

# Outline

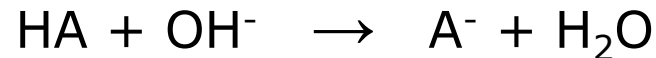
- Buffer Solutions
- Titrations
- Solubility Equilibria
- Precipitation Problems
- Lewis Acids and Bases
- Complex Ion Equilibria
- Solubility – An Equilibrium Position

# Buffers

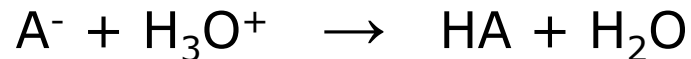
Buffers are solutions that resist changes in pH

Buffers contain significant amounts of a weak acid (HA) and its conjugate base (A<sup>-</sup>)

HA neutralizes added base:

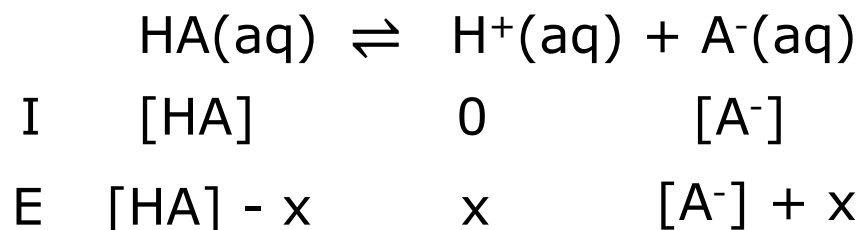


A<sup>-</sup> neutralizes added acid:



Resistance to pH change increases with increasing concentrations of the weak acid and its conjugate base

Acids ionize to form the conjugate base...



$$K_a = \frac{[\text{H}^+]_{\text{eq}} ([\text{A}^-] + x)}{([\text{HA}] - x)} \approx \frac{[\text{H}^+]_{\text{eq}} ([\text{A}^-])}{([\text{HA}] )}$$

$$\Rightarrow -\log (K_a) = -\log \left( \frac{[\text{H}^+]_{\text{eq}} ([\text{A}^-])}{([\text{HA}] )} \right)$$

$$\Rightarrow \text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}] } \right) \quad \text{Henderson-Hasselbalch Eq.}$$

The pH of a buffer is determined by the ratio of  $[A^-]$  to  $[HA]$

Solutions resist pH changes when...

$$0.1 < \frac{[A^-]}{[HA]} < 10$$

A buffer is most effective when the  $[A^-] = [HA]$ ...

$$\text{pH} = \text{pK}_a + \log\left(\frac{[A^-]}{[HA]}\right) \Rightarrow \text{pH} = \text{pK}_a + \log(1) \Rightarrow \text{pH} = \text{pK}_a$$

To make an effective buffer at a specific pH... choose weak acid with  $\text{pK}_a \pm 1$  to the desired pH

A buffer is made by mixing...

1. a weak acid and a salt of its conjugate base
2. a weak base and a salt of its conjugate acid
3. a weak acid and a lesser amount of a strong base
4. a weak base and a lesser amount of a strong acid

You want a  $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$  buffer with a pH of 5.00 ( $K_a = 1.8 \times 10^{-5}$ ). Find the  $[\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^-]$  ratio in this buffer.

$$\text{p}K_a = -\log(K_a) = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \Rightarrow 5.00 = 4.74 + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 0.26 \Rightarrow \frac{[\text{A}^-]}{[\text{HA}]} = 1.82 \Rightarrow \frac{[\text{HA}]}{[\text{A}^-]} = \underline{0.55}$$

What must be the molarity of sodium fluoride in a solution of 0.10 M hydrofluoric acid ( $K_a = 3.5 \times 10^{-4}$ ) to make a buffer with a pH of 4.00?

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \Rightarrow 4.00 = 3.46 + \log\left(\frac{[\text{A}^-]}{0.10 \text{ M}}\right)$$

$$\log\left(\frac{[\text{A}^-]}{0.10 \text{ M}}\right) = 0.54 \Rightarrow \frac{[\text{A}^-]}{0.10 \text{ M}} = 3.46 \Rightarrow [\text{A}^-] = \underline{0.35 \text{ M}}$$

Find the pH of 1.00 L of buffer solution that is 1.00 M in acetic acid ( $K_a = 1.76 \times 10^{-5}$ ) and 1.00 M sodium acetate if 0.01 moles of NaOH are added.

$$\frac{0.01 \text{ mol NaOH}}{1.00 \text{ L}} = 0.01 \text{ M NaOH} \Rightarrow \underline{0.01 \text{ M OH}^-}$$

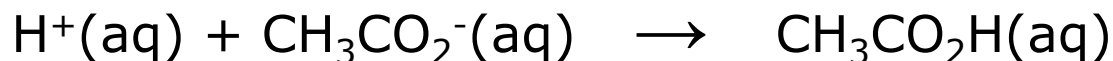
	$\text{OH}^-(\text{aq}) + \text{CH}_3\text{CO}_2\text{H}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CH}_3\text{CO}_2^-(\text{aq})$		
I	0.01	1.00	1.00
F	0	0.99	1.01

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log(1.76 \times 10^{-5}) + \log\left(\frac{1.01}{0.99}\right) = \underline{4.76}$$



Find the pH of 1.00 L of buffer solution that is 1.00 M in acetic acid ( $K_a = 1.76 \times 10^{-5}$ ) and 1.00 M sodium acetate if 0.01 moles of HCl are added.

$$\frac{0.01 \text{ mol HCl}}{1.00 \text{ L}} = 0.01 \text{ M HCl} \Rightarrow \underline{0.01 \text{ M H}^+}$$

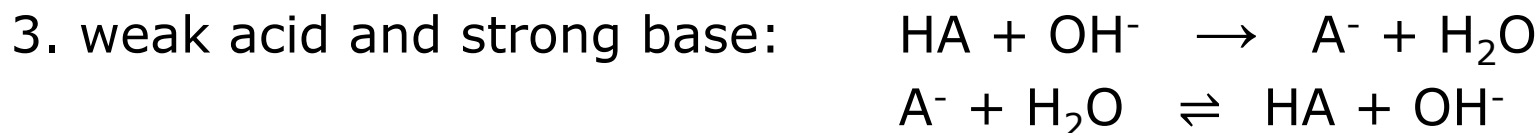
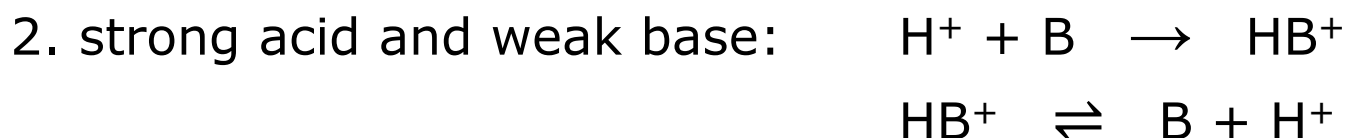


I	0.01	1.00	1.00
F	0	0.99	1.01

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log(1.76 \times 10^{-5}) + \log\left(\frac{0.99}{1.01}\right) = \underline{4.75}$$

# Titration

Three types of titrations to consider...

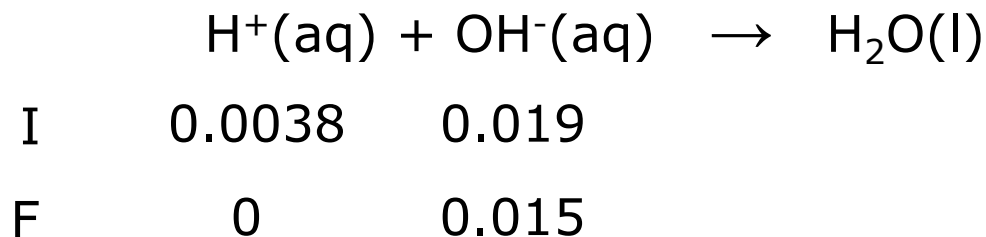


## Strong – Strong Titrations

250.0 mL of 0.020 M NaOH is titrated with 0.10 M HCl. Calculate the pH of the solution after the addition of...

a. 10.0 mL HCl

Find molarities...  $[\text{OH}^-] = 0.019 \text{ M}$  and  $[\text{H}^+] = 0.0038 \text{ M}$

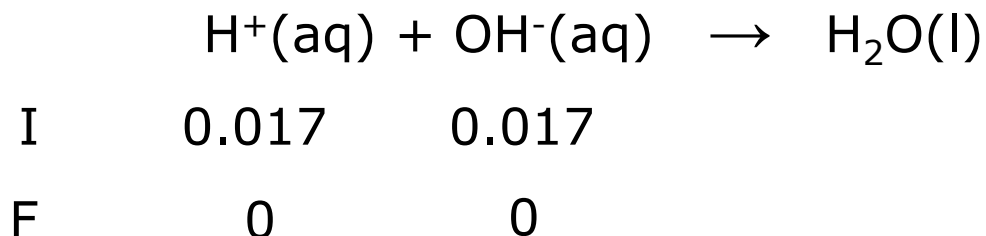


$$\text{pOH} = -\log(0.015) = 1.82$$

$$\text{pH} = 14.00 - 1.82 = \underline{12.18}$$

b. 50.0 mL HCl

Find molarities...  $[\text{OH}^-] = 0.017 \text{ M}$  and  $[\text{H}^+] = 0.017 \text{ M}$



amount acid = amount base... stoichiometric point!

strong acid – strong base titrations:  $\text{pH} = 7.00$  at stoichiometric point

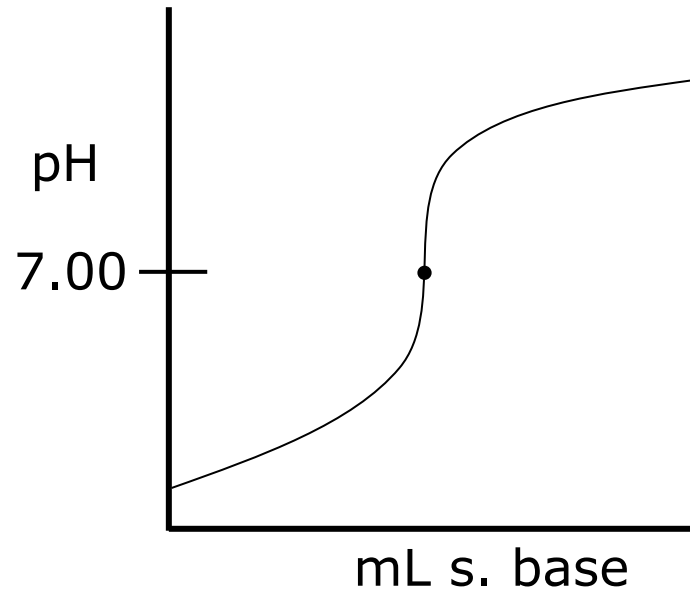
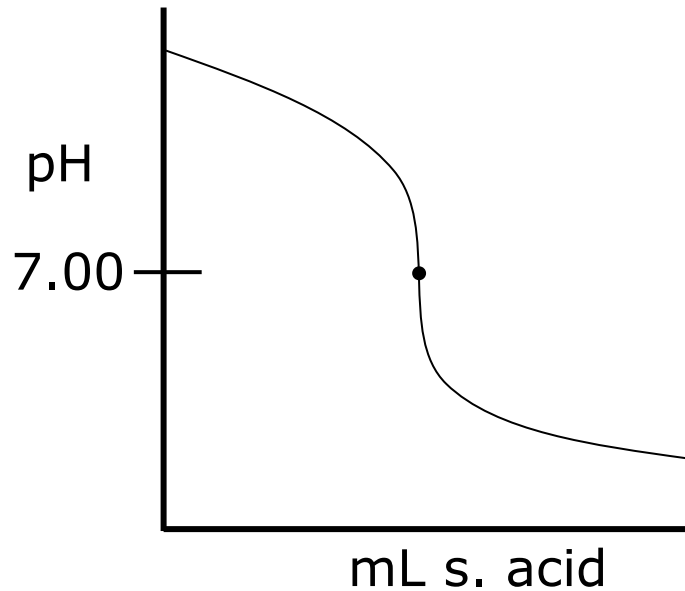
c. 100.0 mL HCl

Find molarities...  $[\text{OH}^-] = 0.014 \text{ M}$  and  $[\text{H}^+] = 0.029 \text{ M}$

	$\text{H}^+(\text{aq})$	$\text{OH}^-(\text{aq})$	$\rightarrow$	$\text{H}_2\text{O}(\text{l})$
I	0.029	0.014		
F	0.015	0		

$$\text{pH} = -\log(0.015) = \underline{1.82}$$

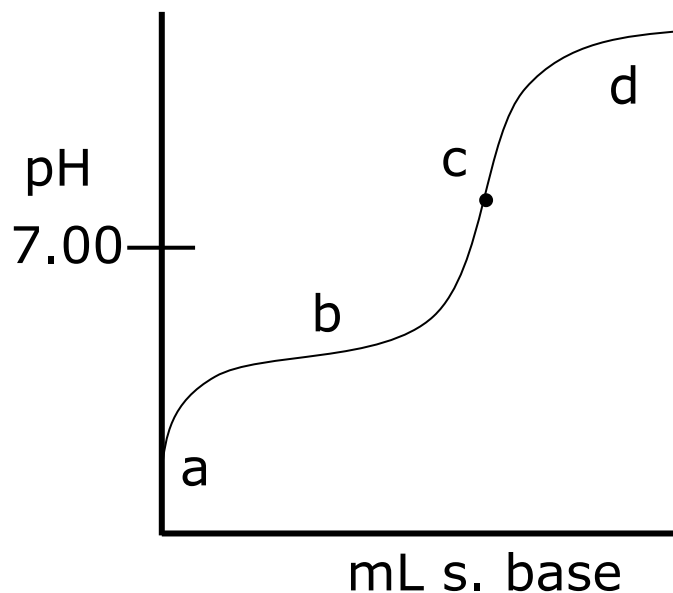
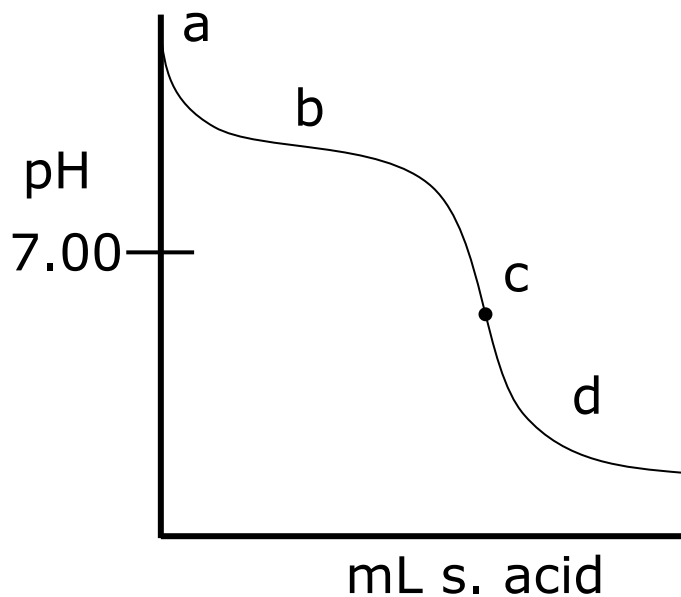
Titration curve is plot of pH vs. acid (base) added



# Strong – Weak Titrations

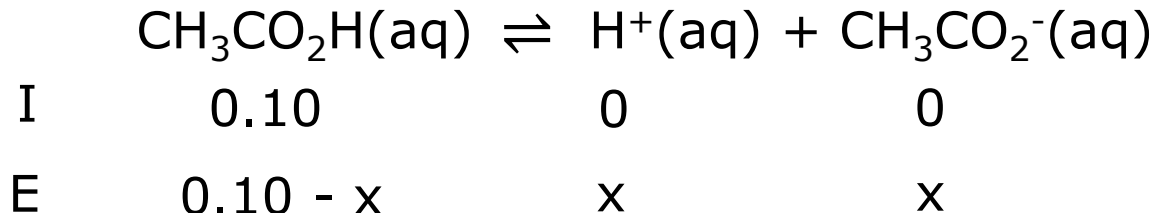
Strong acid (base) – weak base (acid) titration curves have four regions:

(a) initial, (b) buffer, (c) stoichiometric point, (d) excess



100.0 mL of 0.10 M acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ),  $K_a = 1.76 \times 10^{-5}$ , is titrated with 1.0 M sodium hydroxide. Determine the pH of the solution with...

a. 0 mL NaOH added (initial)



$$1.76 \times 10^{-5} = \frac{x^2}{(0.10 - x)} \approx \frac{x^2}{(0.10)} \Rightarrow x = 1.3 \times 10^{-3} \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log(1.3 \times 10^{-3} \text{ M}) = \underline{2.89}$$



b. 2.5 mL NaOH added (buffer)

Find molarities:

$$[\text{CH}_3\text{CO}_2\text{H}] = 0.098 \text{ M and } [\text{OH}^-] = 0.024 \text{ M}$$

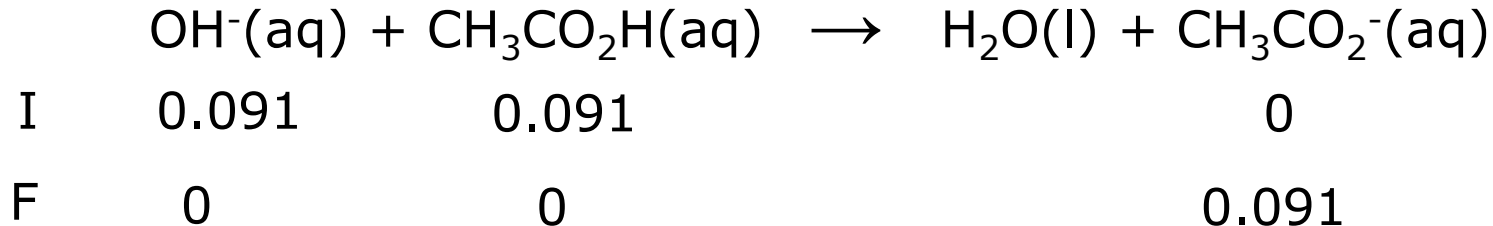
	$\text{OH}^-(\text{aq}) + \text{CH}_3\text{CO}_2\text{H}(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{CH}_3\text{CO}_2^-(\text{aq})$		
I	0.024	0.098	0
F	0	0.074	0.024

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log(1.76 \times 10^{-5}) + \log\left(\frac{0.024}{0.074}\right) = \underline{4.27}$$

c. 10.0 mL NaOH added (stoichiometric point)

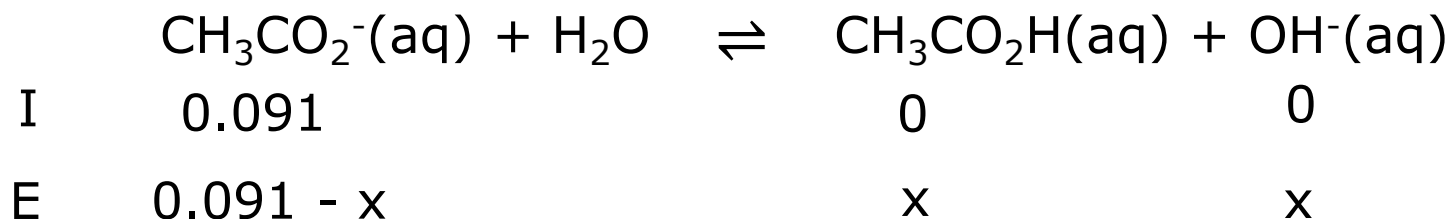
Find molarities:

$$[\text{CH}_3\text{CO}_2\text{H}] = 0.091 \text{ M and } [\text{OH}^-] = 0.091 \text{ M}$$



Not a buffer... Consider the ionization of the conjugate base!

c. 10.0 mL NaOH added (stoichiometric point)



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

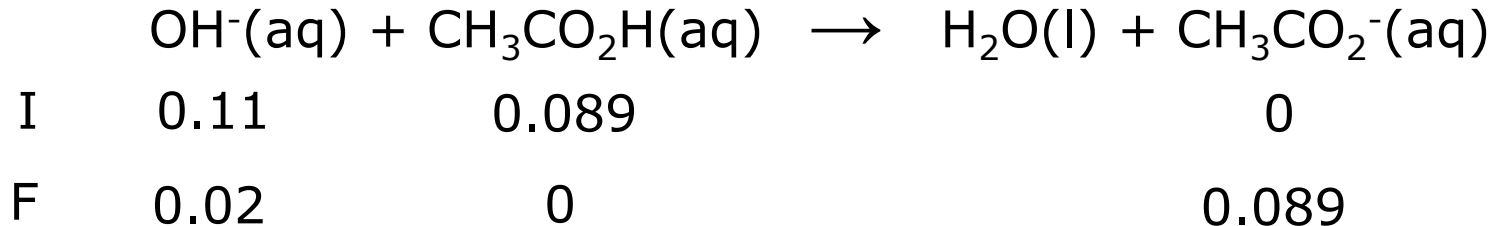
$$5.68 \times 10^{-10} = \frac{x^2}{(0.091 - x)} \approx \frac{x^2}{(0.091)} \Rightarrow x = 7.2 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log (7.2 \times 10^{-6} \text{ M}) = 5.14 \Rightarrow \text{pH} = 14.00 - 5.14 = \underline{8.86}$$

d. 12.5 mL NaOH added (excess)

Find molarities:

$$[\text{CH}_3\text{CO}_2\text{H}] = 0.089 \text{ M and } [\text{OH}^-] = 0.11 \text{ M}$$

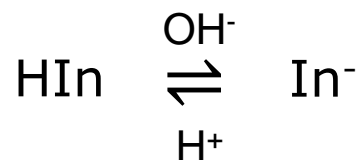


$$\text{pOH} = -\log(0.02 \text{ M}) = 1.7$$

$$\text{pH} = 14.00 - 1.7 = \underline{12.3}$$

Stoichiometric point can be identified with...

1. pH meter: monitor pH during titration  
stoichiometric point is middle of steep change
2. indicator: weak acid (c. base) changes during titration



end point indicated by color change

want  $\text{pK}_a = \text{pH} \pm 1$  at stoichiometric point

A weakly acidic solution is prepared by dissolving 1.016 g benzoic acid into 25.00 mL water, and titrated with 0.2040 M NaOH.

$$\text{MM} = 122.12 \text{ g/mol and } K_a = 6.4 \times 10^{-5}$$

a. How many mL's to reach stoichiometric point?

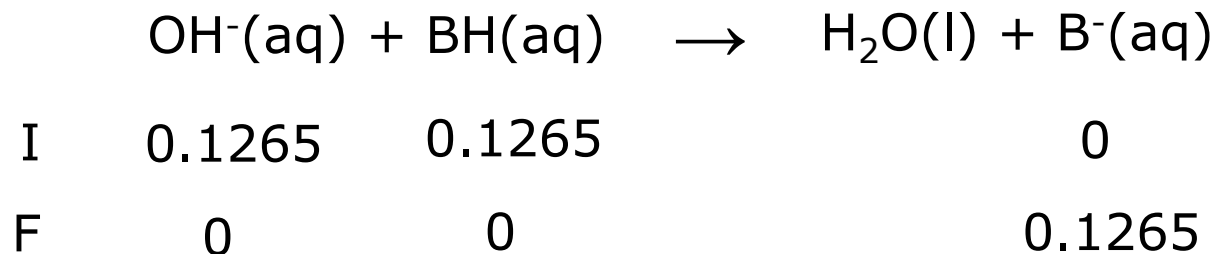
$$1.016 \text{ g BH} \times \frac{1 \text{ mol BH}}{122.12 \text{ g BH}} \times \frac{1}{0.02500 \text{ L}} = 0.3328 \text{ M}$$

$$25.00 \text{ mL} \times \frac{0.3328 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol BH}} \times \frac{1 \text{ L}}{0.2040 \text{ mol}} = 40.78 \text{ mL}$$

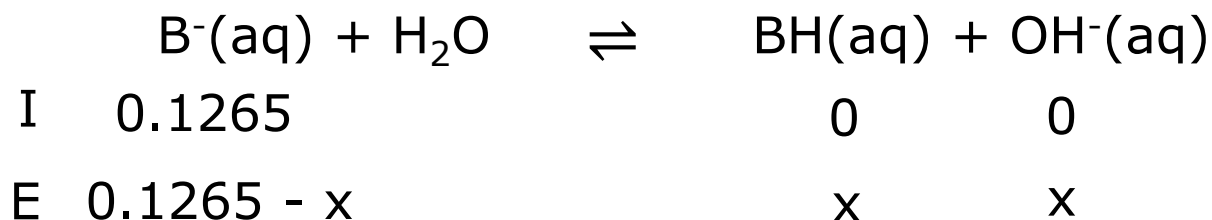
b. What is pH at stoichiometric point?

Find molarities:

$$[\text{BH}] = 0.1265 \text{ M and } [\text{OH}^-] = 0.1265 \text{ M}$$



b. What is pH at stoichiometric point?



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.56 \times 10^{-10}$$

$$1.56 \times 10^{-10} = \frac{x^2}{(0.1265 - x)} \approx \frac{x^2}{(0.1265)}$$

$$x = 4.5 \times 10^{-6} \text{ M} = [OH^-] \quad (0.004\%)$$

$$pOH = -\log(4.44 \times 10^{-6} \text{ M}) = 5.35 \Rightarrow pH = 8.65$$



c. What indicator should be used? What color change occurs?

$$8.65 \pm 1 = 7.65 \text{ and } 9.65$$

thymol blue (chose closest!)

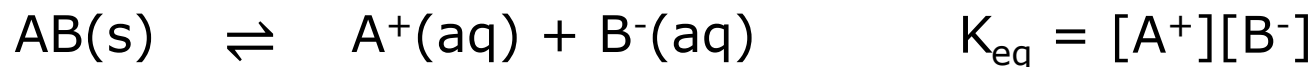
yellow (acidic) → blue (basic)

Indicator	pK <sub>a</sub>	Acidic Color	Basic Color
methyl red	5.0	red	yellow
phenol red	7.9	yellow	red
thymol blue	8.9	yellow	blue
phenolphthalein	9.4	colorless	pink

# Solubility Equilibria

Solids dissolve (dissociate) and ions precipitate (associate) in a competing process

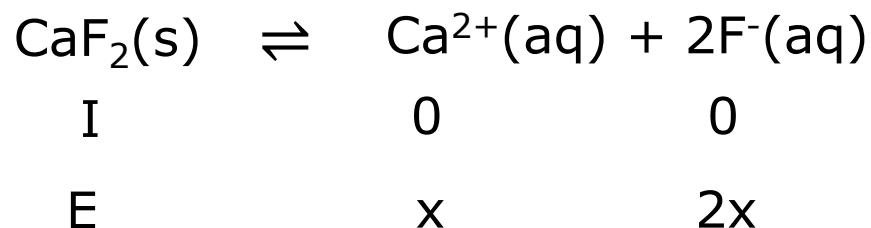
Equilibrium achieved when rate of dissolution and precipitation are equal



A  $K_{\text{eq}}$  for a salt dissociating in water is called a  $K_{\text{sp}}$ , the solubility product constant

Solubility is the amount of substance that can be dissolved

The solubility of calcium fluoride is 0.017 g / L. Find its  $K_{sp}$ .



x = solubility of  $\text{CaF}_2$  in mol / L

$$x = \frac{0.017 \text{ g CaF}_2}{\text{L}} \times \frac{1 \text{ mol CaF}_2}{78.1 \text{ g CaF}_2} = 2.2 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = (x)(2x)^2 = 4x^3 = \underline{4.3 \times 10^{-11}}$$

The solubility of iron (III) hydroxide (MM = 106.8 g/mol) is 0.130 g for every 100. mL.... Find the  $K_{sp}$ .



I	0	0
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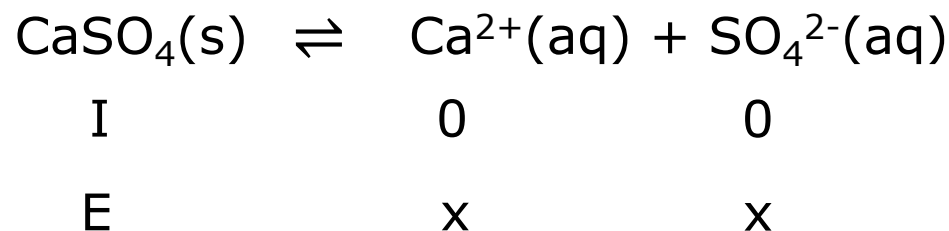
E	x	3x
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$x$  = solubility of  $\text{Fe(OH)}_3$  in mol / L

$$x = \frac{0.130 \text{ g Fe(OH)}_3}{0.100 \text{ L}} \times \frac{1 \text{ mol Fe(OH)}_3}{106.8 \text{ g Fe(OH)}_3} = 1.22 \times 10^{-2} \text{ M}$$

$$K_{sp} = [\text{Fe}^{3+}][\text{OH}^{-}]^3 = (x)(3x)^3 = 27x^4 = \underline{5.98 \times 10^{-7}}$$

Find the molar solubility (mol/L) of calcium sulfate if its  $K_{sp} = 2.40 \times 10^{-5}$ .



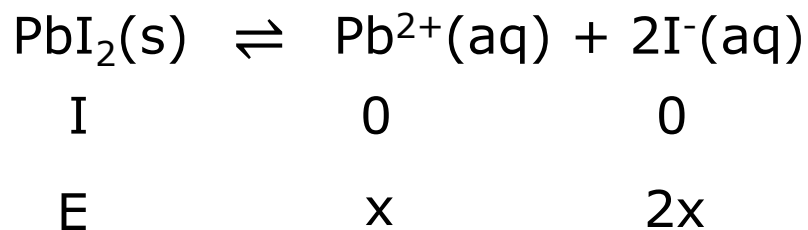
x = molar solubility of  $\text{CaSO}_4$

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \Rightarrow 2.40 \times 10^{-5} = (x)(x) \Rightarrow x = \underline{0.00490 \text{ M}}$$

What is the solubility of  $\text{CaSO}_4$  (136.2 g / mol) in g/100 mL?

$$\frac{0.00490 \text{ mol CaSO}_4}{\text{L}} \times \frac{136.2 \text{ g}}{\text{mol}} \times \frac{0.1 \text{ L}}{100 \text{ mL}} = \frac{0.0667 \text{ g CaSO}_4}{100 \text{ mL}}$$

Find the solubility of lead (II) iodide (MW = 461.2 g / mol) in g / 100 mL if its  $K_{sp} = 8.30 \times 10^{-9}$ .



x = molar solubility of  $\text{PbI}_2$

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 \Rightarrow 8.30 \times 10^{-9} = (x)(2x)^2 \Rightarrow x = 1.28 \times 10^{-3} \text{ M}$$

$$\frac{0.00128 \text{ mol PbI}_2}{\text{L}} \times \frac{461.2 \text{ g}}{\text{mol}} \times \frac{0.1 \text{ L}}{100 \text{ mL}} = \frac{0.0590 \text{ g PbI}_2}{100 \text{ mL}}$$

$K_{sp}$ 's can be used to compare relative solubilities of salts

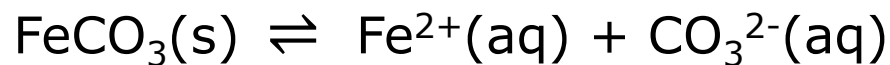
Salts with same number of ions: compare  $K_{sp}$ 's directly!

Salt	$K_{sp}$	Solubility
$\text{NiCO}_3$	$1.4 \times 10^{-7}$	greatest
$\text{AgOH}$	$2.0 \times 10^{-8}$	↓
$\text{MnS}$	$2.3 \times 10^{-13}$	least

Salts with different number of ions: calculate solubility!

Solubility of a salt is decreased by the presence of ions involved in equilibrium reaction: common ion effect

What is the molar solubility of iron (II) carbonate in 0.10 M sodium carbonate?  $K_{sp} = 2.1 \times 10^{-11}$



I	0	0.10
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E	x	x + 0.10
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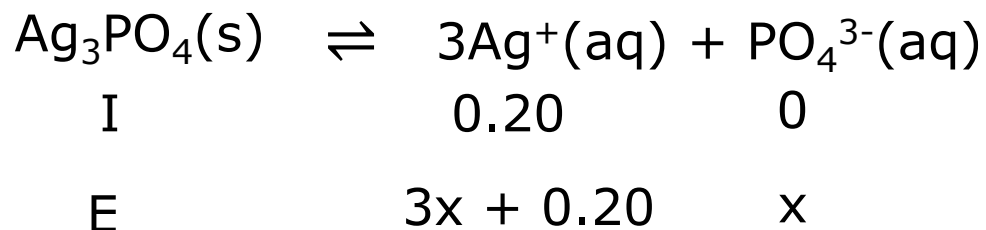
x = molar solubility of  $\text{FeCO}_3$

$$K_{sp} = [\text{Fe}^{2+}][\text{CO}_3^{2-}] \Rightarrow 2.1 \times 10^{-11} = (x)(x + 0.10) \approx (x)(0.10)$$

$$x = \underline{2.1 \times 10^{-10} \text{ M FeCO}_3}$$



What is the molar solubility of silver phosphate ( $K_{sp} = 1.8 \times 10^{-18}$ ) in 0.20 M silver nitrate?



$x$  = molar solubility of  $\text{Ag}_3\text{PO}_4$

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] \Rightarrow 1.8 \times 10^{-18} = (0.20 + 3x)^3(x) \approx (0.20)^3(x)$$

$$x = \underline{2.2 \times 10^{-16} \text{ M Ag}_3\text{PO}_4}$$

Ion product,  $Q$ , is used to predict precipitation

1.  $Q > K$      supersaturated; precipitation occurs
2.  $Q < K$      unsaturated; can dissolve more!
3.  $Q = K$      saturated; precipitation and dissolution occur

# Precipitation Problems

Will barium hydroxide precipitate in a solution that is 0.20 M in sodium hydroxide and 0.10 M in barium nitrate? The  $K_{sp}$  for barium hydroxide is  $5.0 \times 10^{-3}$ .

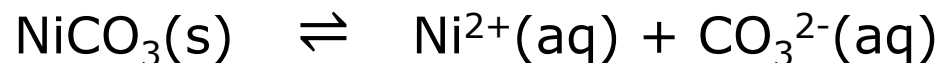


$$K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2 = 5.0 \times 10^{-3}$$

$$Q = (0.10)(0.20)^2 = 4.0 \times 10^{-3}$$

If  $Q < K$ , no precipitate forms

Will nickel (II) carbonate ( $K_{sp} = 1.4 \times 10^{-7}$ ) precipitate in a 1.00 L solution of 0.010 M nickel (II) nitrate and 0.025 M sodium carbonate?



$$K_{sp} = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = 1.4 \times 10^{-7}$$

$$Q = (0.010)(0.025) = 2.5 \times 10^{-4}$$

If  $Q > K$ , precipitate forms

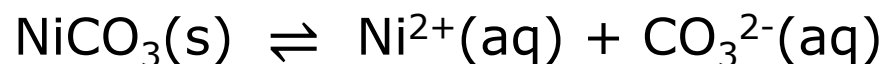
What is the concentration of  $\text{Ni}^{2+}$  at equilibrium?

$\text{Ni}^{2+}$  reacts with  $\text{CO}_3^{2-}$ ...

	$\text{Ni}^{2+}(\text{aq})$	$+$	$\text{CO}_3^{2-}(\text{aq})$	$\rightarrow$	$\text{NiCO}_3(\text{s})$
I	0.010		0.025		"0"
F	0		0.015		"0.010"

What is the concentration of  $\text{Ni}^{2+}$  at equilibrium?

Remaining  $\text{CO}_3^{2-}$  acts as common ion...



I	0	0.015
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E	x	x + 0.015
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$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{CO}_3^{2-}] \Rightarrow 1.4 \times 10^{-7} = (x)(x + 0.015) \approx (x)(0.015)$$

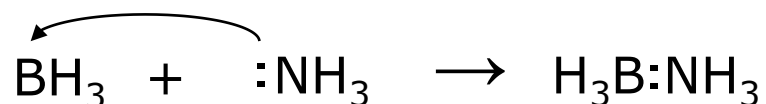
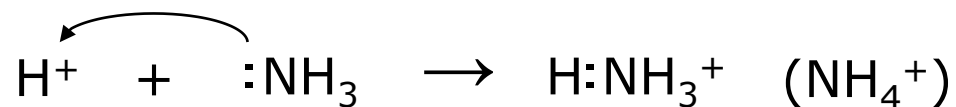
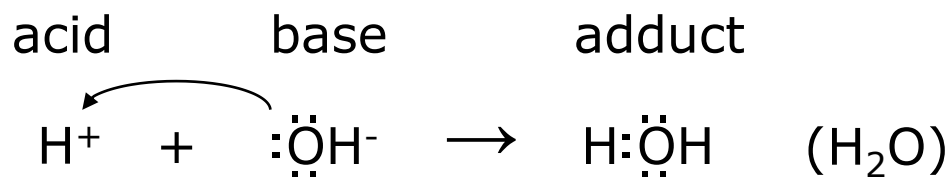
$$[\text{Ni}^{2+}] = x = \underline{9.3 \times 10^{-6} \text{ M}}$$

# Lewis Acids and Bases

Lewis acids are electron pair acceptors

Lewis bases are electron pair donors

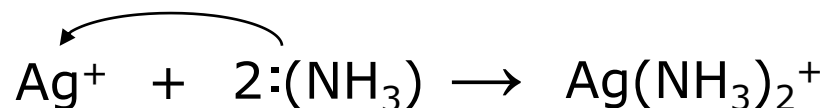
Empty orbital of acid accepts electron pair from base in acid-base reactions



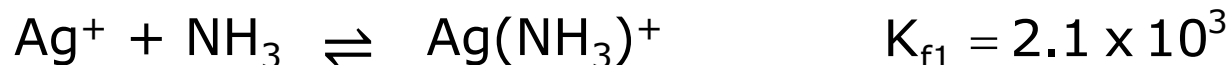
# Complex Ion Equilibria

Complex ions are formed from reactions of metal (atoms) ions and ligands

Ligands are molecules (ions) that donate electron pairs (Lewis bases!)

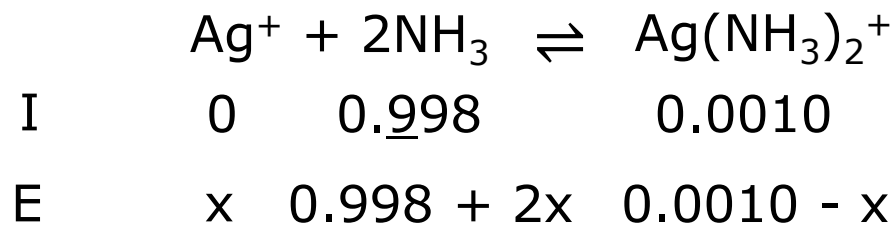
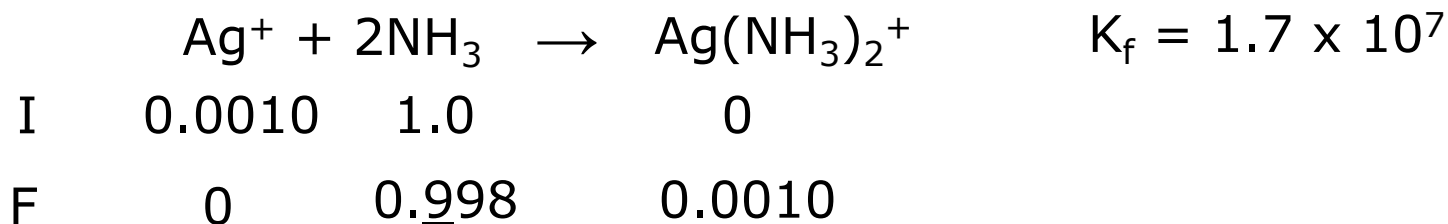


Ligands add to metal ions in individual steps, each step described by a formation constant,  $K_f$





What are the concentrations of all species in a solution that is initially  $1.0 \times 10^{-3} \text{ M Ag}^+$  and  $1.0 \text{ M NH}_3$ ?



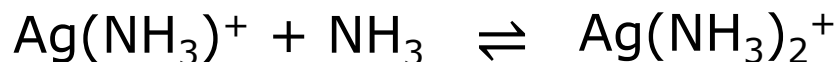
$$1.7 \times 10^7 = \frac{(0.0010 - x)}{(x)(0.998 + 2x)^2} \approx \frac{0.0010}{(x)(0.998)^2} \Rightarrow x = 6 \times 10^{-11} \text{ M}$$

What are the concentrations of all species in a solution that is initially  $1.0 \times 10^{-3} \text{ M Ag}^+$  and  $1.0 \text{ M NH}_3$ ?

$$[\text{Ag}^+] = x = \underline{6 \times 10^{-11} \text{ M}}$$

$$[\text{NH}_3] = 0.\underline{998} + 2x = \underline{1 \text{ M}}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = 0.0010 - x = \underline{0.0010 \text{ M}}$$

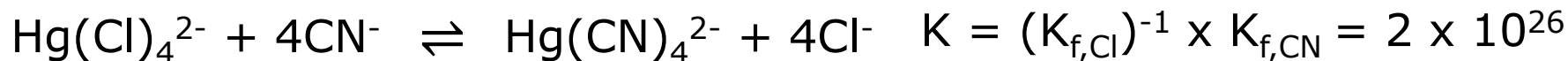
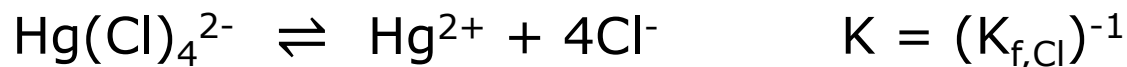
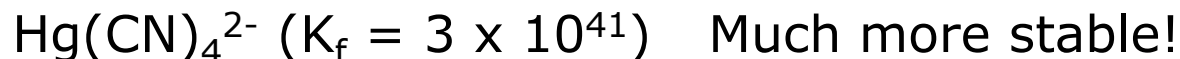
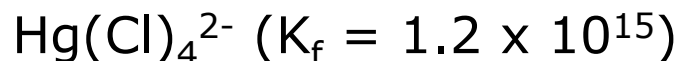


$$K_{f2} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} \Rightarrow [\text{Ag}(\text{NH}_3)^+] = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{K_{f2} [\text{NH}_3]}$$

$$[\text{Ag}(\text{NH}_3)^+] = \frac{(0.0010)}{(8.2 \times 10^3)(1)} = \underline{1 \times 10^{-7} \text{ M}}$$

$K_f$  values can be used to predict stability of complex ions,  
sometimes called stability constants

Which is more stable?



Large  $K$ ,  $\text{Hg}(\text{CN})_4^{2-}$  will be formed!

# Solubility – An Equilibrium Position

The solubility of a salt is an equilibrium position

For a given temperature...

a single value for the solubility product constant ( $K_{sp}$ )

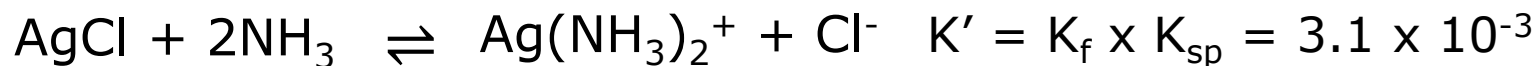
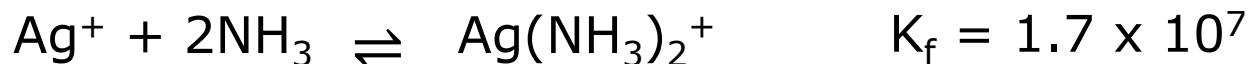
an infinite number of possible solubilities!

Solubility can be affected by:

1. the common ion effect
2. complex ion formation
3. changes in pH

# Complex Ions and Solubility

A number of insoluble salts can be dissolved upon formation of a complex ion...

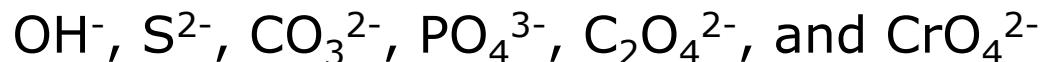


How much greater?  $3.1 \times 10^{-3} / 1.8 \times 10^{-10} = 17,000,000$  times!

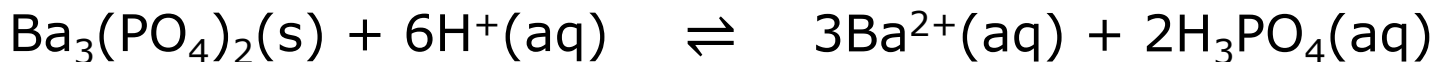
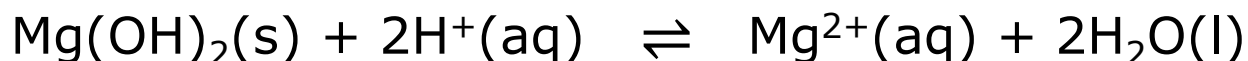
# pH and Solubility

The solubility of a salt containing basic anion increases with increasing acidity

Basic anions are c. bases of weak acids:

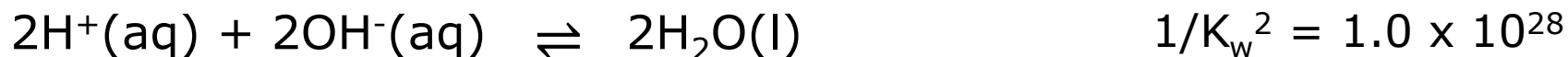
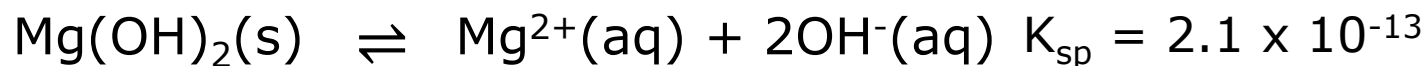


Basic anions react with hydrogen ions to form weak acid



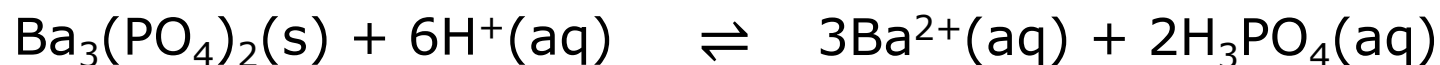
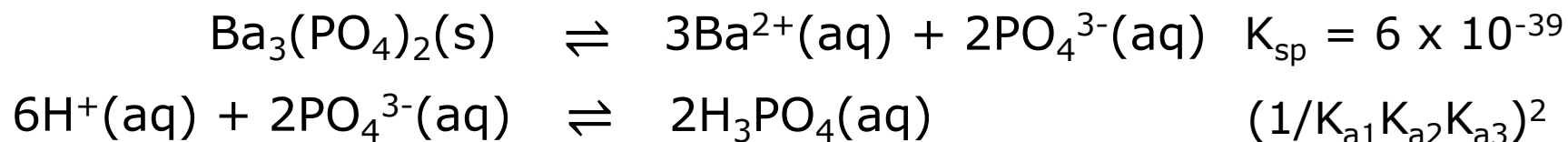
If K is large, salt will be soluble under acidic conditions!

How much more?



$$K'' = K_{\text{sp}}/K_{\text{w}}^2 = 2.1 \times 10^{15} \dots \text{ or } 1.0 \times 10^{28} \text{ times greater!}$$

Again, you say?



$$K'' = K_{\text{sp}}/(K_{\text{a}1}K_{\text{a}2}K_{\text{a}3})^2 = 6 \times 10^{-39}/[(7.5 \times 10^{-3})(6.2 \times 10^{-8})(4.2 \times 10^{-13})]^2$$

$$= 1.6 \times 10^5 \dots \text{ or } \sim 3 \times 10^{43} \text{ times greater!}$$