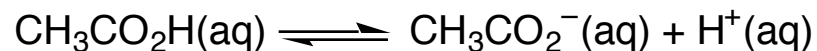


## Common Ion Effects

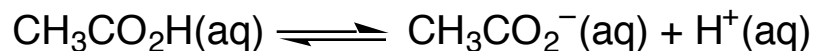
If two reactions both involve the same ion, then one reaction can effect the equilibrium position of the other reaction. The ion that appears in both reactions is the common ion. Buffers are made by combining an acid with its conjugate base.



The acetic acid contains an acetate ion. Sodium acetate also contains an acetate ion. Sodium acetate and acetic acid share a common ion, the acetate ion, so the addition of sodium acetate can affect an acetic acid equilibrium.

## Common Ion Effects

If two reactions both involve the same ion, then one reaction can effect the equilibrium position of the other reaction. The ion that appears in both reactions is the common ion. Buffers are made by combining an acid with its conjugate base.



The acetic acid contains an acetate ion. Sodium acetate also contains an acetate ion. Sodium acetate and acetic acid share a common ion, the acetate ion, so the addition of sodium acetate can affect an acetic acid equilibrium.

### Any common ion

Well, the same thing happens in all equilibria.

$$\text{For CuBr } K_{\text{sp}} = 4.2 \times 10^{-8}$$

The solubility of CuBr will be lower in a 0.05 M NaBr solution than it would be in pure water.

Let's start with a saturated CuBr solution.

In a saturated CuBr solution

$$4.2 \times 10^{-8} = [\text{Cu}^+][\text{Br}^-]$$

$$[\text{Cu}^+] = [\text{Br}^-] = 0.000205 \text{ M}$$

Now, what is the solubility of CuBr in a 0.050 M NaBr solution?

Let's start with a saturated CuBr solution.

In a saturated CuBr solution

$$4.2 \times 10^{-8} = [\text{Cu}^+][\text{Br}^-]$$

$$[\text{Cu}^+] = [\text{Br}^-] = 0.000205 \text{ M}$$

Now, what is the solubility of CuBr in a 0.050 M NaBr solution?

Simply set up an equilibrium table that has a starting conc of  $\text{Br}^- = 0.050 \text{ M}$ ...

	CuBr	Cu <sup>+</sup>	Br <sup>-</sup>
start	solid	0	0.050
change		+ x	+ x
equilibrium		x	0.050 + x
	$4.2 \times 10^{-8} = (x)(0.050 + x)$		

small x approx

$$4.2 \times 10^{-8} = (x)(0.050)$$

$$x = 8.4 \times 10^{-7}$$

$$[\text{Cu}^+] = 8.4 \times 10^{-7} \text{ M}$$

Determine the solubility of  $\text{CaSO}_4$ ,  $K_{\text{sp}} = 6.1 \times 10^{-5}$ , in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution.

Determine the solubility of  $\text{CaCl}_2$  in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution.

Determine the solubility of  $\text{CaSO}_4$ ,  $K_{\text{sp}} = 6.1 \times 10^{-5}$ , in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution.



solid	0	0.0050
solid	+x	+x
solid	x	0.0050 + x

$$x(0.0050 + x) = 6.1 \times 10^{-5}$$

Solubility is 0.0057 M

Determine the solubility of  $\text{CaCl}_2$  in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution.

Determine the solubility of  $\text{CaSO}_4$ ,  $K_{\text{sp}} = 6.1 \times 10^{-5}$ , in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution.



solid	0	0.0050
solid	+x	+x
solid	x	0.0050 + x

$$x(0.0050 + x) = 6.1 \times 10^{-5}$$

Solubility is 0.0057 M

Determine the solubility of  $\text{CaCl}_2$  in a 0.0050 M  $\text{Na}_2\text{SO}_4$  solution. ( $K_{\text{sp}}$  of  $\text{CaCl}_2 \gg K_{\text{sp}}$   $\text{CaSO}_4$ )



solid	0	0.0050
solid	+x	0
solid	x	0.0050

$$x(0.0050) = 6.1 \times 10^{-5}$$

$$x = 0.0122$$

Solubility is 0.012 M

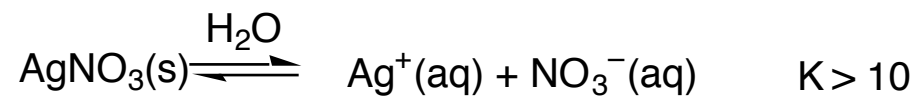
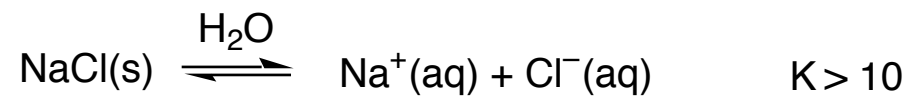
## Precipitation

What concentration of NaCl is required to precipitate AgCl from a 0.10 M AgNO<sub>3</sub> solution?



## Precipitation

What concentration of NaCl is required to precipitate AgCl from a 0.10 M AgNO<sub>3</sub> solution?

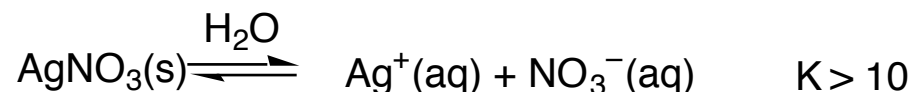
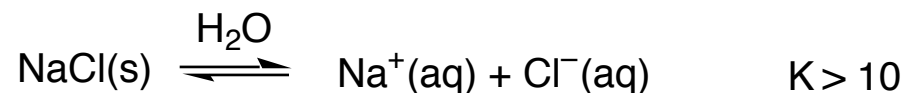


So, all of the NaCl and the AgNO<sub>3</sub> dissolves and dissociates.

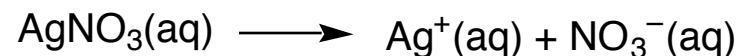
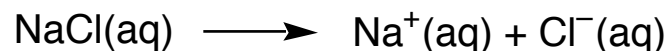


## Precipitation

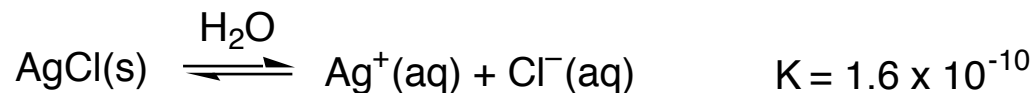
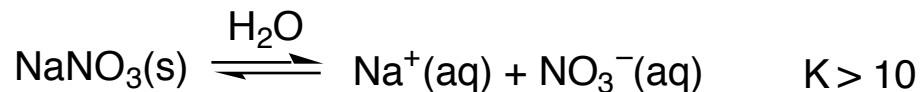
What concentration of NaCl is required to precipitate AgCl from a 0.10 M AgNO<sub>3</sub> solution?



Since we are mixing two solutions, we know all of the NaCl and the AgNO<sub>3</sub> is dissolved and dissociated.

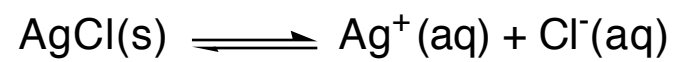


Now, we have to worry about the possibility of a metathesis reaction (ions switching) occurring.



Yes, AgCl can precipitate because it is not very soluble

The reaction is



solid

0.10

?

$$K_{sp} = 1.6 \times 10^{-10}$$

and if  $Q \geq K$  then a precipitate will form.

The reaction is



$$K_{sp} = 1.6 \times 10^{-10}$$

solid

0.10

?

and if  $Q \geq K$  then a precipitate will form.

$$[\text{Ag}^+]_o[\text{Cl}^-]_o \geq 1.6 \times 10^{-10}$$

$$0.10 \cdot [\text{Cl}^-]_o \geq 1.6 \times 10^{-10}$$

$$[\text{Cl}^-]_o \geq 1.6 \times 10^{-9}$$

So, if  $[\text{NaCl}] \geq 1.6 \times 10^{-9}$  then  $Q \geq K$  and a precipitate will form. (There is enough  $\text{Cl}^-$  in tap water to cause  $\text{AgCl}$  to precipitate from a  $\text{AgNO}_3$  solution.)

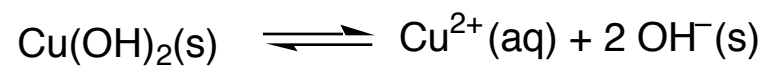
## Common ion and pH dependence

The solubility of some materials displays a pH dependence

This is a common ion effect.

for example....

For  $\text{Cu}(\text{OH})_2$   $K_{\text{sp}} = 2.2 \times 10^{-22}$ .



**What is the solubility of  $\text{Cu}(\text{OH})_2$  in neutral water?**

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-22}$$

Set up a table, before anything dissolves  $[\text{Cu}^{2+}] = 0$ , and  $[\text{OH}^-] \sim 0$  *right?*

$\text{Cu}(\text{OH})_2$   
solid

$\text{Cu}^{2+}$   
0

$\text{OH}^-$   
 $\sim 0$

**What is the solubility of  $\text{Cu}(\text{OH})_2$  in neutral water?**

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-22}$$

Set up a table, before anything dissolves  $[\text{Cu}^{2+}] = 0$ , and  $[\text{OH}^-] \sim 0$  *right?*

$\text{Cu}(\text{OH})_2$ solid	$\text{Cu}^{2+}$ 0	$\text{OH}^-$ $\sim 0$
-----------------------------------	-----------------------	---------------------------

NO,  $\text{OH}^-$  is very small, but it is not zero. In neutral water  $[\text{OH}^-] = 10^{-7}$  M. This reaction goes only slightly toward the products, so a **concentration of  $10^{-7}$**  for one of the products is going to be **significant!**

	$\text{Cu}(\text{OH})_2$ solid	$\text{Cu}^{2+}$ 0	$\text{OH}^-$ $10^{-7}$
initial			
change		+ x	+ 2 x
equilibrium		x	$10^{-7} + 2x$

**What is the solubility of Cu(OH)<sub>2</sub> in neutral water?**

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-22}$$

Set up a table, before anything dissolves  $[\text{Cu}^{2+}] = 0$ , and  $[\text{OH}^-] \sim 0$  *right?*

Cu(OH) <sub>2</sub> solid	Cu <sup>2+</sup> 0	OH <sup>-</sup> ~0
------------------------------	-----------------------	-----------------------

NO, OH<sup>-</sup> is very small, but it is not zero. In neutral water  $[\text{OH}^-] = 10^{-7}$  M. This reaction goes only slightly toward the products, so a **concentration of  $10^{-7}$**  for one of the products is going to be **significant!**

initial	Cu(OH) <sub>2</sub> solid	Cu <sup>2+</sup> 0	OH <sup>-</sup> 10 <sup>-7</sup>
change		+ x	+ 2 x
equilibrium		x	10 <sup>-7</sup> + 2x

$$2.2 \times 10^{-22} = x(10^{-7} + 2x)^2$$

Small X approx? Well, since  $10^{-7}$  is much bigger than  $10^{-22}$ —by a factor of about  $10^{15}$ —the change, x, is going to be small as compared to  $10^{-7}$ , so let's give the small x approx a try.

$$2.22 \times 10^{-22} = 10^{-14}x$$

$$2.22 \times 10^{-8} = x$$

Approximation not valid.  $2.22 \times 10^{-8}/10^{-7} \times 100 = 44\%$

So, I solved it iteratively,

$$x = 2.2 \times 10^{-22}/(10^{-7} + 2x)^2$$

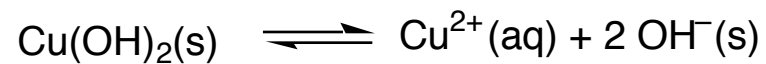


I plugged in  $2.2 \times 10^{-8}$  for the x on the right, evaluated the expression, and repeated until the the x's converged in 12 steps to  $1.36 \times 10^{-8}$

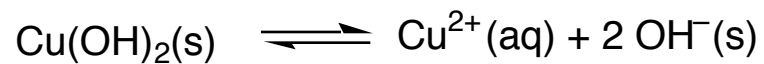
2.2000e-08	1.0610e-08
1.0610e-08	1.4972e-08
1.4972e-08	1.3029e-08
1.3029e-08	1.3845e-08
1.3845e-08	1.3493e-08
1.3493e-08	1.3643e-08
1.3643e-08	1.3579e-08
1.3579e-08	1.3606e-08
1.3606e-08	1.3595e-08
1.3595e-08	1.3600e-08
1.3600e-08	1.3597e-08
1.3597e-08	1.3598e-08
1.3598e-08	1.3598e-08

So, the molar solubility of  $\text{Cu}(\text{OH})_2 = 1.36 \times 10^{-8}$  M in neutral water.

**What is the solubility of  $\text{Cu}(\text{OH})_2$  if the pH of the solution starts at 12.00?** (Remember, if you are given the pH of a solution then you know  $[\text{H}^+]$ , unless the question says something like starting pH.)

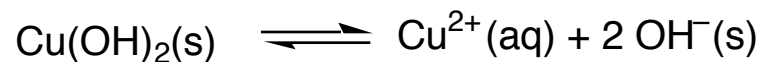


**What is the solubility of  $\text{Cu}(\text{OH})_2$  if the pH of the solution starts at 12.00?** (Remember, if you are given the pH of a solution then you know  $[\text{H}^+]$ , unless the question says something like starting pH)



	$\text{Cu}(\text{OH})_2$	$\text{Cu}^{2+}$	$\text{OH}^-$
initial	solid	0	?
change			
equilibrium			

**What is the solubility of  $\text{Cu}(\text{OH})_2$  if the pH of the solution starts at 12.00?** (Remember if you are given the pH of a solution then you know  $[\text{H}^+]$ , unless the question says something like starting pH)

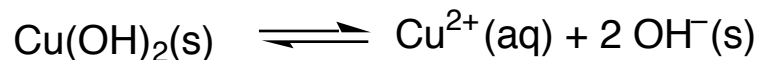


	$\text{Cu}(\text{OH})_2$	$\text{Cu}^{2+}$	$\text{OH}^-$
initial	solid	0	$10^{-2}$
change		+ x	+ 2 x
equilibrium		x	$10^{-2} + 2x$

$$10^{-14} = [10^{-12}][\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-2}$$

**What is the solubility of  $\text{Cu}(\text{OH})_2$  if the pH of the solution starts at 12.00?** (Remember if you are given the pH of a solution then you know  $[\text{H}^+]$ , unless the question says something like starting pH)



	$\text{Cu}(\text{OH})_2$	$\text{Cu}^{2+}$	$\text{OH}^-$
initial	solid	0	$10^{-2}$
change		+ x	+ 2 x
equilibrium		x	$10^{-2} + 2x$

The change, x, is going to be small as compared to  $10^{-2}$ , so

$$2.2 \times 10^{-22} = [\text{Cu}^{2+}](10^{-2})^2$$

$$[\text{Cu}^{2+}] = 2.2 \times 10^{-22}/10^{-4}$$

$$[\text{Cu}^{2+}] = 2.2 \times 10^{-18}$$

Yep, small x approximation is valid.  $4.4 \times 10^{-18}/10^{-2} \times 100 = 4.4 \times 10^{-14} \%$

The molar solubility went down a great deal when the pH went from 7 to 12!

**You must be careful while doing these calculations.** While the solubility is pH dependent pH is not the only factor. Take the following example...

*What is the solubility of  $\text{Cu}(\text{OH})_2$  in a 0.1 M  $\text{HNO}_3$  solution?*

*Find  $[\text{OH}^-]$*

$$\begin{aligned}K_w &= [\text{H}^+][\text{OH}^-] \\10^{-14} &= 0.1 \cdot [\text{OH}^-] \\[\text{OH}^-] &= 10^{-13}\end{aligned}$$

$$\begin{aligned}2.2 \times 10^{-22} &\stackrel{\text{so..}}{=} x(10^{-13})^2 \\2.2 \times 10^{-22} &= 10^{-26}x \\2.2 \times 10^4 &= x\end{aligned}$$

Small x approximation not valid, but lets ignore that fact for a moment and focus on the answer.

**You must be careful while doing these calculations.** While the solubility is pH dependent pH is not the only factor. Take the following example...

*What is the solubility of  $\text{Cu}(\text{OH})_2$  in a 0.1 M  $\text{HNO}_3$  solution?*

*Find  $[\text{OH}^-]$*

$$\begin{aligned}K_w &= [\text{H}^+][\text{OH}^-] \\10^{-14} &= 0.1 \cdot [\text{OH}^-] \\[\text{OH}^-] &= 10^{-13}\end{aligned}$$

$$\begin{aligned}2.2 \times 10^{-22} &= x(10^{-13})^2 \\2.2 \times 10^{-22} &= 10^{-26}x \\2.2 \times 10^4 &= x\end{aligned}$$

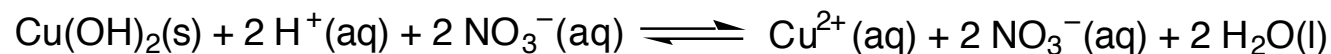
**NO Way is the molar solubility  $2.2 \times 10^4$ .**

That is 22,000 moles of  $\text{Cu}(\text{OH})_2$  dissolved in 1 L.

OK, is 22,000 not big enough for you?

This solution would have approximately 2,100,000 g of  $\text{Cu}(\text{OH})_2$  in a L of water

The problem changed,



The  $\text{HNO}_3$  reacts with the  $\text{Cu(OH)}_2$  to make water and  $\text{Cu(NO}_3)_2$ , and  $\text{Cu(NO}_3)_2$  is soluble in water

$\text{Cu(OH)}_2$  continues to dissolve until the  $\text{HNO}_3$  is used up. Once the  $\text{HNO}_3$  is used up the  $[\text{Cu}^{2+}] = 0.050 \text{ M}$

The  $\text{Cu}^{2+}$  concentration is determined using the stoichiometry of the neutralization reaction.

$$0.1 \text{ M HNO}_3 \times \frac{1 \text{ mol Cu(NO}_3)_2}{2 \text{ mol HNO}_3} = 0.050 \text{ M Cu(NO}_3)_2$$

Since  $[\text{Cu}^{2+}] = 0.050 \text{ M}$  no more  $\text{Cu(OH)}_2$  will dissolve!

This was an acid base neutralization in disguise.



## Less obvious examples of pH dependent solubility

The solubility of any salt that dissociates and forms a weak acid or a weak base will demonstrate pH dependence.

For example  $\text{Ag}_2\text{SO}_4$  is only very slightly soluble in water,  $K_{\text{sp}}$  for  $\text{Ag}_2\text{SO}_4 = 1.4 \times 10^{-5}$ .



The solubility of  $\text{Ag}_2\text{SO}_4$  will be higher in 1 M  $\text{HNO}_3$ . Why?

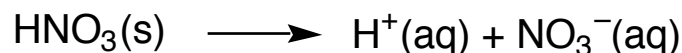
## Less obvious examples of pH dependent solubility

The solubility of any salt that dissociates and forms a weak acid or a weak base will demonstrate pH dependence.

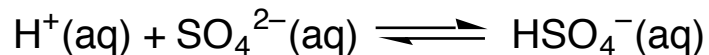
For example  $\text{Ag}_2\text{SO}_4$  is only very slightly soluble in water,  $K_{\text{sp}}$  for  $\text{Ag}_2\text{SO}_4 = 1.4 \times 10^{-5}$ .



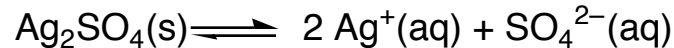
The solubility of  $\text{Ag}_2\text{SO}_4$  will be higher in 1 M  $\text{HNO}_3$ . Why?



Since  $\text{SO}_4^{2-}$  is a weak base....



The K for this reaction is  $1/K_a = 1/(1.2 \times 10^{-2}) = 83$



So, the presence of  $\text{H}^+$  lowers the concentration of  $\text{SO}_4^{2-}$ , and, according to Le Châtelier's principle, more  $\text{Ag}_2\text{SO}_4$  will dissolve to replace the  $\text{SO}_4^{2-}$  that was converted to  $\text{HSO}_4^-$ .

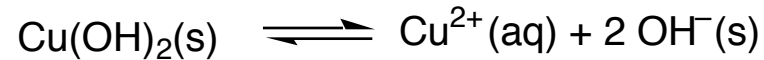
## Common ion and pH dependence

The solubility of some materials displays a pH dependence

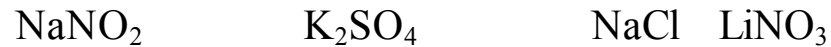
This is a common ion effect.

for example....

For  $\text{Cu}(\text{OH})_2$   $K_{\text{sp}} = 2.2 \times 10^{-22}$ .



The solubility of any salt that produces an acid or base when it dissolves in water will be pH dependent.



The solubility of any metal that can form an insoluble metal hydroxide will be pH dependent.



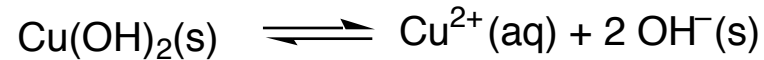
## Common ion and pH dependence

The solubility of some materials displays a pH dependence

This is a common ion effect.

for example....

For  $\text{Cu}(\text{OH})_2$   $K_{\text{sp}} = 2.2 \times 10^{-22}$ .



The solubility of any salt that produces an acid or base when it dissolves in water will be pH dependent.

$\text{NaNO}_2$	$\text{K}_2\text{SO}_4$	$\text{NaCl}$	$\text{LiNO}_3$
yes	yes	no	no

The solubility of any metal that can form an insoluble metal hydroxide will be pH dependent.

$\text{NaCl}$	$\text{FeCl}_3$	$\text{Ba}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$
no	yes	yes	yes