Chapter 16 Acid Base Equilibria - Buffer Solutions

Chemistry by Chang and Goldsby

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16.1 Homogeneous Versus Heterogeneous Solution Equilibria. This refers to K_{sp} which has already been covered.

16.2-16.3 The Common Ion Effect and **Buffer Solutions**

The core understanding all buffer problems is that you are only dealing with two substances, a weak acid and its conjugate base. **Once you identify the weak acid and its conjugate base, you are good to go**.

However, the weak acid and its conjugate base can be difficult to identify. Here are examples of the different weak acids and conjugate bases which will help you spot the conjugate acid-base pair in buffer problems. In going over these examples note that an **acid always has one more H^+ than its corresponding conjugate base**.

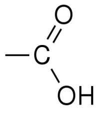
(1) Simple weak acids and their corresponding conjugate base.

weak acid		conjugate base	
HNO_2	nitrous acid	NO_2^-	nitrite
HF	hydrofluoric acid	F^-	fluoride
NH_4^+	ammonium ion	NH_3	ammonia

(2) In polyprotic acids with their conjugates.

weak acid		conjugate base	
H_2S	hydrosulfuric acid	HS^-	hydrogen sulfide
H_2SO_3	sulfurous acid	HSO_3^-	hydrogen sulfite

(3) Organic acids have -COOH and conjugate bases have $-COO^-$ and can be viewed as HA and A^-.



Carboxylic acids have the -COOH functional group and are commonly named “organic name”–ic acid

e.g	$HC_2H_3O_2$	acetic acid or CH_3COOH ethanoic acid
	$HC_6H_7O_2$	sorbic acid
	C_2H_5COOH	propionic acid
	$HC_8H_7O_2^-$	hydrogen phthalate[1]

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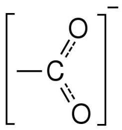
[1] Hydrogen phthalate would be difficult to identify as an acid because it has a negative charge. In a question, you would definitively be told that it was acting as a weak acid.

The conjugate base of carboxylic acids have the functional group $-COO^-$ and are named "organic acid root name"-ate or -oate.



e.g.	$C_2H_3O_2^-$	acetate or CH_3COO^- ethanoate (from acetic or ethanoic acid)
	$C_6H_7O_2^-$	sorbate
	$C_2H_5COO^-$	propionate
	$C_8H_7O_2^{2-}$	phthalate

These will typically be shown in a problem with their sodium or potassium salts, e.g. potassium sorbate, $KC_6H_7O_2$.

It is acceptable to use an acronym instead of the organic compound's formula to make working with an acid-base conjugate pair easier.

Acetic acid:	HAc	and	Ac^-	instead of	$HC_2H_3O_2$	and $C_2H_3O_2^-$
Sorbic acid:	HSorb	and	$Sorb^-$	instead of	$HC_6H_7O_2$	and $C_6H_7O_2^-$
Propionic acid:	HProp	and	$Prop^-$	instead of	C_2H_5COOH	and $C_2H_5COO^-$
Hydrogen phthalate	HPh^-	and	Ph^{2-}	instead of	$HC_8H_7O_2^-$	and $C_8H_7O_2^{2-}$

(4) One twist that is often used in the AP test is to disguise a weak base using a spectator ion, sodium or potassium. Discard the spectator ion to reveal the weak base.

Here are examples of weak acids and bases hidden with spectator ions.

$NaNO_2$	sodium nitrite	~~Na~~NO_2	NO_2^-	nitrite
KF	potassium fluoride	~~K~~F	F^-	fluoride
NH_4Cl	ammonium chloride	NH_4~~Cl~~	NH_4^+	ammonium
$NaC_2H_3O_2$	sodium acetate	~~Na~~ $C_2H_3O_2$	$C_2H_3O_2^-$	acetate
$KC_6H_7O_2$	potassium sorbate	~~K~~$C_6H_7O_2$	$C_6H_7O_2^-$	sorbate
C_2H_5COONa	sodium propionate	C_2H_5COO~~Na~~	$C_2H_5COO^-$	propionate

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Now, that you can spot the weak acid and conjugate base of a buffer, it's time to examine how buffers work.

Buffers are a way of keeping solutions "locked" at a specific pH to resist the rapid changes in pH caused by addition of strong acids or bases.

Every **buffer** has a **weak acid and** its **conjugate base** present in significant concentrations. So, there will be comparable amounts of HA and A^- present ready to react.

> If a strong base is added to a buffered solution, the OH^- is neutralized by the buffer's weak acid, HA.
> If a strong acid is added to the buffered solution, the H^+ is neutralized by the buffer's weak base A^-.

Thus, a buffered solution is protected from pH swings in either direction.

The concentrations of both the weak acid and its corresponding conjugate base work together in solution to produce a specific pH. Adjusting a buffer's [Acid] and [Base] fine-tunes a solution's pH to a stable, accurate pH.

The equation to find the $[H^+]$ of a buffer can be found by rearranging the equilibrium expression to show the ratio of the weak acid to its conjugate base.

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{rearranged to} \Rightarrow \quad [H^+] = K_a \times \frac{[HA]}{[A^-]} \quad \text{or more generally } [H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]}$$

N.B. **Viewing all buffer solutions from the acid perspective simplifies buffer problems.**

To deal with basic buffers using a weak base, B, do not view the problem from the pOH or basic view. **View the buffer from the weak acid point of view, HB^+.** Rewrite the equation making the base's conjugate acid, HB^+ as the reactant. This also will necessitate converting the K_b of B to the K_a of HB^+.

$$K_a = \frac{1.00 \times 10^{-14}}{K_b}$$

As a result, you may use the same buffer equilibrium equation.

$$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]}$$

The pH of buffer systems is so important that there is a special equation, the Henderson-Hasselbalch equation[2] which is on the AP Equation sheet.

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

I advise thinking of the equation in a more generalized manner to fit all buffered equations as

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$$

The Henderson-Hasselbalch equation allows the pH to be directly calculated based on the $\text{p}K_a$ of the acid and the ratio of the conjugate base and acid.

Again, it is best to view basic buffers from the conjugate acid's point of view. So, if given a $\text{p}K_b$ of a weak base of the conjugate pair, switch over to the conjugate acid's $\text{p}K_a$.

$$\text{p}K_a = 14.00 - \text{p}K_b$$

Summarizing: A buffer has significant concentrations of a weak conjugate acid-base pair.
Buffers are used to stabilize a solution's $[H^+]$ and pH.

$$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]} \qquad \text{pH} = \text{p}K_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$$

Use the K_a and $\text{p}K_a$ of the weak acid in the buffer conjugate acid-base pair $[H^+]$ and pH calculations.

There are three possible conjugate acid-base buffer mixture scenarios:

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[2] It is possible to derive the Henderson-Hasselbalch equation from the general equilibrium expression if your log skills are good.

1. When the [Acid] equals [Base]: $[H^+]$ equals the K_a and pH equals the pK_a

If [Acid] = [Base] in the equilibrium expression, $\left[H^+\right] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]}$ becomes $[H^+] = K_a \times 1$, thus $[H^+] = K_a$.

If [Acid] = [Base] in the He-Ha equation, $\log\frac{[\text{Base}]}{[\text{Acid}]}$ becomes log 1, and $\text{pH} = \text{p}K_a + 0$, thus $\text{pH} = \text{p}K_a$.

Special note!

This type of buffer, a perfect buffer, is on every AP Chem exam. You want to be on the lookout for perfect buffers because they are easy to calculate and a fast point.

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2. When the [Acid] is greater than the [Base]: $[H^+]$ is greater than the K_a and pH is smaller than the pK_a

If [**Acid**] > [Base] in the equilibrium expression, $\left[H^+\right] = K_a \times \frac{[\textbf{Acid}]}{[\text{Base}]}$ then $[H^+] > K_a$

If [**Acid**] > [Base] in the He-Ha equation, $\log\frac{[\text{Base}]}{[\textbf{Acid}]}$, log (less than 1) is a negative value

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Base}]}{[\textbf{Acid}]}$$ and the pH < pK_a

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3. When the [Acid] is smaller than the [Base]: $[H^+]$ is smaller than the K_a and pH is greater than the pK_a

If [Acid] < [**Base**] in the equilibrium expression $\left[H^+\right] = K_a \times \frac{[\text{Acid}]}{[\textbf{Base}]}$ then $[H^+] < K_a$

If [Acid] < [**Base**] in the He-Ha equation, $\log\frac{[\textbf{Base}]}{[\text{Acid}]}$, log (greater than 1) is a positive value

$$\text{pH} = \text{p}K_a + \log\frac{[\mathbf{A^-}]}{[\text{HA}]}$$ and the pH > pK_a

Examine math so that it makes sense to you in these equations.

These skills will be used in each of the remaining chapters where ratios of competing factors and their logarithms are used to explain chemical processes.

Now, to go over the three major types of buffer problems.

First, the simplest and most direct way of making a buffer.

1. A buffer can be made by putting together a mixture of a weak acid and an ionic compound of its conjugate base.

(a) 1.00 liter of 0.54 *M* $CH_3COOH(aq)$ is converted into a buffer solution by adding 0.54 moles of $CH_3COONa(s)$. The sodium acetate dissolves, and the solution reaches equilibrium.

What is the pH of the buffered solution?
CH_3COOH $K_a = 1.8 \times 10^{-5}$

Reaction	CH_3COOH	+	$H_2O(l)$	$\leftrightarrows$	H_3O^+	+	CH_3COO^-
Initial	0.54				0		0.54
Change	-x insignificant in buffers		-x		+x		+x insignificant in buffers
Equilibrium	0.54				x		0.54

Because buffer problems do not have significant changes of reactants as equilibrium is reached and the stoichiometry is 1:1 you can simplify the ICE chart to just the reaction equation and the concentration of the two buffer species.

It is important to identify the species in the solution. The most common error in buffer problems is mixing up the acid/base with their conjugates.

HA acid CH_3COOH	+	$H_2O(l)$	$\leftrightarrows$	H_3O^+	+	***A^- conjugate base*** CH_3COO^-
0.54				x		0.54

$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]}$ $\quad [H^+] = 1.8 \times 10^{-5} \times \frac{[0.54]}{[0.54]}$ $\quad [H^+] = 1.8 \times 10^{-5}$ $\quad$ pH=4.74

This buffered solution has the ideal buffer ratio of 1:1, with 0.54 mol/L acid and 0.54 mol/L acid conjugate base.

This problem could be solved using the Henderson Hasselbalch equation once you find the pK_a

$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$ $\quad pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$ $\quad pH = 4.74 + \log\frac{[0.54]}{[0.54]}$ $\quad pH = 4.74$

In buffer problems, volume is not significant since the units in the ratio of the two concentrations in the equilibrium equation cancel. **Either mol or molar can be used in the ratio**. Another factor in buffer solution stability is that diluting a buffered solution does not significantly change its pH.

A sharp student would have seen that this was a perfect buffer, $[HA] = [A^-]$ so: $[H^+] = K_a$ and $pH = pK_a$

This is an important simplification. Always be on the lookout for the perfect ratio!
This can save you valuable time in many FRQ or MC questions.

(b) A mildly alkaline buffer can be made using ammonia and ammonium chloride. What is the pH of 240. mL of 0.500 *M* NH_3 solution mixed with 100. mL of 0.600 *M* NH_4Cl?
NH_3 $K_b = 1.8 \times 10^{-5}$

Convert this to an acid and conjugate base reaction and find the amounts of each species.

HB^+ conjugate acid **NH_4^+**	+	$H_2O(l)$	$\leftrightarrows$	H_3O^+	+	***B base*** NH_3
100. mL × 0.600 *M*						240. mL × 0.500 *M*
60.0 mmol				x		120. mmol

Next convert K_b to K_a and find pK_a

$$1.0 \times 10^{-14} = K_a \times K_b \qquad 1.0 \times 10^{-14} = K_a \times 1.8 \times 10^{-5} \qquad 5.6 \times 10^{--10} = K_a \qquad pK_a = 9.26$$

You can use concentration or mol amounts in the buffer equations since the ratio units cancel.
Using the equilibrium expression equation

$$[H^+] = K_a \times \frac{\text{Acid}}{\text{Base}}$$

$$[H^+] = 5.6 \times 10^{-10} \times \frac{60.0 \text{ mmol}}{120. \text{ mmol}}$$

$$[H^+] = 2.8 \times 10^{-10}\,M$$

Note: The $[H^+]$ is less than the K_a because there is more base than acid

$$\text{pH} = 9.56$$

or the Henderson-Hasselbalch equation

$$\text{pH} = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$$

$$\text{pH} = 9.26 + \log\frac{[120.]}{[60.0.]}$$

$$\text{pH} = 9.56$$

Note: The pH is greater than the pK_a because there is more base than acid.

It is important to check if your answer makes sense relative to the K_a or pK_a since it is easy to mix up the ratio.

Double check your answer to see if it makes sense.

(2) You should be able to design a buffer for a specific pH.

Often it is desirable to have a solution with a specific pH that will not readily change its pH.

To make a buffer solution to a specific pH from a list of acids and salts.

1. **Select a weak acid with a pK_a as close as possible to the desired pH.**
2. Identify the conjugate base of the acid that must be used with the acid.
3. Adjust the weak acid-conjugate base ratio to produce the desired pH.

(a) What ratio of acetic acid and sodium acetate must be present in a buffer, given that the pH will be 4.70? $K_a = 1.8 \times 10^{-5}$

HA *acid* CH_3COOH	+	$H_2O(l)$	$\leftrightarrows$	H_3O^+	+	**A^- *conjugate base*** CH_3COO^-
				2.0×10^{-5} *M*		

The desired buffer $[H^+] = 2.00 \times 10^{-5}$ *M*

$$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]} \qquad [2.0 \times 10^{-5}] = 1.8 \times 10^{-5} \times \frac{[\text{Acid}]}{[\text{Base}]} \qquad 1.1 = \frac{[\text{Acid}]}{[\text{Base}]}$$

Any solution with a ratio of 1.1 times more acetic acid than acetate ion will produce a buffered solution with a pH of 4.70. A solution with 1.1 mol CH_3COOH and 1.0 mol CH_3COO^- or a solution of 0.22 mol of CH_3COOH and 0.20 mol CH_3COO^- would produce the same pH.

However, the 1.1 mol solution would have a **greater capacity** to resist change since it would be able to react with a greater amount of acid or base added to it.

(b) Which pair of substances would be best used for making a buffered solution with a pH of 7.44?

The original compounds for the three substances:

phosphoric acid H_3PO_4
sodium dihydrogen phosphate, NaH_2PO_4
sodium hydrogen phosphate, Na_2HPO_4

Given K_a's

	K_a
H_3PO_4	$7\ .1 \times 10^{-3}$
$H_2PO_4^-$	6.3×10^{-8}
HPO_4^{2-}	4.5×10^{-13}

The chosen pair must be conjugates so there are two possible pairs:

H_3PO_4 and NaH_2PO_4 or NaH_2PO_4 and $Na_2HPO_4^{2-}$

Find the pK_a's of the three substances.

	K_a	pK_a
H_3PO_4	7.1×10^{-3}	2.15
$H_2PO_4^-$	6.3×10^{-8}	7.20
HPO_4^{2-}	4.5×10^{-13}	12.35

The closest pK_a to the desired pH of 7.44 is that of $H_2PO_4^-$ with a pK_a of 7.20.
A perfect buffer with a 50:50 mixture of this acid and its conjugate would have a pH of 7.20. By using a greater amount of conjugate base of $H_2PO_4^-$, you can make the solution more basic and raise the pH to the desired 7.44. So $[H_2PO_4^-] < [HPO_4^{2-}]$ should be used.

(c) What would be the ratio of moles of the two substances in the previous question to produce a buffer with a pH of 7.44?

The buffer with a pH of 7.44 would have a $[H_3O^+]$ of 3.65×10^{-8} *M*.
Using the $H_2PO_4^-$ ($K_a = 6.3 \times 10^{-8}$ and $pK_a = 7.20$) as the acid and HPO_4^{2-} as the conjugate base :

HA acid $H_2PO_4^-$	+	$H_2O(l)$	⇆	H_3O^+	+	***A⁻ conjugate base*** HPO_4^{2-}
[Acid]				3.65×10^{-8} *M*		[Base]

$$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]} \qquad [H^+] = K_a \times \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

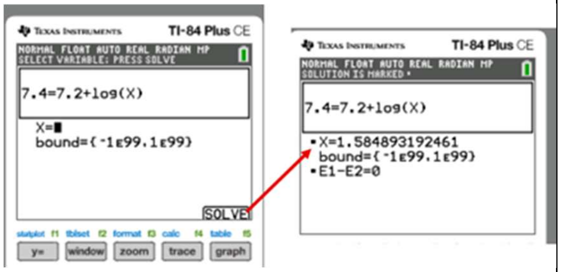
$$[3.65 \times 10^{-8}] = 6.30 \times 10^{-8} \times \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

$$\frac{3.65 \times 10^{-8}}{6.30 \times 10^{-8}} = \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$$

$$0.58 = \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} \quad (\text{Acid/Base})$$

Or 1.74 Base/Acid

$$pH = pK_a + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$



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7.4=7.2+log(X)
  X=█
  bound={⁻1ᴇ99,1ᴇ99}
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7.4=7.2+log(X)
▪X=1.584893192461
 bound={⁻1ᴇ99,1ᴇ99}
▪E1-E2=0
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The ratio of base, HPO_4^{2-}, to acid, $H_2PO_4^-$ is 1.74 times more base than acid.
Or only 0.58 times as much acid as base.

Note the pH desired was higher than the pK_a of the acid (7.44 vs 7.20), so there would need to be more base than acid in this buffer.

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(3) The third type of buffer problem is the sneakiest type of problem which involves strong acids or bases.

Strong acids and bases cannot be buffered since their conjugates do not hydrolyze. So, there is no way to buffer a strong acid or strong base with their conjugates.

However, a strong acid or base can be used with a weak acid or base to make a buffer solution.

A strong acid reacting with a weak base would have the reaction:

$$B + H^+ \rightarrow HB^+$$

If stoichiometric amounts of strong acid reaction and base there is a 100% reaction that proceeds stoichiometrically. All that is left is the weak acid HB^+.

However, if a smaller amount of strong acid were used and only half of the B reacted with the strong acid, the resulting solution would have some B left over and newly produced HB^+ and with the weak acid and left over weak base its buffer time!

For example: 50. mL of 0.10 *M* methyl amine, $H_3CNH_2(aq)$ is reacted with 25. mL of 0.10 M HCl(*aq*).

$$H_3CNH_2(aq) + HCl(aq). \rightarrow H_3CNH_3^+(aq) + Cl^-(aq)$$

The HCl reacts with the weak base to produce the weak acid, $H_3CNH_3^+$, and the Cl^- is a spectator ion.

The reaction leaves behind 25 mmol of unreacted $H_3CNH_2(aq)$ weak base to be buffered with the 25 mmol of the conjugate acid of methyl amine $H_3CNH_3^+$.

Likewise, a weak acid can be converted to a buffer solution by reacting some of the weak acid with the strong base, OH^-.

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

If the amount of base used is less than the amount of acid, HA is left in solution with the newly produced A^-. Thus, what is left is a buffered solution.

Buffers produced by the partial neutralization of a weak acid or a weak base by a strong base or strong acid are calculated as a two-step process.

(1) Use the strong acid or strong base stoichiometric reaction to find the amounts of unreacted weak species and the resulting conjugate.

(2) The amounts of weak acid and conjugate base are used to calculate the properties of the buffered solution.

For example:

(a) 50.0 mL of 0.200 *M* acetic acid solution, CH_3COOH (*aq*), is mixed with 50.0 mL of 0.100 *M* sodium hydroxide solution, NaOH(*aq*). What will be the pH of the resulting solution?
CH_3COOH $K_a = 1.8 \times 10^{-5}$

(1) The reaction of the strong base and the weak acid. This is a simple stoichiometry reaction with no equilibrium complications.

Reaction	***HA acid*** CH_3COOH	+	$OH^-(aq)$	→	H_2O	+	***A^- conjugate base*** CH_3COO^-
Initial	10.0 mmol		5.00 mmol				
Change	-5.00 mmol		-5.00 mmol				+5.00 mmol
Final	5.0 mmol		0.00 mmol				5.00 mmol

With both acetic acid and the acetate ion in solution there will now be this equilibrium in the solution.

CH_3COOH	□	H^+	+	CH_3COO^-
5.0 mmol		?		5.0 mmol

(2) The remaining amounts of HA and A^- and K_a are used with the buffer equation to find the pH.

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \qquad [H^+] = 1.8 \times 10^{-5} \times \frac{5.0}{5.0} \qquad [H^+] = 1.8 \times 10^{-5} \quad pH = 4.74$$

A faster way to do this problem would be to notice that half the weak acid was changed to a weak base (half-equivalence point). Therefore, pK_a = pH.

If half of a weak acid is “neutralized” by a strong base, the pH of the resulting solution equals the pK_a of the weak acid. This is called the half-titration point.

(b) 50.0 mL of 0.200 *M* ammonia solution, $NH_3(aq)$, is mixed with 25.0 mL of 0.100 *M* hydrochloric acid solution, $HCl(aq)$. What will be the pH of the resulting solution?
NH_3 $K_b = 1.8 \times 10^{-5}$

(1) The reaction of the strong acid and the weak base. This is a simple stoichiometry reaction.

Reaction	***B base*** NH_3	+	H_3O^+	→	H_2O	+	***HB^+ conjugate acid*** NH_4^+
Initial	10.0 mmol		2.50 mmol				
Change	-2.50 mmol		-2.50 mmol				+2.50 mmol
Final	7.5 mmol		0.00 mmol				2.50 mmol

(2) Weak acid-base conjugate pair buffers may be basic but should still be approached using the acid point of view of the acid-bas conjugate pair.

NH_4^+	□	H^+	+	NH_3
5.0 mmol		?		5.0 mmol

$1.0 \times 10^{-14} = K_a \times K_b$ $1.0 \times 10^{-14} = K_a \times 1.8 \times 10^{-5}$ $5.6 \times 10^{-10} = K_a$ p$K_a = 9.26$

$$[H+] = K_a \times \frac{[NH_4^+]}{[NH_3]} \qquad [H+] = 5.6 \times 10^{-10} \times \frac{2.50 \text{ mmol}}{7.5 \text{ mmol}} \qquad [H+] = 1.9 \times 10^{-10} \qquad pH = 9.73$$

Or using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} \qquad pH = 9.26 + \log\frac{7.50 \text{ mmol}}{2.5 \text{ mmol}} \qquad pH = 9.73$$

Buffer capacity is how much acid or base a buffer can absorb without significantly changing its pH.

The buffer ratio establishes the pH of the acid and conjugate base.

$$\frac{[HA]}{[A^-]} = \frac{[1.0]}{[1.0]} = \frac{[0.01]}{[0.01]}$$

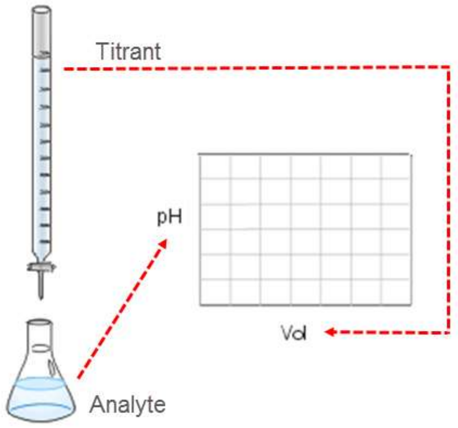
While both of the above ratios produce the same buffered pH, the ratio with the higher concentrations has the higher buffer capacity.

The greater the number of moles within the acid/conjugate base ratio, the greater the buffer’s ability to stay at its pH when it is challenged by the addition of a strong acid or strong base. With a greater number of moles present in the ratio, the ratio will have a smaller change resulting from the addition of an outside acid or base .
Buffer ratio and K_a determine the pH of an acid/conjugate base buffer.
Buffer capacity is the actual amounts inside the buffer ratio.

That’s it! You’ve made it through buffers, the most complex of all the AP Chemistry situations.
Just remember to identify the weak conjugate acid-base pair and

$$[H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Base}]} \quad \text{or} \quad pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$$

16.4 Acid-Base Titrations

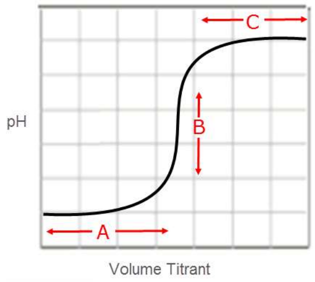


Titrations are best understood using pH graphs.

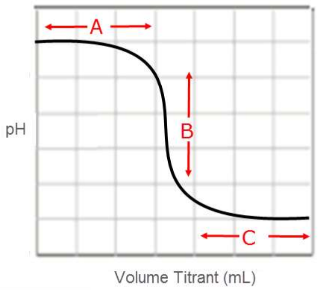
A titration starts with the analyte in a flask. A chosen titrant is added to the flask and reacts with the analyte. The analyte's pH or conductivity is monitored either using an electronic probe which provides data on the condition of the analyte or an acid-base indicator that changes color with the pH of the analyte. The measured volume of titrant is plotted on the x-axis and the pH or conductivity of the analyte is plotted on the y-axis.

Usually the purpose of the titration is to discover the concentration or properties of the analyte based on its reaction with the titrant.

A complete acid/base titration that proceeds from analyte to excess titrant has three parts.



Acidic analyte - basic titrant



Basic analyte - acidic titrant

(A) This horizontal section involves the reaction of the titrant and analyte from the starting point of the titration to the inflection of the curve.
A starting pH of close to 1 or 14 indicates a strong analyte.
A starting pH closer to 3 or 11 indicates a weak analyte.
The midpoint of (A) is the **half-equivalence point** (often called the half-titration point)
The half-equivalence point occurs when half of the analyte has reacted with the titrant.
The half-equivalence point pH = pK_a can be used to calculate the ionization constant, K, for the analyte.

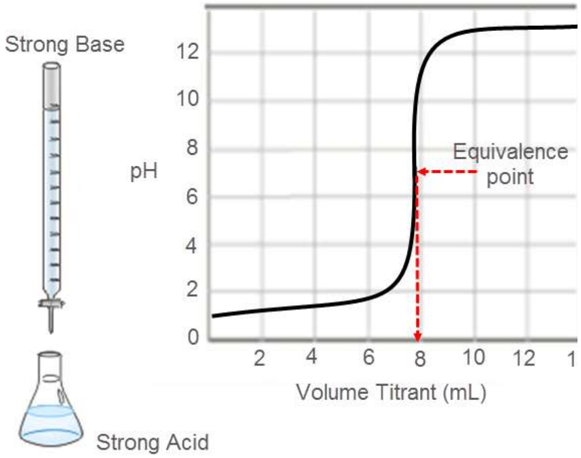
(B) This vertical inflection in the titration curve involves the complete exhaustion of the analyte.
The midpoint of (B) is called the **equivalence point** (also called the equimolar point, end point, or "neutralization" point).
The equivalence point occurs when the mol of titrant delivered equals the initial mol of analyte in the flask.

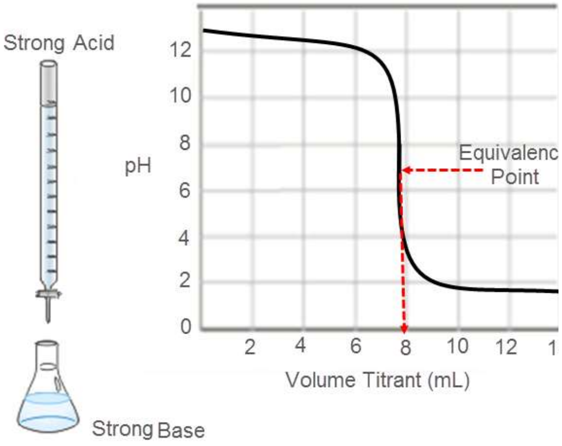
(C) Since the reaction of the titrant with the analyte was completed at the equivalence point, this horizontal segment of the graph will be dominated by the properties of the excess titrant.

The acid-base titrations are divided into two major types based on the strengths of the acids and bases involved.

Strong Acid and Strong Base

This titration is the simplest type of titration.





Net ionic reaction: $H^+ + OH^- \rightarrow H_2O$

The explanation is written primarily from the view of the strong acid as the analyte, but the same principles apply for a strong base as the analyte.

For strong acids the analyte (in the flask) starting pH would start at 1

The pH curve from 0 to 6 mL is relatively flat. There is **no buffering** because the conjugates merely act as spectator ions. Therefore, the half-equivalence point is irrelevant in strong acid-strong base titrations.

Because there is still strong acid present before the inflection, remaining acid keeps the pH low. Typically, the pH of a titration will only change 1.5 units in this region.

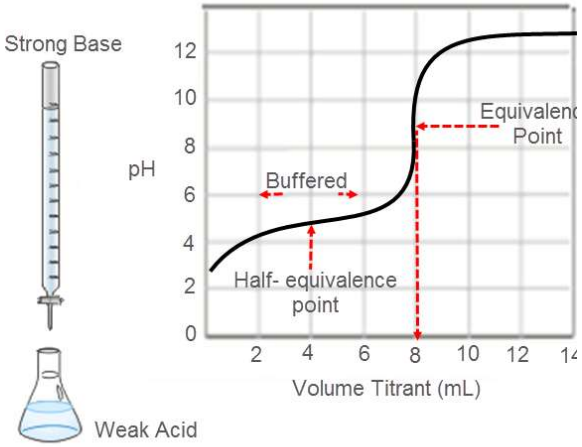
When the amount of acid is almost exhausted, the pH changes dramatically creating a vertical inflection point. The equivalence point is reached when the moles of acid originally in the analyte equals the moles of base from the titrant.
The **equivalence point is the middle of the vertical line.**
All the acid in the flask has been converted to water and spectator ions.
For a strong acid-strong base titration, the equivalence point will have a pH of 7.

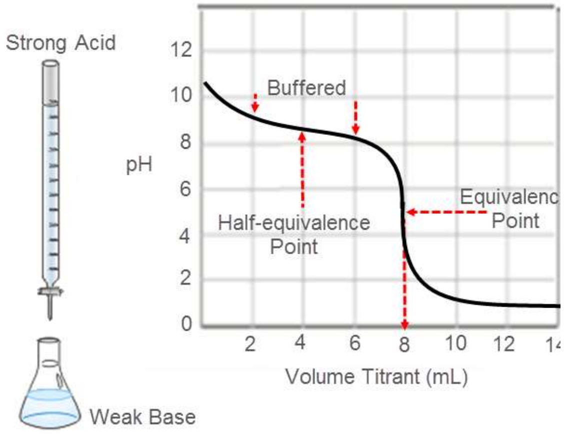
The stoichiometric volume of the titrant is determined from the volume of base at equivalence point on the curve. The concentration-volume equation is valid at the equivalence point since the mol of analyte reacted will equal the mol of titrant that was dispensed. Usually, the volume is given in mL so the use of millimol makes this calculation easier than converting the mL to liters.

$$C_{acid} \times V_{acid} = C_{base} \times V_{base}$$

The last horizontal section of the curve is due to the excess titrant of strong base which quickly raises the pH to 13.

Weak and Strong
This titration type is more complicated and will always be found on the AP Chem exam.





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

$B + H^+ \rightarrow HB^+$

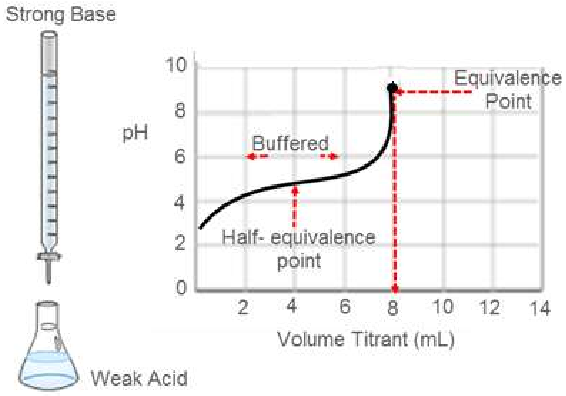
The explanation is written primarily from the view of the weak acid as the analyte, but the same principles apply for a weak base as the analyte. Be sure to understand both.

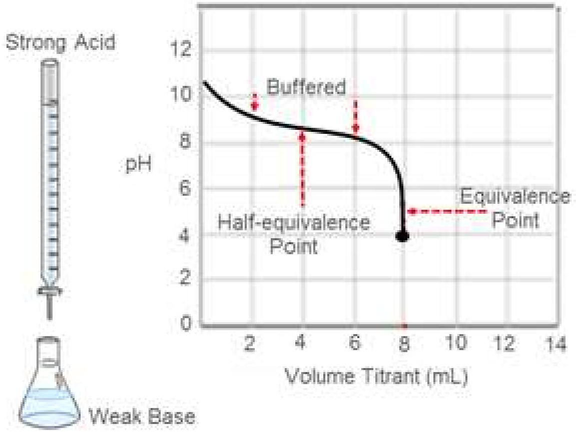
The pH of the weak acid solution usually starts around 3 and the pH of a weak base solution normally starts at around 10.

There is a quick, short increase in pH since the weak acid is reacting with the strong base, but after about 2 mL the amount of conjugate base produced in the reaction becomes significant creating a buffered solution that will resist changes in pH.

At the point where half the weak acid has reacted, the amount of weak acid, HA = A^-.
This is the **half-equivalence point** and the pH = pK_a.
Every AP Chemistry test has at least one problem that involves the values at a half-equivalence point.

Also, often the AP exam will use a pH curve that only goes to the equivalence point. So don't expect to see the full pH curve on a test.





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

$B + H^+ \rightarrow HB^+$

When the buffer has been exhausted, there will be a steep inflection in the curve.
The midpoint of the vertical inflection is the equivalence point of the titration. For a weak acid – strong base titration the pH of the equivalence point will be around 9.

At the equivalence point solution of a weak acid-strong base titration, all of the HA has reacted with the strong base.
The solution will be controlled by the equilibrium of the conjugate base of the weak acid, A^-. The pOH can be calculated from the concentration and the K_b of the weak acid's conjugate base.
At this point the neutralization equation can be used.

$$C_{acid} \times V_{acid} = C_{base} \times V_{base}$$

The equivalence point for a weak acid-strong base titration > 7 because of the conjugate base produced.

The equivalence point for a weak base-strong acid titration is < 7 because of the conjugate acid produced.

After the equivalence point, the extra added strong base will quickly elevate the pH to around 13 since the solution will be primarily the OH^-.

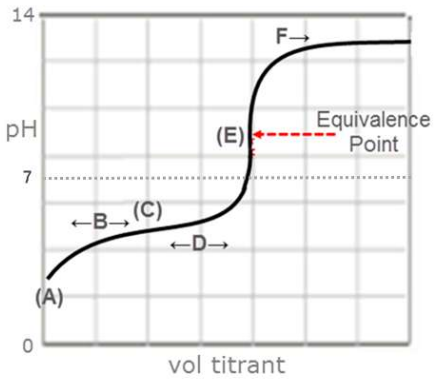
You should not try to memorize every particular of the titration sequence because there are too many items to memorize. Instead, you should apply the principles of acid base equilibria to understand the logical sequence of a titration.

Each titrant addition starts with a simple stoichiometric reaction → that then produces either an acidic or alkaline equilibrium ⇆. These equilibria expressions can be used to understand each equilibrium.

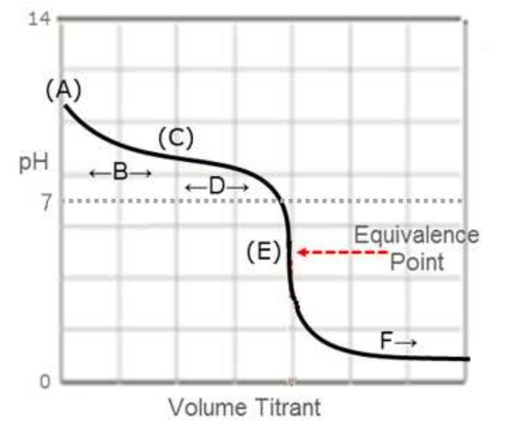
$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad K_b = \frac{[HB^+][OH^-]}{[B]}$$

Go through the two titration sequences and be sure that you understand every statement and equation.

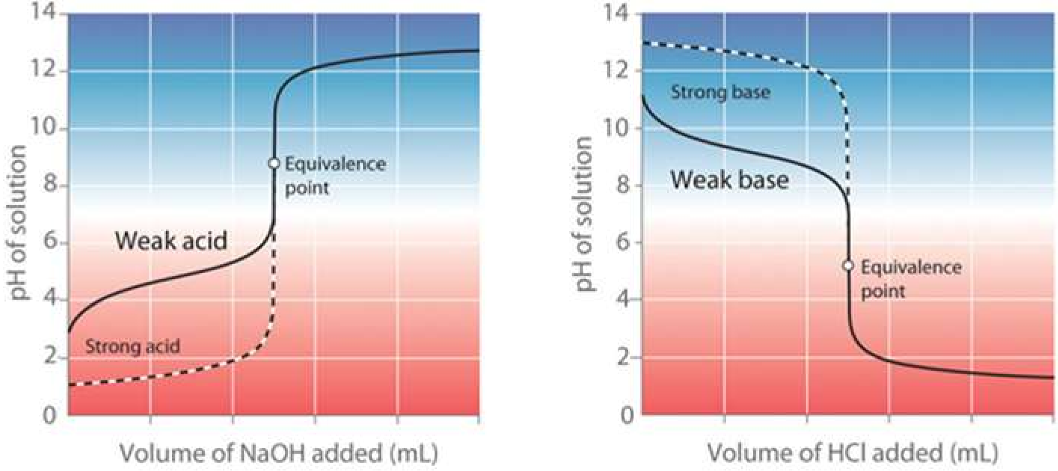
Weak-acid analyte, strong-base titrant: $HA + OH^- \rightarrow A^- + H_2O$.

(A)	Start, [HA] equilibrium determines pH.	$[H+] = \sqrt{K_a \times [HA]}$	
←B→	Buffering starts as HA changed to A^-.	$[HA] > [A^-]$	
(C)	**Half-equivalence point.** Perfect buffer, pH =pK_a	$[HA] = [A^-]$ $pH = pK_a$	
←D→	Buffering decreases after half equivalence.	$[HA] < [A^-]$	
(E)	**Equivalence point, HA titration is over:** HA completely converted to A^-. Only spectator ions and A^- are present. K_b of conjugate base and $[A^-]$ are used to find the slightly alkaline pH	$1.00 \times 10^{14} = K_a \times K_b$ $[OH^-] = \sqrt{K_b \times [A^-]}$	
F→	Excess strong base titrant, OH^-, determines pH	$pOH = -\log[OH^-]$	

Weak-base analyte, strong-acid titrant: $B + H^+ \rightarrow HB^+$

<table>
<tr><td>(A)</td><td>Start, [B] equilibrium determines pH.</td><td>$[OH^-] = \sqrt{K_b \times [B]}$</td><td rowspan="6"> </td></tr>
<tr><td>←B→</td><td>Buffering starts as B changes to HB^+.</td><td>$[B] > [HB^+]$</td></tr>
<tr><td>(C)</td><td>Half-equivalence point.
Perfect buffer,
$pH = pK_a$ of HB^+
$14.0 = pK_a + pK_b$
$pOH = pK_b$</td><td>$[B] = [HB^+]$
$pOH = 14.00 - pH$
$pOH = pK_b$</td></tr>
<tr><td>←D→</td><td>Buffering decreases after half-equivalence.</td><td>$[B] < [HB^+]$</td></tr>
<tr><td>(E)</td><td>Equivalence point, titration is over:
B completely converted to HB^+.
Only spectator ions and conjugate acid are present.
K_a of conjugate base and $[HB^+]$ are used to find the mildly acidic pH.</td><td>$1.00 \times 10^{14} = K_a \times K_b$
$[H^+] = \sqrt{K_a \times [HB^+]}$</td></tr>
<tr><td>F→</td><td>Excess strong acid titrant, H^+, determines pH</td><td>$pH = -\log[H^+]$</td></tr>
</table>

These two titration graphs show the contrast between strong vs strong and weak vs strong titrations.

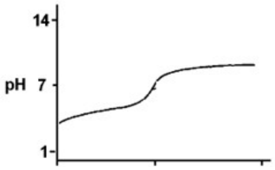


acid titrated with strong base **base titrated with strong acid**

From the **half-titration points** in these curves:

Weak Acid titration: pH halfway to the equivalence point is 4.7. So, the pK_a of the weak acid is 4.7.
Weak Base titration: pH halfway to the equivalence point is 9.2. So, the pK_b of the weak base is 4.8 because the pOH = 14.0-9.2.

The titration of a weak acid and weak base is rarely done because the changes in pH are small.



16.5 Acid-Base Indicators

An acid-base titration can be done with an indicator that changes color near the equivalence point. An indicator must be selected that changes color in the pH range of the vertical inflection of the titration. Because the vertical inflection segment spans a small mL range, the equivalence point (also called the endpoint) will be a well-defined volume.

Indicators are weak Brønsted acid-base conjugate pairs that change color on gaining or losing protons.

[HA color 1] € H^+ + [A^- color 2]

In a low pH (high [H^+]) solution, the HA form of the indicator dominates. Le Châtelier shift ← will force the concentration of HA to predominate. **[HA color 1]** , **H^+** + [A^- color 2]	In a high pH solution, the A^- form of the indicator dominates. High pH solution therefore low [H^+] Le Châtelier shift → will force the A^- to predominate. [HA color 1] H^+ + **[A^- color 2]**

At the indicator's half-equivalence point, the concentrations of the two colors are equal and the indicator is ready to switch colors. The half-equivalence point is reached when the pH is equal to the pK_a of the indicator.

$$[H^+] = K_a \times \frac{[\cancel{\text{HA color1}}]}{[\cancel{\text{A}^- \text{ color2}}]} \qquad \text{pH} = \text{p}K_a$$

Bottom line: An indicator changes color at its pK_a.
Because indicators are weak acids with different strengths, they have different pK_a's.

	pH													
Indicator	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Bromocresol green pK_a = 4.0 Color change pH ≈ 4	Yellow HA			..pK_a = 4..		Blue A^-								
Litmus pK_a = 7 Color change pH ≈ 7	Pink HA						..pK_a =7...		Blue A^-					
Phenolphthalein pK_a= 9.7 Color change pH ≈ 10	Clear HA								..pK_a=10..		Magenta A^-			

Indicators are used to find the equimolar or equivalence point (endpoint) of a titration. To have an indicator that signals the endpoint of the titration by changing color, you must find an indicator that has a pK_a at the equivalence point pH for the type of acid-base titration.

Titration type	Equimolar (endpoint) pH and also the pK_a of the indicator to be used
strong acid-strong base	7
strong acid-weak base	6-5
weak acid-strong base	8-9
weak acid-weak base	use pH meter

Polyprotic Acids

Polyprotic acids are covered in Chapter 15, but the AP Chemistry curriculum emphasizes the pH curve as a way of explaining polyprotic acids, so I have included it in this summary.

Polyprotic acids are often used in buffers since they have more than one acid form and accompanying conjugate base.

This is a typical polyprotic titration curve of a triprotic acid.

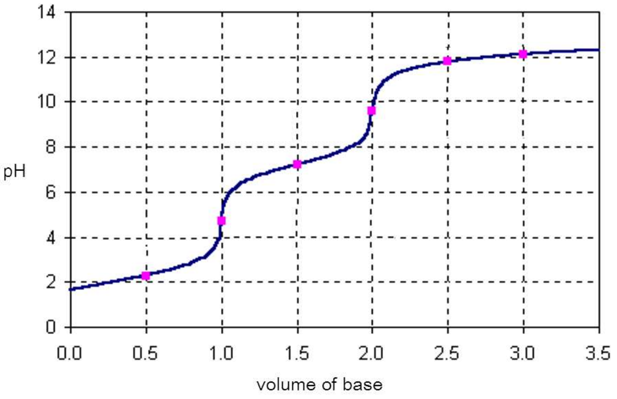
The midpoints of the flat sections are half-equivalence points indicating the pK_a of each.

$H_3A \leftrightarrows H^+ + H_2A^-$ K_{a1} $pK_{a1} \approx 2$

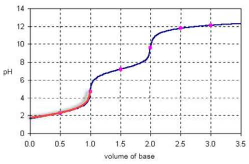
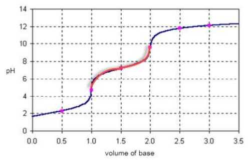
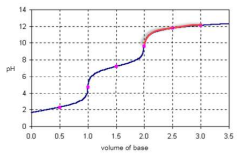
$H_2A^- \leftrightarrows H^+ + HA^{2-}$ K_{a2} $pK_{a3} \approx 7$

$HA^{2-} \leftrightarrows H^+ + A^{3-}$ K_{a3} $pK_{a3} \approx 12$

The midpoints of the vertical inflections are endpoints where each proton of the polyprotic acid is completely removed. Usually, the third proton of a polyprotic acid has such a small K_a that the third part of the curve is hard to discern.



The stages in the titration of a weak triprotic acid, H_3A. You will not be asked to calculate concentrations, but you must be able to identify the dominant species at each point in the titration.

Volume of base	Stage of titration	Species present in significant concentrations	
0	start of titration	H_3A	
0.5	$H_3A + OH^- \rightarrow H_2A^- + H_2O$ 1st half-equivalence point	$[H_3A] = [H_2A^-]$	
1.0	1st equimolar point End of first proton titration	$[H_2A^-]$	
1.5	$H_2A^- + OH^- \rightarrow HA^{2-} + H_2O$ 2nd half-equivalence point	$[H_2A^-] = [HA^{2-}]$	
2.0	2nd equimolar point	$[HA^{2-}]$	
2.5	$HA^{2-} + OH^- \rightarrow A^{3-} + H_2O$ 3rd half-equivalence point	$[HA^{2-}] = [A^{3-}]$	
3.0	Third equivalence point	A^{3-}	

You should be able to distinguish the sections of a polyprotic acid titration and know which species are present at the key parts of the titration.

16.6 Solubility Equilibria was covered in the last unit.

16.7 Separation of Ions by Fractional Precipitation – not part of AP Chem

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16.8 The Common Ion Effect and Solubility was covered in the last unit.

16.9 pH and Solubility is not part of AP Chem.

16.10 The Complex Ion Equilibria and Solubility was covered in the last unit.

16.11 Application of Solubility Product Principle to Qualitative Analysis – not part of AP Chem.