# Titration curves

A **titration** is a procedure for carrying out a chemical reaction between two solutions by the controlled addition from a buret of one solution (the titrant) to the other, allowing measurements to be made throughout the reaction. For a reaction between an acid and a base, a titration is useful for measuring the pH at various points throughout the reaction.

A **titration curve** is a graph of the pH as a function of the amount of titrant (acid or base) added.

Strong Acid-Strong Base Titrations

Here is an example of a titration curve, produced when a strong base is added to a strong acid. This curve shows how pH varies as 0.100 M NaOH is added to 50.0 mL of 0.100 M HCl.
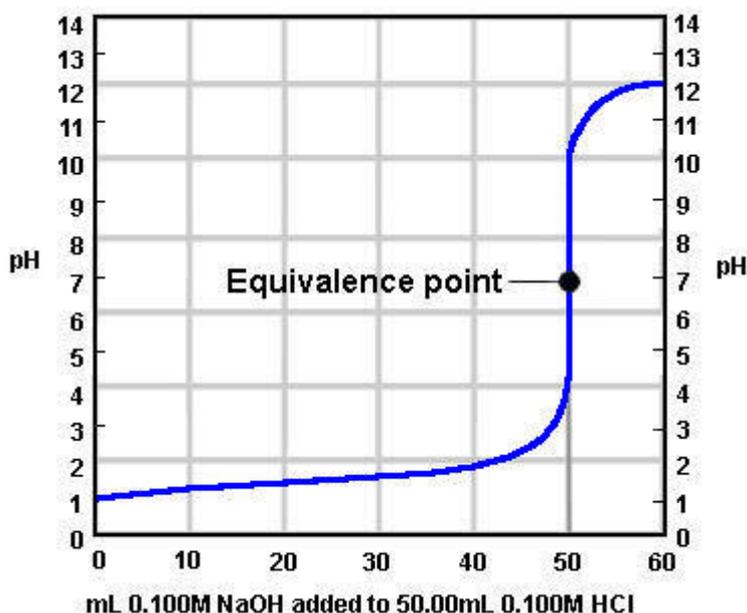
The **equivalence point** of the titration is the point at which exactly enough titrant has been added to react with all of the substance being titrated with no titrant left over. In other words, at the equivalence point, the number of moles of titrant added so far corresponds exactly to the number of moles of substance being titrated according to the reaction stoichiometry. (In an acid-base titration, there is a 1:1 acid:base stoichiometry, so the equivalence point is the point where the moles of titrant added equals the moles of substance initially in the solution being titrated.)

Notice that the pH increases slowly at first, then rapidly as it nears the equivalence point. Why?

Learning Goal 25

Calculate the pH at any point, including the equivalence point, in an acid-base titration.

At the equivalence point, the pH = 7.00 for strong acid-strong base titrations. However, in other types of titrations, this is not the case.

EXAMPLE:

What is the pH when 49.00 mL of 0.100 M NaOH solution have been added to 50.00 mL of 0.100 M HCl solution?

Because it is a strong acid-base reaction, the reaction simplifies to:

$$H^+ (aq) + OH^- (aq) \longrightarrow H_2O (l)$$
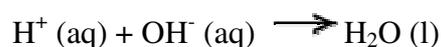
The original number of moles of H^+ in the solution is:

$$50.00 \times 10^{-3} \text{ L} \times 0.100 \text{ M HCl} = 5.00 \times 10^{-3} \text{ moles}$$

The number of moles of OH^- added is :

$$49.00 \times 10^{-3} \text{ L} \times 0.100 \text{ M OH}^- = 4.90 \times 10^{-3} \text{ moles}$$
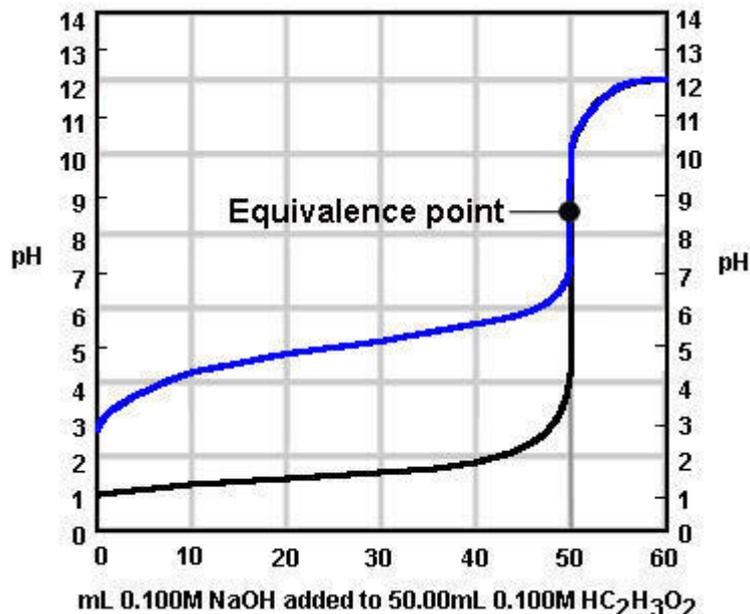
Thus there remains:

$$(5.00 \times 10^{-3}) - (4.90 \times 10^{-3}) = 1.0 \times 10^{-4} \text{ moles H}^+ (aq)$$

The total volume of solution is 0.04900 L + 0.05000 L = 0.09900 L

$$[H^+] = \{1.0 \times 10^{-4} \text{ moles} / 0.09900 \text{ L} \} = 1.0 \times 10^{-3} \text{ M}$$
$$pH = 3.00$$

Titrations Involving a Weak Acid or Weak Base

Titration curve of a weak acid being titrated by a strong base:

mL 0.100M NaOH added to 50.00mL 0.100M $HC_2H_3O_2$

Here, 0.100 M NaOH is being added to 50.0 mL of 0.100 M acetic acid.

There are three major differences between this curve (in blue) and the one we saw before (in black):

1. The weak-acid solution has a higher initial pH.

2. The pH rises more rapidly at the start, but less rapidly near the equivalence point.

3. The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS : The equivalence point for a weak acid-strong base titration has a pH > 7.00.

For a strong acid-weak base or weak acid-strong base titration, the pH will change rapidly at the very beginning and then have a gradual slope until near the equivalence point. The gradual slope results from a buffer solution being produced by the addition of the strong acid or base, which resists rapid change in pH until the added acid or base exceeds the buffer's capacity and the rapid pH change occurs near the equivalence point.

EXAMPLE:

What is the pH when 30.0 mL of 0.100 M NaOH have been added to 50.0 mL of 0.100 M acetic acid?

STEP 1: Stochiometric calculation:

The original number of moles of $HC_2H_3O_2$ in the solution is :

$$50.0 \times 10^{-3} \text{ L} \times 0.100 \text{ M} = 5.00 \times 10^{-3} \text{ moles } HC_2H_3O_2$$

Similarly, there are 3.00×10^{-3} moles of OH⁻ due to the NaOH solution.

The reaction goes to completion:

$$OH^- (aq) + HC_2H_3O_2 (aq) \longrightarrow C_2H_3O_2^- (aq) + H_2O (l)$$

	OH⁻	HC₂H₃O₂	C₂H₃O₂⁻
INITIAL	3.00×10^{-3} mol	5.00×10^{-3} mol	0
CHANGE	-3.00×10^{-3} mol	-3.00×10^{-3} mol	$+3.00 \times 10^{-3}$ mol
FINAL	0	2.00×10^{-3} mol	3.00×10^{-3} mol

The total volume is 80.0 mL.

We now calculate the resulting molarities :

$$[HC_2H_3O_2] = \{ 2.00 \times 10^{-3} \text{ mol } HC_2H_3O_2 / 0.0800 \text{ L} \} = 0.0250 \text{ M}$$
$$[C_2H_3O_2^-] = \{ 3.00 \times 10^{-3} \text{ mol } C_2H_3O_2^- \} / 0.0800 \text{ L} \} = 0.0375 \text{ M}$$

STEP 2: Equilibrium calculation, using simplification:

$$K_a = \{ [H^+][C_2H_3O_2^-] / [HC_2H_3O_2] \} = 1.8 \times 10^{-5}$$
$$[H^+] = \{ K_A [HC_2H_3O_2] / [C_2H_3O_2^-] \} = \{ (1.8 \times 10^{-5})(0.0250) / (0.0375) \} = 1.2 \times 10^{-5} \text{ M}$$

$$pH = -\log(1.2 \times 10^{-5}) = \textbf{4.92}$$

Titration curve of a weak base being titrated by a strong acid:

mL 0.100M HCl added to 50.00mL 0.100M NH₃
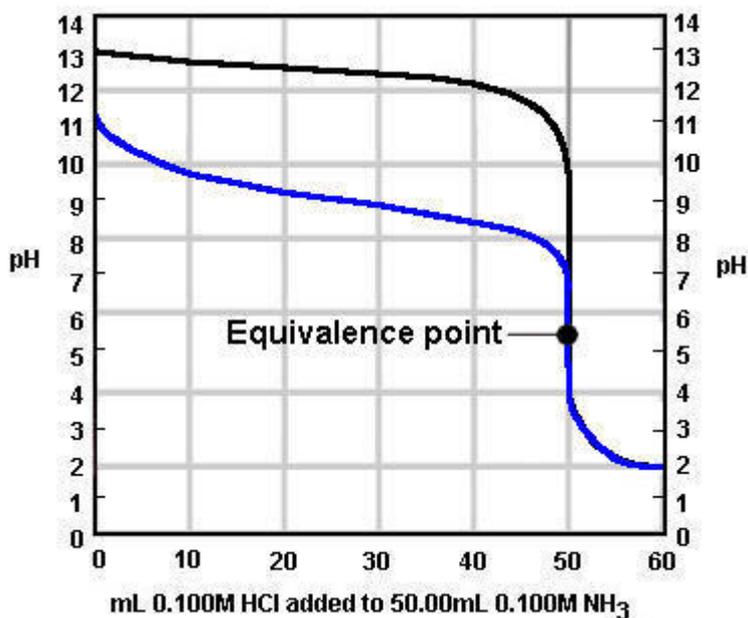
Here, 0.100 M HCl is being added to 50.0 mL of 0.100 M ammonia solution.

As in the weak acid-strong base titration, there are three major differences between this curve (in blue) and a strong base-strong acid one (in black): (Note that the strong base-strong acid titration curve is identical to the strong acid-strong base titration, but flipped vertically.)

1. The weak-acid solution has a lower initial pH.

2. The pH drops more rapidly at the start, but less rapidly near the equivalence point.

3. The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS : The equivalence point for a weak base-strong acid titration has a pH < 7.00.

Titrations of Polyprotic Acids

An example of a polyprotic acid is H_2CO_3 which neutralizes in two steps:

$$H_2CO_3 \text{ (aq)} + OH^- \text{ (aq)} \longrightarrow H_2O \text{ (l)} + HCO_3^- \text{ (aq)}$$

$$HCO_3^- \text{ (aq)} + OH^- \text{ (aq)} \longrightarrow H_2O \text{ (l)} + CO_3^{2-} \text{ (aq)}$$

The titration curve for these reactions will look like this, with two equivalence points.
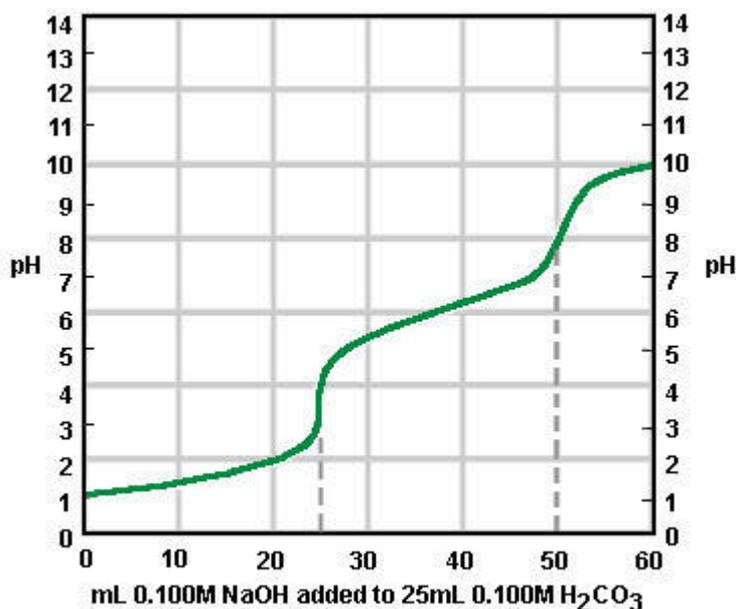
Uses of Titrations

Learning Goal 26
Use titration data or a titration curve to calculate reaction quantities such as the concentration

The most common use of titrations is for measuring unknown concentrations. This is done by titrating a known volume of the unknown solution with a solution of known concentration (where the two react in a predictable manner) and finding the volume of titrant needed to reach the equivalence point using some method appropriate to the particular reaction. Then, the volume and concentration of titrant can be used to calculate the moles of titrant added, which, when used with the reaction stoichiometry, gives the number of moles of substance being titrated. Finally, this quantity, along with the volume of substance being titrated, gives the unknown concentration.

For acid-base titrations, the equivalence point can be found very easily. A pH meter is simply placed in the solution being titrated and the pH is measured after various volumes of titrant have been added to produce a titration curve. The equivalence point can then be read off the curve.

EXAMPLE:

If 80.0 mL of 0.200 M NaOH are required to reach the equivalence point in a titration of 50.0 mL of hydrofluoric acid, what is the concentration of the hydrofluoric acid?

The neutralization reaction goes to completion:

$$HF + OH^- \longrightarrow F^- + H_2O$$

The number of moles of NaOH added was:

$$n_{NaOH} = [NaOH] \times V_{NaOH}$$
$$n_{NaOH} = 0.200 \text{ M} \times 80.0 \text{ mL}$$
$$n_{NaOH} = 16 \text{ mmol}$$

Since each NaOH produces 1 OH^-, $n_{OH} = n_{NaOH} = 16$ mmol

From the 1:1 stoichiometry between HF and OH^-, $n_{HF} = n_{OH} = 16$ mmol

So, the concentration of the original hydrofluoric acid solution was:

$$[HF] = n_{HF} / V_{HF}$$
$$[HF] = 16 \text{ mmol} / 50 \text{ mL}$$
$$[HF] = 0.320 \text{ M}$$

In the same way, knowing the equivalence point can also be used to calculate other unknown quantities of interest in acid base reactions, such as concentration of titrant or volume of solution being titrated, provided that enough other information is known to perform the calculations.

Acid-base indicators

Certain chemicals have the special property of appearing one colour when in a solution of one pH and a different colour when in a solution of a different pH. Such chemicals are known as **acid-base indicators**, or simply as **indicators** because, when a few drops of indicator are added to a solution, the colour of the solution serves as an indication of its pH.

Most acid-base indicators are simply weak acids with a protonated (acidic) form that is one colour and a deprotonated (basic) form that is a different colour. Like all weak acids, they dissocate according to their K_a value. For a generic indicator HIn,

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq) \quad so \quad K_a = \{ [H^+][X^-] / [HX] \}$$
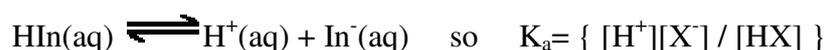
Converting this equation into the form of the Henderson-Hasselbalch equation, we get

$$pH = pK_a + \log([In^-]/[HIn])$$

This shows us that the pH of the solution and the pK_a of the indicator together determine the ratio of In^- to HIn. Since the two species are different colours, this ratio in turn determines the overall colour of the solution.

EXAMPLE:

Consider the indicator phenol red, which has a yellow HIn form, a red In^- form, and a K_a of $5.0x10^{-8}$. Now imagine that a few drops of this indicator are added to a solution of pH 2.3. What colour would the solution be?

To figure this out, we need the above equation:

$$pH = pK_a + \log([In^-]/[HIn])$$
$$pH = -\log(K_a) + \log([In^-]/[HIn])$$
$$2.3 = 7.3 + \log([In^-]/[HIn])$$
$$-5.0 = \log([In^-]/[HIn])$$
$$1.0x10^{-5} = [In^-]/[HIn]$$

Thus, the ratio of In^- to HIn is 1 to 100 000. Since In^- is red and HIn is yellow, there are 100 000 yellow molecules in solution for every red molecule. For coloured species, this is an enormous ratio, and the red molecules will be undetectable. Thus, the solution will appear yellow.

EXAMPLE:

Imagine we have a solution of acetic acid of unknown concentration. How could we measure the concentration of the solution using only indicators?

STEP 1: Use the indicators to estimate the pH of the solution

To do this, we remove a small amount of the solution and add a drop of indicator. Based on the resulting colour of the solution, we will know whether the pH is below, within or above the pH range in which the indicator changes colour. We could just do this with several random indicators and hope that they will provide enough information for us. However, we will use a more systematic approach.

Since we do not know the pH of our solution, an indicator that changes colour in the middle of the pH range is a good one to start with since it will split the pH range into roughly equal parts, each significantly smaller than the whole range. Let's say we add a drop of phenol red and the solution turns yellow. Since phenol red is yellow in solutions below pH 6.6, we know that the pH of our acetic acid solution is below 6.6.

Now we can narrow down the pH range with another indicator. A good choice would be one that will further narrow down the pH range that we know contains the solution's pH. For example, let's say we add a drop of methyl red to a new sample of the solution and it turns red. Now we know that the pH is below 4.8, which gives us more information than we had before. In contrast, if we had used alizarin yellow, it would have turned yellow, telling us that the pH is below 10.1. Since the phenol red told us that the pH is below 6.6, the alizarin yellow test gives us no new information.

Using the results of the phenol red and methyl red tests, our third indicator needs to have a colour-change range even lower than 4.8. Suppose we use thymol blue, and it turns yellow. This tells us that the pH of the solution is above 2.8 AND that it is below 8.0. (Since thymol blue changes colour twice, the colour tells us where the pH of the solution lies relative to *both* of the pK_a's of thymol blue.) So, we now know that the pH is between 2.8 and 4.8.

Suppose we now use methyl orange as a final indicator and it turns yellowish orange. This is an intermediate colour for methyl orange, meaning that the pH is within its colour-change range of 3.2 to 4.4. Since it is closer to the yellow end of the range than the red end, we can assume that the pH is in the upper half of the range, namely between 3.8 and 4.4.

Unfortunately, none of our indicators has a range with one endpoint within this range. Thus, additional tests will not give us any more conclusive information, so we have locallized the pH as much as possible.

STEP 2: Convert the pH range into a range of H^+ concentrations:

Using $[H^+] = 10^{-pH}$, we find that a pH range of 3.8 to 4.4 corresponds to an H^+ concentration range of 4.0×10^{-5}M to 1.6×10^{-4}M.

STEP 3: Use an I.C.E. table and the K_a of acetic acid to convert the H^+ concentration range to a range of acetic acid concentrations. 4.0×10^{-5}M:

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
INITIAL	x	0	0
CHANGE	-4.0×10^{-5}M	$+4.0 \times 10^{-5}$M	$+4.0 \times 10^{-5}$M
EQUILIBRIUM	$(x-4.0 \times 10^{-5})$M	4.0×10^{-5}M	4.0×10^{-5}M

$$K_a = \{ \ [H^+][C_2H_3O_2^-] \ / \ [HC_2H_3O_2] \ \}$$

$$1.8 \times 10^{-5} = \{ \ (4.0 \times 10^{-5})(4.0 \times 10^{-5}) \ / \ (x - 4.0 \times 10^{-5}) \ \}$$

$$x = 1.3 \times 10^{-4} M = [HC_2H_3O_2]$$

Similarly, an H^+ concentration of 1.6×10^{-4}M corresponds to an $HC_2H_3O_2$ concentration of 1.5×10^{-3}M.

So, the indicators have told us that the concentration of the acetic acid solution is between 1.3×10^{-4}M and 1.5×10^{-3}M.

Indicators and Titrations

Learning Goal 29
Explain how indicators are used in titrations and be able to choose an appropriate indicator for a given titration.

Indicators can also be used to track the pH in a titration, usually as a means of detecting the equivalence point of the titration.

Consider the titration of an acid with a base in which a few drops of indicator have been added to the acid being titrated. Initially, the pH of the acid will probably be low enough that the indicator is almost entirely in its acidic (HIn) form. As base is added the pH will increase, causing the indicator to change to its basic (In⁻) form, causing a visible colour change. The point in the titration at which the colour changes is known as the **endpoint** of the titration.

IMPORTANT POINT

The endpoint of a titration is NOT the same thing as the equivalence point. The equivalence point is a single point defined by the reaction stoichiometry as the point at which the base (or acid) added exactly neutralizes the acid (or base) being titrated. The endpoint is defined by the choice of indicator as the point at which the colour changes. Depending on how quickly the colour changes, the endpoint can occur almost instantaneously or be quite wide.

If an appropriate indicator is chosen such that the endpoint of the titration occurs at the equivalence point, then a colour change in the solution being titrated can be used as a signal that the equivalence point has been reached. The volume of titrant needed to reach the equivalence point can then be read, allowing us to calculate concentrations, volumes, K_a's etc. as described in the previous section.

Intuition may suggest that the endpoint of the titration will occur at the equivalence point if we choose an indicator whose pK_a is equal to the pH of the equivalence point. If such an indicator was chosen, the colour change would be half complete at the equivalence point. Unfortunately, it is very difficult to tell when the colour change is precisely half complete, making it difficult to precisely identify the equivalence point. Since it is easiest to tell when the colour first starts to change, we want the equivalence point to occur then.

EXAMPLE:

What is the best pK_a for the indicator if a strong acid is being titrated with a strong base? If a strong base is being titrated with a strong acid?

For a strong acid-strong base titration, the equivalence point occurs at pH 7.

When an acid is being titrated with a base, the first observable colour change will occur when the In^- to HIn ratio is approximately 1 to 10.

$$pH = pK_a + \log([In^-]/[HIn])$$
$$7 = pK_a + \log(1/10)$$
$$7 = pK_a - 1$$
$$8 = pK_a$$

When a base is being titrated with an acid, the first observable colour change will occur when the In^- to HIn ratio is approximately 10 to 1.

$$pH = pK_a + \log([In^-]/[HIn])$$
$$7 = pK_a + \log(10)$$
$$7 = pK_a + 1$$
$$6 = pK_a$$

So, we see that we actually want different indicators for the two titrations.

In practice, the first colour change does not necessarily have to happen right at the equivalence point. Since we only care about being able to use the colour change to detect when the equivalence point has been reached, the crucial requirement for choosing a good indicator is that it begins to change colour after the volume of titrant required to reach the quivalence point has been added.

For example, a strong acid-strong base has a very sharp equivalence point, meaning that a very large change in pH occurs due to the addition of a very small amount of titrant, often a single drop. Therefore, any pH in this range will be reached after the addition of the same number of drops. This means that any indicator that starts to change colour in this range will signal equally well that the equivalence point has been reached. It also means that the pH range over which the indicator changes colour will likely be passed in a single drop of titrant, resulting in a very sharp endpoint.

A titration involving a weak acid or base, however, has a less steep equivalent point with a less dramatic pH change. Thus, there is a smaller range of pH's that will be passed at the same time as the pH as the equivalence point, meaning that the chosen indicator must begin to change colour closer to the equivalence point than in a strong acid-strong base titration, and that the endpoint will be wider.

Here are the titrations of both a strong acid and a weak acid with a strong base, using methyl red and thymol blue as possible indicators.

mL 0.100M NaOH added to 50.00mL 0.100M HCl

mL 0.100M NaOH added to 50.00mL 0.100M $HC_2H_3O_2$
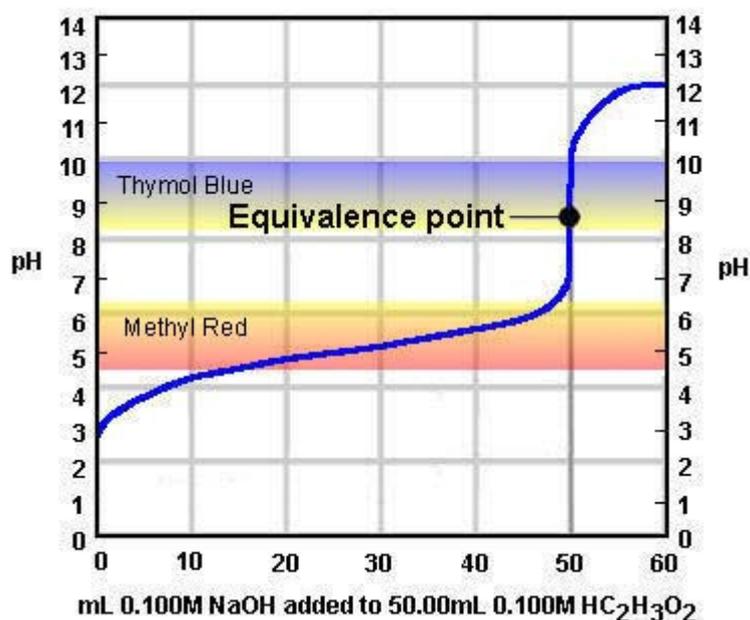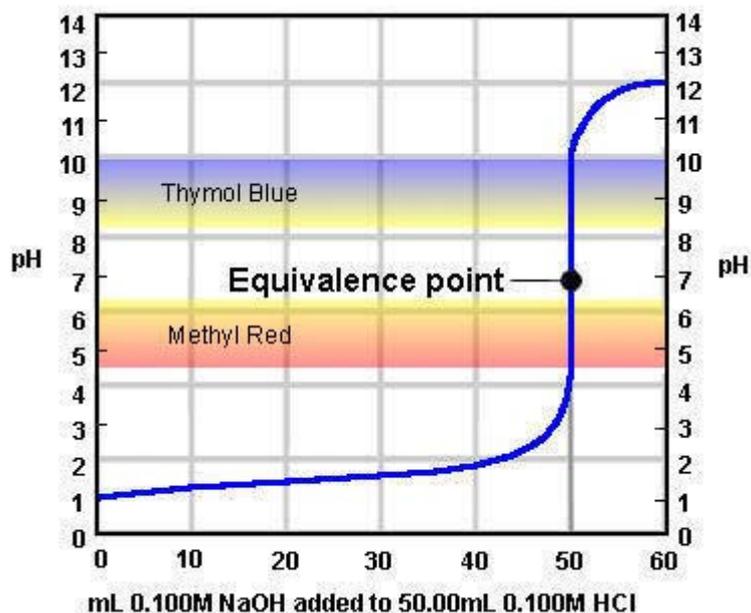
In the strong acid titration, both indicators begin to change colour at the equivalence point (50 mL of base) so both work equally well. In the weak acid titration, thymol blue changes colour at the equivalence point, but methyl red begins to change colour after only 15mL of base are added, which is far from the equivalence point, illustrating the importance of choosing an appropriate indicator.

In general, the faster the pH changes in the range where the indicator changes colour, the sharper the endpoint of the titration will be and the more different indicators will be suitable for the titration.

One limitation of using indicators to find the equivalence point of a titration is that the approximate pH of the equivalence point must be known in order to choose an indicator that will accurately locate the equivalence point. This means that if the approximate pH of the equivalence point is not known, it will be difficult to locate the equivalence point. However,

even if we do not know the pH of the equivalence point, we can get around this problem by using trial and error to choose the best indicator. To do this, we can repeat the titration several times with several different indicators, taking note of how sharp or wide the endpoints are- that is, how quickly the colour changes. Since the endpoint is sharpest when it is closest to the equivalence point, we can simply look for the indicator that gave the sharpest endpoint and assume that that one will be most accurate for finding the equivalence point.

Composition and Action of Buffered Solutions

Learning Goal 21
Describe how a buffer of a certain pH is made, and how it works to control pH.

Buffered solutions or **buffers** are solutions which resist a change in pH when small amounts of acid or base are added.

Buffers contain an acidic species to neutralize OH^- ions and a basic species to neutralize H^+ ions. However, these two species must be able to coexist in a solution, without completely neutralizing each other. Buffers are therefore made of weak acid-base conjugate pairs, such as $HC_2H_3O_2$ and $C_2H_3O_2^-$.

If we have a weak acid, HX, and its conjugate base, X^-, the following equilibrium occurs:

$$HX\ (aq) \rightleftharpoons H^+\ (aq) + X^-\ (aq)$$

For this reaction,

$$K_a = \{\ [H^+][X^-]\ /\ [HX]\ \}$$

If an amount of H^+ ions are added, the above reaction will shift to the left. This will cause the $[H^+]$ to decrease, to close to what it was before, and thus the pH will stay fairly constant.

If OH^- ions are added they will remove H^+ ions to form water, thus increasing the pH. However, the equilibrium reaction will shift to the right as H^+ ions are removed. The $[H^+]$ will therefore remain fairly constant, as will the pH.

The most effective buffering solutions are those which have similar concentrations of HX and X^-, because then the buffer has the capacity to absorb both acid and base, with the same effectiveness in either direction.

When choosing an appropriate conjugate acid-base pair to form a buffer at a specific pH, the most effective buffers have the desired pH within 1.0 of the conjugate acid's pKa.

Ways to make a buffer

Buffering Capacity and pH

The **buffering capacity** is the amount of acid or base a buffer can accept without the pH changing appreciably. The greater the amounts of the conjugate acid-base pair, the more resistant they are to change in pH.

If we solve the acid-dissociation-constant expression for $[H^+]$ we get:

$$[H^+] = K_a \{ [HX] / [X^-] \},$$

assuming that the amount of added acid or base is less than 5% of the conjugate acid / base molarity.

We can use this to determine the pH of a buffer:

We first take the negative log of both sides:

$$-\log [H^+] = -\log [K_a \{ [HX] / [X^-] \}] = -\log K_a - \log \{ [HX] / [X^-] \}$$

We know $-\log [H^+] = pH$ and $-\log K_a = pK_a$.

$$pH = pK_a - \log \{ [HX] / [X^-] \} = pK_a + \log \{ [X^-] / [HX] \}$$

In general:

$$\textbf{pH} = \textbf{pK}_a + \textbf{log \{ [base] / [acid] \}}$$

This is known as the **Henderson-Hasselbalch equation**.

Additions of Acids or Bases to Buffers

Learning Goal 22
Calculate the change in pH of a simple buffer solution, whose composition is known, caused by adding small amounts of strong acid or strong base.

EXAMPLE

A 1 L solution containing 0.100 moles of $HC_2H_3O_2$ *and 0.100 moles of* $C_2H_3O_2$ *forms a buffer solution, pH = 4.74. What is the pH after 0.020 moles of NaOH are added?*

STEP 1: Stoichiometry calculation:

The OH⁻ will react completely with the weak acid $HC_2H_3O_2$:

$$HC_2H_3O_2 \text{ (aq)} + OH^- \text{ (aq)} \longrightarrow H_2O \text{ (l)} + C_2H_3O_2^- \text{ (aq)}$$

	$HC_2H_3O_2$	OH^-	$C_2H_3O_2^-$
INITIAL	0.100 mol	0.020 mol	0.100 mol
CHANGE	-0.020 mol	-0.020 mol	+0.020 mol
FINAL	0.080 mol	0 mol	0.120 mol

STEP 2: Equilibrium calculation:

The solution contains the weak acid and its conjugate base. We shall therefore use their equilibrium equation, and create an I.C.E. table :

$$HC_2H_3O_2 \text{ (aq)} \rightleftharpoons H^+ \text{ (aq)} + C_2H_3O_2^- \text{ (aq)}$$
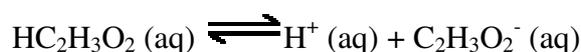
	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
Initial	0.080 M	0	0.120 M
Change	-x M	+x M	+x M
Equilibrium	(0.080 - x) M	x M	(0.120 + x) M

$$K_a = \{ [C_2H_3O_2^-][H^+] / [HC_2H_3O_2] \} = \{ (0.120 + x)(x) / (0.080 - x) \} = 1.8 \times 10^{-5}$$
$$1.8 \times 10^{-5} = \{ (0.120) \, x / (0.080) \}$$
$$x = [H^+] = 1.2 \times 10^{-5} \text{ M}$$
$$pH = -\log (1.2 \times 10^{-5}) = 4.92$$

Applications of Buffer Calculations

In many systems, such as biological applications, there is extreme sensitivity to minute pH changes. To study these systems, the pH must be controlled by a buffer that is effective within given limits. How does one determine what the buffer concentration is?

Learning Goal 23
Calculate the specific amounts of species necessary to make the buffer effective within given requirements.

EXAMPLE

What must the minimum concentration of $HC_2H_3O_3$ be in a one litre buffer solution of $HC_2H_3O_3$-$C_2H_3O_3^-$ (pH = 4.74) if the pH changes by less than 0.1 if 0.050 moles of HCl are added?

STEP 1: Stoichiometry calculation:

The amount of HCl added will react completely with the conjugate base, $C_2H_3O_3^-$:

$$C_2H_3O_3^- + H^+ \longrightarrow HC_2H_3O_3$$
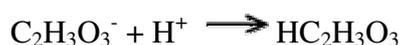
The pH of the buffered solution, 4.74, matches the pK_a of acetic acid, so from the Henderson-Hasselbach equation, we know that there are originally equal concentrations of acid and conjugate base, which we denote as x:

	$HC_2H_3O_3$	H^+	$C_2H_3O_3^-$
INITIAL	x mol	0.050 mol	x mol
CHANGE	+0.050 mol	-0.050 mol	-0.050 mol
FINAL	(x+0.050) mol	0 mol	(x-0.050) mol

Because there is one litre of solution, $[H_2H_3O_3] = (x + 0.050)$M and $[C_2H_3O_3^-] = (x - 0.050)$M.

STEP 2: Calculate the equilibrium concentration that will produce the desired pH:

Having added acid, the pH will decrease. However, the tolerance given is 0.1, so the lowest pH that the final solution can have is 4.64.

The hydronium concentration is thus:

$$[H^+] = 10^{-pH}$$
$$[H^+] = 10^{-4.64} = \mathbf{2.29 \times 10^{-5} \ M}$$

STEP 3: Equilibrium calculation:

I.C.E. table:

$$HC_2H_3O_3 \rightleftharpoons H^+ + C_2H_3O_3^-$$

	$HC_2H_3O_3$	H^+	$C_2H_3O_3^-$
INITIAL	(x+0.050)M	0M	(x-0.050)M
CHANGE	-2.29×10^{-5}M	$+2.29 \times 10^{-5}$M	$+2.29 \times 10^{-5}$M
EQUILIBRIUM	(x+0.050)M	2.29×10^{-5}M	(x-0.050)M

$$K_a = \{ [H^+][C_2H_3O_2^-] \} / [HC_2H_3O_2] = \{ (2.29\times10^{-5})(x-0.050) \} / (x+0.050) = 1.8\times10^{-5}$$
$$x = [HC_2H_3O_2] = 0.417M$$

Thus, the molarity of both $[HC_2H_3O_2]$ and $[C_2H_3O_2^-]$ must be equal to or greater than 0.417M to produce the required effectiveness.