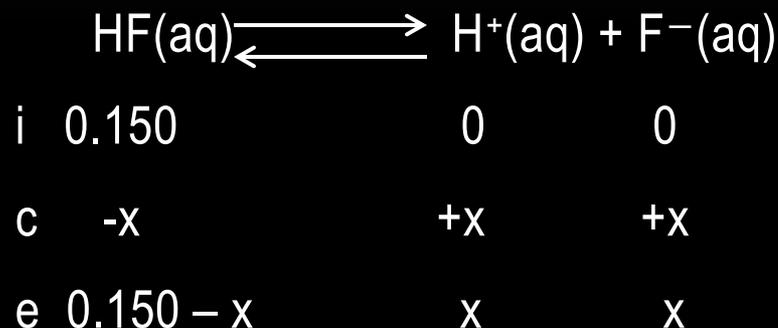


ACID-BASE EQUILIBRIA/SOLUBILITY AND COMPLEX ION EQUILIBRIA

THE COMMON ION EFFECT

Common Ions

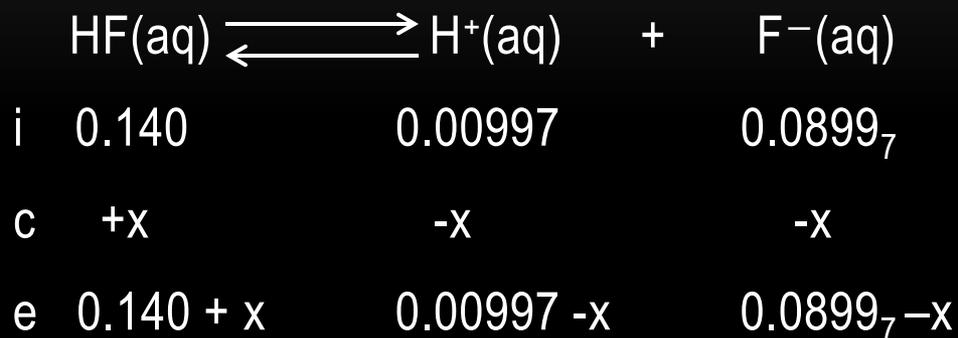
Consider the equilibrium, where we start with 1.00 L of 0.150 M HF ($K_a = 7.1 \times 10^{-4}$):



At equilibrium $[\text{H}^{\text{+}}] = 0.00997 \text{ M} = [\text{F}^{-}]$, $[\text{HF}] = 0.140 \text{ M}$, and $\text{pH} = 2.001$

Suppose we then add 0.0800 moles of KF. KF is a strong electrolyte, so we've added 0.0800 moles of F^{-} . We've disturbed the equilibrium, and Le Châtelier tells us the equilibrium should shift to the left.

Common Ions



Solving the equilibrium expression for x , we get $x=0.00867$, so at the new equilibrium: $[\text{H}^{\text{+}}]=0.00130 \text{ M}$, $[\text{F}^{-}]=0.0813 \text{ M}$, $[\text{HF}]=0.149 \text{ M}$, and $\text{pH}=2.886$

The equilibrium has shifted to the left. This is called the common ion effect.

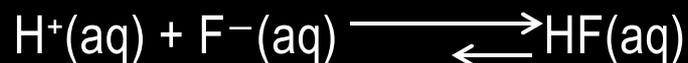
BUFFER SOLUTIONS

Buffers

A solution that has a weak acid and a salt of a conjugate base, or a weak base and a salt of its conjugate acid, is a buffer.

A buffer maintains the pH of a solution even when acid or base is added (up to a certain point called the buffer capacity).

Consider a solution that is made up to be 1.0 M in HF and 1.0 M in NaF. When a strong acid is added to the solution:



The addition of a strong acid lowers the pH, but the effect is minimized because the buffer essentially converts the strong acid into a weak acid.

Buffers

The same sort of thing happens when a strong base is added to the buffer solution:



The strong base is effectively converted into a weak base, and while the pH rises a little, the effect is minimized.

Calculating the pH of a Buffer Solution

Suppose we have 1.00 L of the 1.00 M HF/NaF buffer solution.



$$\text{i} \quad 1.00 \qquad \qquad 0 \qquad \qquad 1.00$$

$$\text{c} \quad -x \qquad \qquad +x \qquad \qquad +x$$

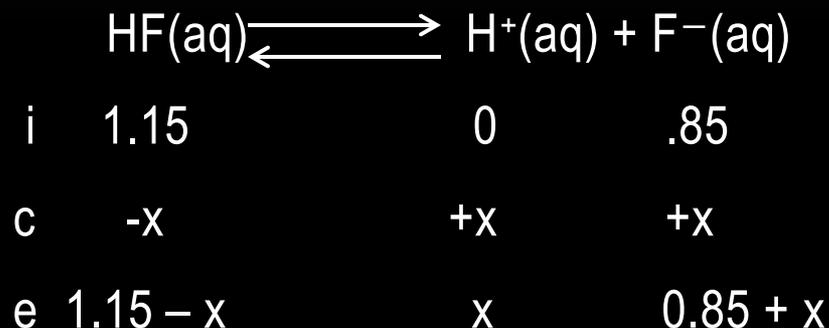
$$\text{e} \quad 1.00 - x \qquad \qquad x \qquad \qquad 1.00 + x$$

$$7.1 \times 10^{-4} = \frac{(x)(1.00 + x)}{(1.00 - x)} \approx \frac{(x)(1.00)}{(1.00)} = x$$

And so the pH = 3.15.

Calculating the pH of a Buffer Solution

No suppose we add 0.15 moles of a strong acid, assume the volume stays at 1.00 L.



$$7.1 \times 10^{-4} = \frac{(x)(0.85 + x)}{(1.15 - x)} \approx \frac{(x)(0.85)}{(1.15)} = 0.74x, x = 9.6 \times 10^{-4}$$

And so the pH = 3.02. The pH has been lowered a little, but not much. A solution that has $[\text{H}^{\text{+}}] = 0.15 \text{ M}$ has a pH of 0.82.

The Henderson-Hasselbalch Equation

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

(The Henderson-Hasselbalch equation)

ASSUMES THE CHANGE IN CONCENTRATION (“x”) IS << INITIAL CONCENTRATIONS!

For the previous example:

$$\begin{aligned}\text{pH} &= -\log(7.1 \times 10^{-4}) + \log \frac{0.85}{1.15} \\ &= 3.01_7 = 3.02\end{aligned}$$

Designing A Buffer

A buffer only has the ability to resist pH changes if the concentrations of the acid and conjugate base are within a factor of 10 of each other:

$$10 \geq \frac{[\text{base}]}{[\text{acid}]} \geq 0.1$$

This means the log term in the Henderson-Hasselbalch equation ranges from -1 to +1, or $\text{pH} = \text{pK}_a \pm 1$.

So, choose a weak acid whose pK_a is within 1 unit of the desired pH. Then, plug the pH and pK_a into the Henderson-Hasselbalch equation to get the ratio of conjugate base molarity to weak acid molarity.

Then, make up the solution and measure its pH. You will almost certainly have to adjust it.

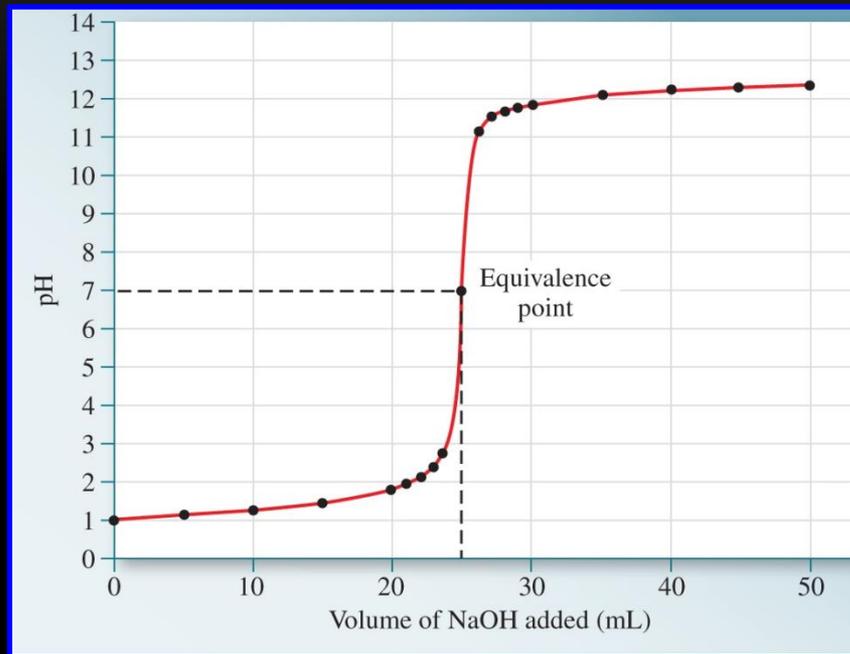
Designing A Buffer

Describe how to make 1.0 L of a buffer whose pH = 4.5 using benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ ($\text{pK}_a = 4.19$), and its conjugate base, sodium benzoate, $\text{NaC}_6\text{H}_5\text{CO}_2$.

ACID-BASE TITRATIONS

Strong Acid – Strong Base Titrations

Consider the titration of 25.0 mL of 0.100M HCl with 0.100 M NaOH.

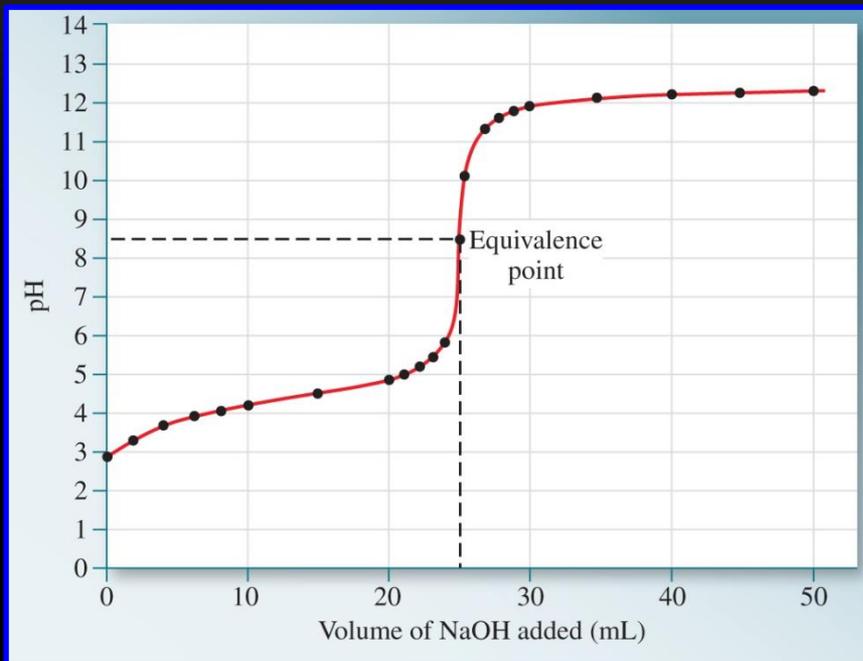


Calculate these

Volume OH ⁻ added (mL)	OH ⁻ added (mmol)	H ⁺ remaining (mmol)	Total volume (mL)	[H ⁺] (mol/L)	pH	
0	0	2.5	25.0	0.100	1.000	
5.0	0.50	2.0	30.0	0.0667	1.176	
10.0	1.0	1.5	35.0	0.0429	1.364	
15.0	1.5	1.0	40.0	0.0250	1.602	
20.0	2.0	0.5	45.0	0.0111	1.955	
25.0	2.5	0	50.0	1.00×10^{-7}	7.000	
Volume OH ⁻ added (mL)	OH ⁻ added (mmol)	Excess OH ⁻ (mmol)	Total volume (mL)	[OH ⁻] (mol/L)	pOH	pH
30.0	3.0	0.5	55.0	0.0091	2.04	11.96
35.0	3.5	1.0	60.0	0.0167	1.78	12.223

Weak Acid-Strong Base

Look at the titration of 25.0 mL of 0.10 M acetic acid with 0.10 M NaOH:



Calculate these

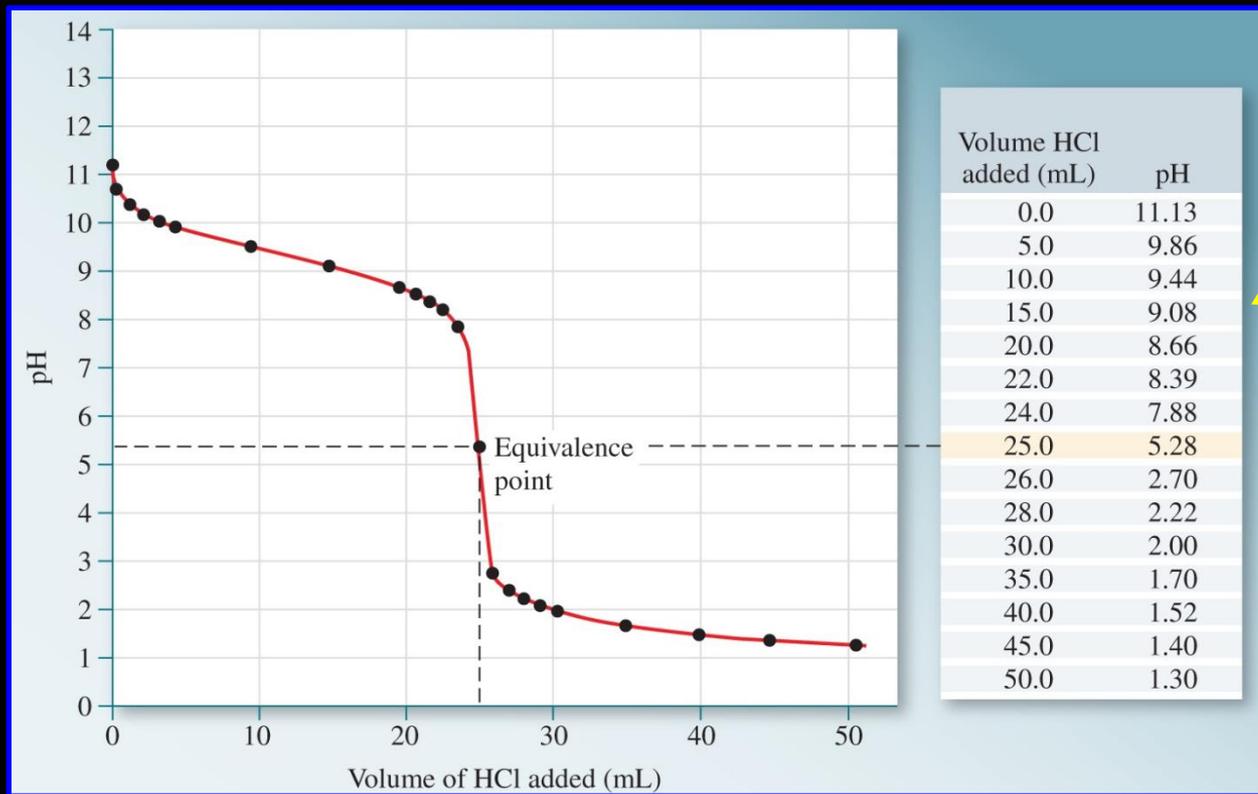
Volume OH ⁻ added (mL)	OH ⁻ added (mmol)	CH ₃ COOH remaining	CH ₃ COO ⁻ produced	pH		
0	0	2.5	0.0	2.87*		
5.0	0.50	2.0	0.50	4.14		
10.0	1.0	1.5	1.0	4.56		
15.0	1.5	1.0	1.5	4.92		
20.0	2.0	0.5	2.0	5.34		
25.0	2.5	0.0	2.5	8.72†		
Volume OH ⁻ added (mL)	OH ⁻ added (mmol)	Excess OH ⁻ (mmol)	Total volume (mL)	[OH ⁻] (mol/L)	pOH	pH
30.0	3.0	0.5	55.0	0.0091	2.04	11.96
35.0	3.5	1.0	60.0	0.017	1.78	12.22

*[CH₃COOH] = 0.10 M, $K_a = 1.8 \times 10^{-5}$.

†[CH₃COO⁻] = 0.050 M, $K_b = 5.6 \times 10^{-10}$.

Strong Acid-Weak Base

Let's look at the titration of 25.0 mL of 0.10 M NH_3 with 0.10 M HCl:

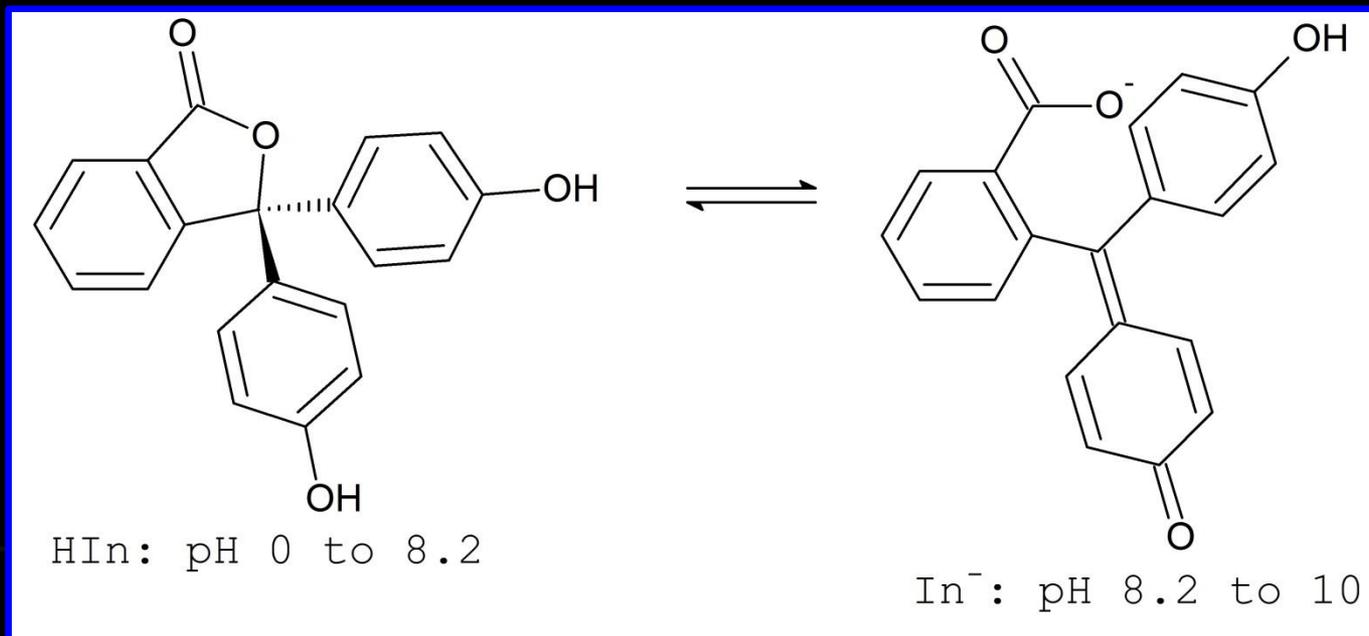


Calculate these

Acid-Base Indicators

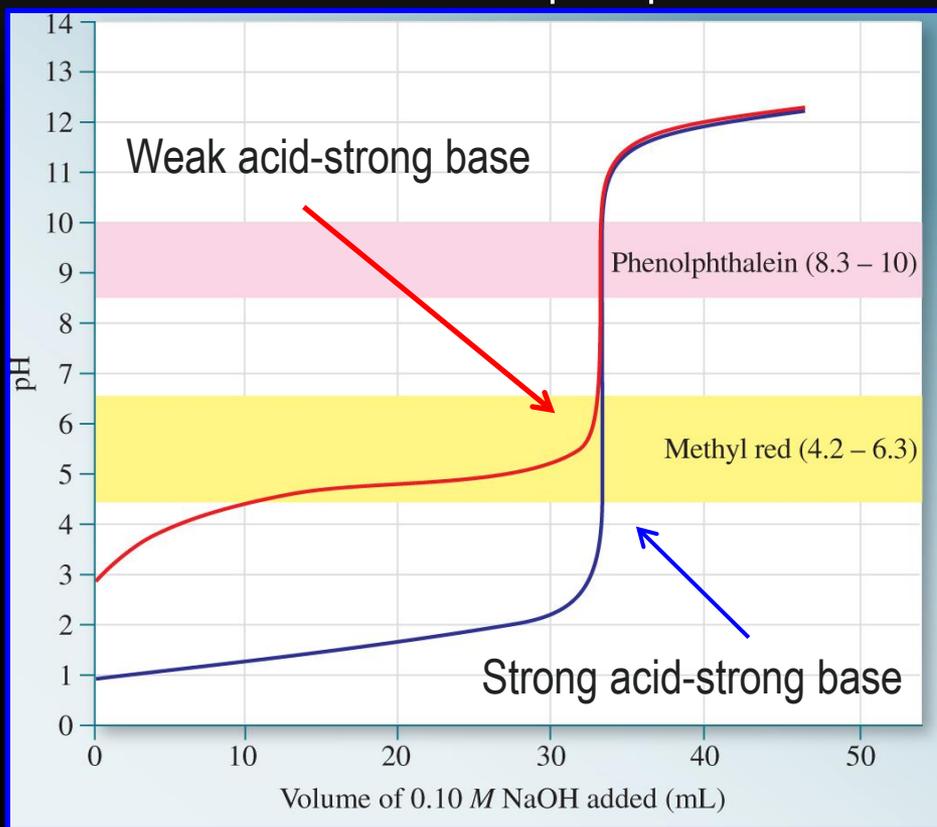
The equivalence point is where exactly enough of one reactant has been added to react with all of the other reactant. For an acid base titration this can be monitored with a pH meter, or the use of an indicator.

An acid-base indicator (such as phenolphthalein) changes color over a certain pH range.



Acid-Base Indicators

To be effective, the pH range over which an indicator changes color must coincide with the steepest part of a titration curve.



Indicator	Color		pH range
	In acid	In base	
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

Phenolphthalein would work for either titration.

Methyl red would only work for the strong acid-strong base titration.

SOLUBILITY EQUILIBRIA

K_{sp}

The solubility rules we learned in chapter 9 were just a generalization of the solubility product expression. The solubility product expression for the dissolution of lead (II) iodide,



is

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 1.4 \times 10^{-8}$$

K_{sp} is called the solubility product constant. The smaller K_{sp} is, the less soluble a compound is in water.

Unless otherwise noted, all K_{sp} 's assume the temperature is 25 °C and the solvent is water.

Compound	Dissolution equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$	1.8×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	8.1×10^{-9}
Barium fluoride	$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$	1.7×10^{-6}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Bismuth sulfide	$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$	1.6×10^{-72}
Cadmium sulfide	$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$	8.0×10^{-28}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	8.7×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	8.0×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	1.2×10^{-26}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	2.4×10^{-5}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$	3.0×10^{-29}
Cobalt(II) sulfide	$CoS(s) \rightleftharpoons Co^{2+}(aq) + S^{2-}(aq)$	4.0×10^{-21}
Copper(I) bromide	$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$	4.2×10^{-8}
Copper(I) iodide	$CuI(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$	5.1×10^{-12}
Copper(II) hydroxide	$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$	2.2×10^{-20}
Copper(II) sulfide	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	6.0×10^{-37}
Iron(II) hydroxide	$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$	1.6×10^{-14}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$	1.1×10^{-36}
Iron(III) phosphate	$FePO_4(s) \rightleftharpoons Fe^{3+}(aq) + PO_4^{3-}(aq)$	1.3×10^{-22}
Iron(II) sulfide	$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$	6.0×10^{-19}
Lead(II) bromide	$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$	6.6×10^{-6}
Lead(II) carbonate	$PbCO_3(s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$	3.3×10^{-14}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$	2.4×10^{-4}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.0×10^{-14}
Lead(II) fluoride	$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$	4.0×10^{-8}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	1.4×10^{-8}
Lead(II) sulfate	$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$	1.8×10^{-8}
Lead(II) sulfide	$PbS(s) \rightleftharpoons Pb^{2+}(aq) + S^{2-}(aq)$	3.4×10^{-28}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	4.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$	1.2×10^{-11}
Manganese(II) sulfide	$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq)$	3.0×10^{-14}
Mercury(I) bromide	$Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Br^-(aq)$	6.4×10^{-23}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$	3.5×10^{-18}
Mercury(I) sulfate	$Hg_2SO_4(s) \rightleftharpoons Hg_2^{2+}(aq) + SO_4^{2-}(aq)$	6.5×10^{-7}
Mercury(II) sulfide	$HgS(s) \rightleftharpoons Hg^{2+}(aq) + S^{2-}(aq)$	4.0×10^{-54}
Nickel(II) sulfide	$NiS(s) \rightleftharpoons Ni^{2+}(aq) + S^{2-}(aq)$	1.4×10^{-24}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	7.7×10^{-13}
Silver carbonate	$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$	8.1×10^{-12}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.6×10^{-10}
Silver chromate	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$	1.2×10^{-12}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.3×10^{-17}
Silver sulfate	$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$	1.5×10^{-5}
Silver sulfide	$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$	6.0×10^{-51}
Srntium carbonate	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	1.6×10^{-9}
Srntium hydroxide	$Sr(OH)_2(s) \rightleftharpoons Sr^{2+}(aq) + 2OH^-(aq)$	3.2×10^{-4}
Srntium sulfate	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.8×10^{-7}
Tin(II) sulfide	$SnS(s) \rightleftharpoons Sn^{2+}(aq) + S^{2-}(aq)$	1.0×10^{-26}
Zinc hydroxide	$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$	1.8×10^{-14}
Zinc sulfide	$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$	3.0×10^{-23}

Calculating Solubility (g/L) And Molar Solubility (mol/L)

What is the molar solubility (moles solute/L solution) and solubility (grams solute/L solution) for PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$)?

$$s = 0.0015 \text{ mol/L}$$

$$s = 0.70 \text{ g/L}$$

Predicting Precipitation

For a solution of an ionic compound, not yet at equilibrium, there are three possibilities:

- 1.) The solution is unsaturated $Q < K_{sp}$
- 2.) The solution is saturated $Q = K_{sp}$
- 3.) The solution is supersaturated $Q > K_{sp}$

Remember Q looks like K except not at equilibrium.

Predicting Precipitation

Determine whether or not a precipitate will form when 1.000 gram of NaF is added to 150.0 mL of 0.04914 M BaCl₂ solution. K_{sp} for BaF₂ = 1.7×10^{-6} .

FACTORS AFFECTING SOLUBILITY

The Common Ion Effect

What is the molar solubility of magnesium carbonate ($K_{sp} = 4.0 \times 10^{-5}$)? What is the molar solubility of magnesium carbonate in a 0.0500 M solution magnesium nitrate?

$$s = 0.0063 \text{ M in water}$$

$$s = 0.00079 \text{ M in the MgNO}_3 \text{ solution}$$

pH

This is really just another example of the common ion effect. For example, a solution of strontium hydroxide.



$$K_{\text{sp}} = 3.2 \times 10^{-4}$$

$$s = 0.043 \text{ M}, \text{ pOH} = 1.37, \text{ pH} = 12.63$$

At any pH higher than 12.63 the equilibrium will shift to the left, decreasing the solubility of Sr(OH)_2 . At a pH lower than 12.63 the solubility would increase.

WHY?

pH

pH also affects the solubility of the salt of a weak base. For example, CaF_2 .



If the solution is acidic, the protons will react with the conjugate base, F^{-} , of a weak acid, HF.

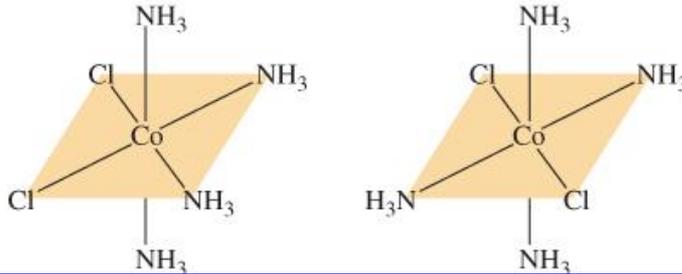
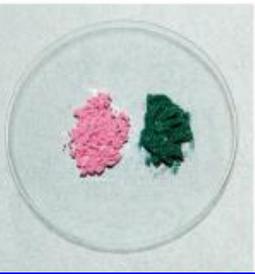


reducing the amount of F^{-} in solution, which will increase the solubility of the calcium fluoride.

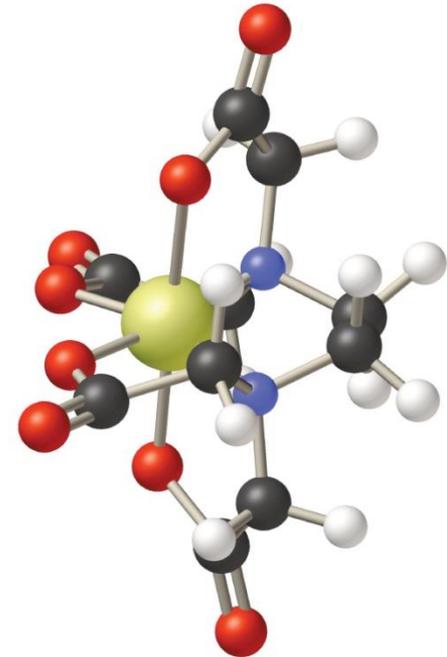
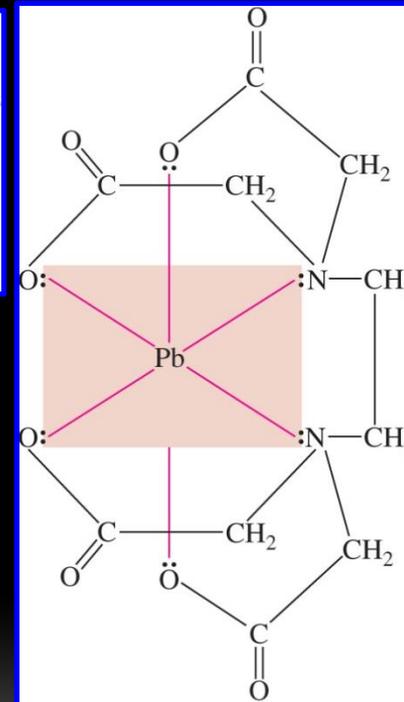
The solubilities of the salts of the conjugate bases of strong acids are not affected by the pH of the solution.

Complex Ion Formation

A complex ion has a metal cation with one or more molecules bonded to it. Many transition metals form complex ions.



Two forms (called cis and trans) of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (the tetraaminodichloro cobalt(III) ion)



An EDTA complex of the lead (II) ion

K_f and Complex Ion Formation

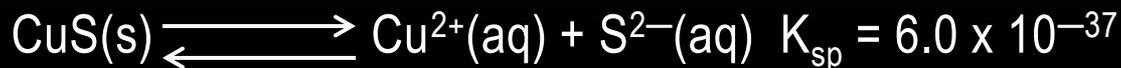
K_f is the equilibrium constant for the formation of a complex ion (also called the stability constant).



$$K_f = \frac{[\text{Cr}(\text{OH})_4^-]}{[\text{Cr}^{3+}][\text{OH}^-]^4} = 8 \times 10^{29}$$

How Complex Ion Formation Affects Solubility

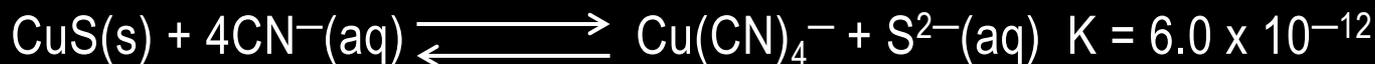
CuS is very insoluble in water:



Now if we add some sodium cyanide to the solution this happens:



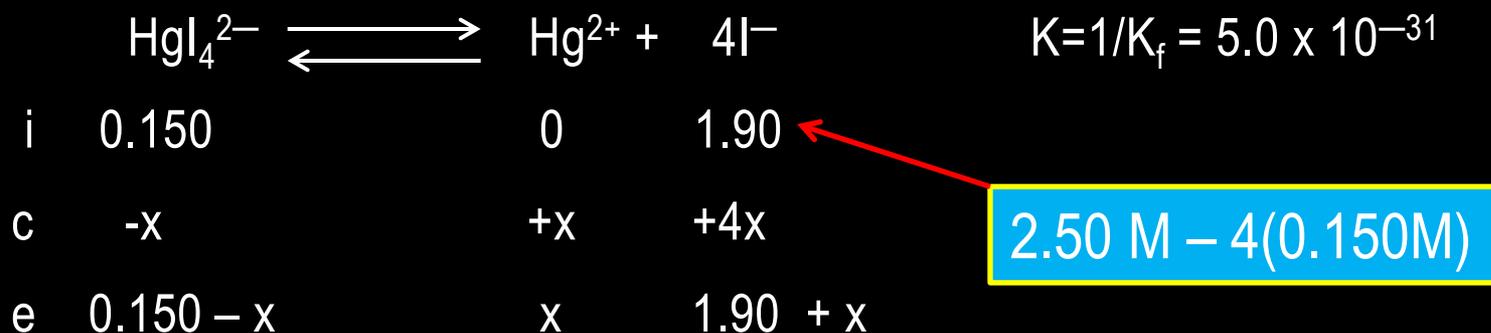
The net result is the sum of the two equations:



The solubility of the copper(II) sulfide has increased dramatically.

Equilibrium Calculations with Complex Ion Formation

Calculate the concentration of free mercury(II) ion in a solution that is made by dissolving 0.150 moles of $\text{Hg}(\text{NO}_3)_2$ in 1.00 L of a solution that is 2.50 M in potassium iodide. The K_f for HgI_4^{2-} is 2.0×10^{30} . If we try to set up an i.c.e. table for the formation of this complex ion we will have a hard time solving the resulting quartic equation. What we do instead is assume that all of the mercury(II) reacts, and then find out how much dissociates. Now set up an ice table and determine the solubility.

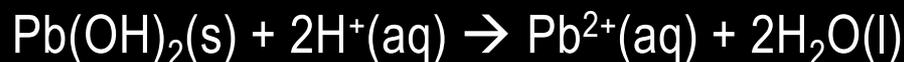


$$x = \text{solubility} = [\text{Hg}^{2+}] = 1.84 \times 10^{-38} \text{ M}$$

Amphoteric Hydroxides

Can react with both acids and bases. Either will increase their solubility.

Some common amphoteric hydroxides are $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Cd}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, and $\text{Pb}(\text{OH})_2$. For example:



Here lead(II)hydroxide is acting as a Lewis acid and hydroxide is a Lewis base.

ION SEPARATION BY SOLUBILITY

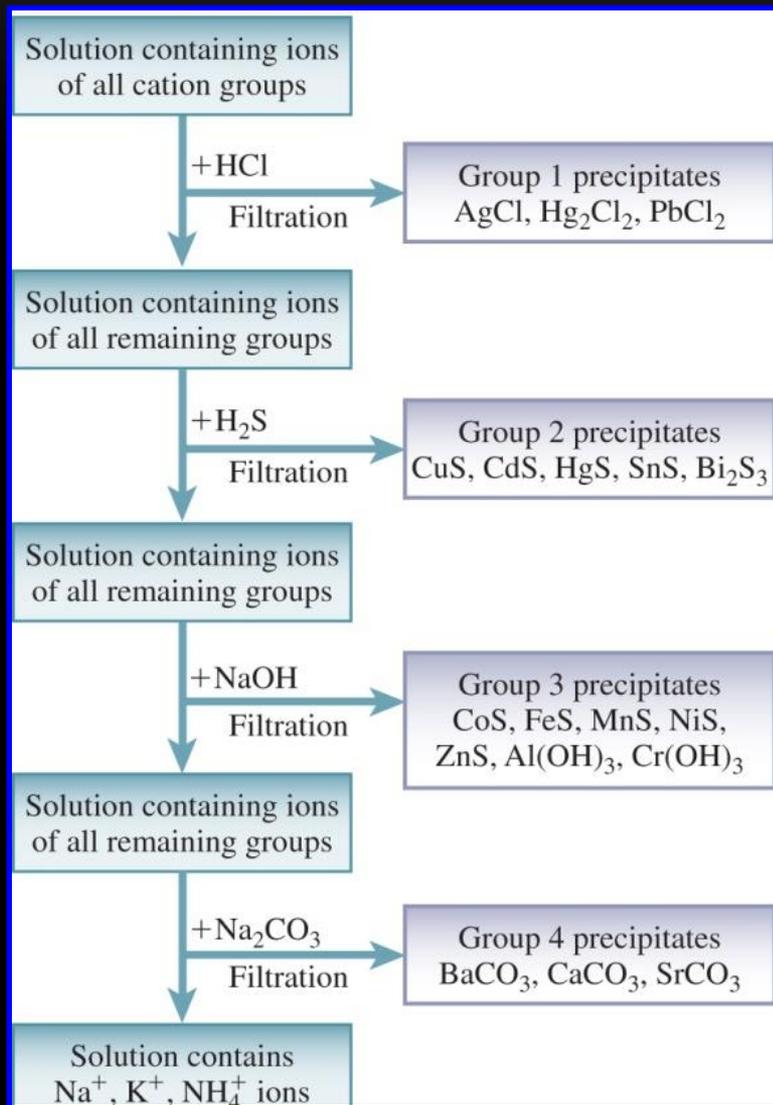
Fractional Precipitation

If we have a solution that contains several ions, and we need to separate the ions, we can use fractional precipitation if there are counter ions that give precipitates with significantly different K_{sp} 's (at least 2 orders of magnitude different)

For example, if we had a solution with chloride and bromide ions in it we could separate them by judiciously adding the silver ion:



Qualitative Analysis of Metal Ions in Solution



Sodium

Potassium