Chapter 17

ACID-BASE EQUILIBRIA

(Part I)

The Common Ion Effect

- A phenomenon known as the ***common ion effect*** states that:

  When a compound containing an ion *in common* with an already dissolved substance (a weak electrolyte) is added to an aqueous solution at equilibrium, the equilibrium shifts to the left.

  The ionization of the weak electrolyte is being suppressed by adding the common ion to the solution.

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The Common Ion Effect

- A 1.0 L of 0.10 *M* solution of CH_3COOH.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Adding 0.050 mol of CH_3COONa:

$$CH_3COONa(aq) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

CH_3COO^- is a common ion

Addition

$$CH_3COOH(aq) \leftarrow H^+(aq) + CH_3COO^-(aq)$$

Le *Châtelier's principle*

Equilibrium is driven toward reactant.

The result is that fewer H^+ ions present.

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Equilibrium Calculation Involving Common Ion Effect

- Before adding the CH_3COO^- ions:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

1.0 L of 0.10 *M*

(*M*)	CH_3COOH	H^+	CH_3COO^-
Initial conc.	0.10	0	0
Change in conc.	- *x*	+ *x*	+ *x*
Equilibrium conc.	0.10 - *x*	*x*	*x*

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.10\ M - x} \approx \frac{x^2}{0.10\ M} = 1.8 \times 10^{-5}$$

$x = 1.34 \times 10^{-3}\ M$ $(1.34 \times 10^{-3} / 0.1) \times 100\% = 1.34\%$

Approximation is valid

$[H^+] = 1.34 \times 10^{-3}\ M$

pH = -log (1.34×10^{-3}) = 2.87

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Equilibrium Calculation Involving Common Ion Effect

Method I

- When 0.050 mol of CH_3COONa salt is added:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

We assume that adding 0.050 mol of CH_3COONa doesn't affect the volume

(*M*)	CH_3COOH	H^+	CH_3COO^-
Initial conc.	0.09866	1.34×10^{-3}	5.134×10^{-2}
Change in conc.	+ *y*	- *y*	- *y*
Equilibrium conc.	0.09866 + *y*	1.34×10^{-3} - *y*	5.134×10^{-2} - *y*

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(1.34\times10^{-3} - y)(5.134\times10^{-2} - y)}{0.09866 + y}$$

$y = 1.304 \times 10^{-3}$ *M*

$[H^+] = 1.34 \times 10^{-3}$ *M* – 1.304×10^{-3} *M* = 3.6×10^{-5} *M*

pH = -log (3.6×10^{-5}) = 4.44

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Equilibrium Calculation Involving Common Ion Effect

Method II

- Assuming both acetic acid and sodium acetate are dissolved in water at the same time:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

(*M*)	CH_3COOH	H^+	CH_3COO^-
Initial conc.	0.10	0	0.050
Change in conc.	- *x*	+ *x*	+ *x*
Equilibrium conc.	0.10 - *x*	*x*	0.050 + *x*

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(0.050 + x)}{0.10 - x} \approx \frac{(0.050)(x)}{0.10} = 1.8 \times 10^{-5}$$

x here is even smaller than the ionization without adding the common ion, so the approximation must be valid.

$x = 3.6 \times 10^{-5}$ *M*

$[H^+] = x = 3.6 \times 10^{-5}$ *M*

pH = -log (3.6×10^{-5}) = 4.44 ← pH is the same either way

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The Common Ion Effect

- <u>Exercise:</u>

  Which of the following when dissolved in aqueous NH_3 solution is (are) going to decrease the dissociation of NH_3?

  (a) $Ca(OH)_2$

  (b) HNO_2

  (c) CH_3COONa

  (d) NH_4NO_3

17.2

Buffer Solutions

- A ***buffer solution*** is the one that resists the change in its pH when small amounts of either H^+ or OH^- ions are added.

  Buffers are useful application of the *common ion effect*.

- Buffer solutions are important for:
  - Biological systems. (some enzymes can only function at a specific pH, pH of blood is always about 7.4, gastric “stomach” juices maintain a pH of about 1.5)
  - Chemical applications. (fermentation processes, dyes used in coloring fabrics, calibration for pH meters).

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Buffer Solutions

- A buffer solution can be:
  - a solution containing a weak acid and its conjugate base, or

    $CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$

    weak acid — *conjugate base*

    It is known as an *acidic* buffer solution and it maintains a pH value that is less than 7.

  - a solution containing a weak base and its conjugate acid.

    $NH_3\ (aq) + H_2O(l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

    weak base — *conjugate acid*

    It is known as a *basic* buffer solution and it maintains a pH value that is greater than 7.

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How Does a Buffer Solution Work?

- Consider a solution that is 1.0 *M* in acetic acid (CH_3COOH) and 1.0 *M* in sodium acetate (CH_3COONa).
  - When a small amount of a *strong acid (H^+)* is added, the following will happen:

Case I

1. The pH of the solution will go lower because of the addition of the H^+ ions, then
2. The acetate ions (CH_3COO^-) start consuming the H^+ ions and convert them to acetic acid.

   $CH_3COO^-\ (aq) + H^+\ (aq) \rightleftharpoons CH_3COOH\ (aq)$
3. As a result, the pH goes back close to its original value.
4. Also, $[CH_3COOH]$ increases and $[CH_3COO^-]$ decreases.

17.2

How Does a Buffer Solution Work?

- Consider again the same solution which is 1.0 *M* in acetic acid (CH_3COOH) and 1.0 *M* in sodium acetate (CH_3COONa).
  - When a small amount of a *strong base (OH^-)* is added, the following will happen:

Case II

1. The pH of the solution will go higher because of the addition of the OH^- ions, then
2. The acetic acid (CH_3COOH) consumes the OH^- ions and converts them to acetate ions.

   $$CH_3COOH\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H_2O(l)$$

3. As a result, the pH goes back close to its original value.
4. Also, $[CH_3COO^-]$ increases and $[CH_3COOH]$ decreases.

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Calculating the pH of a Buffer

- Exercise:

  What will be the change in the pH of a 1.0-L solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate when 0.1 mol of HCl is added? Assume that the change in the volume when HCl is added is too small.

  This solution is a buffer since it contains a weak acid and its conjugate base.

  First, we calculate the buffer pH before adding HCl.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

(*M*)	CH_3COOH	H^+	CH_3COO^-
Initial conc.	1.0	0	1.0
Change in conc.	- *x*	+ *x*	+ *x*
Equilibrium conc.	0.10 - *x*	*x*	1.0 + *x*

Continue on the next slide →

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$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(1.0+x)}{1.0-x} \approx \frac{(1.0)(x)}{1.0} = 1.8 \times 10^{-5}$$

Remember that the common ion effect suppresses the ionization of CH_3COOH (the forward reaction). Thus, the change in conc. (x) is assumed to be very small.

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

$pH = -\log(1.8 \times 10^{-5}) = 4.74$

- ***Second***, we calculate the pH after adding 0.1 mol of the strong acid HCl.

1.0 mol | 0.1 mol | 1.0 mol

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

1.0 mol + 0.1 mol | 0.0 mol | 1.0 mol – 0.1 mol

The equilibrium concentrations after adding 0.1 mol become:

(*M*)	CH_3COOH	H^+	CH_3COO^-
Initial conc.	1.1	0	0.9
Change in conc.	- *x*	+ *x*	+ *x*
Equilibrium conc.	0.11 – *x*	*x*	0.9 + *x*

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17.2

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(0.9+x)}{1.1-x} \approx \frac{(0.9)(x)}{1.1} = 1.8 \times 10^{-5}$$

$x = 2.2 \times 10^{-5}$ *M* => $[H^+] = x = 2.2 \times 10^{-5}$ *M*

$pH = -\log(2.2 \times 10^{-5}) = 4.66$ *(compared to 4.74 before adding HCl)*

- What do we conclude?

  There was a change in the pH of only 0.08 units.

  In our calculations for buffer solution we always treat *x* (the change in concentration of H^+) as a very small quantity because of the common ion effect that suppresses the weak acid to ionize and favors the backward reaction.

- Think about it.

  If we had added the 0.1 mol HCl to 1 L of pure water, the pH would have gone from 7.00 to 1.00.

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Henderson-Hasselbalch Equation

- For any buffer solution when a valid approximation is applied, its equilibrium expression is:

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

HA is the weak acid
A^- is the conjugate base

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

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

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

From H-H equation, when the concentrations of the weak acid and its conjugate base in a buffer are equal, its pH = its pK_a.
The slight change in the pH of the buffer is due to change in the concentrations of the weak acid and its conjugate base when small amounts of either H^+ or OH^- ions are added to the buffer.

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Henderson-Hasselbalch Equation

- Exercise:

  Calculate the pH of 2.0 L of a buffer that is 1.0 *M* in both acetic acid and sodium acetate after adding 0.15 mol of $Ca(OH)_2$.

2.0 mol	2 × 0.15 mol	2.0 mol
$CH_3COOH\,(aq)$ +	$OH^-\,(aq) \rightleftharpoons$	$CH_3COO^-\,(aq) + H_2O(l)$
2.0 mol – 0.30 mol	0.0 mol	2.0 mol + 0.30 mol

After OH^- ions are all consumed, there are 1.7 mol of CH_3COOH and 2.3 mol of CH_3COO^- ions in the buffer solution.

Applying H-H equation:

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log \frac{(2.3\text{ mol} / 2.0\text{ L})}{(1.7\text{ mol} / 2.0\text{ L})} = 4.87$$

The pH has increases by only 0.13 units.

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Buffer Solutions

- Compare the previous exercise with what happens when 0.3 mol of OH^- ions are added to 2.0 L of pure water instead of a buffer solution.

  $[OH^-]$ = 0.3 mol / 2.0 L = 0.15 *M*

  $K_w = [H^+]\,[OH^-]$

  $[H^+] = K_w / [OH^-] = (1 \times 10^{-14})/(0.15) = 6.7 \times 10^{-14}$ *M*

  $pH = -\log(6.7 \times 10^{-14}) = 13.17$

The pH has increased by 13.17 – 7.00 = 6.17 units.

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Buffer Capacity

- A buffer solution performs well when it has the *capacity* to resist a big change in a pH. So any buffer solution has to satisfy the following condition:

$$pK_a + 1 \;\geq\; pH \;\geq\; pK_a - 1$$

  The above condition is satisfied only when the log term in the H-H equation is within the range:

$$10 \;\geq\; \frac{[\text{conjugate base}]}{[\text{weak acid}]} \;\geq\; 0.1$$

- This enables us to prepare the proper buffer solution with the desired pH.

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Preparation of a Buffer

- Choose a weak acid with a pK_a that is close to the pH you need.

  The pK_a value should be roughly within the range of pH ± 1.

pH = 4.5

5.5 > pK_a > 3.5

- Obtain the needed ratio of $\frac{\text{[conjugate base]}}{\text{[weak acid]}}$

Weak Acid	K_a	pK_a
HF	7.1×10^{-4}	3.15
HNO_2	4.5×10^{-4}	3.35
HCOOH	1.7×10^{-4}	3.77
C_6H_5COOH	6.5×10^{-5}	4.19
CH_3COOH	1.8×10^{-5}	4.74
HCN	4.9×10^{-10}	9.31
C_6H_5OH	1.3×10^{-10}	9.89

Possible acids

By choosing C_6H_5COOH acid:

$$pH = pK_a + \log \frac{\text{[conjugate base]}}{\text{[weak acid]}}$$

$$\log \frac{\text{[conjugate base]}}{\text{[weak acid]}} = 0.31$$

$$\frac{\text{[conjugate base]}}{\text{[weak acid]}} = 2.04$$

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Preparation of a Buffer

- Convert the ratio to molar quantities to prepare the solution.

$$\frac{\text{[conjugate base]}}{\text{[weak acid]}} = 2.04$$

Dissolve 2.04 mol of C_6H_5COONa (*conjugate base*) and 1.00 mol of C_6H_5COOH (*weak acid*) in enough water to form 1.00 L of solution

- If the solubility of the substances does not permit these amounts to dissolve,

  then reduce the amounts but maintain the same ratio.

Dissolve 1.02 mol of C_6H_5COONa (*conjugate base*) and 0.50 mol of C_6H_5COOH (*weak acid*) in water to form 1.00 L of solution

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Acid-Base Titration

- ***Titration*** is the addition of a solution of accurately known concentration to another solution of unknown concentration until the reaction is complete.

  Titration enables us to determine the concentration of the solution with the unknown concentration.
  - The ***titrant*** is the solution that is placed in the buret, while the ***analyte*** is the solution to which the titrant is added.
  - A ***standard solution*** is the one of known concentration.
  - The ***equivalence point*** is the point when stoichiometrically equivalent amounts of acid and base have been added.
  - The ***endpoint*** is the point in the laboratory when the titration is stopped.

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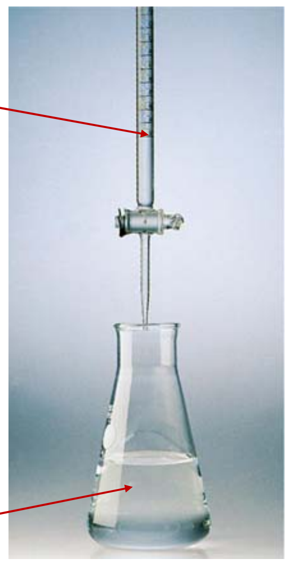
Acid-Base Titration

- Acid-base titration is done by gradually adding an acid (or a base) solution (*titrant*) of known concentration to a base (or an acid) solution (*analyte*) for which the concentration is needed to be determined, with the presence of an *indicator*.



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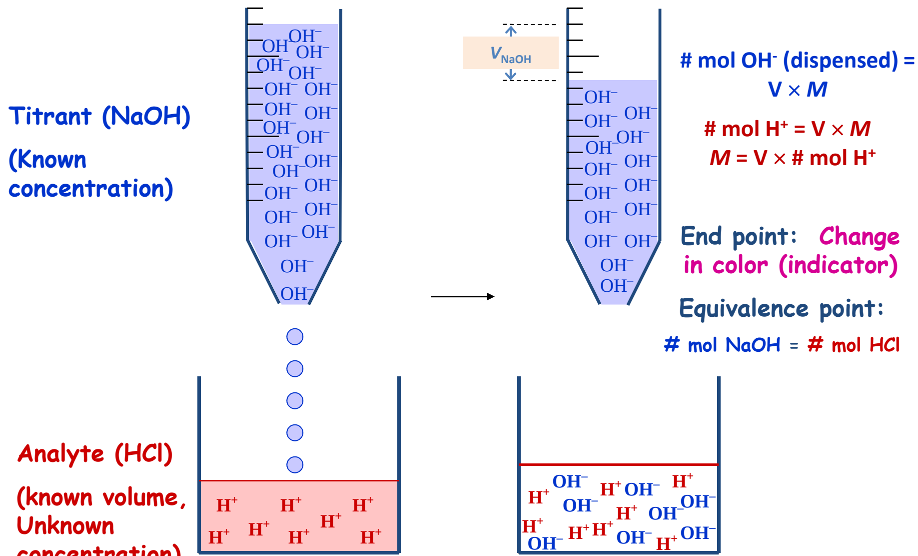
Acid-Base Titration



$H^+(aq) + OH^-(aq) \rightarrow H_2O\ (l)$

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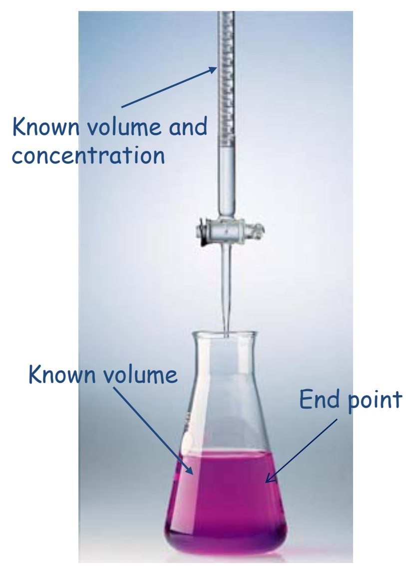
Acid-Base Titration

- In this example, when the reaction is completed, the base titrant neutralizes the acid analyte. The point of neutralization is called the *end point* or *equivalence point*.
- The end point can be visually located by using *indicators* which change their colors when an access of the titrant is present in the solution.
- This experiment has to be done very carefully.



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Acid-Base Titration

- Types of titration systems to be considered:
  - Strong acid – strong base
  - Weak acid – strong base
  - Strong acid – weak base

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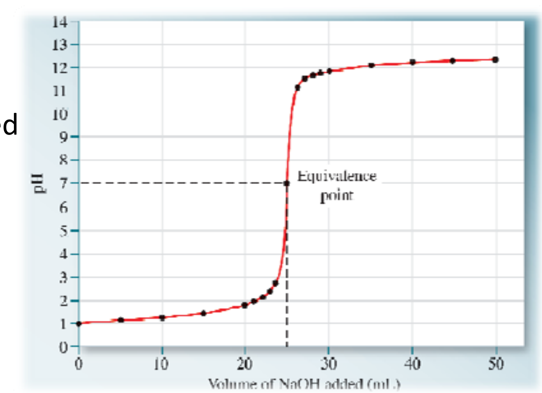
Strong Acid-Strong Base Titration

- The net ionic equation of any strong acid-strong base titration is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\ (l)$$

- The pH values at various points in the titration process can be determined by stoichiometric calculations.
- A titration curve (pH vs. volume of titrant) can be constructed.



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Strong Acid-Strong Base Titration

- We are going to track the change in pH for the solution during a titration process.

  Consider the titration by gradually adding a 0.10 *M* NaOH solution (titrant) to 25.0 mL 0.10 *M* HCl (analyte).

  Before adding any NaOH solution:

Volume OH^- added (mL)	OH^- added (mmol)	H^+ remaining (mmol)	Total volume (mL)	$[H^+]$ (mol/L)	pH
0	0	2.5	25.0	0.100	1.000

1 mmol = 1 millimole = 1×10^{-3} mol

$$\text{Molarity} = \frac{\text{mol}}{\text{Liters}} = \frac{\text{mmol}}{\text{milliliters}}$$

$$pH = -\log [H^+]$$
$$= -\log (0.10\ M)$$
$$= 1.00$$

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We continue by gradually adding the NaOH solution:

Volume OH^- added (mL)	OH^- added (mmol)	H^+ remaining (mmol)	Total volume (mL)	$[H^+]$ (mol/L)	pH
0	0	2.5	25.0	0.100	1.000
5.0					
10.0					
15.0					
20.0					
25.0					

When 5.0 mL of NaOH is added:

$$n_{OH^-} = 5.0\ \text{mL}\ OH^- \times \frac{0.10\ \text{mmol}}{1\ \text{mL}} = 0.50\ \text{mmol}\ OH^-$$

$$n_{H^+}\ \text{before adding NaOH} = 25.0\ \text{mL} \times \frac{0.10\ \text{mmol}}{1\ \text{mL}} = 2.5\ \text{mmol}$$

$$n_{H^+}\ \text{remaining in the solution} = 2.5\ \text{mmol}\ H^+ - 0.50\ \text{mmol}\ OH^-$$
$$= 2.0\ \text{mmol}\ H^+$$

$$[H^+] = \frac{2.0\ \text{mmol}}{(25.0\ \text{mL} + 5.0)} = 0.0667\ M$$

$$pH = -\log (0.0667) = 1.176$$

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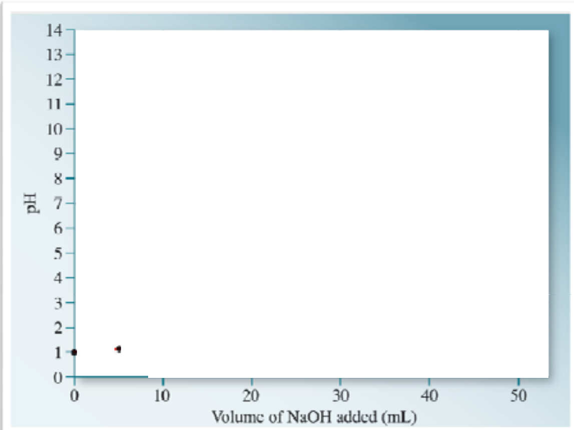
Strong Acid-Strong Base Titration



- A ***titration curve*** (the pH value vs. volume of titrant added) can be constructed.

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We repeat the calculation each time we add 5.0 ml NaOH solution:

Volume OH^- added (mL)	OH^- added (mmol)	H^+ remaining (mmol)	Total volume (mL)	$[H^+]$ (mol/L)	pH
0	0	2.5	25.0	0.100	1.000
5.0	0.50	2.0	30.0	0.0667	1.176
10.0					
15.0					
20.0					
25.0					

When 10.0 mL of NaOH is added:

$$n_{OH^-} = 10.0 \text{ mL } OH^- \times \frac{0.10 \text{ mmol}}{1 \text{ mL}} = 1.0 \text{ mmol } OH^-$$

n_{H^+} remaining in the solution = 2.50 mmol H^+ – 1.0 mmol OH^-

= 1.5 mmol H^+

$$[H^+] = \frac{1.5 \text{ mmol}}{(25.0 \text{ mL} + 10.0)} = 0.0429\ M$$

pH = – log (0.0429) = 1.364

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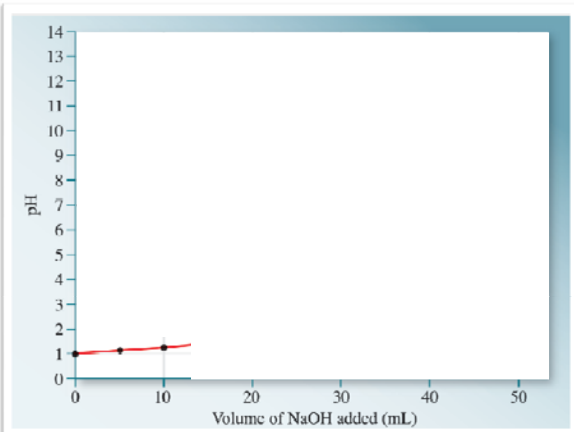
Strong Acid-Strong Base Titration



- A ***titration curve*** (the pH value vs. volume of titrant added) can be constructed.

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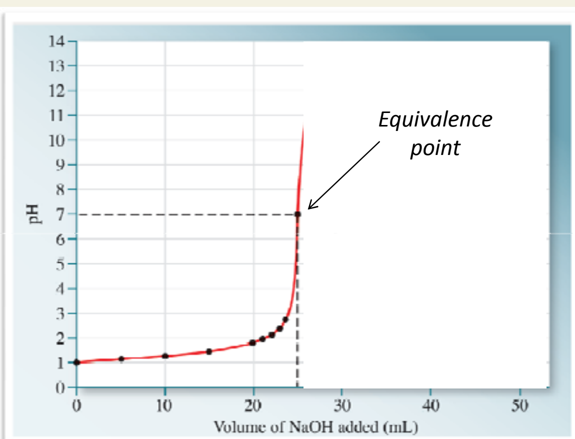
Volume OH^- added (mL)	OH^- added (mmol)	H^+ remaining (mmol)	Total volume (mL)	$[H^+]$ (mol/L)	pH
0	0	2.5	25.0	0.100	1.000
5.0	0.50	2.0	30.0	0.0667	1.176
10.0	1.0	1.5	35.0	0.0429	1.364
15.0	1.5	1.0	40.0	0.0250	1.602
20.0	2.0	0.5	45.0	0.0111	1.955
25.0	2.5	0	50.0	1.00×10^{-7}	7.000



Recall that acid and base combine in a 1:1 mole ratio. Thus, the *equivalence point* in strong acid-strong base titration is where equal amounts of OH^- and H^+ ions have combined.

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Volume OH^- added (mL)	OH^- added (mmol)	H^+ remaining (mmol)	Total volume (mL)	$[H^+]$ (mol/L)	pH
0	0	2.5	25.0	0.100	1.000
5.0	0.50	2.0	30.0	0.0667	1.176
10.0	1.0	1.5	35.0	0.0429	1.364
15.0	1.5	1.0	40.0	0.0250	1.602
20.0	2.0	0.5	45.0	0.0111	1.955
25.0	2.5	0	50.0	1.00×10^{-7}	7.000

When more than 25.0 mL of NaOH solution is added, we pass the equivalence point and all protons are consumed. Only OH^- ions are there in excess.

Upon adding 30.0 mL of NaOH, 3.0 mmol of OH^- are there in the solution.

n_{OH^-} in excess = 3.0 mmol OH^- – 2.5 mmol H^+ = 0.5 mmol OH^-

$$[OH^-] = \frac{0.5 \text{ mmol}}{(25.0 \text{ mL} + 30.0)} = 0.0091\ M$$

pOH = – log (0.0091) = 2.04 => pH = 14.00 – 2.04 = 11.96

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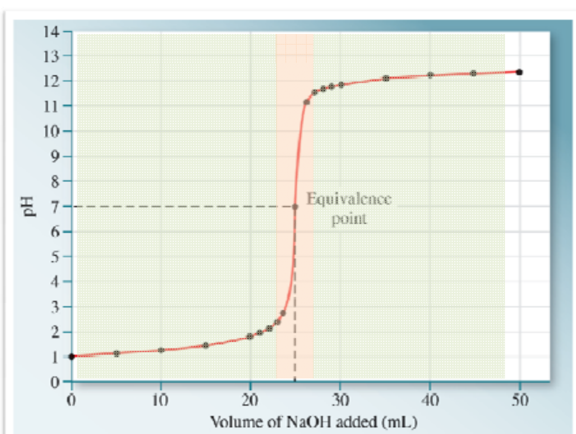
Strong Acid-Strong Base Titration

- Before and beyond the equivalence point, the increase in the pH is very slow.

  Within the small range just before and after the equivalence point, however, the increase in the pH is very steep.



Titration curve

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Weak Acid-Strong Base Titration

- In this case, the weak acid doesn't dissociate completely like the case for the strong acid. So, *equilibrium calculations* are needed in order to track the change in pH during the titration process.
- Example:

  Consider the titration of acetic acid with sodium hydroxide.
  - Before adding NaOH:

    $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$
  - After starting the addition of NaOH:

    $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$

    Also, the acetate ions undergo hydrolysis:

    $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

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Weak Acid-Strong Base Titration

- Consider the titration by gradually adding a 0.10 *M* NaOH solution (titrant) to 25.0 mL 0.10 *M* CH_3COOH.
  - ***Before adding any NaOH solution***, the concentration of H^+ ions can be calculated by constructing an equilibrium table.

	$CH_3COOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CH_3COO^-(aq)$
Initial concentration (*M*):	0.10	0	0
Change in concentration (*M*):	$-x$	$+x$	$+x$
Equilibrium concentration (*M*):	$0.10 - x$	x	x

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.10\,M - x} \approx \frac{x^2}{0.10\,M} = 1.8 \times 10^{-5}$$

$$[H^+] = 1.34 \times 10^{-3}\ M$$

$$pH = 2.87$$

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Volume OH^- added (mL)	OH^- added (mmol)	CH_3COOH remaining	CH_3COO^- produced	pH
0	0	2.5	0.0	2.87*

- ***By adding 5.0 mL of 0.1 M NaOH***, some acetate ions are produced and some acetic acid is consumed. Now we have a *buffer solution*. So we can apply here the H-H equation to calculate the pH.

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \frac{0.0167}{0.0667} = 4.14$$

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

$[CH_3COO^-]$ = 0.50 mmol / (30.0 mL) = 0.0167

$[CH_3COOH]$ = 2.0 mmol / (30.0 mL) = 0.0667

Because the volume is not changed, you can consider just the ratio of the number of moles.

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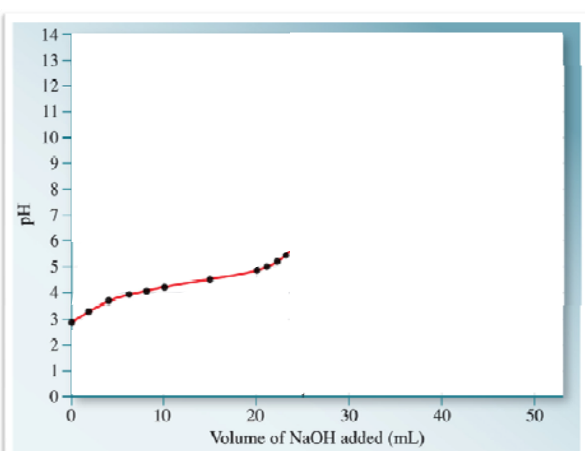
Weak Acid-Strong Base Titration



- To construct the titration curve, we plot the pH vs. the volume of NaOH (titrant).

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- ***At the equivalence point***, 25.0 mL of NaOH is added. Thus, all the acetic acid has been converted to acetate ions which, in their turn, undergo hydrolysis to produce OH^- ions.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

We find the concentration of the acetate ions:

$$[CH_3COO^-] = \frac{2.50\,\text{mmol}}{50.0\,\text{mL}} = 0.050\,M$$

K_b of acetate ions can be calculated from K_a of acetic acid:

$$K_b = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

We calculate $[OH^-]$ by constructing an equilibrium table:

	$CH_3COO^-(aq)$	+ $H_2O(l)$ ⇌	$OH^-(aq)$	+ $CH_3COOH(aq)$
Initial concentration (M):	0.050		0	0
Change in concentration (M):	$-x$		$+x$	$+x$
Equilibrium concentration (M):	$0.050 - x$		x	x

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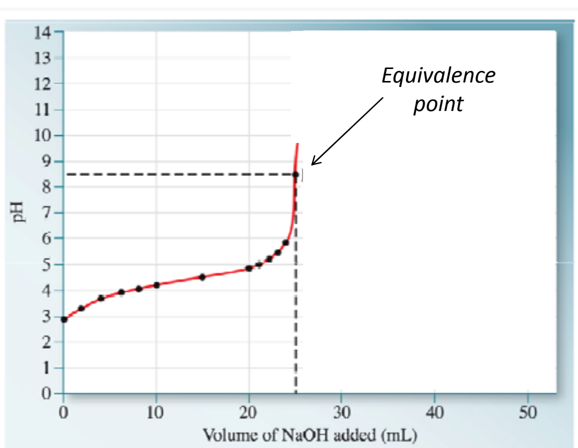
$$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{x^2}{0.050\,M - x} \approx \frac{x^2}{0.050\,M} = 5.6 \times 10^{-10}$$

$$[OH^-] = 5.3 \times 10^{-6}\,M \quad => \quad pOH = 5.28 \quad => \quad pH = 14.00 - 5.28 = 8.72$$



Compared to the strong acid-strong base titration curve, a titration curve for weak acid and strong base has:

- a pH greater than 7.
- a higher initial pH.
- a slightly steeper change in pH as more base is added.
- a shorter vertical region near the equivalence point.

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- ***After the equivalence point***, more than 25.0 mL of NaOH is added. No more acetic acid to be consumed. Thus, there will be an excess of OH^- ions in the solution.

$$\text{added mmol NaOH} = 30.00\,\text{ml x}\,\frac{0.100\,\text{mmol NaOH}}{\text{ml}} = 3.00\,\text{mmol}$$

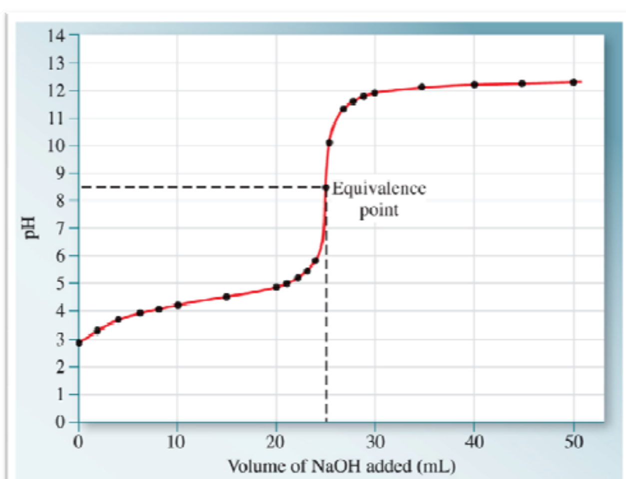
$$\text{remaining mmol NaOH} = 3.00\,\text{mmol} - 2.50\,\text{mmol} = 0.50\,\text{mmol OH}^-$$

$$[OH^-] = \frac{0.50\,\text{mmol}}{60.0\,\text{mL}} = 0.0091\,\text{mmol} \quad => \quad pOH = 2.04 \quad => \quad pH = 11.96$$

Volume OH^- added (mL)	OH^- added (mmol)	CH_3COOH remaining	CH_3COO^- produced	pH
0	0	2.5	0.0	2.87*
5.0	0.50	2.0	0.50	4.14
10.0	1.0	1.5	1.0	4.56
15.0	1.5	1.0	1.5	4.92
20.0	2.0	0.5	2.0	5.34
25.0	2.5	0.0	2.5	8.72†

Volume OH^- added (mL)	OH^- added (mmol)	Excess OH^- (mmol)	Total volume (mL)	$[OH^-]$ (mol/L)	pOH	pH
30.0	3.0	0.5	55.0	0.0091	2.04	11.96
35.0	3.5	1.0	60.0	0.017	1.78	12.22

Weak Acid-Strong Base Titration



Titration curve

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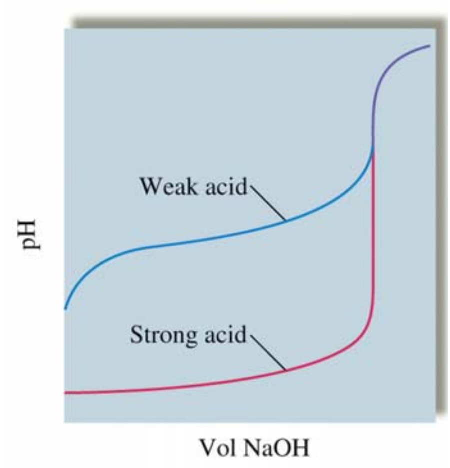
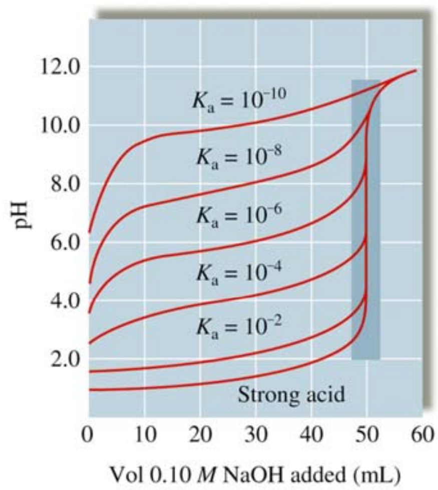
Titration Curve Dependence on Acid Strength





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Acid-Base Titration

- Exercise:

  Calculate the pH at the equivalence point of formic acid (HCOOH) titration with NaOH, assuming both titrant and analyte concentrations are 0.10 *M*. The pK_a value for formic acid is 3.75.

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Acid-Base Titration

- Exercise:
  Calculate the pH at the equivalence point in the titration of 30 mL of 0.25 *M* CH_3COOH with 0.25 *M* KOH. The K_a value of CH_3COOH is 1.8×10^{-5}.

Answer is 8.92

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Strong Acid-Weak Base Titration

- The calculation followed here is similar to the one used for the weak acid-strong base titration.
- An example for strong acid-weak base titration is the titration of ammonia (NH_3) with hydrochloric acid (HCl).

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

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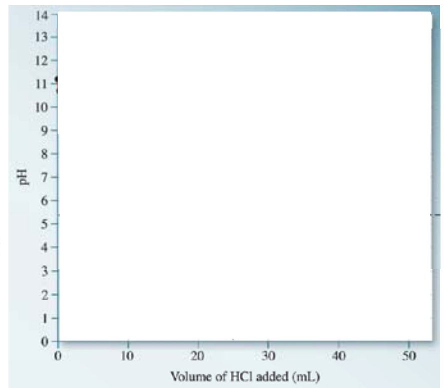
Strong Acid-Weak Base Titration

- *From the first drop* of HCl added and before reaching to the equivalence point, the pH is of a high value and slightly decreases as more HCl is added.

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

To find the pH values, you need to follow the same procedure done for the weak acid-strong base titration.



Strong Acid-Weak Base Titration

At the equivalence point, all of NH_3 has been converted to ammonium ions (NH_4^+), and NH_4^+ hydrolyzes to produce hydronium ions.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Thus, at the equivalence point, the pH is expected to be less than 7 since the solution is slightly acidic.

Past the equivalence point, [H^+] increases as more HCl is added. The pH continues to decrease very slowly.

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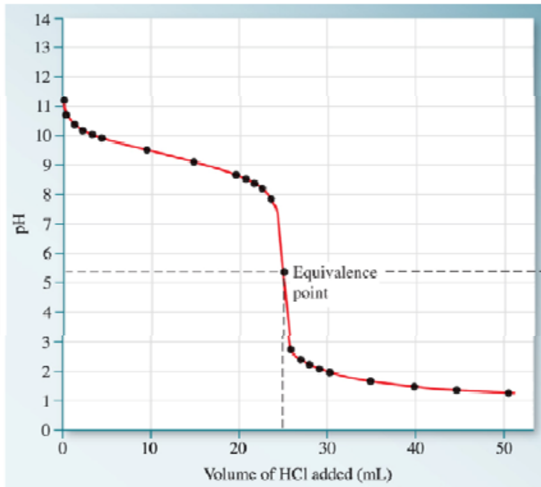
Strong Acid-Weak Base Titration



Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

Titration curve

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Acid-Base Indicators

- An ***acid-base indicator*** is a weak organic acid (or base) for which the ionized and non-ionized forms are of different colors.

$$HIn\ (aq) \rightleftharpoons H^{+}\ (aq) + In^{-}(aq)$$

- o In an acidic medium (from *Le Châtelier's principle*):

$$HIn\ (aq) \leftarrow H^{+}\ (aq) + In^{-}(aq)$$

- o In a basic medium, on the other hand, :

$$HIn\ (aq) \rightarrow H^{+}\ (aq) + In^{-}(aq)$$

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Acid-Base Indicators

- The ***end point*** for a titration process is the point where the color of an indicator changes.
  - It is different from the *equivalence point* which is the point where neutralization between an acid and base is complete (the numbers of moles of an acid and base are equal).
  - The end points (*ranges*) of different indicators are different.

	Color		
Indicator	**In Acid**	**In Base**	**pH Range**
Thymol blue	Red	Yellow	1.2−2.8
Bromophenol blue	Yellow	Bluish purple	3.0−4.6
Methyl orange	Orange	Yellow	3.1−4.4
Methyl red	Red	Yellow	4.2−6.3
Chlorophenol blue	Yellow	Red	4.8−6.4
Bromothymol blue	Yellow	Blue	6.0−7.6
Cresol red	Yellow	Red	7.2−8.8
Phenolphthalein	Colorless	Reddish pink	8.3−10.0

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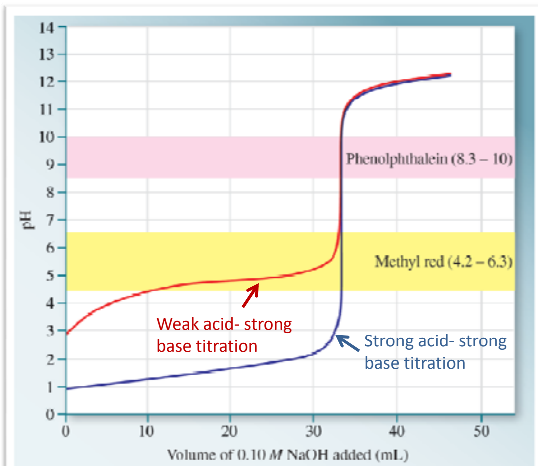
Acid-Base Indicators

- In order to choose an appropriate indictor, the pH at the equivalence point of a specific titration must be within the pH range where the indicator changes its color.



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Acid-Base Indicators

- Many acid-base indicators are plant pigments.

  For example, solutions containing extracts of *red cabbage* have different colors at different pH values.

pH increases

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