

Chapter 15 Outline – Applications of Aqueous Equilibria**Solutions of Acids or Bases Containing a Common Ion**

- A common ion often refers to an ion that is added by two or more species. For example, if sodium fluoride (NaF) is added to a solution of hydrofluoric acid (HF), fluoride is the common ion because it occurs in hydrofluoric acid and sodium fluoride.
 - $\text{HF(aq)} \rightleftharpoons \text{H}^{\text{+}}(\text{aq}) + \text{F}^{-}(\text{aq})$
 - $\text{NaF(s)} \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{F}^{-}(\text{aq})$
- The shift in equilibrium position because of the addition of an ion already involved in the equilibrium reaction is called the common ion effect.
- Remember, addition of a common ion pushes the reaction AWAY from the ion added.
- Recall your solubility rules for whether or not a salt is soluble,
- For example: Calculate the pH of a 0.750 M HF ($K_{\text{a}} = 7.2 \times 10^{-4}$) solution containing 0.450 M NaF.

	HF	H ⁺	F ⁻
Initial	0.750 M	0	0.450
Change	-x	+x	+x
Equilibrium	0.750	x	0.450

$$K_{\text{a}} = \frac{[\text{H}^{\text{+}}][\text{F}^{-}]}{[\text{HF}]}$$

$$\frac{7.2 \times 10^{-4}}{1} = \frac{[x][0.450]}{0.750}$$

$$x = 0.0012 = [\text{H}^{\text{+}}]$$

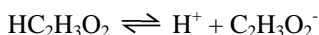
$$\text{pH} = 2.92$$

You try: Calculate the pH and percent ionization of a 0.250 M solution of $\text{HC}_2\text{H}_3\text{O}_2$ ($K_{\text{a}} = 1.8 \times 10^{-5}$) containing 0.500 M $\text{NaC}_2\text{H}_3\text{O}_2$.

Buffered Solutions

- A buffered solution is one that resists a change in its pH when hydroxide ions or protons (hydrogen ions) are added.
- An important buffer solution is blood. The pH of blood is important because cells can only survive in a very narrow pH range.
- Buffered solutions are either made up of a weak acid and its salt or a weak base and its salt.

- Calculating the pH of a buffered solution:
 - Calculate the pH of a solution that contains 0.50 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) and a 0.50 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$).



$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$\frac{1.8 \times 10^{-5}}{1} = \frac{[x][0.50]}{0.50}$$

$$x = 1.8 \times 10^{-5} = [\text{H}^+]$$

$$\text{pH} = 4.74$$

- As you can see from the above example, this type of problem is just like the common ion problem shown earlier.
 - Another example: Calculate the pH change that occurs when 0.010 mol NaOH is added to 1.0 L of a solution that contains 0.50 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) and a 0.50 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$).

Keep in mind that the addition of NaOH will react with $\text{HC}_2\text{H}_3\text{O}_2$, moving the reaction to the right to produce water and more acetate ion. So the ice chart looks like:

	$\text{HC}_2\text{H}_3\text{O}_2$	H^+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.50 M	0	0.50
Change	-x	+x	+x
Equilibrium	0.49	x	0.51

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$\frac{1.8 \times 10^{-5}}{1} = \frac{[x][0.51]}{0.49}$$

$$x = 1.7 \times 10^{-5} = [\text{H}^+]$$

$$\text{pH} = 4.76$$

- You try: Calculate the pH change that occurs when 0.050 mol of solid NaOH is added to 0.750 L of a solution that contains 0.250 M solution of $\text{HC}_2\text{H}_3\text{O}_2$ ($K_a = 1.8 \times 10^{-5}$) and 0.500 M $\text{NaC}_2\text{H}_3\text{O}_2$.

- Some important formulas when working with buffers:
 - $\text{p}K_a = -\log(K_a)$ this one is just like $\text{pH} = -\log[\text{H}^+]$ and $\text{pOH} = -\log[\text{OH}^-]$
 - $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ or $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$ This formula is known as the Henderson-Hasselbalch equation and is useful for calculating pH when [acid] & [base] is known.

- Calculate the pH of a solution containing 0.85 M lactic acid ($K_a = 1.4 \times 10^{-4}$) and 0.45 M sodium lactate.
 - $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$
 - $\text{pH} = 3.85 + \log\left(\frac{[0.45]}{[0.85]}\right)$
 - $\text{pH} = 3.85 + (-0.22)$
 - $\text{pH} = 3.63$
- You try. Calculate the pH of a solution containing 0.250 M hydrofluoric acid ($K_a = 7.2 \times 10^{-4}$) and 0.350 M sodium fluoride.
- The same equations can also be used when considering a solution composed of a weak base and its salt. It is important to remember to convert K_b to K_a using the equation: $1 \times 10^{-14} = K_a \times K_b$.
- For example: Calculate the pH of a buffered solution containing 0.250 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.300 M NH_4Cl .
 - $1 \times 10^{-14} = K_a \times K_b$
 - $1 \times 10^{-14} = K_a \times 1.8 \times 10^{-5}$
 - $K_a = 5.6 \times 10^{-10}$
 - Note: In this problem NH_4^+ is the acid and NH_3 is the base.
 - $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$
 - $\text{pH} = 9.25 + \log\left(\frac{[0.250]}{[0.300]}\right)$
 - $\text{pH} = 9.25 + (-0.079)$
 - $\text{pH} = 9.17$

Buffering Capacity

- The buffering capacity is the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH.
- The pH of a buffered solution is determined by the ratio $[\text{A}^-]/[\text{HA}]$.
- The buffering capacity is determined by the magnitude of $[\text{A}^-]$ and $[\text{HA}]$. The bigger the magnitude, the greater the buffering capacity.
- For example: Calculate the pH when 0.010 moles of HCl (gaseous) is added to 1.0 liter of each of the following solutions: $K_a(\text{HC}_2\text{H}_3\text{O}_2) = 1.8 \times 10^{-5}$
 - Solution A 5.00 M $\text{HC}_2\text{H}_3\text{O}_2$ and 5.00 M $\text{NaC}_2\text{H}_3\text{O}_2$
 - Solution B 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.050 M $\text{NaC}_2\text{H}_3\text{O}_2$
 - $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$
 - The addition of HCl, adds H^+ and shifts the reaction left. Acetate concentration will decrease by 0.010 and acetic acid concentration will increase by 0.010.
 - Solution A:
 - $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$
 - $\text{pH} = 4.74 + \log\left(\frac{[4.99]}{[5.01]}\right)$
 - $\text{pH} = 4.74 + (-0.0017)$
 - $\text{pH} = 4.74$
 - Solution B:
 - $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$
 - $\text{pH} = 4.74 + \log\left(\frac{[0.040]}{[0.060]}\right)$
 - $\text{pH} = 4.74 + (-0.18)$
 - $\text{pH} = 4.56$
 - Although solution B did not change its pH significantly, it can still be seen that the greater the magnitude of the concentrations of the acid and base, the greater the buffering capacity.

- Because large changes in the ratio of $[A^-]/[HA]$ will produce large changes in pH. Optimal buffering occurs when $[A^-] = [HA]$.
- $pH = pK_a + \log([A^-]/[HA])$, if $[A^-] = [HA]$, then $pH = pK_a + \log(1)$, then $pH = pK_a + 0$
- When choosing a buffer, choose the weak acid with a pK_a closest to the desired pH.
- For example: In order to buffer a solution at a pH of 4.30, which of the following weak acids (and their sodium salts) would be the best choice?
 - a. chloroacetic acid ($K_a = 1.35 \times 10^{-3}$)
 - b. propanoic acid ($K_a = 1.3 \times 10^{-5}$)
 - c. benzoic acid ($K_a = 6.4 \times 10^{-5}$)
 - d. hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)

$$[H^+] = 10^{-pH}$$

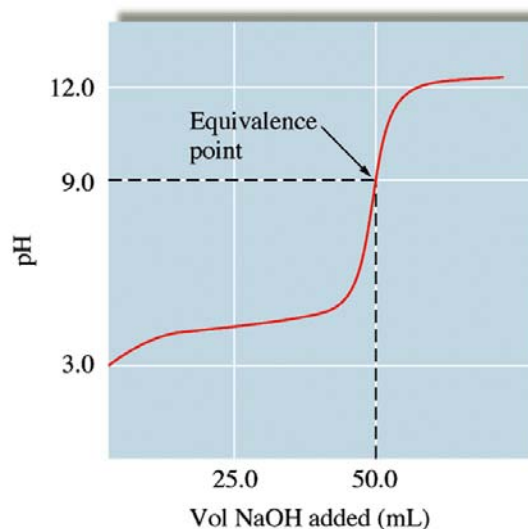
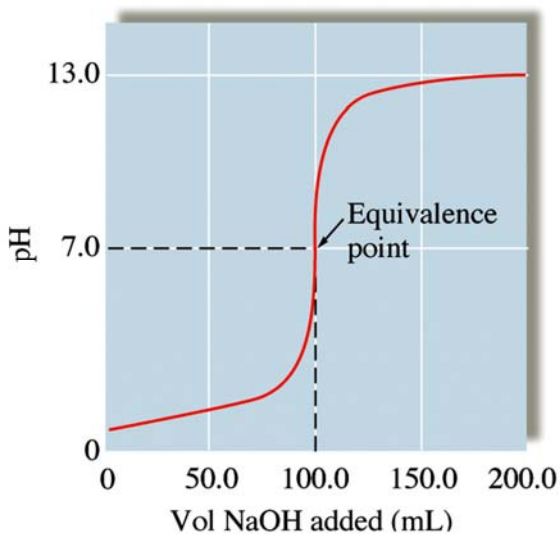
$$[H^+] = 5.0 \times 10^{-5}$$

Since choice C has a K_a value closest to the $[H^+]$, (and thus a pK_a closest to desired pH)

- You try: In order to buffer a solution at a pH of 7.50, which of the above weak acids (and their sodium salts) would be the best choice?

Titration and pH Curves

- A titration is commonly used to determine the amount of acid or base in solution.
- The process involves a solution of known concentration (the titrant) delivered from a buret into the unknown solution until the substance being analyzed is just consumed.
- The stoichiometric (equivalence) point is often signaled by the color change of an indicator.
- The equivalence point is defined by stoichiometry, not the pH. When the number of moles of the acid = the number of moles of base, the equivalence point has been reached.
- The diagram above shows the graph of a titration of a strong acid using a strong base. The equivalence (stoichiometric) point is at 7.0.
- The diagram to the right shows the graph of a titration of a weak acid using a strong base. The stoichiometric (equivalence) point is always above 7 because the anion of the acid is a base. The additional base in the solution causes the pH to be above 7 at the equivalence point.



For example: (I will do this one in class – please copy)

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a weak acid ($K_a = 6.2 \times 10^{-10}$) when dissolved in water. If a 50.0 mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, calculate the pH of the solution:

- the initial pH of the weak acid
- after 8.00 mL of 0.100 M NaOH has been added
- at the halfway point of the titration
- at the equivalence point of the titration

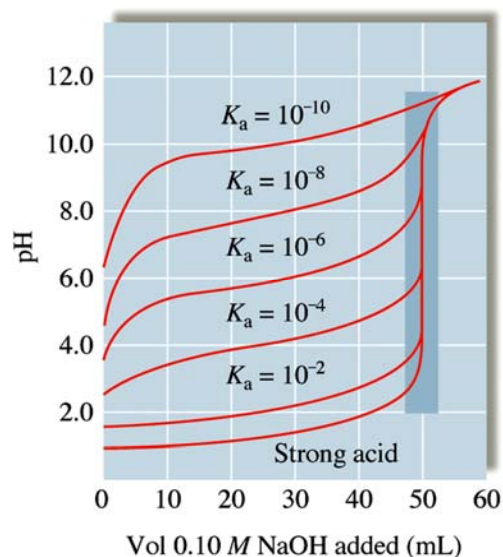
You try: Consider the titration of 100.0 mL of a 0.200 M acetic acid ($K_a = 1.8 \times 10^{-5}$) by 0.100 M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added:

- the initial pH of the acetic acid
- after 50.0 mL of KOH has been added
- after 100.0 mL of KOH has been added
- after 200.0 mL of KOH has been added
- after 250.0 mL of KOH has been added

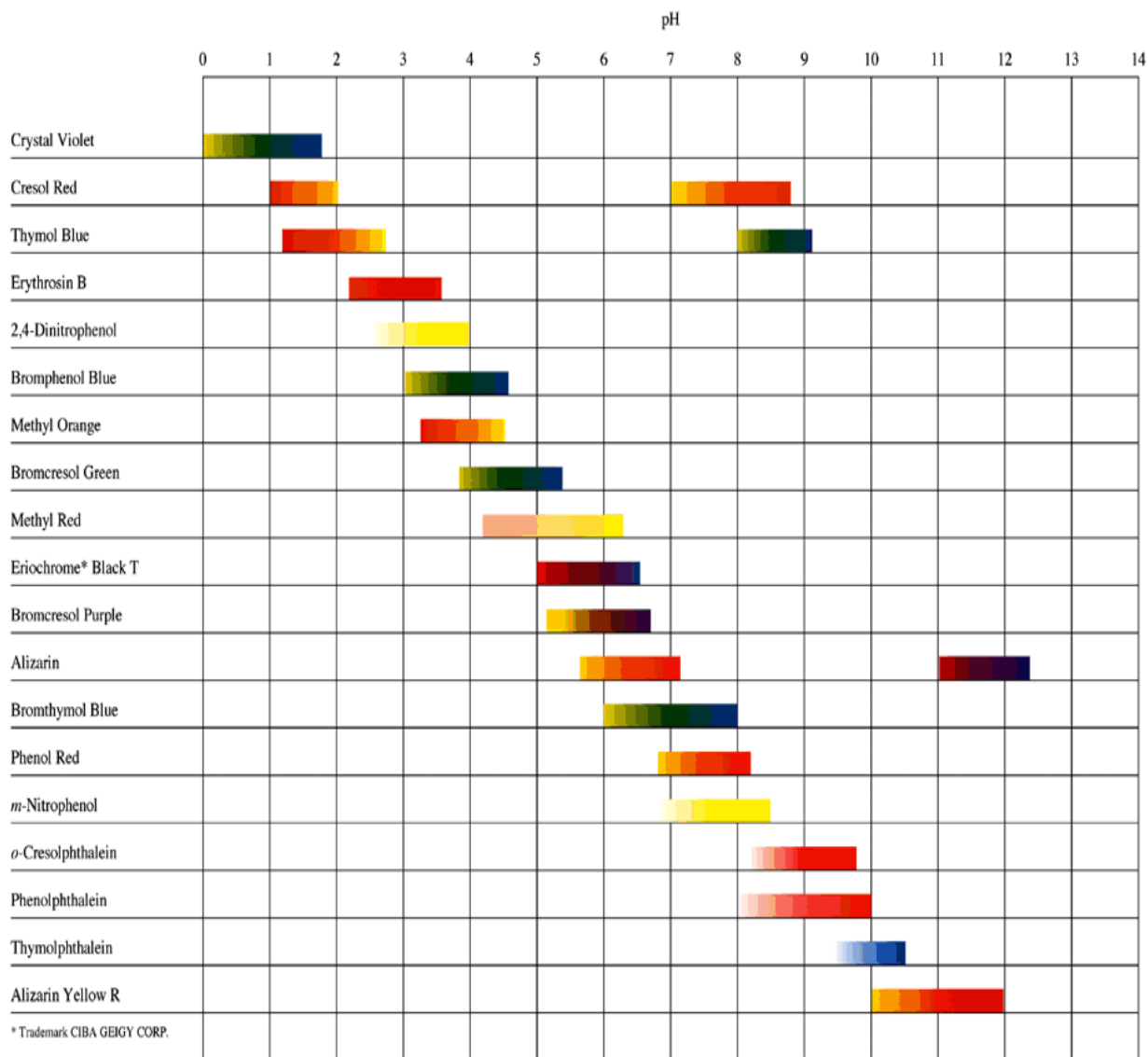
- The diagram to the right shows that the strength of a weak acid has a significant effect on the shape of its pH curve.
- The weaker the acid, the greater the pH value at the equivalence point.

Acid-Base Indicators

- The two common methods for determining the equivalence point of an acid base titration are to use a pH meter or an acid base indicator.
- The most common acid-base indicators are complex molecules that are themselves weak acids (represented by HIn).
- They exhibit one color when the proton is attached to the molecule and a different color when the proton is absent.
- An indicator's color change can be detected by the human eye when the $[In^-]/[HIn] = 1/10$. Basically, this equates to: $pH = pK_a \pm 1$
- For example: Bromthymol blue has a K_a value of 1.0×10^{-7} . At what pH would the color change be first noticed if a strong acid is being titrated by a strong base?
 - $pH = pK_a + 1$
 - $pH = -\log(1.0 \times 10^{-7})$
 - $pH = 7$
 - The color change of bromthymol blue would first be seen at a pH of 6. (If a strong acid was titrating a strong base the pH would be 8.)
- You try: Calculate the pH where color change would first be noticed if methyl red was used in a basic solution to which a strong acid is being added. $K_a = 3.16 \times 10^{-6}$



- The point in a titration changes color is called the end point.
- When choosing an indicator for a titration, you should choose one where the equivalence point and the indicator end point are as close as possible.
- A plethora of acid-base indicators are listed below along with their color changes – but you will only see shades of gray because our copy machine is b/w only.



The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.

Solubility Equilibria and the Solubility Product

- Solubility is a very important function and can explain many interesting chemical behaviors. For example, Tooth enamel contains a mineral called hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Treating teeth with fluoride causes the hydroxyapatite to be converted into fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and calcium fluoride, CaF_2 . Both fluoroapatite and calcium fluoride are less soluble in acids than hydroxyapatite.
- Salts that are generally referred to as being insoluble in water, do actually dissociate in water to a very small degree. This value is referred to as the solubility product constant, K_{sp} .
- Consider the following: $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$
 - $K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^{-}]^2$
 - Note $\text{CaF}_2(\text{s})$ was not included in the solubility product expression. Only aqueous ions are listed.
- The solubility of a salt does not depend on the amount of excess solid.
- The amount of surface area of the salt exposed to water also does not increase the amount of ions produced. Instead, increased surface area only speeds up the rate at which the salt dissociates and reforms.

- **The only factor that can increase the solubility of a salt is temperature.** Note that K_{sp} values are only at 25°C.

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		$Hg_2CrO_4^*$	2×10^{-9}	$Co(OH)_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	$BaCrO_4$	8.5×10^{-11}	$Ni(OH)_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$Zn(OH)_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	$PbCrO_4$	2×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$Hg(OH)_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	Carbonates		$Sn(OH)_2$	3×10^{-27}
		$NiCO_3$	1.4×10^{-7}	$Cr(OH)_3$	6.7×10^{-31}
Chlorides		$CaCO_3$	8.7×10^{-9}	$Al(OH)_3$	2×10^{-32}
$PbCl_2$	1.6×10^{-5}	$BaCO_3$	1.6×10^{-9}	$Fe(OH)_3$	4×10^{-38}
$AgCl$	1.6×10^{-10}	$SrCO_3$	7×10^{-10}	$Co(OH)_3$	2.5×10^{-43}
$Hg_2Cl_2^*$	1.1×10^{-18}	$CuCO_3$	2.5×10^{-10}		
		$ZnCO_3$	2×10^{-10}	Sulfides	
Bromides		$MnCO_3$	8.8×10^{-11}	MnS	2.3×10^{-13}
$PbBr_2$	4.6×10^{-6}	$FeCO_3$	2.1×10^{-11}	FeS	3.7×10^{-19}
$AgBr$	5.0×10^{-13}	Ag_2CO_3	8.1×10^{-12}	NiS	3×10^{-21}
$Hg_2Br_2^*$	1.3×10^{-22}	$CdCO_3$	5.2×10^{-12}	CoS	5×10^{-22}
		$PbCO_3$	1.5×10^{-15}	ZnS	2.5×10^{-22}
Iodides		$MgCO_3$	6.8×10^{-6}	SnS	1×10^{-26}
PbI_2	1.4×10^{-8}	$Hg_2CO_3^*$	9.0×10^{-15}	CdS	1.0×10^{-28}
AgI	1.5×10^{-16}			PbS	7×10^{-29}
$Hg_2I_2^*$	4.5×10^{-29}	Hydroxides		CuS	8.5×10^{-45}
		$Ba(OH)_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
Sulfates		$Sr(OH)_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
$CaSO_4$	6.1×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}		
Ag_2SO_4	1.2×10^{-5}	$AgOH$	2.0×10^{-8}	Phosphates	
$SrSO_4$	3.2×10^{-7}	$Mg(OH)_2$	8.9×10^{-12}	Ag_3PO_4	1.8×10^{-18}
$PbSO_4$	1.3×10^{-8}	$Mn(OH)_2$	2×10^{-13}	$Sr_3(PO_4)_2$	1×10^{-31}
$BaSO_4$	1.5×10^{-9}	$Cd(OH)_2$	5.9×10^{-15}	$Ca_3(PO_4)_2$	1.3×10^{-32}
		$Pb(OH)_2$	1.2×10^{-15}	$Ba_3(PO_4)_2$	6×10^{-39}
Chromates		$Fe(OH)_2$	1.8×10^{-15}	$Pb_3(PO_4)_2$	1×10^{-54}
$SrCrO_4$	3.6×10^{-5}				

- **Calculating K_{sp} from solubility. Example:** Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. What is the K_{sp} value?
 - $CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$
 - $K_{sp} = [Cu^+][Br^-]$
 - Solubility represents how much CuBr dissociates. In the ICE chart, the solubility = x.

	Cu^+	Br^-
Initial	0	0
Change	+x	+x
Equilibrium	2.0×10^{-4}	2.0×10^{-4}

- $K_{sp} = [2.0 \times 10^{-4}][2.0 \times 10^{-4}]$
- $K_{sp} = 4.0 \times 10^{-8}$

- **You try:** Calculating K_{sp} from solubility. Example: Silver chloride has a measured solubility of 1.3×10^{-5} mol/L at 25°C. What is the K_{sp} value?

- **Calculating K_{sp} from solubility when more than two ions are produced. Example:** Bismuth sulfide, Bi_2S_3 , has a measured solubility of 1.0×10^{-15} mol/L at 25°C . What is the K_{sp} value?
 - $\text{Bi}_2\text{S}_3(\text{s}) \rightleftharpoons 2\text{Bi}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq})$
 - $K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$
 - Solubility represents how much Bi_2S_3 dissociates. In the ICE chart, the solubility = x.

	Bi^{3+}	S^{2-}
Initial	0	0
Change	+2x	+3x
Equilibrium	2.0×10^{-15}	3.0×10^{-15}

- $K_{sp} = [2.0 \times 10^{-15}]^2 [3.0 \times 10^{-15}]^3$
 - $K_{sp} = 1.1 \times 10^{-73}$
- **You try:** Calculating K_{sp} from solubility. Example: Magnesium hydroxide has a measured solubility of 1.31×10^{-4} mol/L at 25°C . What is the K_{sp} value? Determine the pH of 1.0 L of this solution.

- **Calculating solubility from K_{sp} . Example:** The K_{sp} value for copper(II) iodate is 1.4×10^{-7} . Calculate its solubility at 25°C .

- $\text{Cu}(\text{IO}_3)_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{IO}_3^-(\text{aq})$
- $K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$

	$[\text{Cu}^{2+}]$	$[\text{IO}_3^-]^2$
Initial	0	0
Change	+x	+2x
Equilibrium	+x	+2x

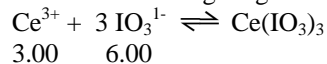
- $K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$
 - $1.4 \times 10^{-7} = [x][2x]^2$
 - $1.4 \times 10^{-7} = 4x^3$
 - $3.5 \times 10^{-8} = x^3$
 - $x = 3.3 \times 10^{-3}$ mol/L = solubility at 25°C .
- **You try:** The K_{sp} value for aluminum hydroxide is 2×10^{-32} . Calculate its solubility at 25°C .

- **Relative Solubilities:**
 - When making relative comparisons of the solubility of different salts, be sure to note the number of ions being produced. If each substance will dissociate to form the same number of ions, then you can refer to the K_{sp} values for comparison.
 - When comparing solubilities of salts that dissociate to form different amounts of ions, you must **calculate** (as you did above) the solubility of each.
- **Common Ion Effect:**
 - The common ion effect is a decrease in the solubility of a compound when it is dissolved in a solution that already contains an ion in common with the salt being dissolved.
 - For example, barium sulfate is an insoluble salt which means very little dissolves in solution. Doctors use barium sulfate to take X-rays of the digestive tract. Barium sulfate is safe but barium ions are very poisonous. Doctors must be sure that there are no barium ions in the solution. To do so, they add sodium sulfate, a very soluble solid. When sodium sulfate dissolves in solution, a large amount of sulfate ions are added to solution. The excess of sulfate ions means that all the barium ions will be bonded to the sulfate ions and none will be free floating.
 - $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ by adding $Na_2SO_4 \rightleftharpoons 2Na^{1+} + SO_4^{2-}$ there is an excess of SO_4^{2-} . This means the reaction will shift left and all of the Ba^{2+} ions will be bonded to SO_4^{2-} ions, forming $BaSO_4$. SO_4^{2-} is the common ion because it appears in both compounds.
- **pH and Solubility:**
 - pH can greatly affect a salt's solubility.
 - For example: magnesium hydroxide is more soluble in acidic solutions than basic solutions.
 - $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$
 - In a basic solution, the presence of hydroxide ions would push the reaction left.
 - In an acidic solution, the acid will react with the magnesium hydroxide, producing magnesium ions and water.
 - **The general rule for solubility and pH is that if the anion X^- is an effective base – meaning that HX is a weak acid – the salt MX will show increased solubility in an acidic solution.**
 - Common anions that are effective bases are: OH^- , S^{2-} , CO_3^{2-} , $C_2O_4^{2-}$ and CrO_4^{2-} .

Precipitation and Qualitative Analysis

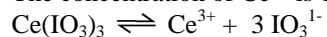
- So far we have looked at solids dissolving in solution. In this section we will look at solids formed when solutions mix.
 - **Ion product (Q)** is just like the expression for K_{sp} , except initial concentrations are used, instead of equilibrium concentrations.
 - If $Q > K_{sp}$: Precipitation occurs until K_{sp} is reached
 - If $Q < K_{sp}$: No precipitation
- For example: A solution is prepared by adding 750.0 mL of 4.00×10^{-3} M $Ce(NO_3)_3$ to 300.0 mL of 2.00×10^{-2} M KIO_3 . Will $Ce(IO_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution? If so, what is the concentration of $[Ce^{3+}]$ and $[IO_3^{1-}]$ ions.
- Calculate the amount of Ce^{3+} ions in solution IO_3^{1-} .
 Ce^{3+} : $750.0 \text{ mL} \times 4.00 \times 10^{-3} \text{ M} = 3.00 \text{ mmol}$; Total volume: $750.0 + 300.0 = 1050.0 \text{ mL}$
Molarity: $3.00 \text{ mmol} / 1050.0 \text{ mL} = 0.00286 \text{ M}$
 - IO_3^{1-} : $300.0 \text{ mL} \times 2.00 \times 10^{-2} \text{ M} = 6.00 \text{ mmol}$; Total volume: $750.0 + 300.0 = 1050.0 \text{ mL}$
Molarity: $6.00 \text{ mmol} / 1050.0 \text{ mL} = 0.00571 \text{ M}$
- $$Ce(IO_3)_3 \rightleftharpoons Ce^{3+} + 3 IO_3^{1-}$$
- $$Q = [Ce^{3+}] [IO_3^{1-}]^3$$
- $$Q = [0.00286] [0.00571]^3$$
- $$Q = 5.32 \times 10^{-10}$$
- Since $Q > K_{sp}$; $Ce(IO_3)_3$ will precipitate**

Determine limiting reagent using the amount of mmoles of each.



IO_3^{1-} is the limiting reagent. If all 6.00 mmoles of IO_3^{1-} is used, you will use up 2.00 mmoles of Ce^{3+} . That leaves an excess of 1.00 mmol of Ce^{3+} .

The concentration of Ce^{3+} is 1.00 mmol / 1050.0 mL = **$9.52 \times 10^{-4} \text{ M}$**



$$K_{\text{sp}} = [\text{Ce}^{3+}] [\text{IO}_3^{1-}]^3$$

$$1.9 \times 10^{-10} = [9.52 \times 10^{-4}] [x]^3$$

$$\text{IO}_3^{1-} = \mathbf{0.0058 \text{ M}}$$

- **You try:** A solution is prepared by mixing 150.0 mL of $1.00 \times 10^{-2} \text{ M Mg}(\text{NO}_3)_2$ and 250.0 mL of $1.00 \times 10^{-1} \text{ M NaF}$. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{\text{sp}} = 6.4 \times 10^{-9}$).

• Selective Precipitation

- Selective precipitation is a process where mixtures of metal ions in aqueous solution are separated by using a reagent whose anion forms a precipitate with only a few of the metal ions in the mixture.
- **For example:** A solution contains $1.0 \times 10^{-4} \text{ M Cu}^+$ and $2.0 \times 10^{-3} \text{ M Pb}^{2+}$. If a source of I^- is added gradually to this solution, will PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) or CuI ($K_{\text{sp}} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I^- necessary to begin precipitation of each salt.

For PbI_2

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

$$1.4 \times 10^{-8} = [2.0 \times 10^{-3}] [\text{I}^-]^2$$

$$[\text{I}^-] = 2.6 \times 10^{-3} \text{ M}$$

For CuI

$$K_{\text{sp}} = [\text{Cu}^+] [\text{I}^-]$$

$$5.3 \times 10^{-12} = [1.0 \times 10^{-4}] [\text{I}^-]$$

$$[\text{I}^-] = 5.3 \times 10^{-8} \text{ M}$$

A concentration of I^- in excess of $5.3 \times 10^{-8} \text{ M}$ will cause formation of solid CuI . CuI precipitates first.

- Since metal sulfide salts differ dramatically in their solubilities, the sulfide ion is often used to separate
- One advantage of the sulfide ion as a precipitating reagent is that because it is basic, its concentration can be controlled by regulating the pH of the solution.

Sulfide	Ksp
MnS	3.0×10^{-11}
FeS	8.0×10^{-19}
CoS	5.0×10^{-22}
NiS	4.0×10^{-20}
CuS	8.0×10^{-37}
Cu_2S	3.0×10^{-49}
Ag_2S	8.0×10^{-51}
Ti_2S	6.0×10^{-22}
ZnS	2.0×10^{-25}
CdS	1.0×10^{-27}
HgS	2.0×10^{-53}
SnS	1.3×10^{-26}
PbS	3.0×10^{-28}
In_2S_3	4.0×10^{-70}