Buffers

- Buffers are exceptionally important in biology. For example, our blood pH is precisely controlled by a buffer involving the bicarbonate (HCO_3^-) ion.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

A. The Common-Ion Effect

- Consider the following ionization of a weak acid:

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

- What happens if we added a strong acid (source of H^+, a *common ion*) to the solution already in equilibrium?
    - The reaction quotient Q will be larger than K_a, so the system shifts to the left to re-establish equilibrium. *i.e.* the presence a common ion = less HA ionization

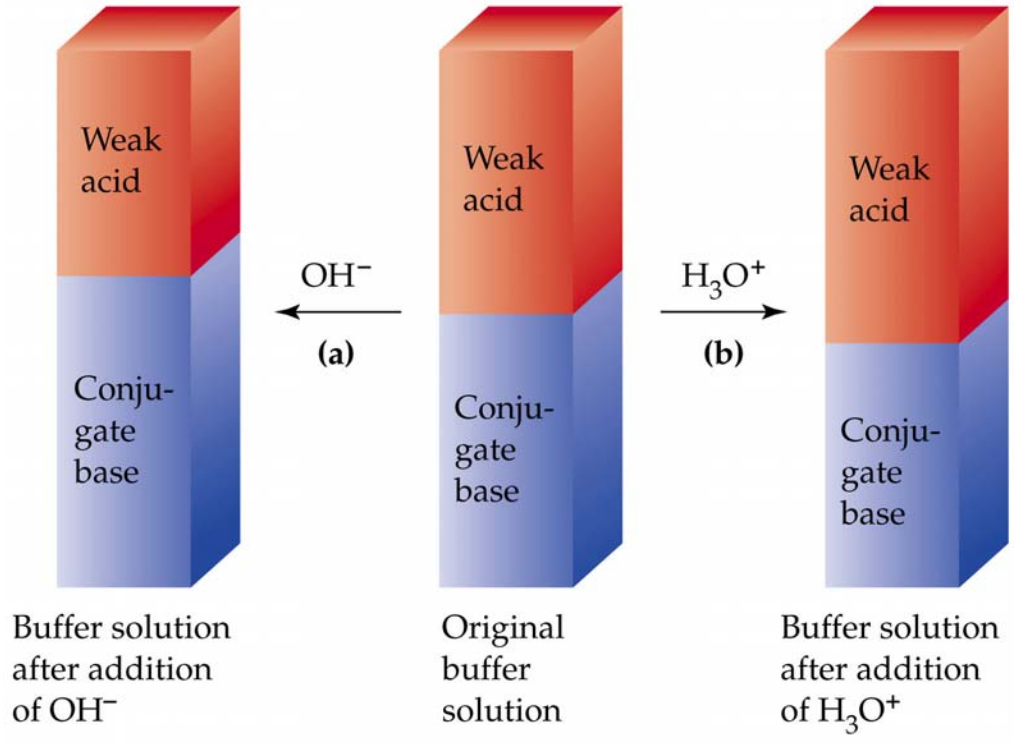
- Example: What is the pH of a solution containing 0.20 M acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.05 M HCl? What is the % ionization of acetic acid?

B. Buffers

- In the last example, we added a strong acid and a weak acid together (the common ion was H^+).
- What if we had a solution of *approx equal amounts* of both weak acid (HA) and its conjugate base (as salt, *e.g.* NaA)?
- Under these circumstances, we could have a buffer solution. Buffers are solutions that are able to resist drastic changes in pH upon the addition of strong acid or base.

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

  - If we have enough A^-, the reaction could use up any strong acid that is added (by shifting to the left). If we have enough HA, it could shift to the right and replace the H^+ that is used by the addition of strong base



- Buffers therefore must have both the *weak acid* and its conjugate base (or a weak base and its conjugate acid). A weak acid alone is not a buffer, because there aren't appreciable quantities of the conjugate base.
- Buffers cannot be made from a strong acid (or strong base) and its conjugate. This is because they ionize completely!
- It is important to be able to recognize buffer solutions! Once recognized, their calculations are typical of equilibria.
- Mixing equal volumes of which of the following gives a buffer?
    - 0.5 M $NaHCO_3$ and 0.5 M Na_2CO_3
    - 0.5 M HCl and 0.5 M NaCl
    - 0.5 M acetic acid and 0.5 M sodium acetate
    - 0.5 M NH_3 and 0.5 M NH_4Cl
    - 0.5 M H_2SO_4 and 0.5 M $NaHSO_4$
- Buffers can also be made by starting with just weak acid and then converting a portion of that weak acid via neutralization with a strong base. *e.g.* mixing same volumes of 1.0 M acetic acid with 0.5 M sodium hydroxide (this makes 0.5 M acetate)
- Or, we could start with 1.0 M sodium acetate and add 0.5 M hydrochloric acid (this makes 0.5 M acetic acid).

C. Calculating the pH of Buffer Solutions

- Buffer calculations are quite easy! This is because the equilibrium concentration of HA and A^- are approximated to be equal to the initial amounts present.
- Example: A solution is made by dissolving 0.20 mol CH_3COOH and 0.10 mol CH_3COONa a total volume of a litre. What is the pH of the solution? ($K_a = 1.8 \times 10^{-5}$)
    - Buffers made from a weak acid and its conj base will be on the acidic side of the pH scale

- This assumption that x is negligible is true because ionization is suppressed by the large amounts of conjugate based present (common ion effect!).
- So, in any buffer, all we have to look at are the initial concs!

- Thus, for any buffer consisting of a weak acid and its conjugate base, the concentration of H^+ can be calculated as

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

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]}$$

- How about dilution? If we dilute a buffer with pure water, the pH of a buffer does not change.
  - This is because the two concentrations correspond to the same volume, so the volumes cancel out

$$[H^+] = K_a \times \frac{(\text{mol acid}) \div V}{(\text{mol conj base}) \div V}$$

$$\boxed{[H^+] = K_a \times \frac{(\text{mol acid})}{(\text{mol conj base})}}$$

  - So when mol acid = mol conj base, the concentration of $H^+ = K_a$. At the midpoint of a titration, pH = pK_a.

- Buffers can also be made from weak bases and their conjugate acids. In this case, the pH will be on the basic side.

$$K_b = \frac{[OH^-][\text{conj acid}]}{[\text{base}]}$$

$$[OH^-] = K_b \times \frac{[\text{base}]}{[\text{conj acid}]}$$

$$[OH^-] = K_b \times \frac{(\text{mol base})}{(\text{mol conj acid})}$$

- Example: 25.0 g of NH_4Cl was added to 1.50 L of 0.25 M NH_3(aq). What is the pH of the solution? ($K_b = 1.8 \times 10^{-5}$)

- As previously mentioned, we could also prepare a buffer by having only a weak acid/base species and then partially neutralizing it.
- Example: What is the pH of the solution formed by mixing 0.1 mol HCl with 0.2 mol NH_3 in 1.0 L water? ($K_b = 1.8 \times 10^{-5}$)
    - Realize that the HCl will convert exactly 0.1 mol ammonia into ammonium chloride by neutralization

- Example: How many mL of 2.0 M HCl must be added to 1.00 L of a 0.100 M solution of sodium formate to produce a buffer with pH 4.00? (K_a formic acid = 1.9×10^{-4})

- Always be alert and make sure that you're dealing with buffers before doing buffer calculations.
- Example: A solution is made by adding 25.0 mL of a 0.123 M solution of the weak base CH_3NH_2 to 35.0 mL of a 0.213 M solution of HCl. What is the resulting pH?

- Example: What is the pH of a solution made by mixing 500 mL of 1.00 M HCN and 1.50 L of 0.250 M NaOH, and then diluting the entire solution to 3.00 L? (K_a HCN = 4.0×10^{-10})

D. Buffering Against H^+ or OH^- Addition

- Suppose we have an acetate buffer consisting of 1.0 mol acetic acid and 1.0 mol sodium acetate in 1.0 L water.
    - At this point, $K_a = [H^+] = 1.8 \times 10^{-5}$ (so pH = 4.74)
- What happens if we add 100 mL of 1.0 M HCl? (0.10 mol)
    - We convert the same amount of acetate to acetic acid
    - The pH does not change appreciably, and this is the whole purpose of a buffer. (Adding 0.10 mol HCl to 0.1 L pure water alone would cause the pH to drop to 1).

- What happens if we add 100 mL of 1.0 M NaOH (0.10 mol) to the original solution?
    - We convert the 0.10 mol of acetic acid to acetate

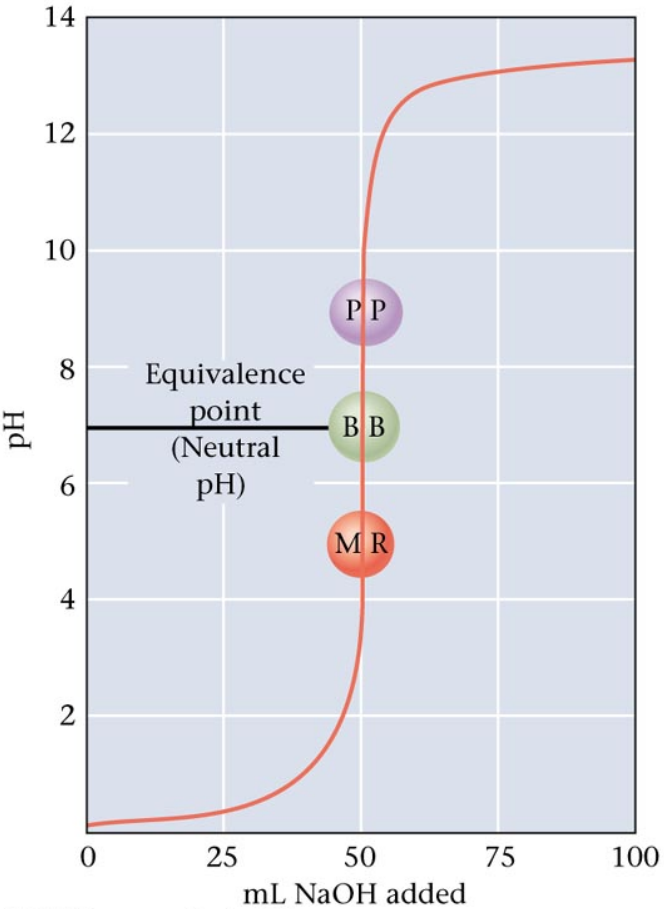
E. Titration Curves

- In the previous chapter, we had discussed the equivalence point of a titration. We considered three cases:
  - Strong acid + strong base — EP = neutral
  - Weak acid + strong base — EP = basic
  - Weak base + strong acid — EP = acidic
- We will now examine the shapes of these titration curves, which plot the pH against the amount of strong a/b added.

1. Strong acid + strong base

- Suppose we titrate HCl and NaOH. At equivalence point, the pH is neutral (NaCl does not cause hydrolysis).

- Recall that buffers can't be made from strong acids and strong bases. So, near the EP, the pH rises quickly (from about 4 to 10) when one drop of base is added.
- pH measured by pH meter
- If we want to use an indicator for the titration, it must change colour within the quick rise. (Different indicators change color at different pH)

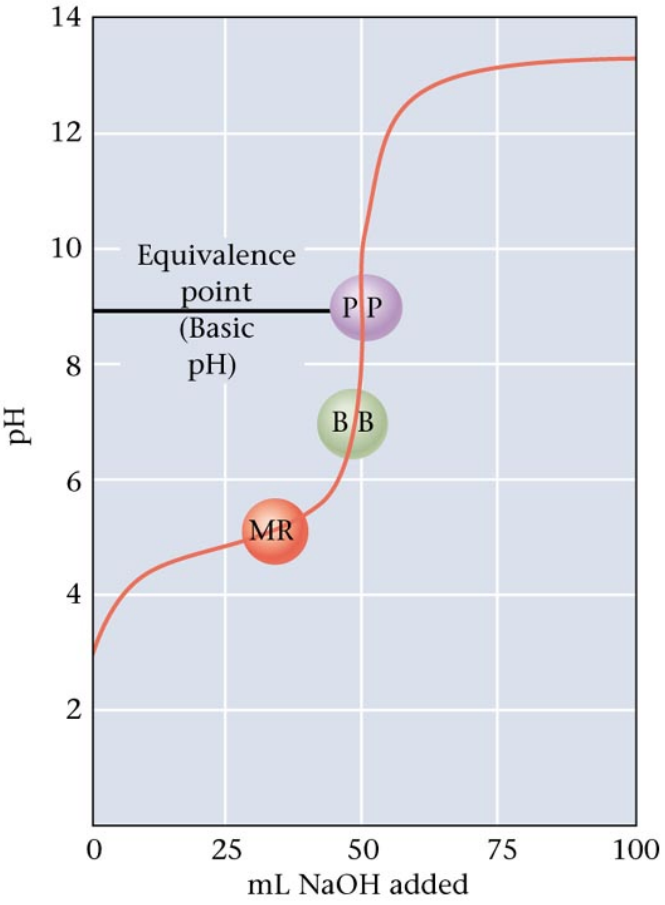


2. Weak acid + strong base

- Suppose we titrate 50 mL of 1.0 M acetic acid with 1.0 M NaOH.

$$CH_3COOH + OH^- \rightarrow H_2O + CH_3COO^-$$

- As we are neutralizing acid, we are making its conjugate base. After the addition of 25 mL NaOH, we have a buffer where the ratio of conjugate base to acid is 1:1.
- At this midpoint, pH = pK_a
- Near this region, the pH changes gradually because of the buffering action (note the $pK_a \pm 1$ usefulness on plot)



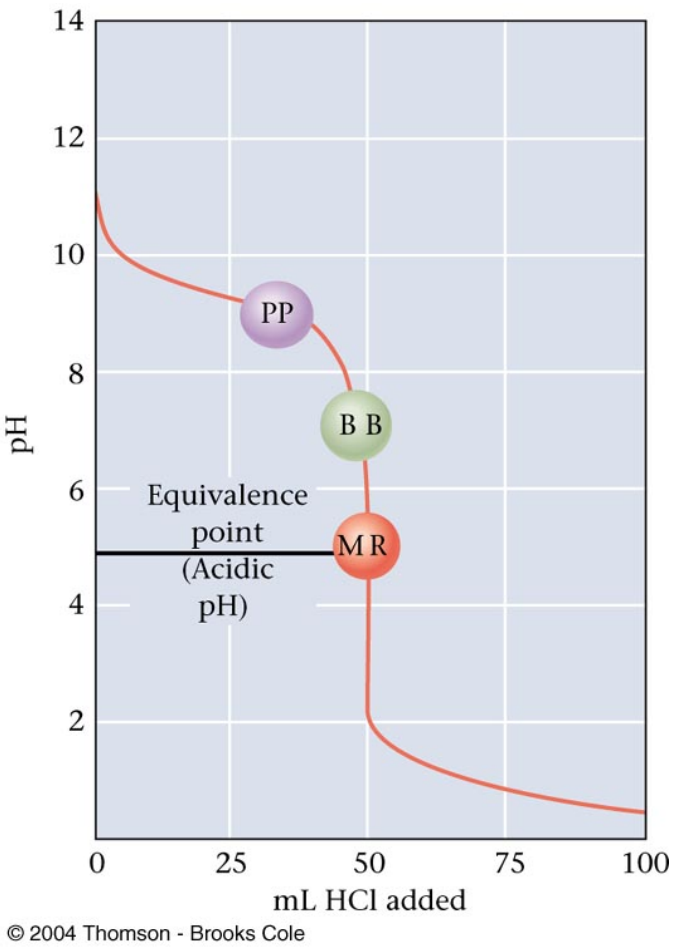
- At EP, the solution is basic because only acetate is present. Acetate hydrolyzes to acetic acid and OH^-.
- The quick rise corresponds to only about 1 pH only, so the choice of indicator is more important (phenolphthalein works; methyl red or bromothymol blue change color too early).

3. Weak base + strong acid titration

- Suppose we titrate 50 mL of 1.0 M NH_3 with 1.0 M HCl

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

- As we are neutralizing NH_3, we are making its conjugate acid. After the addition of 25 mL HCl, we have a buffer where the ratio of conjugate acid to base is 1:1.
- At this midpoint, pH = pK_b
- Near this region, the pH changes gradually because of the buffering action (note the $pK_b \pm 1$ usefulness on plot)



- At EP, the solution is acidic because only NH_4^+ is present. It ionizes to NH_3 and H^+.

- Here, we see that that methyl red would be a good indicator. (Since we're titrating from high to low pH, colour disappears!)

F. Indicators for Titrations

- We've already seen how we could select an indicator: we choose one that changes colour within the rise corresponding to the equivalence point. Recall that different indicators will change colours at different pH values; *e.g.* methyl red at pH 5
- Now the chemical side: what happens when an indicator changes colour? An indicator is simply an organic weak acid that has different colours in the unionized and ionized forms. They are used in tiny quantities and do not affect the titration.
- Since they are weak acids, we can write the equilibrium

$$HIn \rightleftharpoons In^- + H^+ \qquad K_{a(indicator)} = \frac{[H^+][In^-]}{[HIn]}$$

- With most indicators, the coloured form is the conjugate base of the indicator, In^-. At low pH, most of the indicator is in the colourless HIn form. At high pH, In^- predominates.
- If $K_{a(indicator)} = [H^+]$, half the indicator is ionized, so $[In^-] = [HIn]$. Therefore, the indicator is in the process of changing colour when $K_{a(indicator)} = [H^+]$.
- When do we want this change to happen? At equivalence point! Thus, we want an indicator with $K_{a(indicator)}$ equal to the $[H^+]$ at the equivalence point.

Ideal indicator: $pK_{a(indicator)}$ = pH at equivalence point

- Interestingly, our eyes first detect colour changes when the ratio of $\frac{[In^-]}{[HIn]} = 0.1$ and this occurs when the $[H^+]$ is 10 times greater than $K_{a(indicator)}$.
  - *i.e.* when pH is exactly one unit less than $pK_{a(indicator)}$

- Our eyes then stop noticing colour changes when the ratio of $\frac{[In^-]}{[HIn]} = 10$ is reached, which occurs when $[H^+]$ is one-tenth the value of $K_{a(indicator)}$.
  - *i.e.* when pH is exactly one unit greater than $pK_{a(indicator)}$

- So, we want an indicator that has a pK_a value within one unit of the pH at equivalence point.
- Some common indicators (look back at the titration curves and see why they are useful)

	HIn colour	**In^- colour**	**pK_a**
Methyl Red	Red	Yellow	5
Bromothymol Blue	Yellow	Blue	7
Phenolphthalein	Colourless	Pink	9