# AP* Chemistry
# Buffers Made Easy
## (At least as easy as they are going to get!)

There are many ways to solve buffer problems. Some folks prefer using simply the equilibrium expression, some prefer Henderson-Hasselbalch and some I've converted to my way, which is probably closer to the latter than the former. Some of the methods are more time intensive than others. Never lose sight of the fact that your students need a method that works for THEM. This method should be reliable and quick since they will always be under a time crunch! After moderate success with every method I could find, this handout presents the approach I've found the most student-friendly. Is it the method WE learned? NO! If *you've* had trouble teaching buffers, or your *students* have had trouble working buffer problems, give this a try….

First, we need to know what a buffer is, what it does, and how it does it. A buffer is just a case of the common ion effect.

**IS**: A buffer is a solution of a weak acid or base and its salt [which is its conjugate].

**DOES**: A buffer resists a change in pH.

**HOW IT WORKS**: Since a buffer consists of both an acid or base and its conjugate which is its complement, an acid and a base are present in all buffer solutions. If a small amount of strong acid is added to the buffer, there is a base component ready and waiting to neutralize the "invader".

There are a few background concepts/skills at which students need to be proficient before any method of solving buffer problems becomes effective:

- Students must know the conjugate A/B concept to be successful at buffer problems. This means they understand that HA has A⁻ as it's conjugate and that NaA is not only the salt, but that any soluble salt releases the conjugate
- $pH = -\log[H^+]$
- $K_a \times K_b = K_w$
- Realize that any titration involving a weak A/B is a buffer problem. If I titrate HA with NaOH, then as soon as the first drop splashes into the container, I've made NaA⁻ which promptly dissociates into A⁻

I use one and only one formula to solve buffer problems, this lessens student [and in my case, teacher] confusion! Here it is:

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

If acid is added to the buffer, simply add acid to the numerator AND subtract the same quantity from the base since it was self-sacrificing and neutralized the acid. If base is added, simply add the base to the denominator and subtract from the numerator. *Add or subtract in moles NOT molarity! Moles = M ×V*

When equal concentrations (or moles) of Acid and Base are present [which occurs at the ½ equivalence point of a titration] the ratio of acid to base equals ONE and therefore, the pH = p$K_a$. IF you are asked to construct a buffer of a specific pH and given a table of $K_a$'s, choose a $K_a$ with an exponent close to the desired pH and use equal concentrations of the acid and base.

Let's try it! Here's a common calculate the pH of a buffer before and after an "invader" is added. Convert to moles when doing the adding and subtracting! The $K_a$ of formic acid is $1.8 \times 10^{-4}$

**Exercise 1**

Calculate the pH of 0.500 L of a buffer solution composed of 0.50 $M$ formic acid and 0.70 $M$ sodium formate before and after adding 10.0 mL of 1.00 $M$ HCl.

**PREPARING BUFFER SOLUTIONS:**

Use 0.10 $M$ to 1.0 $M$ solutions of reagents & choose an acid whose $K_a$ is near the [$H_3O^+$] concentration we want. The p$K_a$ should be as close to the pH desired as possible. Adjust the ratio of weak A/B and its salt to fine tune the pH.

**Exercise 2**

Using an acetic acid\sodium acetate buffer solution, what ratio of acid to conjugate base will you need to maintain the pH at 5.00? Explain how you would make up such a solution.

It is the relative # of moles of acid/CB or base/CA that is important since they are in the same solution and share the same solution volume.

This allows companies to make concentrated versions of buffer and let the customer dilute--this will not affect the # of moles present--just the dilution of those moles.

What if you're given a $K_b$?

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**Exercise 3**

A buffered solution contains 0.25 $M$ NH$_3$ ( $K_b = 1.8 \times 10^{-5}$) and 0.40 $M$ NH$_4$Cl.

a) Calculate the pH of this solution.

b) Calculate the pH when 0.10 mol of gaseous HCl is added to 1.0 L of the buffered solution.

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**Exercise 4**

A chemist needs a solution buffered at pH 4.30 and can choose from the following list of acids and their soluble salt:

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.  hypochlorus acid  $K_a = 3.5 \times 10^{-8}$

Calculate the ratio of A/B required for each system to yield a pH of 4.30.  Which system works best?

## ACID-BASE TITRATION CURVES

Only when the acid AND base are both strong is the pH at the equivalence point 7. Any other conditions and you get to do a nasty equilibrium problem. It's really a stoichiometry problem with a limiting reactant. The "excess" is responsible for the pH

Weak acid + strong base ☞ eq. pt. > pH 7

Strong acid + weak base ☞ eq. pt. < pH 7

There is a distinction between the equivalence point and the end point. The end point is when the indicator changes color. If you've made a careful choice, the equivalence point, when the number of moles of acid = number of moles of base, will be achieved at the same time.

**Exercise 5**
For the titration of 50.0 mL of 0.200 $M$ $HNO_3$ with 0.100 $M$ NaOH calculate the pH of the solution at the following selected points of the titration:
a) NO NaOH has been added:




b) 10.0 mL of NaOH has been added:




c) 20.0 mL (total as opposed to additional) of NaOH has been added:





d) 50.0 mL (total) of NaOH has been added:





e) 100.0 mL (total) of NaOH has been added:





f) 200.0 mL (total) of NaOH has been added:

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**FIVE POINTS OF INTEREST ALONG A TITRATION CURVE** for weak acids/bases:

1. The pH before the titration begins. Treat as usual, the acid or base in the flask determines the pH. If weak, a RICE table is in order.

2. The pH on the way to the equivalence point. You are in the "land of buffer" as soon as the first drop from the buret makes a splash and reacts to form the salt. Whatever is in the burette is the "added" part. Use $\left[H^+\right] = K_a \dfrac{\left[\text{Acid}\right]}{\left[\text{Base}\right]}$ to solve for the hydrogen ion concentration and subsequently the pH. Either the acid or the base [whichever is in the burette] starts at ZERO.

3. The pH at the midpoint of the titration (½ equivalence point): $\left[H^+\right] = K_a \dfrac{\left[\text{Acid}\right]}{\left[\text{Base}\right]}$ on the way *to* the equivalence point as explained above; once the midpoint is reached, $[H^+] = K_a$ since ½ of the acid or base has been neutralized, AND the resulting solution in the beaker is composed of the half that remains AND the salt. That means the A/B term is a big tall ONE so, it follows that pH = p$K_a$.

4. The pH *at* the equivalence point.—you are simply calculating the pH of the *salt*, all the acid or base is now neutralized [to salt + water!]. Write the hydrolysis reaction as the "R" of your RICE table. [Examples follow the fifth point of interest...]

5. The pH beyond the equivalence point—it's stoichiometry again with a limiting reactant. Calculate the *molarity* of the EXCESS and solve for either pH directly (excess $H^+$) or pOH (excess $OH^-$) and subtract it from 14 to arrive at pH. Be sure to track the total volume when calculating the *molarity*!

## LEARNING TO WRITE SALT HYDROLYSIS REACTIONS

Recall that when quantities of acid and base react, a neutralization reaction takes place and the products of such a reaction are salt and water. The trouble is that not all salts are neutral. However, reasoning through the pH of a salt is *easy* as is writing the subsequent hydrolysis reaction. Ponder the following points:

- "Hydrolysis" translates into "water splitting" but the salt is also split. The rest of this will be much easier if you think of $H_2O$ as HOH and as a reactant. Essentially, a hydrolysis reaction is the reverse of a neutralization reaction and is written in net ionic form for all *soluble* salts.
- IF a strong base is reacted with a weak acid, "Strong wins!" and the salt is basic, thus $OH^-$ forms as a product.
- IF a strong acid is reacted with a weak base, "Strong wins!" and the salt is acidic, thus $H^+$ forms as a product.
- The "Strong" portion of the acid or base is source of the "Spectator" ion.
- The remaining ion (or neutral molecule) is the reactant that reacts with the water.

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**Example 1** Write the hydrolysis reaction for the salt, NaCN.

Explanation: First, recognize NaCN as a salt if that information is not given—the polyatomic ion is a dead give away! Next, ask yourself which acid reacted with which base to generate the salt in the first place?

Which base? NaOH.   Which acid? HCN.

Now, ask yourself: Is the base strong or weak? NaOH, strong.  Is the acid strong or weak? HCN, weak.  "Strong wins!", so it is a basic salt, AND "Strong is also the Spectator."  So, sodium ion is not in the net ionic hydrolysis equation, leaving $CN^-$ as the reacting species.  Ah, you are ready to write the hydrolysis reaction.

Start the same way every time you try to write a hydrolysis reaction…draw the arrow in the center of your answer space!

$$\rightarrow$$

It's a hydrolysis reaction, water is a reactant and splits into $H^+$ and $OH^-$, so write it as HOH until you get the hang of this process.  Your reaction looks like this so far:

$$+ \quad HOH \quad \rightarrow$$

Recap what you now know:  NaCN is a <span style="color:red">basic</span> salt.  Since it is basic, $OH^-$ is a product. Your reaction improves…

$$+ \quad HOH \quad \rightarrow \quad OH^-$$

More knowledge: <span style="color:red">$Na^+$ is a spectator</span> (since "Strong, Spectator"—it's an alliteration, get it? Strong and Spectator both start with an "S".) leaving <span style="color:red">$CN^-$ as the other reactant</span>. Your reaction improves yet again…
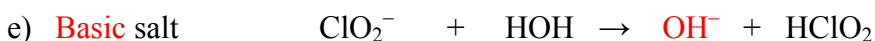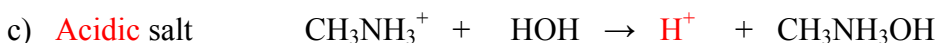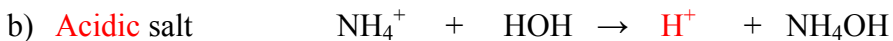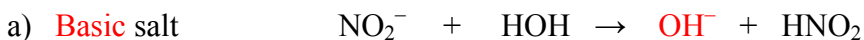
$$CN^- \quad + \quad HOH \quad \rightarrow \quad OH^-$$

Now, think…think…think.  IF HOH released $OH^-$ as a product, then $H^+$ is left to react with the negative cyanide ion.  Your final improvement to the reaction finishes it off…

$$CN^- \quad + \quad HOH \quad \rightarrow \quad OH^- \quad + \quad HCN$$
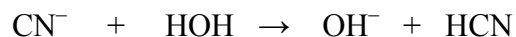
Why is this such a big deal?  A hydrolysis reaction is what you must plop into your RICE table to solve for the pH (or pOH) of an acid-base titration where *either* participant is weak. BECAUSE, at the equivalence point *moles acid = moles base = moles salt formed*.  Just be sure and calculate the molarity of the salt by tracking the total volume before putting its concentration into the rice table.

**Example 2** Write the hydrolysis reactions for the following salts:

    a) $KNO_2$
    b) $NH_4NO_3$
    c) $CH_3NH_3Cl$
    d) $NaClO_2$

    a) <span style="color:red">Basic</span> salt          $NO_2^- \ + \ HOH \ \rightarrow \ $<span style="color:red">$OH^-$</span>$ \ + \ HNO_2$

    b) <span style="color:red">Acidic</span> salt         $NH_4^+ \ + \ HOH \ \rightarrow \ $<span style="color:red">$H^+$</span>$ \ + \ NH_4OH$

    c) <span style="color:red">Acidic</span> salt       $CH_3NH_3^+ \ + \ HOH \ \rightarrow \ $<span style="color:red">$H^+$</span>$ \ + \ CH_3NH_3OH$

    e) <span style="color:red">Basic</span> salt          $ClO_2^- \ + \ HOH \ \rightarrow \ $<span style="color:red">$OH^-$</span>$ \ + \ HClO_2$

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**Exercise 6**

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a very weak acid ($Ka = 6.2 \times 10^{-10}$) 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

a) after 8.00 mL of 0.100 $M$ NaOH has been added.

b) at the halfway point of the titration.

c) at the equivalence point of the titration.

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## CHOOSING INDICATORS FOR TITRATIONS

Choose and indicator with a $K_a$ near that of the acid you're titrating AND whose color changes strongly at the equivalence point. Those blasted "e" words! moles acid equal moles base at the equivalence point...the color changes at the end point. Choose your indicator wisely, and the two coincide!

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**Exercise 7**
Use table 15.8 to decide which indicator would be best to use in the titration of ammonia with hydrochloric acid.

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**Exercise 8**
Bromthymol blue has a $Ka$ value of $1.0 \times 10^{-7}$, is yellow in its HIn form and blue in its In⁻ form. Suppose we put a few drops of this indicator in a strongly acidic solution. If the solution is then titrated with NaOH, at what pH will the indicator color change first be visible?

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Shall we try this with some retired AP questions?
 [Go to the *AP Buffers Free Response Questions* handout.]