

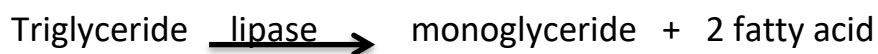
Principles of Neutralization Titrations

Neutralization titrations are widely used to determine the amounts of acids and bases.

In addition, neutralization titrations can be used to monitor the progress of reactions that produce or consume hydrogen ions.

In clinical chemistry, for example, pancreatitis can be diagnosed by measuring the activity of serum lipase. Lipases hydrolyze the long-chain fatty acid triglyceride.

The reaction liberates two moles of fatty acid and one mole of monoglyceride for each mole of triglyceride present according to



1. Solutions and Indicators for Acid/Base Titrations

Like all titrations, neutralization titrations depend on a chemical reaction of the analyte with a standard reagent. There are several different types of acid/base titrations.

- ✚ One of the most common is the titration of a strong acid, such as hydrochloric or sulfuric acid, with a strong base, such as sodium hydroxide.
- ✚ Another common type is the titration of a weak acid, such as acetic or lactic acid, with a strong base.
- ✚ Weak bases, such as sodium cyanide or sodium salicylate, can also be titrated with strong acids.

In all titrations, we must have a method of determining the point of chemical equivalence. Typically, a chemical indicator or an instrumental method is used to locate the end point, which we hope is very close to the equivalence point.

1.1 Standard Solutions

- ✚ The standard reagents used in acid/base titrations are always strong acids or strong bases, most commonly HCl, HClO₄, H₂SO₄, NaOH, and KOH.
- ✚ Because these substances react completely with an, and as a result, they produce sharper end points.

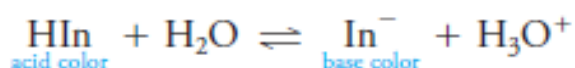
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- ✚ Weak acids and bases are never used as standard reagents because they react incompletely with analytes.

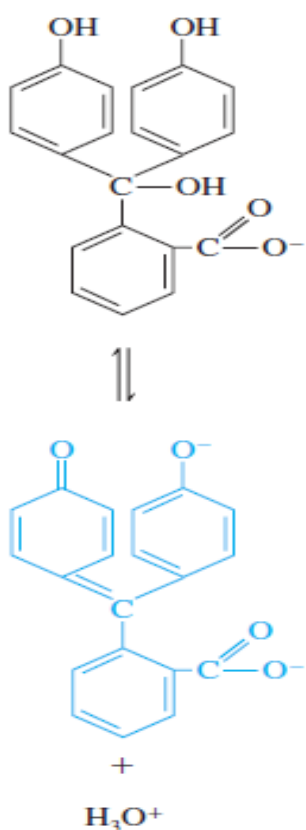
1.2 Acid/Base Indicators

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form.

For example, the behavior of an acid-type indicator, HIn, is described by the equilibrium:

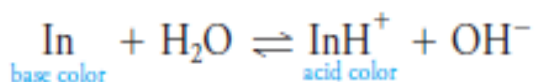


In this reaction, internal structural changes accompany dissociation and cause the color change (for example, see **Figure below**)



Color change and molecular modes for phenolphthalein.
(a) Acidic form after hydrolysis of the lactone form.
(b) Basic form.

The equilibrium for a base-type indicator, In, is



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The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \quad [\text{H}_3\text{O}^+] = K_a \frac{[\text{HIn}]}{[\text{In}^-]}$$

We see then that the hydronium ion is proportional to the ratio of the concentration of the acid form to the concentration of the base form of the indicator, which in turn controls the color of the solution.

The color change detected by an average observer occurs within a limited range of concentration ratios from about 10 to about 0.1

$$\frac{[\text{HIn}]}{[\text{In}^-]} \geq \frac{10}{1} \quad \frac{[\text{HIn}]}{[\text{In}^-]} \leq \frac{1}{10}$$

$$[\text{H}_3\text{O}^+] = 10K_a \quad [\text{H}_3\text{O}^+] = 0.1 K_a$$

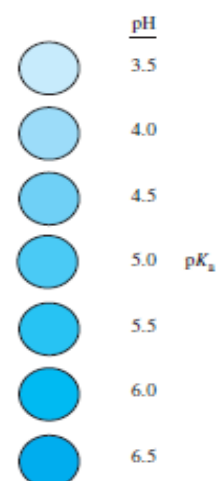
$$\text{pH}(\text{acid color}) = -\log(10K_a) = \text{p}K_a + 1$$

$$\text{pH}(\text{basic color}) = -\log(0.1K_a) = \text{p}K_a - 1$$

The pH transition range of most acid type indicators is roughly $\text{p}K_a \pm 1$

$$\text{indicator pH range} = \text{p}K_a \pm 1$$

This expression shows that an indicator with an acid dissociation constant 1×10^{-5} ($\text{p}K_a=5$) typically shows a complete color change when the pH of the solution in which it is dissolved changes from 4 to 6.



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Titration Errors with Acid/Base Indicators

We find two types of titration error in acid/base titrations.

- 1) The first is a determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point.

This type of error can usually be minimized by choosing the indicator carefully or by making a blank correction.

- 2) The second type is an indeterminate error that originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator.

The magnitude of this error depends on

- a) The change in pH per milliliter of reagent at the equivalence point
- b) The concentration of the indicator
- c) The sensitivity of the eye to the two indicator colors.

- ❖ The visual uncertainty with an acid/base indicator is in the range of ± 0.5 to ± 1 pH unit.
- ❖ This uncertainty can often be decreased to as little as ± 0.1 pH unit by matching the color of the solution being titrated with that of a reference standard containing a similar amount of indicator at the appropriate pH.

Variables That Influence the Behavior of Indicators

The pH interval over which a given indicator exhibits a color change is influenced by

- a) Temperature
- b) The ionic strength of the medium
- c) The presence of organic solvents and colloidal particles.
 - ❖ Some of these effects, particularly the last two, can cause the transition range to shift by one or more pH units

The Common Acid/Base Indicators

A few common indicators and their properties are listed in Table below

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Some Important Acid/Base Indicators			
Common Name	Transition Range, pH	pK_a^*	Color Change [†]
Thymol blue	1.2–2.8	1.65§	R – Y
	8.0–9.6	8.96§	Y – B
Methyl yellow	2.9–4.0		R – Y
Methyl orange	3.1–4.4	3.46§	R – O
Bromocresol green	3.8–5.4	4.66§	Y – B
Methyl red	4.2–6.3	5.00§	R – Y
Bromocresol purple	5.2–6.8	6.12§	Y – P
Bromothymol blue	6.2–7.6	7.10§	Y – B
Phenol red	6.8–8.4	7.81§	Y – R
Cresol purple	7.6–9.2		Y – P
Phenolphthalein	8.3–10.0		C – R
Thymolphthalein	9.3–10.5		C – B
Alizarin yellow GG	10–12		C – Y

Titration of a Strong Acid with a Strong Base:

Three types of calculations must be done in order to construct the hypothetical curve for titrating a solution of a strong acid with a strong base. Each of these types corresponds to a distinct stage in the titration:

- (1) Preequivalence
- (2) Equivalence
- (3) Postequivalence

Generate the hypothetical titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH at 25°C.

Initial Point

Before any base is added, the solution is 0.0500 M in H_3O^+ , and

$$pH = -\log[H_3O^+] = -\log 0.0500 = 1.30$$

After Addition of 10.00 mL of Reagent

The hydronium ion concentration is decreased as a result of both reaction with the base and dilution. So, the remaining HCl concentration, c_{HCl} , is

$$\begin{aligned} c_{HCl} &= \frac{\text{no. mmol HCl remaining after addition of NaOH}}{\text{total volume soln}} \\ &= \frac{\text{original no. mmol HCl} - \text{no. mmol NaOH added}}{\text{total volume soln}} \\ &= \frac{(50.00 \text{ mL} \times 0.0500 \text{ M}) - (10.00 \text{ mL} \times 0.1000 \text{ M})}{50.00 \text{ mL} + 10.00 \text{ mL}} \\ &= \frac{(2.500 \text{ mmol} - 1.00 \text{ mmol})}{60.00 \text{ mL}} = 2.50 \times 10^{-2} \text{ M} \end{aligned}$$

$$[H_3O^+] = 2.50 \times 10^{-2} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(2.50 \times 10^{-2}) = 1.602 \approx 1.60$$

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After Addition of 25.00 mL of Reagent: The Equivalence Point

At the equivalence point, neither HCl nor NaOH is in excess, and so, the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M}$$
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-7}) = 7.00$$

After Addition of 25.10 mL of Reagent

The solution now contains an excess of NaOH, and we can write

$$c_{\text{NaOH}} = \frac{\text{no. mmol NaOH added} - \text{original no. of mmoles HCl}}{\text{total volume soln}}$$
$$= \frac{25.10 \times 0.1000 - 50.00 \times 0.0500}{75.10} = 1.33 \times 10^{-4} \text{ M}$$

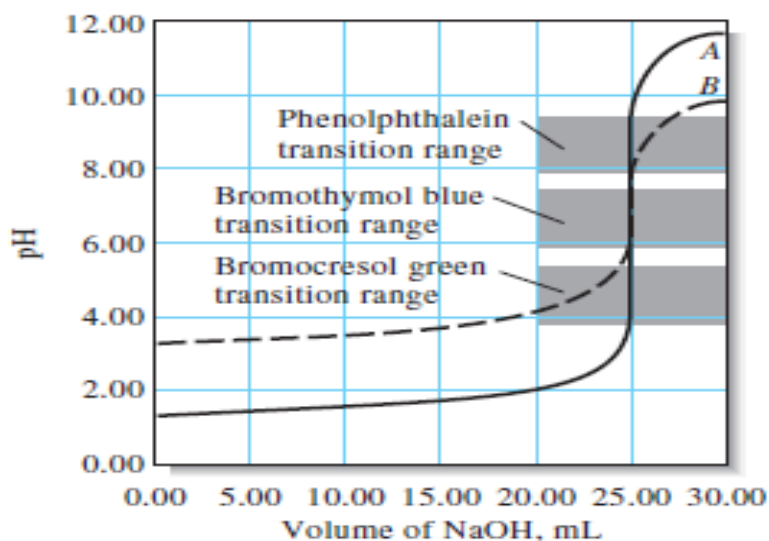
The equilibrium concentration of hydroxide ion is

$$[\text{OH}^-] = c_{\text{NaOH}} = 1.33 \times 10^{-4} \text{ M}$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.33 \times 10^{-4}) = 3.88$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.88 = 10.12$$

Changes in pH during the Titration of a Strong Acid with a Strong Base

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

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Titration curves for HCl with NaOH. Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve B: 50.00 mL of 0.000500 M HCl with 0.00100 M NaOH

The Effect of Concentration

The effects of reagent and analyte concentration on the neutralization titration curves for strong acids are shown by the two sets of data in table and the plots in **above**.

Note that with 0.1 M NaOH as the titrant, the change in pH in the equivalence-point region is large. With 0.001 M NaOH, the change is much smaller, but still pronounced.

Choosing an Indicator

Figure above shows that the selection of an indicator is not critical when the reagent concentration is approximately 0.1 M. In that case, the volume differences in titrations with the three indicators shown are of the same magnitude as the uncertainties associated with reading the buret and so are negligible.

Note, however, that **bromocresol green** is unsuited for a titration involving the 0.001 M reagent because The color change occurs over a 5-mL range well before the equivalence **phenolphthalein** is subject to similar objections. Of the three indicators, then, only **bromothymol blue** provides a satisfactory end point with a minimal systematic error in the titration of 0.001 M NaOH.

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Titration of a Strong Base with a Strong Acid

Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl at 25°C after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

Solution

(a) At 24.50 mL added, $[\text{H}_3\text{O}^+]$ is very small and cannot be computed from stoichiometric considerations but can be obtained from $[\text{OH}^-]$:

$$\begin{aligned}[\text{OH}^-] &= c_{\text{NaOH}} = \frac{\text{original no. mmol NaOH} - \text{no. mmol HCl added}}{\text{total volume of solution}} \\ &= \frac{50.00 \times 0.0500 - 24.50 \times 0.1000}{50.00 + 24.50} = 6.71 \times 10^{-4} \text{ M}\end{aligned}$$

$$\begin{aligned}[\text{H}_3\text{O}^+] &= K_w / (6.71 \times 10^{-4}) = 1.00 \times 10^{-14} / (6.71 \times 10^{-4}) \\ &= 1.49 \times 10^{-11} \text{ M}\end{aligned}$$

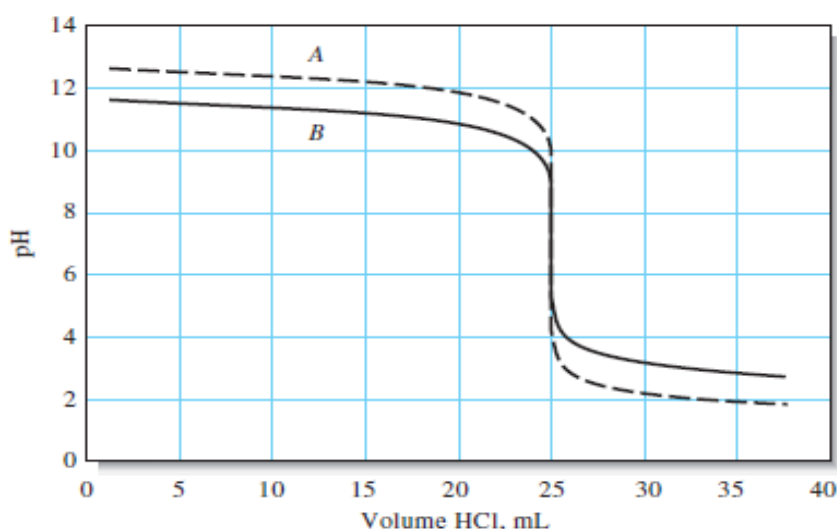
$$\text{pH} = -\log(1.49 \times 10^{-11}) = 10.83$$

(b) 25.00 mL added is the equivalence point where $[\text{H}_3\text{O}^+] = [\text{OH}^-]$:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ M} \\ \text{pH} &= -\log(1.00 \times 10^{-7}) = 7.00\end{aligned}$$

(c) At 25.50 mL added

$$\begin{aligned}[\text{H}_3\text{O}^+] &= c_{\text{HCl}} = \frac{25.50 \times 0.1000 - 50.00 \times 0.0500}{75.50} \\ &= 6.62 \times 10^{-4} \text{ M} \\ \text{pH} &= -\log(6.62 \times 10^{-4}) = 3.18\end{aligned}$$



Titration curves for NaOH with HCl. Curve A: 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl. Curve B: 50.00 mL of 0.00500 M NaOH with 0.0100 M HCl