Chapter 8: Applications of Aqueous Equilibria

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Solutions of Acids or Bases Containing a Common Ion

- Have calculated pH and % dissociation of a weak acid HA
- Now we assume that both the acid and its salt are present (i.e. HF and NaF).
- The effect of the simultaneous presence of the salt is to lower the extent of dissociation of the acid.
- This is called the common ion effect.
- The common ion effect occurs with polyprotic acids and mono- and polyprotic bases as well.

EP 137: pH of a Weak Acid With and Without a Common Ion

Acetic acid (HAc) is a weak acid: $K_a = 1.8 \text{ x } 10^{-5}$. Calculate the pH and percent dissociation of acetic acid in a solution 0.10 M in acetic acid and 0.050 M in sodium acetate (NaAc). This is a sufficiently concentrated solution that the autoionization of water can be neglected.

The major species in solution are:

HAc, H^+, Ac^-, Na^+ and H_2O

The relevant equilibrium is

$HAc(aq) = H^+(aq) + Ac^-(aq)$

$$K_a = 1.8\times10^{-5} = \frac{[H^+][Ac^-]}{[HAc]}$$

$HAc(aq) = H^+(aq) + Ac^-(aq)$

Conc. (M)	HAc	$H^+(aq)$	$Ac^-(g)$
Init.	0.10	0	0.050
Change			
Equil.			

$HAc(aq) = H^+(aq) + Ac^-(aq)$

Conc. (M)	HAc	$H^+(aq)$	$Ac^-(g)$
Init.	0.10	0	0.050
Change	-x	+x	+x
Equil.			

$HAc(aq) = H^+(aq) + Ac^-(aq)$

Conc. (M)	HAc	$H^+(aq)$	$Ac^-(g)$
Init.	0.10	0	0.050
Change	-x	+x	+x
Equil.	0.10 - x	x	0.050 + x

$$K_a = 1.8\times10^{-5} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{Ac}^-\right]}{\left[\mathrm{HAc}\right]} = \frac{(x)(.050+x)}{0.10-x}$$

$$x^2 + 5.0\times10^{-2}x - 1.8\times10^{-6} = 0$$

Solving this quadratic and keeping the positive root:

$x = \left[\mathrm{H}^+\right] = 3.6\times10^{-5}$ M; pH = 4.44

no Ac^-, $\left[\mathrm{H}^+\right] = 1.3\times10^{-3}$ M; pH = 2.88

The percent dissociation is

$$\frac{[\mathrm{H}+]}{[\mathrm{HAc}]_0}\times100\% = \frac{3.6\times10^{-5}\ \mathrm{M}}{0.10\ \mathrm{M}}\times100\% = 0.036\%$$

no Ac^-, dissociation is 1.3%

$x = \left[\mathrm{H}^+\right] = 3.6\times10^{-5}$ M; pH = 4.44

no Ac^-, $\left[\mathrm{H}^+\right] = 1.3\times10^{-3}$ M ; pH = 2.88

The percent dissociation is 0.036%

no Ac^-, dissociation is 1.3%

The large difference clearly shows the presence of the Ac^- ions from the dissolved NaAc greatly inhibits the dissociation of HAc. The position of the acid dissociation equilibrium has been shifted to the left by the presence of Ac^- ions from NaAc. **Predicted by Le Chatelier principle.**

Buffered Solutions

- A buffered solution is one that resists changing pH when acid or bases is added.
- A buffered solution contains a weak acid **and its salt (conjugate base)** , i.e.HOac +Oac^-

or a weak base **and its salt (conjugate acid),** i.e. $\mathrm{NH_3}$ +$\mathrm{NH_4^+}$

- By choosing appropriate components buffering can be had at virtually any pH.
- The calculations for a buffer solution are similar to those for the common ion effect.

EP 138: pH of a Buffer Solution Before and After Addition of Strong Base

Hydrofluoric acid (HF) is a weak acid with $K_a = 6.8 \times 10^{-4}$. Calculate the pH and percent dissociation of HF in a solution containing 0.50 M HF and 0.45 M sodium fluoride (NaF) (a) before, and (b) after addition of 0.010 mol NaOH to 1.0 L of the buffer. (c) Calculate the change in pH if the same amount of base is added to 1.0 L of pure water. This is a sufficiently concentrated solution that the autoionization of water can be neglected.

The major species in solution are: HF, $\mathrm{H^+}$, $\mathrm{F^-}$, $\mathrm{Na^+}$ and $\mathrm{H_2O}$

The relevant equilibrium is

$\mathrm{HF(aq) = H^+(aq) + F^-(aq)}$

$$K_a = 6.8\times10^{-4} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{F}^-\right]}{[\mathrm{HF}]}$$

$\mathrm{HF(aq) = H^+(aq) + F^-(aq)}$

Conc. (M)	HF(*aq*)	$\mathrm{H^+}$(*aq*)	$\mathrm{F^-}$(*aq*)
Init.	0.50	0	0.45
Change			
Equil.			

$\mathrm{HF(aq) = H^+(aq) + F^-(aq)}$

Conc. (M)	HF(*aq*)	$\mathrm{H^+}$(*aq*)	$\mathrm{F^-}$(*aq*)
Init.	0.50	0	0.45
Change	-x	+x	+x
Equil.			

$HF(aq) = H^+(aq) + F^-(aq)$

Conc. (M)	HF(*aq*)	H^+(*aq*)	F^-(*aq*)
Init.	0.50	0	0.45
Change	-x	+x	+x
Equil.	0.50 - x	x	0.45 + x

$$K = 6.8\times10^{-4} = \frac{\left[H^+\right]\left[F^-\right]}{\left[HF\right]} = \frac{(x)(.45+x)}{0.50-x}$$

$$x^2 + 4.5\times10^{-1}x - 3.4\times10^{-4} = 0$$

solving this quadratic and keeping the positive root:

$$x = \left[H^+\right] = 7.5\times10^{-4}\ \text{M}; \qquad \text{pH} = 3.12$$

$$\%\ \text{dissociation} = 100\times\frac{7.5\times10^{-4}\ \text{M}}{0.50\text{M}} = 0.15\%$$

What happens after addition of 0.010 mol NaOH to 1.0 L of the buffer of 2(a)?

The major species in solution are: HF, F^-, Na^+, OH^- and H_2O

The reaction that occurs is:

$OH^-(aq) + HF(aq) = H_2O(aq) + F^-(aq)$

First assume the reaction goes to completion, then let the resultant species establish a new equilibrium according to:

$$K_a = 6.8\times10^{-4} = \frac{\left[H^+\right]\left[F^-\right]}{\left[HF\right]}$$

After 0.50 M HF reacts with 0.010 M NaOH we can construct the reaction table:

$HF(aq) = H^+(aq) + F^-(aq)$

Conc. (M)	HF(*aq*)	H^+(*aq*)	F^-(*aq*)
Init.	0.49	0	0.46
Change			
Equil.			

After 0.50 M HF reacts with 0.010 M NaOH we can construct the reaction table:

$HF(aq) = H^+(aq) + F^-(aq)$

Conc. (M)	HF(*aq*)	H^+(*aq*)	F^-(*aq*)
Init.	0.49	0	0.46
Change	-x	+x	+x
Equil.			

After 0.50 M HF reacts with 0.010 M NaOH we can construct the reaction table:

$HF(aq) = H^+(aq) + F^-(aq)$

Conc. (M)	HF(*aq*)	H^+(*aq*)	F^-(*aq*)
Init.	0.49	0	0.46
Change	-x	+x	+x
Equil.	0.49 - x	x	0.46 + x

$$K = 6.8\times10^{-4} = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} = \frac{(x)(.46+x)}{0.49-x}$$

$$x^2 + 4.6\times10^{-1}x - 3.33\times10^{-4} = 0$$

solving this quadratic and keeping the positive root:

$$x = [\mathrm{H}^+] = 7.2\times10^{-4}\ \mathrm{M}; \qquad \mathrm{pH} = 3.14$$

Change in pH is only 3.14 - 3.12 = 0.02

$$\%\ \text{dissociation} = 100\times\frac{7.2\times10^{-4}\ \mathrm{M}}{0.49\mathrm{M}} = 0.15\%$$

Compare a Buffer to an Unbuffered Solution

(c): Suppose that the same 0.010 mol NaOH is added to 1.0 L of water to give 0.010 M NaOH. In this case,

$[\mathrm{OH}^-]$ = 0.010 M and

$$[\mathrm{H}^+] = \frac{K_w}{[\mathrm{OH}^-]} = \frac{1.0\times10^{-14}}{1.0\times10^{-2}} = 1.0\times10^{-12}$$

$$\mathrm{pH} = 12.00$$

Thus the change in pH is

$$12.00 - 7.00 = +5.00$$

The increase is 5.00 pH units.

How Does a Buffer Work?

Start by considering what happens to a buffered solution when OH^- is added. The following reaction occurs:

$$\mathrm{OH}^-(aq) + \mathrm{HA}(aq) = \mathrm{A}^-(aq) + \mathrm{H_2O}(l)$$

Note that OH^- does not increase; instead A^- increases **from a nonzero value**.

The stability of pH under these conditions can be seen from the equilibrium expression:

$$K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]} \text{ or rearranging, } \quad [\mathrm{H}^+] = K_a\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

Clearly, the pH is determined by the ratio [HA]/[A-]

Henderson-Hasselbach Equation

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) = \mathrm{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

In using this equation, assume [base] =$[\text{base}]_0$ and [acid = $[\text{acid}]_0$

For a particular buffering solution (acid-conjugate base pair), all solutions that have the same ratio $[\mathrm{A}^-]/[\mathrm{HA}]$ have the same pH.

EP 139: Buffer Calculation Using the Henderson-Hasselbach Equation

A buffered solution is 0.35 M in $\mathrm{CH_3NH_2}$ (K_b = 4.38 x 10^{-4} and 0.55 M in $\mathrm{CH_3NH_3^+}$

a. Calculate the pH of this solution by solving the equilibrium problem.

b. Calculate the pH of this solution using the Henderson-Hasselbach equation.

c. Calculate the pH of the solution that results when 0.10 mol of gaseous HCl is added to 1.00 L of the buffered solution from part a.

$$\mathrm{CH_3NH_2}(aq) + \mathrm{H_2O} \rightleftarrows \mathrm{CH_3NH_3^+}(aq) + \mathrm{OH^-}(aq)$$

Conc. (M)	$\mathrm{CH_3NH_2}$	$\mathrm{CH_3NH_3^+}$	$\mathrm{OH^-}$
Init.	0.35	0	0.55
Change			
Equil.			

$$CH_3NH_2(aq) + H_2O \rightleftarrows CH_3NH_3^+(aq) + OH^-(aq)$$

Conc. (M)	CH_3NH_2	$CH_3NH_3^+$	OH^-
Init.	0.35	0	0.55
Change	-x	+x	+x
Equil.			

$$CH_3NH_2(aq) + H_2O \rightleftarrows CH_3NH_3^+(aq) + OH^-(aq)$$

Conc. (M)	CH_3NH_2	$CH_3NH_3^+$	OH^-
Init.	0.35	0	0.55
Change	-x	+x	+x
Equil.	0.35 - x	x	0.55 + x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.55+x)(x)}{(0.35-x)} \approx \frac{(0.55)(x)}{(0.35)}$$

$x = 2.79\times10^{-4}$ exact: 2.78×10^{-4}

The approximations is valid, so

$[H^+] = 1.0 \times 10^{-14}/2.79 \times 10^{-4} = 3.59 \times 10^{-11}$

$pH = -\log(3.59 \times 10^{-11}) = 10.44$

b. Calculate the pH of this solution using the Henderson- Hasselbach equation

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log\frac{K_w}{K_b} + \log\left(\frac{[CH_3NH_2]}{[CH_3NH_3^+]}\right)$$

$$pH = -\log\left(\frac{1.00\times10^{-14}}{4.38\times10^{-4}}\right) + \log\left(\frac{0.35}{0.55}\right) = 10.44$$

Justification for using Henderson- Hasselbach equation

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{[CH_3NH_3^+]K_w}{[CH_3NH_2][H^+]}$$

$$[H^+] = \frac{[CH_3NH_3^+]K_w}{[CH_3NH_2]K_b}$$

$$-\log[H^+] = -\log\frac{K_w}{K_b} - \log\frac{[CH_3NH_3^+]}{[CH_3NH_2]}$$

$$pH = pK_a + \log\frac{[CH_3NH_2]}{[CH_3NH_3^+]} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

c. Calculate the pH of the solution that results when 0.10 mol of gaseous HCl is added to 1.00 L of the buffered solution from part a.

assume that the reaction goes essentially to completion. So for [acid] 0.55M → 0.65 M; for [base]= 0.35M → 0.25M

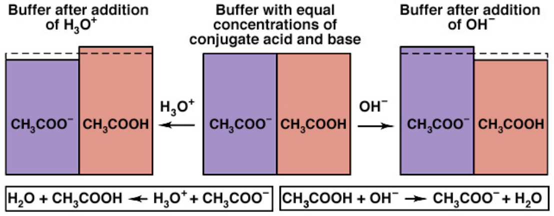
$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = -\log\frac{K_w}{K_b} + \log\left(\frac{[CH_3NH_2]}{[CH_3NH_3^+]}\right)$$

$$pH = -\log\left(\frac{1.00\times10^{-14}}{4.4\times10^{-4}}\right) + \log\left(\frac{0.25}{0.65}\right) = 10.23$$

The pH has decreased only 0.21 units with this large addition of H^+

How a Buffer Works

In each case the pH stays NEAR the pK_a



[base]/[acid] < 1 — $pH < pK_a$

[base]/[acid] = 1 — $pH = pK_a$

[base]/[acid] > 1 — $pH > pK_a$

pH and Capacity of Buffered Solutions

The pH of a buffered solution is determined by the ratio$[A^-]/[HA]$. The buffer should be prepared by selecting the acid/conjugate base pair so the pK_a is near the desired pH.

The capacity of a buffered solution is the ability of the solution to resist pH change due to adding H^+ or OH^-. It is determined by the magnitudes of $[HA]$ and $[A^-]$.

Buffered solutions contain relatively large concentrations of a weak acid HA and the conjugate base A^- or a weak base B and the conjugate acid BH^+.

When H^+ is added to a buffered solution, it reacts essentially to completion with the base present:

$$H^+ + A^- \longrightarrow HA$$

or $$H^+ + B \longrightarrow BH^+$$

When OH^- is added to a buffered solution, it reacts essentially to completion with the acid present.

$$OH^- + HA \longrightarrow A^- + H_2O$$

or $$OH^- + BH^+ \longrightarrow B + H_2O$$

The pH of the buffered solution is determined by the ratio of the concentrations of the weak base and weak acid. As long as this ratio remains virtually constant, the pH will remain virtually constant.

This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with the amounts of H^+ or OH^- added.

TITRATION

An experimental method to determine the concentration of an acid in a sample using a base as the titrant,

Or conversely, to determine the concentration of a base in a sample using an acid as the titrant.

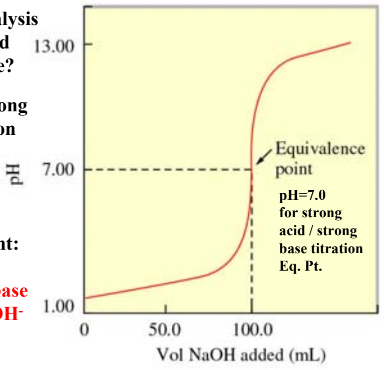
The method is QUANTITATIVE. We determine when

mol acid (H+) = mol base (OH- or equivalent)

using pH meter or a visual indicator.

Quantitative Analysis
How concentrated is the acid sample?

Titration of a strong acid (HCl) solution by a strong base (NaOH).



Equivalence point:

mol acid = mol base
mol H^+ = mol OH^-

Quantify!

Why does pH change so rapidly near equivalence point?

Titrate 50.0mL 0.200M HNO_3 (10.0 mmol H^+) with 0.100M NaOH

1) Add 10.0 mL NaOH (1.00 mmol)

1.0 mmol OH^- + 10.0 mmol H^+ = 9.0 mmol H^+

$[H^+]$ = 9.0 mmol/(50.0mL + 10.0 mL)=0.15M **pH = 0.82**

2) Add 2 mL more NaOH

1.2 mmol OH^- + 10.0 mmol H^+ = 8.8 mmol H^+

$[H^+]$ = 8.8 mmol/(50.0mL + 12.0 mL)= 0.14M **pH = 0.85**

Change in pH = 0.03

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3) After 99.0 mL NaOH added (9.90 mmol)

9.9 mmol OH^- + 10.0 mmol H^+ = 0.1 mmol H^+

$[H^+]$ = 0.1 mmol/(149.0 mL) = 7 x 10^{-4}M

pH = 3.2

2) Add 2 mL more NaOH

10.1 mmol OH^- + 10.0 mmol H^+ = 0.1 mmol OH^-

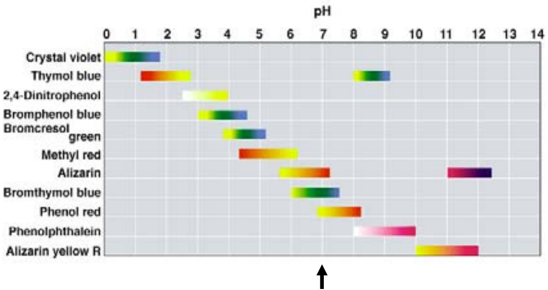
$[OH^-]$ = 0.1 mmol/(151 mL) = 7 x 10^{-4}M

pOH = 3.2

pH = 14 - 3.2 = 10.8

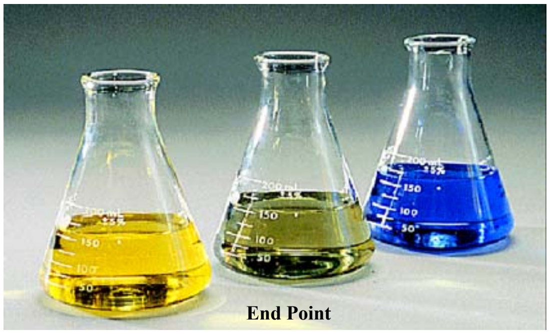
Change in pH = +7.6

Colors and Approximate pH Range of Some Common Acid-Base Indicators



Strong acid / strong base

The Color Change of the Indicator Bromthymol Blue, BTB



pH < 7 pH = 7 pH > 7

$$HIn \rightleftarrows H^+ + In-$$

Red Blue

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad \frac{[In^-]}{[HIn]} = \frac{K_a}{[H^+]}$$

$$\text{Solution red if } \frac{[In^-]}{[HIn]} \approx 0.1 \text{ and blue if } \frac{[In^-]}{[HIn]} \approx 10$$

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} = pK_a - 1$$

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} = pK_a + 1$$

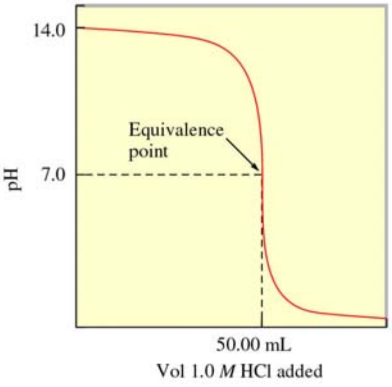
Range over which color change occurs ~ 2 pH units.

At equivalence point, $pH = pK_a$

How about a strong base for a sample?

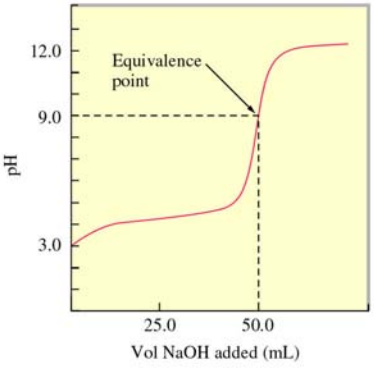
Titration of strong base by a strong acid.

Eq. Pt. is still at pH = 7.0

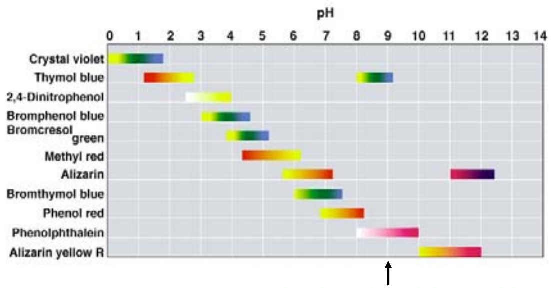


Titration of acetic acid (weak acid) sample using NaOH as the titrant.

Form H_2O and NaAc
pH > 7

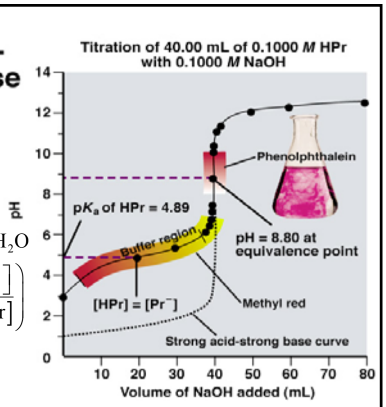


Colors and Approximate pH Range of Some Common Acid-Base Indicators



Titration of weak base with Eq. Pt. at a pH = 9

Weak Acid-Strong Base Titration Curve



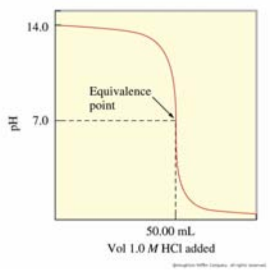
$$HPr + OH^- \rightleftarrows Pr^- + H_2O$$

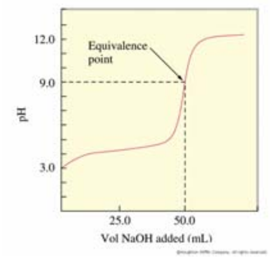
$$pH = pK_a + \log\left(\frac{[Pr^-]}{[HPr]}\right)$$

At halfway point,

$$[Pr^-] = [HPr]$$

$$pH = pK_a$$



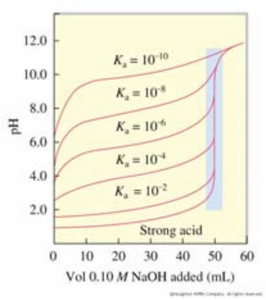


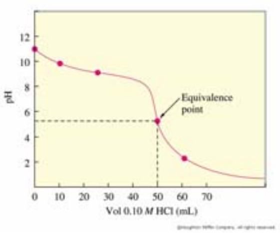
NaOH(aq) + HCl(aq)

Strong acid titrating strong base

NaOH(aq) + HAc(aq)

Strong base titrating weak acid

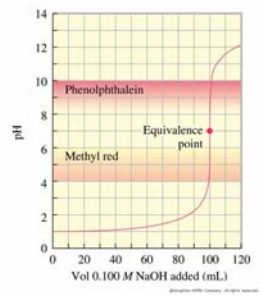


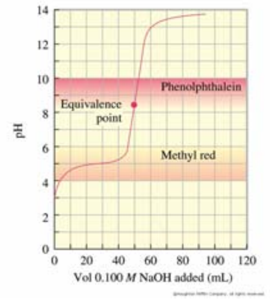


Note shift in pH of equivalence point with K_a

NH_3(aq) + HCl(aq)

Strong acid titrating weak base

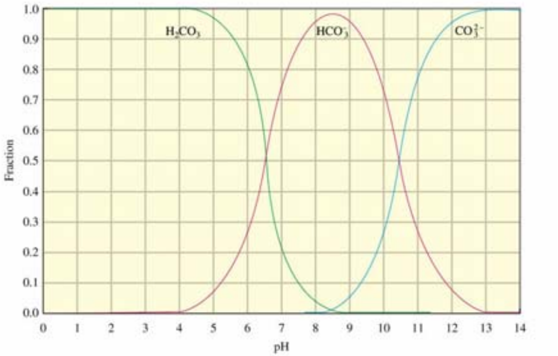




Both indicators suitable

Methyl red unsuitable

Dominant species for titration of polyprotic acid determined by pH



Major species at first equivalence point:

Na^+, $H_2PO_4^-$, and H_2O

As more NaOH is added, dominant reaction is

$H_2PO_4^-(aq) + OH^-(aq) = HPO_4^{2-}(aq) + H_2O(l)$

Major species at second equivalence point:

Na^+, HPO_4^{2-}, and H_2O

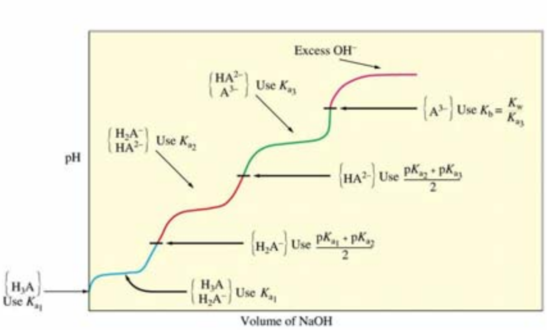
As more NaOH is added, dominant reaction is

$HPO_4^{2-}(aq) + OH^-(aq) = PO_4^{3-}(aq) + H_2O(l)$

Major species at third equivalence point:

Na^+, PO_4^{3-}, and H_2O

Titration of a polyprotic acid leads to multiple equivalence points



Calculating the pH at first equivalence point

At first equivalence point, H_3PO_4 (aq) converted to $H_2PO_4^-$(aq) and a new equilibrium is established because $H_2PO_4^-$(aq) is both an acid and a base

$H_2PO_4^-(aq) = HPO_4^{2-}(aq) + H^+(aq)$ K_{a2}

$H_2PO_4^-(aq) + H^+(aq) = H_3PO_4\,(aq)$ $1/K_{a1}$

Add two equations

$2H_2PO_4^-(aq) + H^+(aq) = H_3PO_4\,(aq) + HPO_4^{2-}(aq)$ K_{a2}/K_{a1}

$$2H_2PO_4^-(aq) \rightleftarrows H_3PO_4(aq) + HPO_4^{2-}(aq)$$

If this is only important reaction involving 3 species

$$[H_3PO_4] = [H_2PO_4^-]$$

$$\frac{K_{a2}}{K_{a1}} = \frac{[H_3PO_4][HPO_4^{2-}]}{[H_2PO_4^-]^2} = \frac{[H_3PO_4]^2}{[H_2PO_4^-]^2}$$

Can get same ratio from first ionization constant

$$\frac{[H^+]}{K_{a1}} = \frac{[H_3PO_4]}{[H_2PO_4^-]} \text{ therefore}$$

$$\frac{K_{a2}}{K_{a1}} = \frac{[H_3PO_4]^2}{[H_2PO_4^-]^2} = \left(\frac{[H^+]}{K_{a1}}\right)^2 \text{ solving for } [H^+]$$

$$\text{At equiv point } [H^+] = \sqrt{K_{a1}K_{a2}}; \quad pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Precipitation

- **Precipitation** - The formation of a solid from solution. The reverse of **dissolution**.
- Importance - (a) Selective precipitation is an important industrial purification process, especially when crystals are formed. (b) Scales that form on boilers and teeth are to be prevented, as are kidney stones. (c) Precipitation forms minerals - dissolution removes them.

Saturation

- **Saturated Solution** - dissolution - precipitation equilibrium exists between a solid and its dissolved form. The equilibrium is dynamic and the rate of dissolution is equal to the rate of precipitation.
- **Unsaturated Solution** - the concentration of dissolved solid is not sufficient to cause precipitation.
- A quantitative description of this type of heterogeneous equilibrium is subject to the law of mass action, and the concentration of various species at equilibrium can be calculated.

Solubility

Solubility - The greatest amount of a substance that will dissolve in equilibrium in a specified volume of solvent at a particular temperature.

Example - The solubility of silver chloride in water at 25 ^{o}C is .0018 g/L or a saturated solution is 1.3 x 10^{-5} M in AgCl.

The solubility of most salts increases with temperature.

Classification of Ionic Materials by Solubility

Soluble Ionic Materials - have solubilities in excess of 10 g L^{-1}.

Insoluble Ionic Materials - have solubilities less than 0.1 g L^{-1}.

Slightly Soluble Materials - have solubilities between 0.1 and 10 g L^{-1}.

The Nature of Ionic Equilibria

Most salts dissociate into ions when they dissolve. Equilibrium exists between the solid salt and its aqueous ions, and not between the solid salt and dissolved molecules of the salt.

$$PbSO_4(s) = Pb^{2+}(aq) + SO_4^{2-}(aq)$$

This equilibrium system may be described by the mass-action expression:

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$ **solubility product**

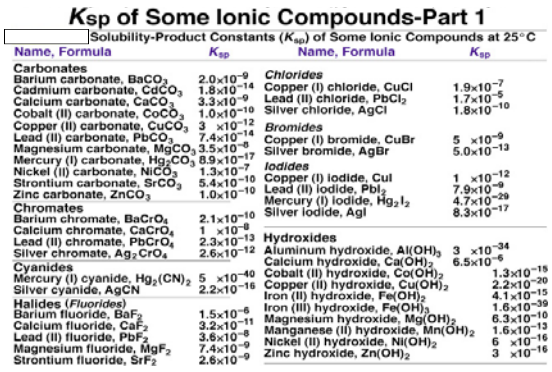
Note that the pure solid does not enter into the solubility product.

The solubility product constant, K_{sp}, can be ***compared*** to the ion product constant, Q_{sp}, to understand the characteristics of a solution with respect to forming a precipitate.

$Q_{sp} = K_{sp}$: These are the conditions when the solution is saturated with the ions and a precipitate is just beginning to form.

$Q_{sp} > K_{sp}$: A precipitate will form, depleting the solution until $Q_{sp} = K_{sp}$

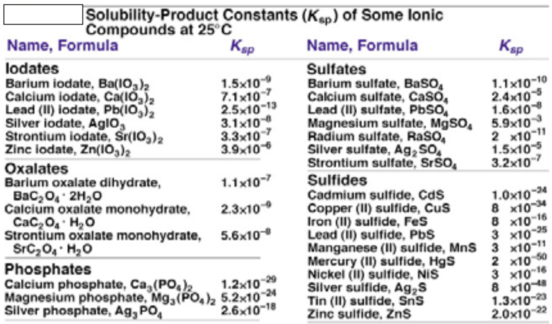
$Q_{sp} < K_{sp}$: Solution is unsaturated with the ions, and no precipitate will form.



Ksp of Some Ionic Compounds-Part 1

Solubility-Product Constants (K_{sp}) of Some Ionic Compounds at 25°C

Name, Formula	K_{sp}
Carbonates	
Barium carbonate, $BaCO_3$	2.0×10^{-9}
Cadmium carbonate, $CdCO_3$	1.8×10^{-14}
Calcium carbonate, $CaCO_3$	3.3×10^{-9}
Cobalt (II) carbonate, $CoCO_3$	1.0×10^{-10}
Copper (II) carbonate, $CuCO_3$	$3\ \times10^{-12}$
Lead (II) carbonate, $PbCO_3$	7.4×10^{-14}
Magnesium carbonate, $MgCO_3$	3.5×10^{-8}
Mercury (I) carbonate, Hg_2CO_3	8.9×10^{-17}
Nickel (II) carbonate, $NiCO_3$	1.3×10^{-7}
Strontium carbonate, $SrCO_3$	5.4×10^{-10}
Zinc carbonate, $ZnCO_3$	1.0×10^{-10}
Chromates	
Barium chromate, $BaCrO_4$	2.1×10^{-10}
Calcium chromate, $CaCrO_4$	$1\ \times10^{-8}$
Lead (II) chromate, $PbCrO_4$	2.3×10^{-13}
Silver chromate, Ag_2CrO_4	2.6×10^{-12}
Cyanides	
Mercury (I) cyanide, $Hg_2(CN)_2$	$5\ \times10^{-40}$
Silver cyanide, AgCN	2.2×10^{-16}
Halides (*Fluorides*)	
Barium fluoride, BaF_2	1.5×10^{-6}
Calcium fluoride, CaF_2	3.2×10^{-11}
Lead (II) fluoride, PbF_2	3.6×10^{-8}
Magnesium fluoride, MgF_2	7.4×10^{-9}
Strontium fluoride, SrF_2	2.6×10^{-9}
Chlorides	
Copper (I) chloride, CuCl	1.9×10^{-7}
Lead (II) chloride, $PbCl_2$	1.7×10^{-5}
Silver chloride, AgCl	1.8×10^{-10}
Bromides	
Copper (I) bromide, CuBr	$5\ \times10^{-9}$
Silver bromide, AgBr	5.0×10^{-13}
Iodides	
Copper (I) iodide, CuI	$1\ \times10^{-12}$
Lead (II) iodide, PbI_2	7.9×10^{-9}
Mercury (I) iodide, Hg_2I_2	4.7×10^{-29}
Silver iodide, AgI	8.3×10^{-17}
Hydroxides	
Aluminum hydroxide, $Al(OH)_3$	$3\ \times10^{-34}$
Calcium hydroxide, $Ca(OH)_2$	6.5×10^{-6}
Cobalt (II) hydroxide, $Co(OH)_2$	1.3×10^{-15}
Copper (II) hydroxide, $Cu(OH)_2$	2.2×10^{-20}
Iron (II) hydroxide, $Fe(OH)_2$	4.1×10^{-15}
Iron (III) hydroxide, $Fe(OH)_3$	1.6×10^{-39}
Magnesium hydroxide, $Mg(OH)_2$	6.3×10^{-10}
Manganese (II) hydroxide, $Mn(OH)_2$	1.6×10^{-13}
Nickel (II) hydroxide, $Ni(OH)_2$	$6\ \times10^{-16}$
Zinc hydroxide, $Zn(OH)_2$	$3\ \times10^{-16}$



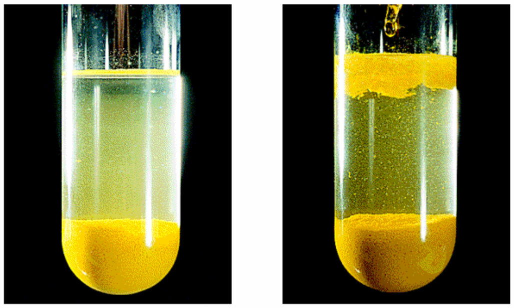
K_{sp} of Some Ionic Compounds-Part 2

Solubility-Product Constants (K_{sp}) of Some Ionic Compounds at 25°C

Name, Formula	K_{sp}
Iodates	
Barium iodate, $Ba(IO_3)_2$	1.5×10^{-9}
Calcium iodate, $Ca(IO_3)_2$	7.1×10^{-7}
Lead (II) iodate, $Pb(IO_3)_2$	2.5×10^{-13}
Silver iodate, $AgIO_3$	3.1×10^{-8}
Strontium iodate, $Sr(IO_3)_2$	3.3×10^{-7}
Zinc iodate, $Zn(IO_3)_2$	3.9×10^{-6}
Oxalates	
Barium oxalate dihydrate, $BaC_2O_4\cdot 2H_2O$	1.1×10^{-7}
Calcium oxalate monohydrate, $CaC_2O_4\cdot H_2O$	2.3×10^{-9}
Strontium oxalate monohydrate, $SrC_2O_4\cdot H_2O$	5.6×10^{-8}
Phosphates	
Calcium phosphate, $Ca_3(PO_4)_2$	1.2×10^{-29}
Magnesium phosphate, $Mg_3(PO_4)_2$	5.2×10^{-24}
Silver phosphate, Ag_3PO_4	2.6×10^{-18}

Name, Formula	K_{sp}
Sulfates	
Barium sulfate, $BaSO_4$	1.1×10^{-10}
Calcium sulfate, $CaSO_4$	2.4×10^{-5}
Lead (II) sulfate, $PbSO_4$	1.6×10^{-8}
Magnesium sulfate, $MgSO_4$	5.9×10^{-3}
Radium sulfate, $RaSO_4$	2×10^{-11}
Silver sulfate, Ag_2SO_4	1.5×10^{-5}
Strontium sulfate, $SrSO_4$	3.2×10^{-7}
Sulfides	
Cadmium sulfide, CdS	1.0×10^{-24}
Copper (II) sulfide, CuS	8×10^{-34}
Iron (II) sulfide, FeS	8×10^{-16}
Lead (II) sulfide, PbS	3×10^{-25}
Manganese (II) sulfide, MnS	3×10^{-11}
Mercury (II) sulfide, HgS	2×10^{-50}
Nickel (II) sulfide, NiS	3×10^{-16}
Silver sulfide, Ag_2S	8×10^{-48}
Tin (II) sulfide, SnS	1.3×10^{-23}
Zinc sulfide, ZnS	2.0×10^{-22}

The Effect of a Common Ion on Solubility



$$\longleftarrow$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$$

Adding more iodide increases the amount of pcpt and decreases the [Pb^{2+}]

Solubility and the K_{sp}

- One may provide solubility information as the solubility, S or as the solubility product, K_{sp}.
- These two quantities are obviously related to each other.

EP 140: Given Solubility, Calculate K_{sp}

Problem: What is the K_{sp} of $Pb(IO_3)_2$ if 0.00896 g dissolves in 400. mL of water at 25 °C?

Strategy:

1) Write the balanced reaction

2) Calculate the molar solubility, S.

3) Calculate the equilibrium constant from $K_{sp} = S(2S)^2 = 4S^3$

$Pb(IO_3)_2 = Pb^{2+}(aq) + 2IO_3^-(aq)$

S 2S

S = (.00896 g / 556.994 g/mol)/0.400 L = 4.02 x 10^{-5} M

$K_{sp} = S(2S)^2 = 4S^3 = 4(4.02 \times 10^{-5})^3$ = **2.60×10^{-13}**

EP 141: Given K_{sp}, Calculate Solubility

Given $K_{sp} = 5.6 \times 10^{-6}$ at 20°C for $(NH_4)_2(PtCl_6)$ calculate the solubility in g/L.

Strategy:

1)Derive an expression for the molar solubility, S, using the known value of K_{sp}.

2) Calculate S from this expression

For the above compound, we have $K_{sp} = (2S)^2S = 4S^3$. Solving for S, $S = (K_{sp}/4)^{1/3}$.

$S = (5.6 \times 10^{-6} / 4)^{1/3}$ = **0.011 mol L^{-1}**

(0.011 mol/L x 443.88 g mol^{-1}) = **5.0 g L^{-1}**

EP 142: The Common Ion Effect

What is the solubility of $Ca(OH)_2$ in a) pure water and b) 0.10 M $Ca(NO_3)_2$?

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

a) Set up a reaction table, with S = [Ca^{2+}]from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	2 $OH^-(aq)$
Initial	-	0	0
Change	-		
Equil.	-		

What is the solubility of $Ca(OH)_2$ in 0.10 M $Ca(NO_3)_2$?

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

Set up a reaction table, with S = $[Ca^{2+}]$from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	$2\ OH^-(aq)$
Initial	-	0	0
Change	-	+S	+2S
Equil.	-		

What is the solubility of $Ca(OH)_2$ in 0.10 M $Ca(NO_3)_2$?

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

Set up a reaction table, with S = $[Ca^{2+}]$from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	$2\ OH^-(aq)$
Initial	-	0	0
Change	-	+S	+2S
Equil.	-	S	2S

$$K_{sp} = \left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^-\right]^2 = 6.5\times10^{-6} = (S)(2S)^2 = 4S^3$$

$$S = \frac{\sqrt[3]{6.5\times10^{-6}}}{4} = 4.7\times10^{-2}\ \text{moles/L}$$

---

b) Solubility in 0.10 M $Ca(NO_3)_2$

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

Set up a reaction table, with S = $[Ca^{2+}]$from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	$2\ OH^-(aq)$
Initial	-	0.10	0
Change	-		
Equil.	-		

---

b) Solubility in 0.10 M $Ca(NO_3)_2$

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

Set up a reaction table, with S = $[Ca^{2+}]$from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	$2\ OH^-(aq)$
Initial	-	0.10	0
Change	-	+S	+2S
Equil.	-		

---

b) Solubility in 0.10 M $Ca(NO_3)_2$

$Ca(OH)_2(s) = Ca^{2+}(aq) + 2\ OH^-(aq)$; $K_{sp} = 6.5 \times 10^{-6}$

Set up a reaction table, with S = $[Ca^{2+}]$from $Ca(OH)_2$

Conc. M	$Ca(OH)_2(s)$	$Ca^{2+}(aq)$	$2\ OH^-(aq)$
Initial	-	0.10	0
Change	-	+S	+2S
Equil.	-	0.10+S	2S

$$K_{sp} = \left[Ca^{2+}\right]\left[OH^-\right]^2 = 6.5\times10^{-6} = (0.10+S)(2S)^2$$

Make the assumption that K_{sp} is small, so $S << 0.10$ M

$$K_{sp} \approx 0.10(2S)^2$$

Therefore:

$$4S^2 = \frac{6.5\times10^{-6}}{0.10}; S = \sqrt{\frac{6.5\times10^{-6}}{0.40}} = 4.0\times10^{-3} \text{ moles/L}$$

In pure water, $S = 4.7\times10^{-2}$ moles/L

Common ion has reduced solubility!

EP 143: Predicting the Effect of pH on Solubility

Write balanced equations to explain whether addition of H_3O^+ from a strong acid affects the solubility of (a) lead(II) bromide, (b) copper(II) hydroxide, and (c) iron(II) sulfide.

Strategy: Write the balanced dissolution equation and note the anion: anions of weak acids react with H_3O^+ and shift the equilibrium position toward more dissolution. Anions of strong acids do not react, so added H_3O^+ has no effect.

(a) $PbBr_2(s) = Pb^{2+}(aq) + 2\ Br^-(aq)$

No effect. Since Br^- is the anion of HBr a strong acid, it is a very weak base and H_3O^+ does not react with it.

(b) $Cu(OH)_2(s) = Cu^{2+}(aq) + 2\ OH^-(aq)$

Increases solubility. OH^- is the anion of H_2O, a very weak acid, so it reacts with the added H_3O^+:

$OH^-(aq) + H_3O^+(aq) = 2\ H_2O(l)$

(c) $FeS(s) = Fe^{2+}(aq) + S^{2-}(aq)$

$S^{2-}(aq) + H_2O(l) = HS^-(aq) + OH^-(aq)$

$FeS(s) + H_2O(l) = Fe^{2+}(aq) + HS^-(aq) + OH^-(aq)$

Increases solubility. The S^{2-} ion reacts immediately with water to form HS^-. The added H_3O^+ reacts with both weak acid anions, HS^- and OH^-:

$HS^-(aq) + H_3O^+(aq) = H_2S(aq) + H_2O(l)$

$OH^-(aq) + H_3O^+(aq) = 2\ H_2O(l)$

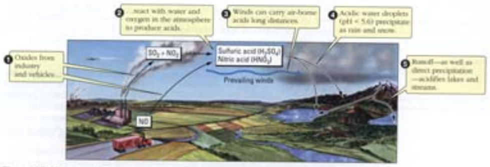


Figure 17.10 How acid deposition occurs.

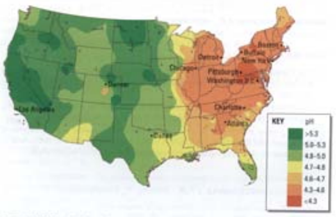


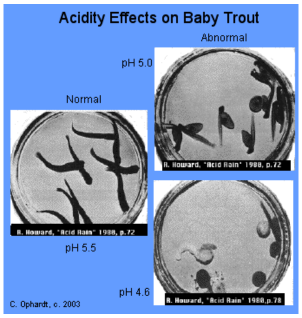
Figure 17.11 pH of precipitation within the United States.

Acid rain

$CaCO_3(s) + H_2SO_4(aq) = CaSO_4(s) + H_2CO_3(aq)$

$H_2CO_3(aq) = CO_2(g) + H_2O(l)$

Aquatic plants and animals have a limited range if pH in which they can live.

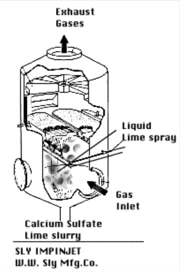


Alkaline soils in the midwest, great plains and west can neutralize acid rain much better than soils in the northeast US

Acid rain in the northeast and Canada threat to aquatic life and to forests

Acid rain solutions

Diagram of a Scrubber



C. Ophardt, c. 2003

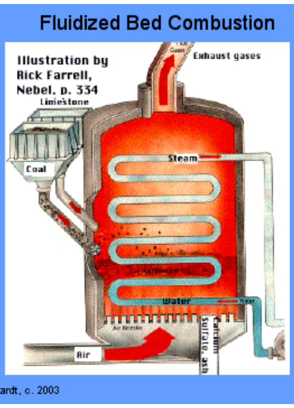
Sludge from Scrubbers

mixture of water, lime, and calcium sulfate

C. Ophardt, c. 2003

Retrofitting scrubbers increases cost of electricity ~15%

Fluidized Bed Combustion



C. Ophardt, c. 2003

In fluidized bed combustion, coal and limestone are combined in firebox. SO_2 reacts with limestone to form $CaSO_4$.

EP 144: Predicting Whether a Precipitate Will Form

Question: Does a precipitate form when 0.100 L of 0.30 M $Ca(NO_3)_2$ is mixed with 0.200 L of 0.06 M NaF?

Strategy:

(1) decide whether any of the ions present will combine to form a slightly soluble salt.

(2) Look up the K_{sp} for the substance. From the initial concentrations after mixing, calculate Q_{sp} and compare it to K_{sp}.

$$\left[Ca^{2+}\right]_{init} = \frac{\text{moles of } Ca^{2+} \text{ added}}{\text{total volume}} = \frac{0.30 \text{ M } Ca^{2+} \times 0.100 \text{ L}}{0.100 \text{ L} + 0.200 \text{ L}} =$$

$0.10 \text{ M } Ca^{2+}$

$$\left[F^-\right]_{init} = \frac{\text{moles of } F^- \text{ added}}{\text{total volume}} = \frac{0.060 \text{ M } F^- \times 0.200 \text{ L}}{0.100 \text{ L} + 0.200 \text{ L}} =$$

$0.040 \text{ M } F^-$

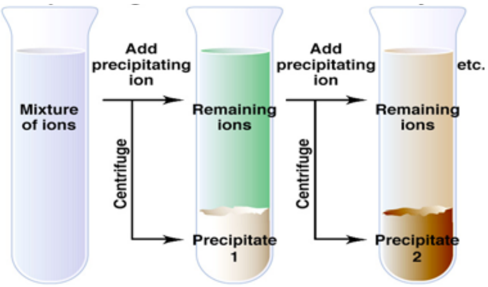
Substituting into the ion product expression and comparing Q_{sp} with K_{sp}:

$$Q_{sp} = \left[Ca^{2+}\right]_{init}\left[F^-\right]_{init}^2 = (0.10)(0.040)^2 = 1.6\times10^{-4}$$

$K_{sp} = 3.2\text{x}10^{-11}$

Since $Q_{sp} > K_{sp}$, CaF_2 will precipitate until $Q_{sp} = 3.2\text{x}10^{-11}$

The General Procedure for Separating Ions in Qualitative Analysis



Sequential precipitation based on value of K_{sp}

Add I^-(aq)

K_{sp} CuI = 5.3 x 10^{-12}

Add more I^-(aq)

K_{sp} PbI_2 = 1.4 x 10^{-8}

EP 145: Separating Ions by Selective Precipitation

Problem: A solution consists of 0.20 M $MgCl_2$ and 0.10 M $CuCl_2$. Calculate the $[OH^-]$ that would precipitate one of the metal ions as a hydroxide, while leaving the other in solution. Calculate the concentration in solution of the metal ion that is precipitated. K_{sp} of $Mg(OH)_2 = 6.3 \times 10^{-10}$; K_{sp} of $Cu(OH)_2 = 2.2 \times 10^{-20}$

Strategy:

1) By comparing the K_{sp} values, $Mg(OH)_2$ is about 10^{10} times more soluble than $Cu(OH)_2$.
2) Thus $Cu(OH)_2$ precipitates first.
3) We solve for the the $[OH^-]$ that will just give a saturated solution of $Mg(OH)_2$
4) Calculate Cu^{2+} from known $[OH^-]$ and K_{sp}

First write the equilibria and ion products

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

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

Calculate the $[OH^-]$ that will give a saturated $Mg(OH)_2$ solution:

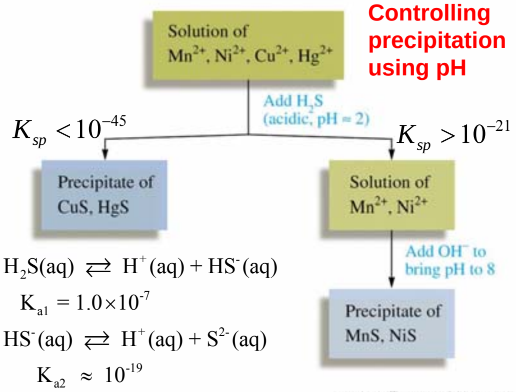
$$\left[OH^-\right] = \sqrt{\frac{K_{sp}}{\left[Mg^{2+}\right]}} = \sqrt{\frac{6.3\times10^{-10}}{0.20}} = 5.6\times10^{-5}\,M$$

This is the maximum $[OH^-]$ that will not precipitate Mg^{2+} ion.

Calculating the $[Cu^{2+}]$ remaining in the solution with this $[OH^-]$:

$$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{2.2\times10^{-20}}{\left(5.6\times10^{-5}\right)^2} = 7.0\times10^{-12}\ \text{M}$$

Controlling precipitation using pH



$H_2S(aq) \rightleftarrows H^+(aq) + HS^-(aq)$

$K_{a1} = 1.0\times10^{-7}$

$HS^-(aq) \rightleftarrows H^+(aq) + S^{2-}(aq)$

$K_{a2} \approx 10^{-19}$

More $S^{2-}(aq)$ in basic than acidic solutions

Separation into Ion Groups

Ion Group 1: Insoluble chlorides
Ag^+, Hg_2^{2+}, Pb^{2+}

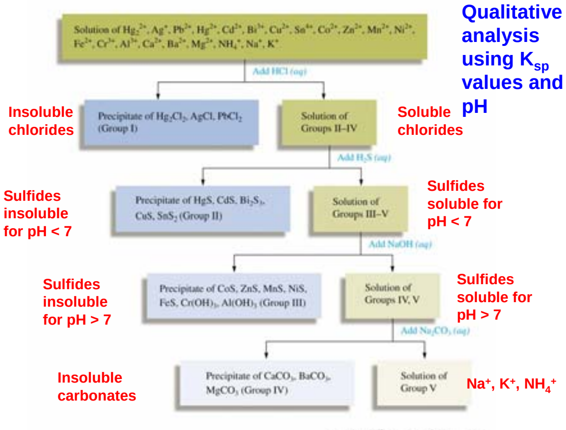
Ion Group 2: Acid-insoluble sulfides
Cu^{2+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}, Sn^{2+}, Sn^{4+}, Pb^{2+}

Ion Group 3: Base-insoluble sulfides and hydroxides
Zn^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+} as sulfides,
and Al^{3+}, Cr^{3+} as hydroxides

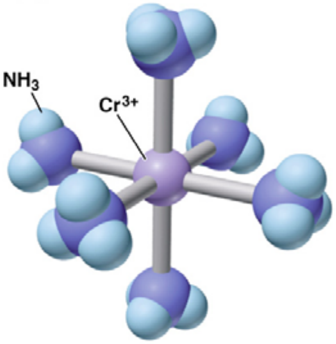
Ion Group 4: Insoluble phosphates
Mg^{2+}, Ca^{2+}, Ba^{2+}

Ion Group 5: Alkali metal and ammonium ions
Na^+, K^+, NH_4^+

Qualitative analysis using K_{sp} values and pH



$Cr(NH_3)_6^{3+}$, a Typical Complex Ion



Complex Ions: Charged species consisting of a metal ion surrounded by ligands

Equilibrium described by formation constant, K_f

$Ag^+(aq) + NH_3(aq) = Ag(NH_3)^+ (aq)$

$K_1 = 2.1 \times 10^3$

$Ag(NH_3)^+ (aq) + NH_3(aq) = Ag(NH_3)_2^+ (aq)$

$K_2 = 8.2 \times 10^3$

Formation Constants (K_f) of Some Complex Ions at 25°C

Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Ag(NH_3)_2^+$	1.7×10^7
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}
AlF_6^{3-}	4×10^{19}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
CdI_4^{2-}	1×10^6
$Co(OH)_4^{2-}$	5×10^9
$Cr(OH)_4^-$	8.0×10^{29}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Fe(CN)_6^{4-}$	3×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}

EP 146: Calculating the Concentrations of Complex Ions

How many moles $Zn(NH_3)_4^{2+}$ are made by mixing 50.0 L of 0.00200 M $Zn(H_2O)_4^{2+}$ and 25.0 L of 0.150 M NH_3? $K_f = 7.8 \times 10^8$ for $Zn(NH_3)_4^{2+}$. What is the concentration of $Zn(H_2O)_4^{2+}$ left in solution?

Strategy:

(1)Write the equation for formation reaction and the K_f expression.

(2)Set up a reaction table.

(3) Because K_f so large, assume that reaction goes nearly to completion. Then establish equilibrium.

The formation reaction:

$Zn(H_2O)_4^{2+}(aq) + 4\ NH_3(aq) = Zn(NH_3)_4^{2+}(aq) + 4\ H_20(l)$

The formation constant:

$$K_f = \frac{\left[Zn\left(NH_3\right)_4^{2+}\right]}{\left[Zn\left(H_2O\right)_4^{2+}\right]\left[NH_3\right]^4} = 7.8 \times 10^8$$

The initial concentrations:

$$\left[Zn\left(H_2O\right)_4^{2+}\right]_0 = \frac{50.0L \times 0.00200M}{50.0L + 25.0L} = 1.25 \times 10^{-3} M$$

$$\left[NH_3\right]_0 = \frac{25.0L \times 0.150M}{50.0L + 25.0L} = 5.00 \times 10^{-2} M$$

The reaction table:

Assume that all the $Zn(H_2O)_4^{2+}$ is converted to $Zn(NH_3)_4^{2+}$ and correct through eq calculation.

$$\left[Zn\left(H_2O\right)_4^{2+}\right] \rightarrow 1.25 \times 10^{-3} M - 1.25 \times 10^{-3} M = 0$$

Change in $\left[NH_3\right]$ given by

$$\left[NH_3\right] \rightarrow 5.00 \times 10^{-2} M - 4 \times 1.25 \times 10^{-3} M = 0.045M$$

Set up a table with $x = [Zn(H_2O)_4^{2+}]$ at equilibrium.

An initial estimate of $[Zn(NH_3)_4^{2+}] = 1.25 \times 10^{-3}$ M

$Zn(H_2O)_4^{2+} + 4\ NH_3 = Zn(NH_3)_4^{2+} + 4H_2O(l)$

Conc., M	$Zn(H_2O)_4^{2+}$	NH_3	$Zn(NH_3)_4^{2+}$
Initial	1.25×10^{-3}	5.00×10^{-2}	0
Change			
Equilibrium			

$Zn(H_2O)_4^{2+}$+ 4 NH_3 = $Zn(NH_3)_4^{2+}$ +$4H_2O(l)$

Conc., M	$Zn(H_2O)_4^{2+}$	NH_3	$Zn(NH_3)_4^{2+}$
Initial	1.25×10^{-3}	5.00×10^{-2}	0
Change	~(-1.25 x10^{-3})	~(-5.00 x 10^{-3})	~(+1.25 x10^{-3})
Equilibrium			

$Zn(H_2O)_4^{2+}$+ 4 NH_3 = $Zn(NH_3)_4^{2+}$ +$4H_2O(l)$

Conc., M	$Zn(H_2O)_4^{2+}$	NH_3	$Zn(NH_3)_4^{2+}$
Initial	1.25×10^{-3}	5.00×10^{-2}	0
Change	~(-1.25 x10^{-3})	~(-5.00 x 10^{-3})	~(+1.25 x10^{-3})
Equilibrium	x	$4.50 \times 10^{-2} + 4x$	$1.25 \times 10^{-3} - x$

$$K_f = \frac{\left[Zn\left(NH_3\right)_4^{2+}\right]}{\left[Zn\left(H_2O\right)_4^{2+}\right]\left[NH_3\right]^4} = 7.7\times10^8$$

$$\frac{1.25\times10^{-3} - x}{x\left(4.50\times10^{-2} + 4x\right)^4} = 7.7\times10^8 \approx \frac{1.25\times10^{-3}}{x\left(4.50\times10^{-2}\right)^4}$$

$$x = 4.0\times10^{-7} M = \left[Zn\left(H_2O\right)_4^{2+}\right]$$

$$\left[Zn\left(NH_3\right)_4^{2+}\right] = 1.25\times10^{-3} - x = 1.25\times10^{-3} M$$

$$\text{moles } Zn\left(NH_3\right)_4^{2+} = 1.25\times10^{-3} M \times 75.0 L = 0.0938 \text{ moles}$$

EP 147: Calculating the Effect of Complex Ion Formation on Solubility

Problem: A critical step in black and white film developing is the removal of excess AgBr from the film negative by 'hypo', an aqueous solution of sodium thiosulfate ($Na_2S_2O_3$), through formation of the complex ion $Ag(S_2O_3)_2^{3-}$. Calculate the concentration of Ag^+ in (a) H_2O: (b) 1.0 M hypo. K_f of $Ag(S_2O_3)_2^{3-}$ = 4.7×10^{13} and K_{sp} of AgBr = 5.0×10^{-13}.

Strategy:

(a) Normal solubility problem

(b) K for overall equation for dissolution of AgBr in hypo found by combining the equations of dissolution of AgBr in water and of formation of the complex of silver thiosulfate.

(a): $K_{sp} = [Ag^+][Br^-]$

$S = [AgBr]_{dissolved} = [Ag^+] = [Br^-]$

$K_{sp} = S^2 = 5.0 \times 10^{-3}$; $S = 7.1 \times 10^{-7}$ moles L^{-1}

(b): Combine the following reactions

$AgBr(s) = Ag^+(aq) + Br^-(aq)$

$Ag^+(aq) + 2\, S_2O_3^{2-}(aq) = Ag(S_2O_3)_2^{3-}(aq)$

Sum: $AgBr(s) + 2\, S_2O_3^{2-}(aq) = Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$

$K_{overall} = K_{sp}$ x K_f = (5.0×10^{-13})x(4.7×10^{13}) = 24

$AgBr(s) + 2\, S_2O_3^{2-}(aq) = Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$

Let x = $[AgBr]_{dissolved}$

Conc., M	$S_2O_3^{2-}$	$Ag(S_2O_3)_2^{3-}$	Br^-
Initial	1.0	0	0
Change			
Equilibrium			

$AgBr(s) + 2\ S_2O_3^{2-}(aq) = Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$

Let x = $[AgBr]_{dissolved}$

Conc., M	$S_2O_3^{2-}$	$Ag(S_2O_3)_2^{3-}$	Br^-
Initial	1.0	0	0
Change	-2x	+x	+x
Equilibrium			

$AgBr(s) + 2\ S_2O_3^{2-}(aq) = Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$

Let x = $[AgBr]_{dissolved}$

Conc., M	$S_2O_3^{2-}$	$Ag(S_2O_3)_2^{3-}$	Br^-
Initial	1.0	0	0
Change	-2x	+x	+x
Equilibrium	1.0 – 2x	x	x

$$K_{overall} = \frac{\left[\mathrm{Ag}\left(\mathrm{S_2O_3}\right)_2^{3-}\right]\left[\mathrm{Br}^-\right]}{\left[\mathrm{S_2O_3}^{2-}\right]^2} = \frac{x^2}{(1.0-2x)^2} = 24$$

Taking the square root of both sides gives:

$$\frac{x}{1.0-x} = \sqrt{24} = 4.9$$

$$\mathrm{x} = \left[\mathrm{Ag}\left(\mathrm{S_2O_3}\right)_2^{3-}\right] = 0.45M$$

$\left[\mathrm{Ag}^+\right]$ in water was $7.1\times10^{-7}M$

Answers to Numerical Problems

EP 137: pH = 4.44, 0.036%
EP 138: a) pH = 3.12, 0.15% b) pH = 3.14, 0.15% c) 5.00pH units
EP 139: a) 10.44 b) 10.44 c) 0.21 pH units
EP 140: 2.60×10^{-13}
EP 141: 5.0g/L
EP 142: 4.7×10^{-2}, $4.0 \mathrm{X} 10^{-3}$ mol/L
EP 145: 5.6×10^{-5}M, 7.0×10^{-12}M
EP 146: 1.25×10^{-3} mol/L, 4.0×10^{-7}M
EP 147: a) 7.1×10^{-7}M b) 0.45M