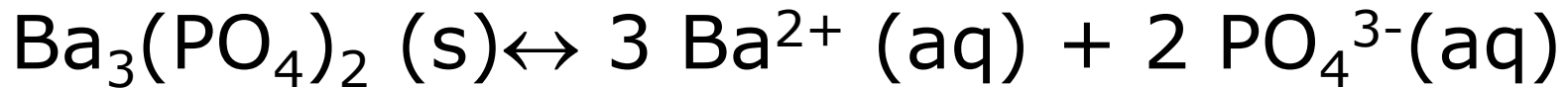
Precipitation:



It's just K "upside down"

# How do you know if something precipitates?

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$$K_{\text{sp}} = 6 \times 10^{-39}$$

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"?

# What's Q?

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

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

$$Q = [\text{Ba}^{2+}]^3[\text{PO}_4^{3-}]^2 = \text{any other number}$$

## 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.

# Q is more than K means...

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

## A little precipitation question:

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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?

# What COULD form...?

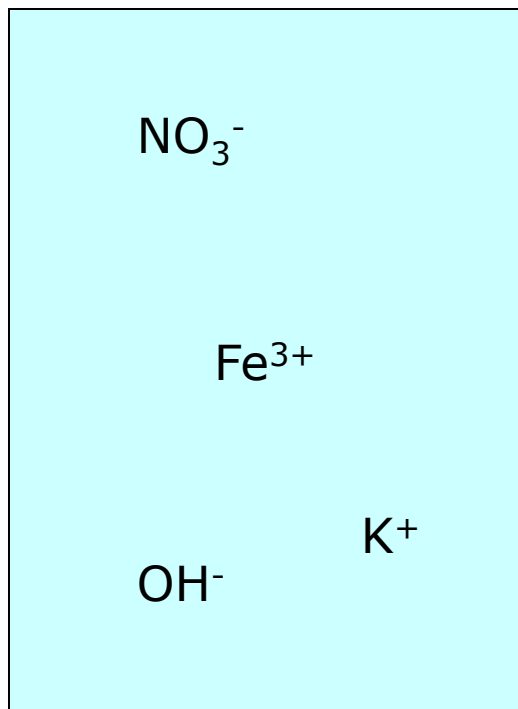
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A beaker of KOH and  $\text{Fe(NO}_3)_3$  has neither KOH nor  $\text{Fe(NO}_3)_3$ , it's all ions!

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

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Opposites attract!

Positive ions like negative ions.

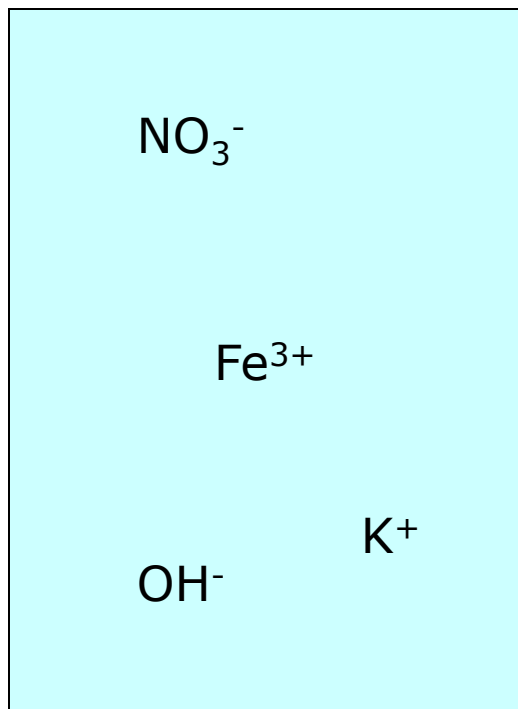
Negative ions like positive ions.

Positive ions hate positive ions.

Negative ions hate negative ions.

# Only possible products are...

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$\text{KOH}$  or  $\text{KNO}_3$

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

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

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

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

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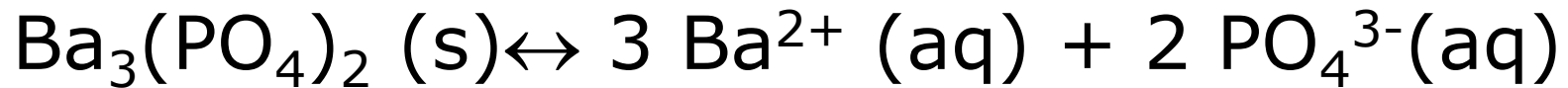
They are both possible products of the reaction. Could they both form? Which one forms first? Do they form together? How would you know?

$K_{sp}$

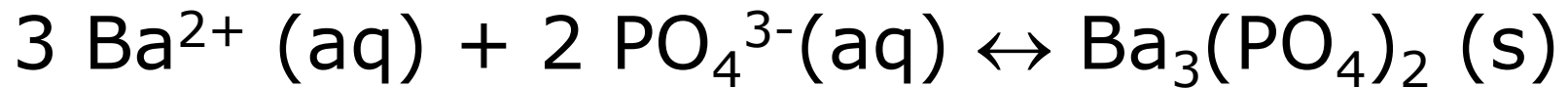
Precipitation is just the reverse of dissolution.

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Solubility Product:



Precipitation:



It's just K "upside down"

# When you have 2 possible reactions...

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**BIGGEST K wins!**

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

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

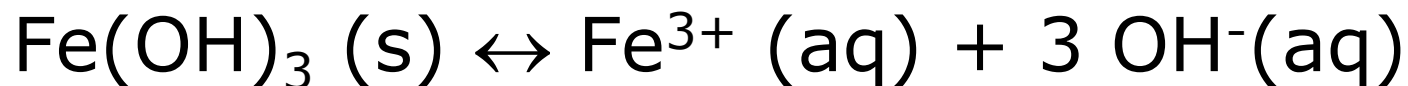
**Small  $K_{sp}$  means big  $K_{\text{precipitation}}$ .**

Precipitation is just the reverse of dissolution.

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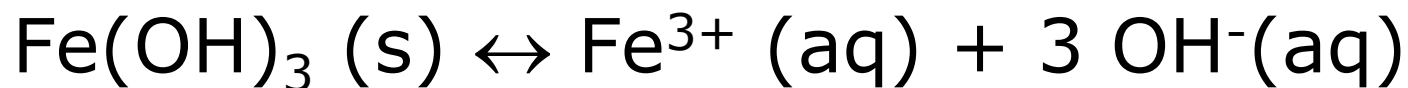
$K_{\text{sp}} (\text{KNO}_3) = \text{HUGE}$  ( $\text{K}^+$  salts are very soluble and nitrates are very soluble)



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

So the only reaction to consider is...

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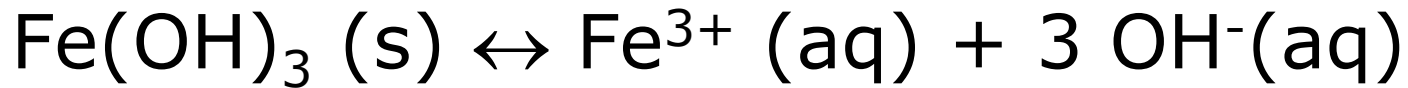


$$K_{\text{sp}} (\text{Fe(OH)}_3) = 2.79 \times 10^{-39}$$

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

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

---



I  
C  
E

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

What do we know?

# Don't forget the dilution

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

So...

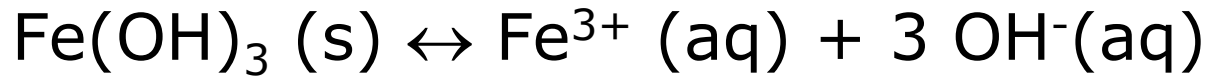
Dilution is the solution!

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

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

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

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I	-	0.067	0.033
C	-	-x	-3x
E	-	0.067-x	0.033-3x

$$K_{sp} = 2.79 \times 10^{-39} = [0.067-x][0.033-3x]^3$$

This is an algebraic mess BUT...K is really small.

*K* is really small...

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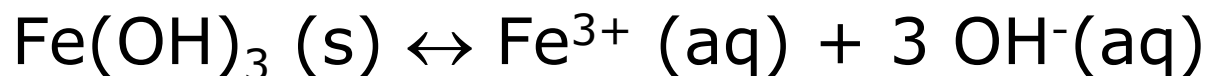
...which means...  $\text{Fe}(\text{OH})_3$  is not very soluble.

So,  $x$  is going to be huge! We can use that to our advantage.

We can mathematically precipitate out ALL of the  $\text{Fe}(\text{OH})_3$  and then redissolve it!

# What is rate limiting?

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$$\text{I} \quad - \quad \quad \quad 0.067 \quad \quad \quad 0.033$$

$$\text{C} \quad - \quad \quad \quad -x \quad \quad \quad -3x$$

$$\text{E} \quad - \quad \quad \quad 0.067-x \quad \quad \quad 0.033-3x$$

$$0.067-x = 0$$

$$X = 0.067$$

$$0.033 - 3x = 0$$

$$X = 0.011$$

The hydroxide runs out first!

# Double your ICE, double your pleasure!

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

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

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

# Double your ICE, double your pleasure!

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

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.

# Double your ICE, double your pleasure!

---

	$\text{Fe(OH)}_3$ (s)	$\leftrightarrow$	$\text{Fe}^{3+}$ (aq)	+	3	$\text{OH}^-$ (aq)
I	-		0.067			0.033
C	+0.011		-0.011		-3*(0.011)	
I	0.011		0.056			0
C	- $1.23 \times 10^{-13}$		+ $1.23 \times 10^{-13}$		+3( $1.23 \times 10^{-13}$ )	
E	0.011		0.056			$3.68 \times 10^{-13}$

0.011 M  $\text{Fe(OH)}_3$  precipitate

$0.011 \text{ M } \text{Fe(OH)}_3 * 0.75 \text{ L} * 106.9 \text{ g/mol} = 0.9 \text{ g}$   
 $\text{Fe(OH)}_3$

# Neat trick, huh?

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Actually, that is another little trick in your ICE arsenal...

We know what to do when  $x$  is small. Now, if we suspect  $x$  is large, we can try this little trick.

In fact, you could always forcibly do a reaction to change the initial condition. After all, in the end the equilibrium will decide where it finishes.

# Clicker question

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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?

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

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

- A.  $1.56 \times 10^{-9}$  M  $\text{CO}_3^{2-}$ , 0.0196 M  $\text{Fe}^{2+}$ , 0.0137 M  $\text{Mg}^{2+}$
- B. 0.078 M  $\text{CO}_3^{2-}$ ,  $3.9 \times 10^{-10}$  M  $\text{Fe}^{2+}$ , 0.014 M  $\text{Mg}^{2+}$
- C. 0.086 M  $\text{CO}_3^{2-}$ , 0.022 M  $\text{Fe}^{2+}$ ,  $7.9 \times 10^{-10}$  M  $\text{Mg}^{2+}$
- D.  $5.82 \times 10^{-4}$  M  $\text{CO}_3^{2-}$ , 0.0216 M  $\text{Fe}^{2+}$ , 0.0117 M  $\text{Mg}^{2+}$

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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:

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

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

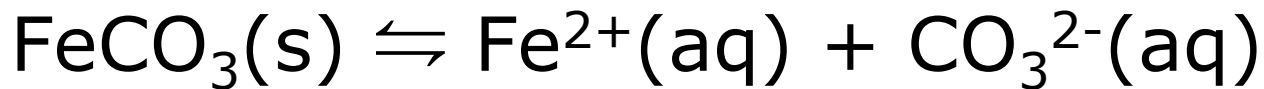
$$0.100 \text{ M} \times \frac{10 \text{ mL}}{510 \text{ mL}} = 0.00196 \text{ M } \text{CO}_3$$

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

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

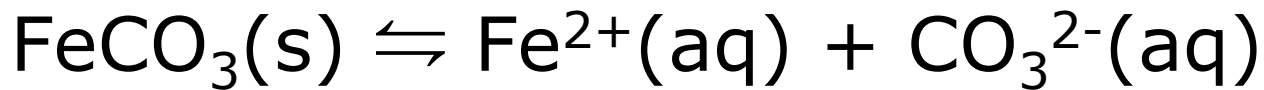
I expect the  $\text{FeCO}_3$  to precipitate first



	<b>0.0216</b>		<b>0.00196</b>
	-x		-x
	0.0216-x		0.00196-x

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

Assume x is LARGE!



	<b>0.0216</b>		<b>0.00196</b>
	-0.00196		-0.00196
	0.0196		0
	+x		+x
	0.0196+x		x

$$3.07 \times 10^{-11} = (0.0196 + x)(x)$$

Assume  $x \ll 0.0196$

$$3.07 \times 10^{-11} = 0.0196x$$

$$X = 1.56 \times 10^{-9}$$

# Check $\text{MgCO}_3$ equilibrium

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

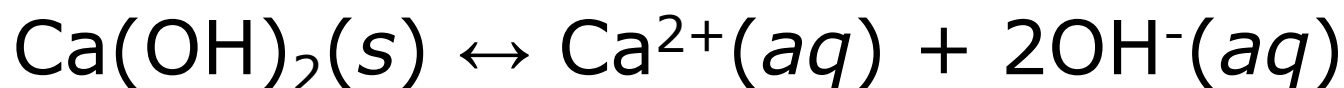
$$K_{\text{sp}}(\text{MgCO}_3) = 6.82 \times 10^{-6}$$

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

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

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CB: For the equilibrium



decreasing the pH would:

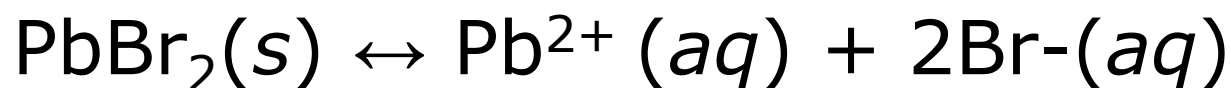
A Decrease solubility

B Increase solubility

C Have no effect on solubility

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CB: For the equilibrium



Adding NaBr(s) would:

A Decrease solubility

B Increase solubility

C Have no effect on solubility