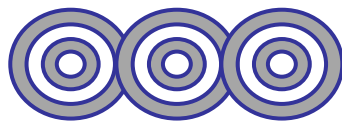




# Fundamentals of Analytical Chemistry



## Acid-Base Titrations

**Ahmad Aqel Ifseisi**

Associate professor of Analytical Chemistry  
College of Science, Department of Chemistry  
King Saud University

P.O. Box 2455 Riyadh 11451 Saudi Arabia

Building: 05, Office: 2A/149 & AA/53

Tel. 014674198, Fax: 014675992

Web site: <http://fac.ksu.edu.sa/aifseisi>

E-mail: [ahmad3qel@yahoo.com](mailto:ahmad3qel@yahoo.com)

[aifseisi@ksu.edu.sa](mailto:aifseisi@ksu.edu.sa)



كرسي أبحاث  
المواد المتقدمة  
Advanced Materials  
Research Chair



جامعة  
الملك سعود  
King Saud University

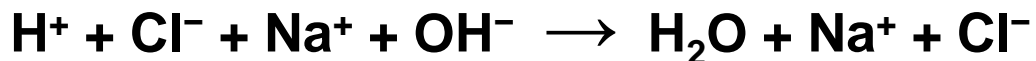


# Strong acid versus strong base

An acid-base titration involves a **neutralization** reaction in which an acid is reacted with an equivalent amount of base. The **end point** signals the completion of the reaction. A **titration curve** is constructed by plotting the pH of the solution as a function of the volume of titrant added. The **titrant** is always a strong acid or a strong base. The **analyte** may be either a strong base or acid or a weak base or acid.

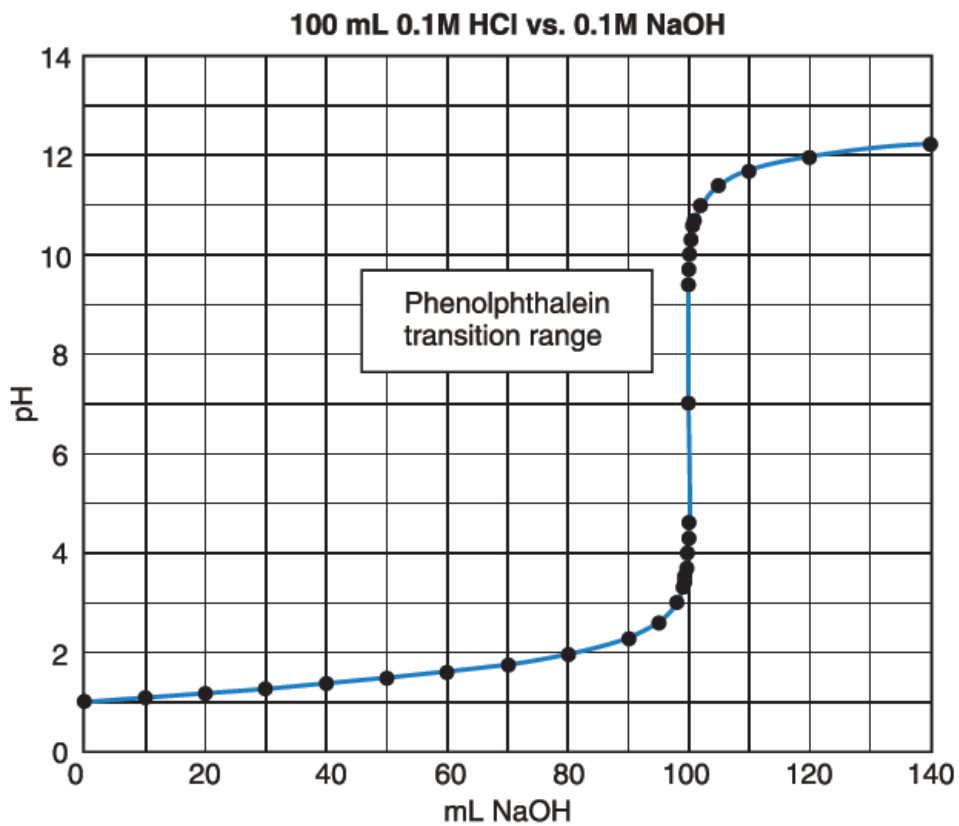
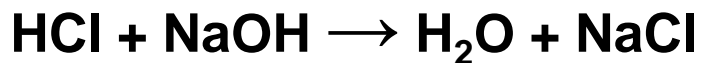
In the case of a **strong acid** versus a **strong base**, both the titrant and the analyte are completely ionized.

An example is the titration of hydrochloric acid **HCl** with sodium hydroxide **NaOH**:



The  $\text{H}^+$  and  $\text{OH}^-$  combine to form  $\text{H}_2\text{O}$ , and the other ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) remain unchanged, so the net result of neutralization is conversion of the HCl to a neutral solution of NaCl.

# Titration of 100 mL of 0.1 M HCl with 0.1 M NaOH



The titration curve for 100 mL of 0.1 M HCl titrated with 0.1 M NaOH

	A	B	C	D	E
1	<b>100.00 mL of 0.1000 M HCl vs. 0.1000 M NaOH</b>				
2	mL <sub>HCl</sub> =	100.00	M <sub>HCl</sub> =	0.1000	
3	M <sub>NaOH</sub> =	0.1000	K <sub>w</sub> =	1.00E-14	
4	mL <sub>NaOH</sub>	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	pOH	pH
5	0.00	0.1			1.00
6	10.00	0.0818182			1.09
7	20.00	0.0666667			1.18
8	30.00	0.0538462			1.27
9	40.00	0.0428571			1.37
10	50.00	0.0333333			1.48
11	60.00	0.025			1.60
12	70.00	0.0176471			1.75
13	80.00	0.0111111			1.95
14	90.00	0.0052632			2.28
15	95.00	0.0025641			2.59
16	98.00	0.0010101			3.00
17	99.00	0.0005025			3.30
18	99.20	0.0004016			3.40
19	99.40	0.0003009			3.52
20	99.60	0.0002004			3.70
21	99.80	0.0001001			4.00
22	99.90	5.003E-05			4.30
23	99.95	2.501E-05			4.60
24	100.00	<b>0.0000001</b>			7.00
25	100.05		<b>2.5E-05</b>	<b>4.60</b>	<b>9.40</b>
26	100.10		5E-05	4.30	9.70
27	100.20		1E-04	4.00	10.00
28	100.40		0.0002	3.70	10.30
29	100.80		0.0004	3.40	10.60
30	101.00		0.0005	3.30	10.70
31	102.00		0.00099	3.00	11.00
32	105.00		0.00244	2.61	11.39
33	110.00		0.00476	2.32	11.68
34	120.00		0.00909	2.04	11.96
35	140.00		0.01667	1.78	12.22

## Equations governing a strong-acid (HX) or strong-base (BOH) titration

Fraction $f$ Titrated	Strong Acid		Strong Base	
	Present	Equation	Present	Equation
$f = 0$	HX	$[H^+] = [HX]$	BOH	$[OH^-] = [BOH]$
$0 < f < 1$	HX/X <sup>-</sup>	$[H^+] = [\text{remaining HX}]$	BOH/B <sup>+</sup>	$[OH^-] = [\text{remaining BOH}]$
$f = 1$	X <sup>-</sup>	$[H^+] = \sqrt{K_w}$	B <sup>+</sup>	$[H^+] = \sqrt{K_w}$
$f > 1$	OH <sup>-</sup> /X <sup>-</sup>	$[OH^-] = [\text{excess titrant}]$	H <sup>+</sup> /B <sup>+</sup>	$[H^+] = [\text{excess titrant}]$

$f$  to denote the fraction of analyte

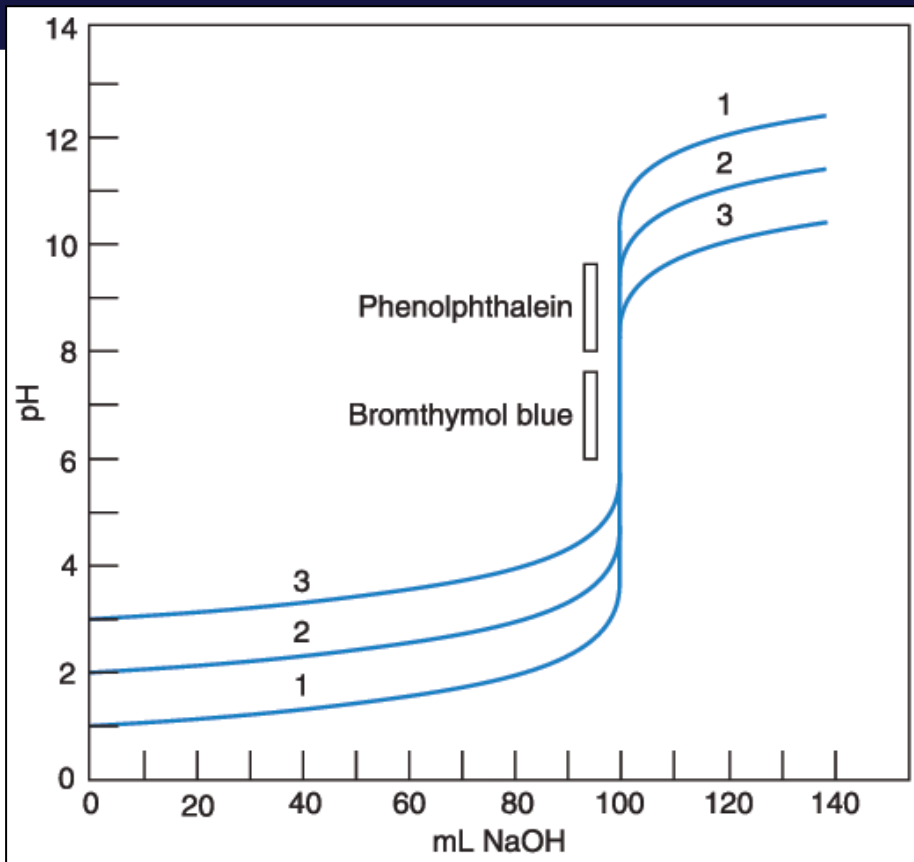
Note that prior to the equivalence point, when there is excess acid, the relationship is

$$[H^+] = (M_{\text{acid}} \times V_{\text{acid}} - M_{\text{base}} \times V_{\text{base}}) / V_{\text{total}}$$

Beyond the equivalence point when there is excess base,

$$[OH^-] = (M_{\text{base}} \times V_{\text{base}} - M_{\text{acid}} \times V_{\text{acid}}) / V_{\text{total}}$$

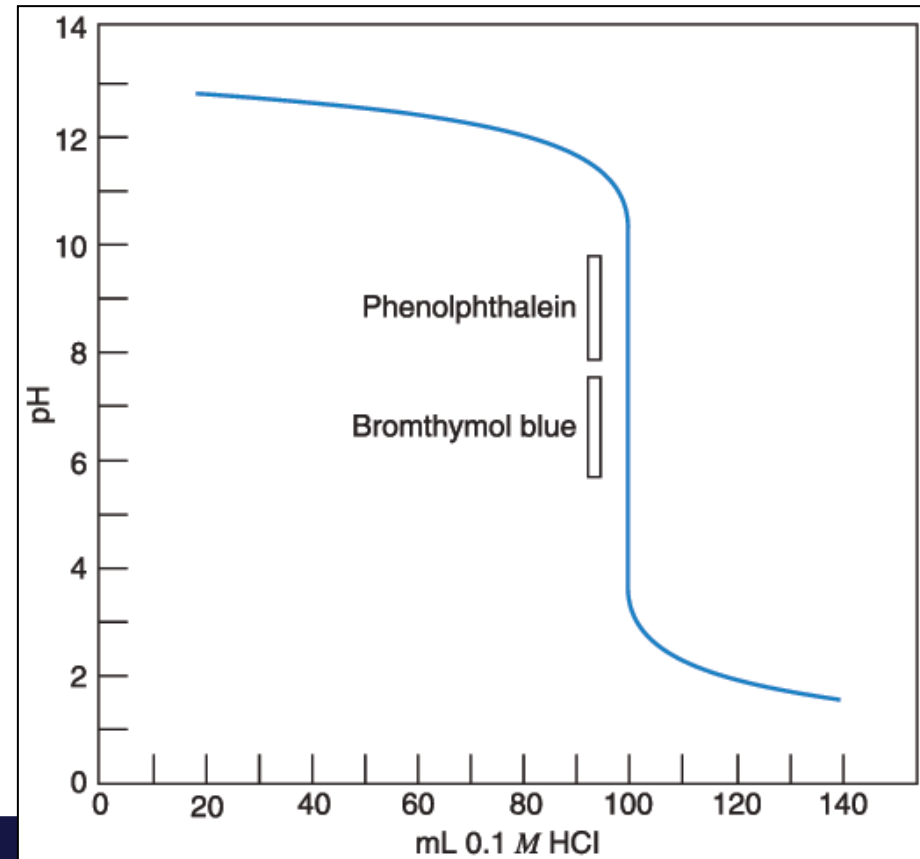
Where:  $V$  is the volume and  $V_{\text{total}}$  is always  $V_{\text{acid}} + V_{\text{base}}$



Titration curve for 100 mL 0.1 M NaOH vs. 0.1 M HCl.  
The equivalence point pH is 7.00.

Dependence of the magnitude of end-point break on concentration.

- Curve 1: 100 mL of 0.1 M HCl vs. 0.1 M NaOH.
  - Curve 2: 100 mL of 0.01 M HCl vs. 0.01 M NaOH.
  - Curve 3: 100 mL of 0.001 M HCl vs. 0.0001 M NaOH.
- The equivalence point pH is 7.00 in all cases.



## Example

Calculate the pH at 0, 10, 90, 100 and 110% titration (% of the equivalence point volume) for the titration of 50.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH.

## Solution

### At 0%:

$$\text{pH} = -\log 0.100 = 1.00$$

### At 10%:

5.0 mL NaOH is added. We start with  $0.100 \text{ M} \times 50.0 \text{ mL} = 5.00 \text{ mmol H}^+$ . Calculate the concentration of  $\text{H}^+$  after adding the NaOH:

$$\text{mmol H}^+ \text{ at start} = 5.00 \text{ mmol H}^+$$

$$\text{mmol OH}^- \text{ added} = 0.100 \text{ M} \times 5.0 \text{ mL} = 0.500 \text{ mmol OH}^-$$

$$\text{mmol H}^+ \text{ left} = 4.50 \text{ mmol H}^+ \text{ in } 55.0 \text{ mL}$$

$$[\text{H}^+] = 4.50 \text{ mmol} / 55.0 \text{ mL} = 0.0818 \text{ M} \quad \text{pH} = -\log 0.0818 = 1.09$$

### At 90%:

$$\text{mmol H}^+ \text{ at start} = 5.00 \text{ mmol H}^+$$

$$\text{mmol OH}^- \text{ added} = 0.100 \text{ M} \times 45.0 \text{ mL} = 4.50 \text{ mmol OH}^-$$

$$\text{mmol H}^+ \text{ left} = 0.50 \text{ mmol H}^+ \text{ in } 95.0 \text{ mL}$$

$$[\text{H}^+] = 0.00526 \text{ M} \quad \text{pH} = -\log 0.00526 = 2.28$$

### At 100%:

All the  $\text{H}^+$  has been reacted with  $\text{OH}^-$ , and we have a 0.050 *M* solution of NaCl. Therefore, the pH is 7.00.

### At 110%:

We now have a solution consisting of NaCl and excess added NaOH.

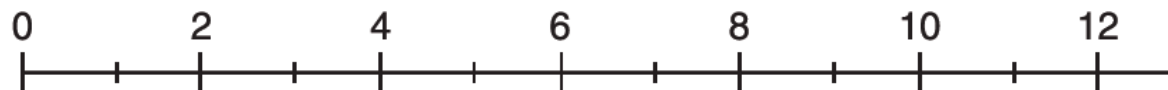
$$\text{mmol OH}^- = 0.100 \text{ M} \times 5.00 \text{ mL} = 0.50 \text{ mmol OH}^- \text{ in } 105 \text{ mL}$$

$$[\text{OH}^-] = 0.00476 \text{ M}$$

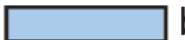
$$\text{pOH} = -\log 0.00476 = 2.32; \quad \text{pH} = 11.68$$


Indicator


pH





Methyl violet ——— yellow  violet


Crystal violet ——— yellow  blue

Cresol red ——— red  yellow

Bromphenol blue ——— yellow  blue

Methyl orange ——— red  yellow


Bromcresol green ——— yellow  blue

Methyl red ——— red  yellow

Methyl purple ——— purple  green

Bromothymol blue ——— yellow  blue


Litmus ——— red  blue

Cresol red ——— yellow  red

Thymol blue ——— red  yellow ——— yellow  blue

Phenolphthalein ——— colorless  red violet

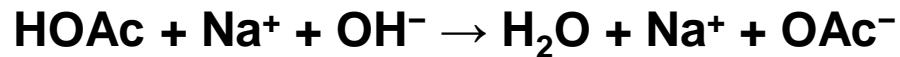
Thymolphthalein ——— colorless  blue

Alizarin yellow R ——— yellow  red

pH transition ranges and colors of some common indicators.

# Weak acid versus strong base

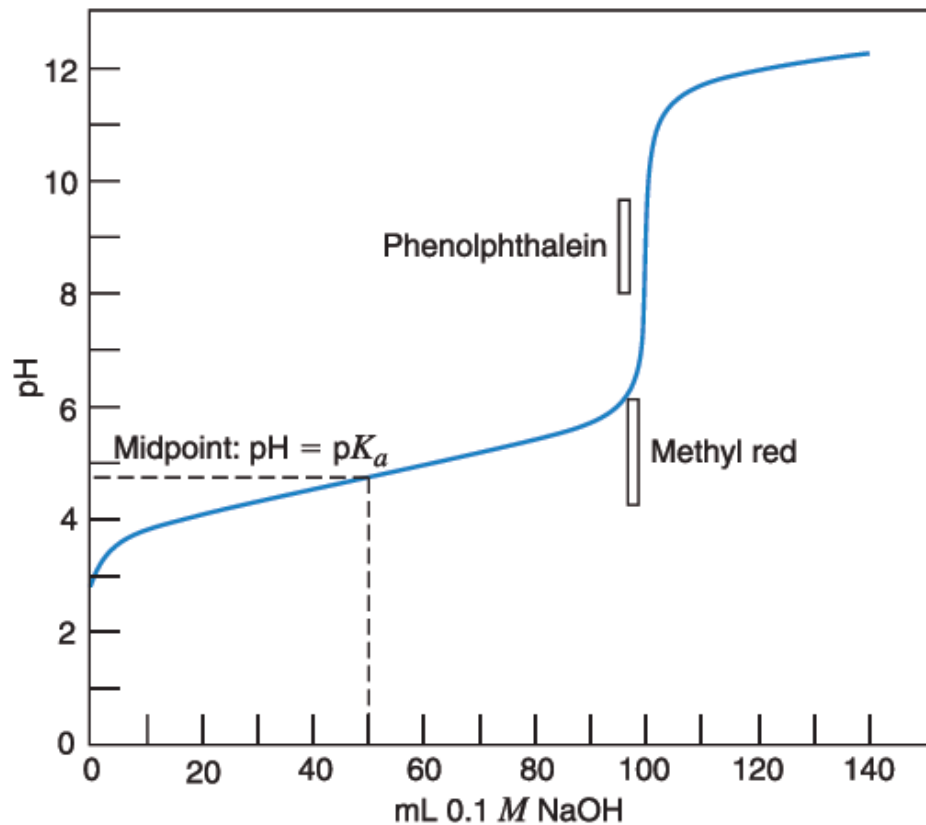
Example, the titration of 100 mL of 0.1 *M* acetic acid (as a weak acid) with 0.1 *M* sodium hydroxide (as a strong base). The neutralization reaction is:



Equations governing a weak-acid (HA) titration

Fraction <i>f</i> Titrated	Weak Acid	
	Present	Equation
$f = 0$	HA	$[\text{H}^+] = \sqrt{K_a \cdot C_{\text{HA}}}$
$0 < f < 1$	HA/A <sup>-</sup>	$\text{pH} = \text{p}K_a + \log \frac{C_{\text{A}^-}}{C_{\text{HA}}}$
$f = 1$	A <sup>-</sup>	$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{\text{A}^-}}$
$f > 1$	OH <sup>-</sup> /A <sup>-</sup>	$[\text{OH}^-] = [\text{excess titrant}]$

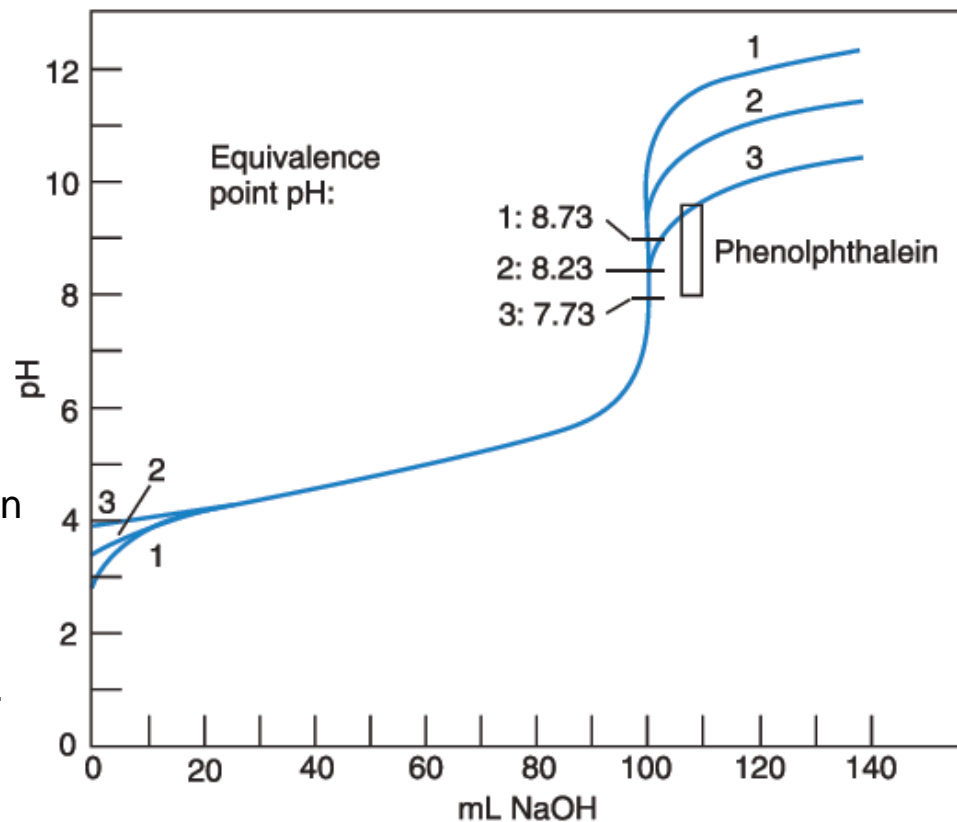




Titration curve for 100 mL 0.1 M HOAc vs 0.1 M NaOH. Note that the equivalence point pH is not 7. At 0.05 M NaOAc, it is 8.73.

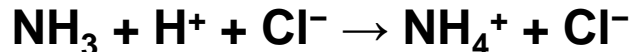
Dependence of the titration curve of weak acid on concentration.

- Curve 1: 100 mL of 0.1 M HOAc vs 0.1 M NaOH.
- Curve 2: 100 mL of 0.01 M HOAc vs 0.01 M NaOH.
- Curve 3: 100 mL of 0.001 M HOAc vs 0.001 M NaOH.



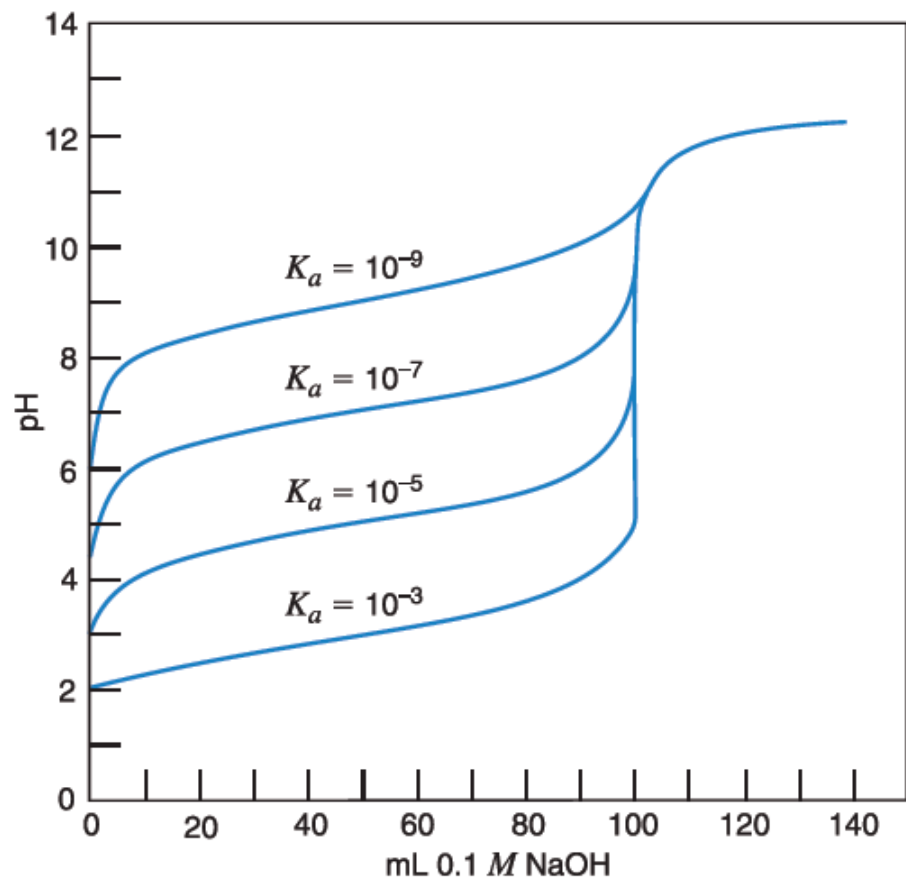
# Weak base versus strong acid

The titration of a weak base with a strong acid is completely analogous to the above case, but the titration curves are the reverse of those for a weak acid versus a strong base. Example, the titration of 100 mL of 0.1 *M* ammonia (as a weak base) with 0.1 *M* hydrochloric acid (as a strong acid). The neutralization reaction is:



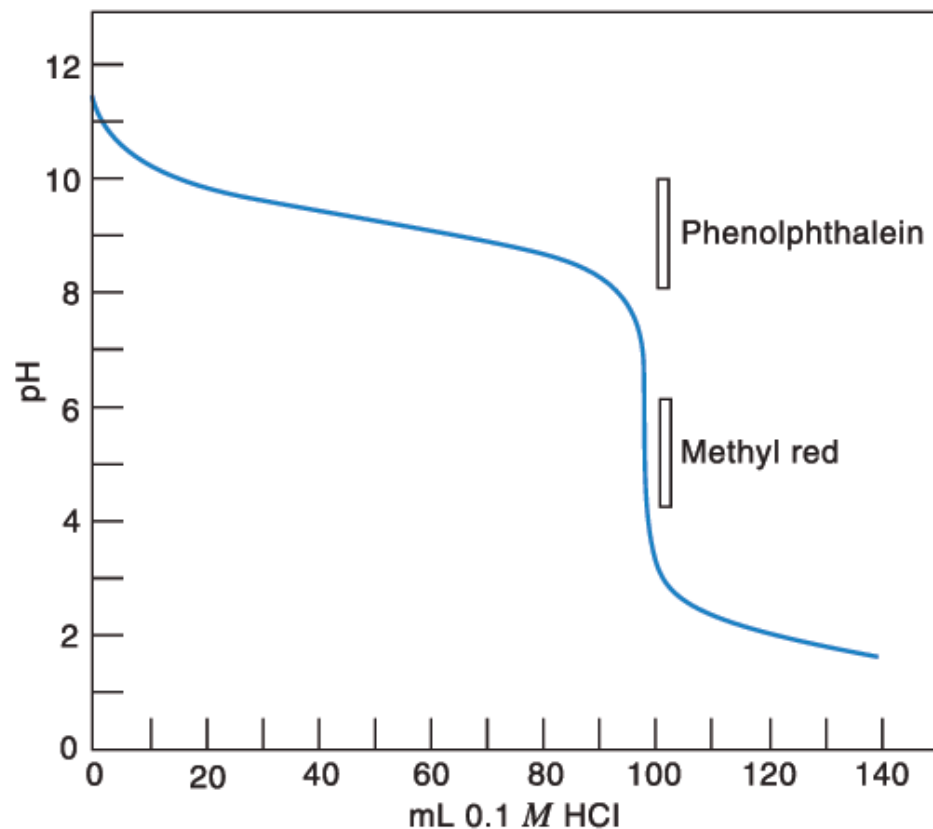
Equations governing a weak-base (B) titration

Fraction <i>f</i> Titrated	Weak Base	
	Present	Equation
$f = 0$	B	$[\text{OH}^-] = \sqrt{K_b \cdot C_B}$
$0 < f < 1$	B/BH <sup>+</sup>	$\text{pH} = (\text{p}K_w - \text{p}K_b) + \log \frac{C_B}{C_{\text{BH}^+}}$
$f = 1$	BH <sup>+</sup>	$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{\text{BH}^+}}$
$f > 1$	H <sup>+</sup> /BH <sup>+</sup>	$[\text{H}^+] = [\text{excess titrant}]$



Titration curve for 100 mL 0.1 M  $\text{NH}_3$  versus 0.1 M HCl.

Titration curves for 100 mL 0.1 M weak acids of different  $K_a$  values versus 0.1 M NaOH.



## Example

Calculate the pH at 0, 10.0, 25.0, 50.0, and 60.0 mL titrant in the titration of 50.0 mL of 0.100 *M* acetic acid with 0.100 *M* NaOH.

## Solution

### At 0 mL

We have a solution of only 0.100 *M* HOAc:

$$\frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$[\text{H}^+] = x = 1.32 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.88$$

### At 10.0 mL

We started with 0.100 *M* × 50.0 mL = 5.00 mmol HOAc; part has reacted with OH<sup>-</sup> and has been converted to OAc<sup>-</sup>:

mmol HOAc at start = 5.00 mmol HOAc

mmol OH<sup>-</sup> added = 0.100 *M* × 10.0 mL = 1.00 mmol OH<sup>-</sup>

= mmol OAc<sup>-</sup> formed in 60.0 mL

mmol HOAc left = 4.00 mmol HOAc in 60.0 mL

We have a buffer. Since volumes cancel, use millimoles:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]}$$

$$\text{pH} = 4.76 + \log \frac{1.00}{4.00} = 4.16$$

### At 25.0 mL

One-half the HOAc has been converted to OAc<sup>-</sup>, so pH = pKa:

mmol HOAc at start = 5.00 mmol HOAc

mmol OH<sup>-</sup> = 0.100 M × 25.0 mL = 2.50 mmol OAc<sup>-</sup> formed

mmol HOAc left = 2.50 mmol HOAc

$$\text{pH} = 4.76 + \log \frac{2.50}{2.50} = 4.76$$

### At 50.0 mL

All the HOAc has been converted to OAc<sup>-</sup> (5.00 mmol in 100 mL, or 0.0500 M):

$$\begin{aligned} [\text{OH}^-] &= \sqrt{\frac{K_w}{K_a} [\text{OAc}^-]} \\ &= \sqrt{\frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} \times 0.0500} = 5.35 \times 10^{-6} \text{ M} \end{aligned}$$

$$\text{pOH} = 5.27 \quad \text{pH} = 8.73$$

### At 60.0 mL

We have a solution of NaOAc and excess added NaOH. The hydrolysis of the acetate is negligible in the presence of added OH<sup>-</sup>. So the pH is determined by the concentration of excess OH<sup>-</sup>:

mmol OH<sup>-</sup> = 0.100 M × 10.0 mL = 1.00 mmol in 110 mL

[OH<sup>-</sup>] = 0.00909 M

pOH = -2.04; pH = 11.96

