Topic 6H - Acid-Base Titrations

Titrations

Acid-Base neutralization reactions ⇒ a salt + water

- Stoichiometric (equivalence) point
- pH curves

Types of Acid-Base Titrations

- Strong Acid - Strong Base
  - Sharp change in pH at equivalence point
  - pH = 7 at equivalence point
- Strong Acid - Weak Base or Weak Acid - Strong Base
  - Less sharp change in pH at equivalence point
  - pH < 7 (strong acid) or pH > 7 (strong base) at equivalence point
- Weak Acid - Weak Base (?)

Acid-Base Indicators

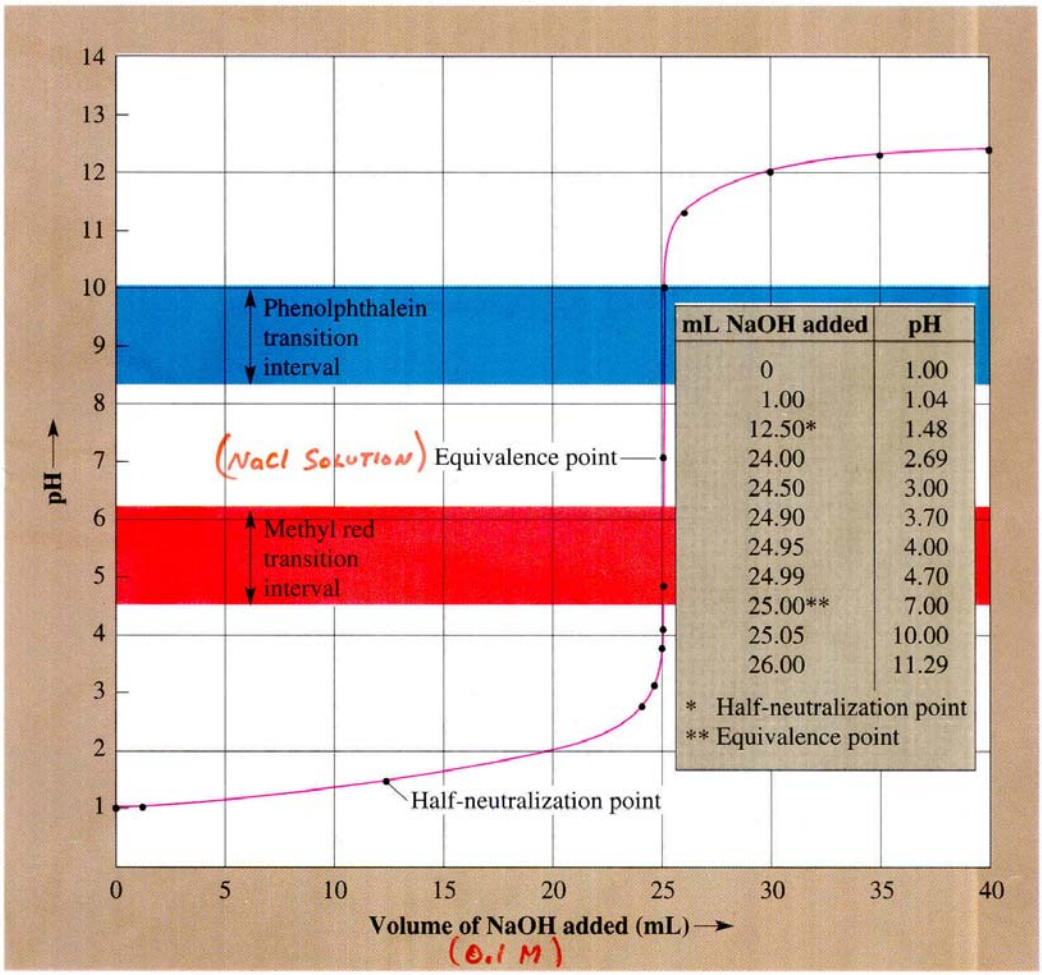
- Weak acids that have one color in their acidic form (HIn) and a different color in their basic form (In^-).
- pH at color change varies widely for different indicators.
  - Selectd to be within ~ 1 pH unit of equivalence point.

Polyprotic Acid Titrations

- Multiple equivalence points and buffer regions, corresponding to # of acidic protons.
- Successive equivalence points may become increasingly indistinct as $K_{a,n}$ approaches K_w.

A Strong Acid–Strong Base Titration Curve

25.00 mL OF 0.1 M HCl

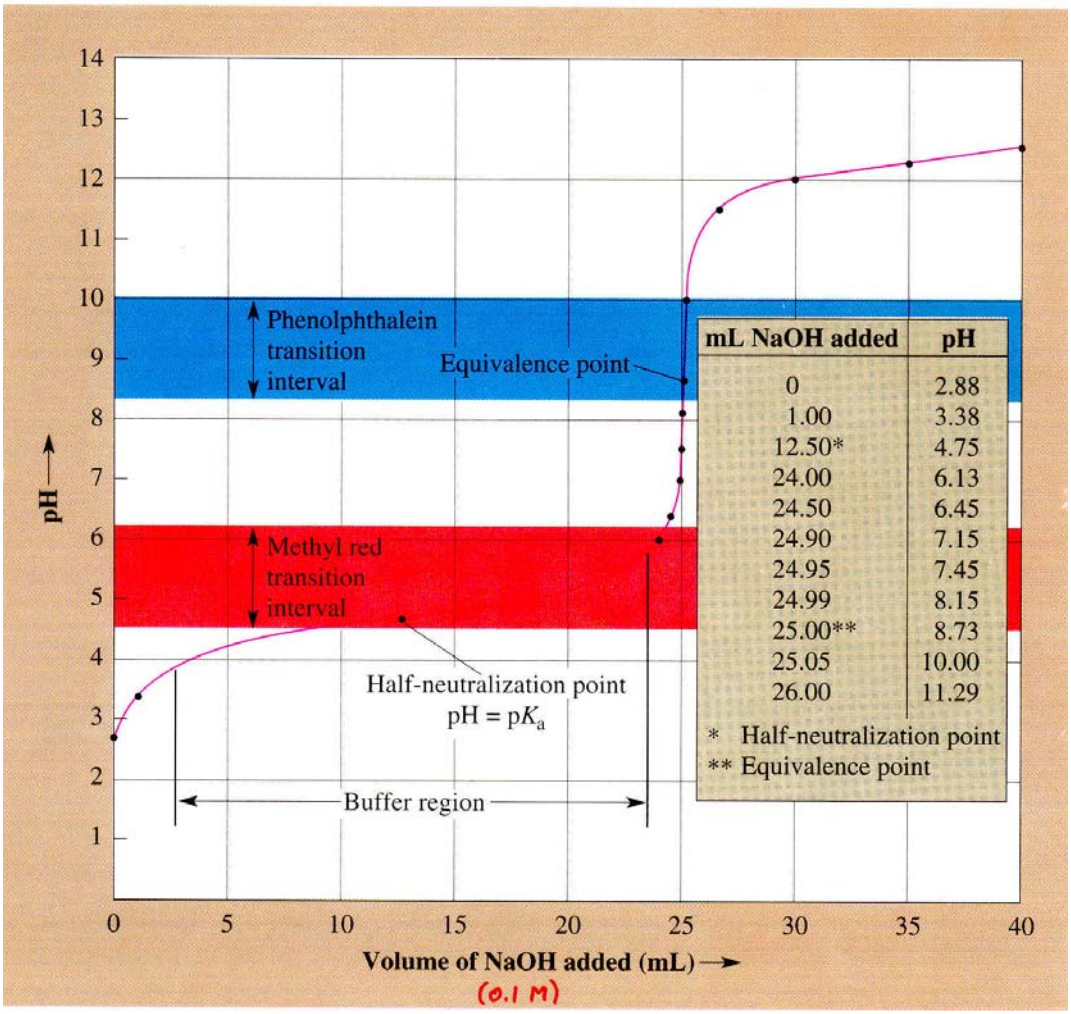


mL NaOH added	pH
0	1.00
1.00	1.04
12.50*	1.48
24.00	2.69
24.50	3.00
24.90	3.70
24.95	4.00
24.99	4.70
25.00**	7.00
25.05	10.00
26.00	11.29

* Half-neutralization point
** Equivalence point

A Weak Acid–Strong Base Titration Curve

25.00 mL ACETIC ACID (0.1 M)



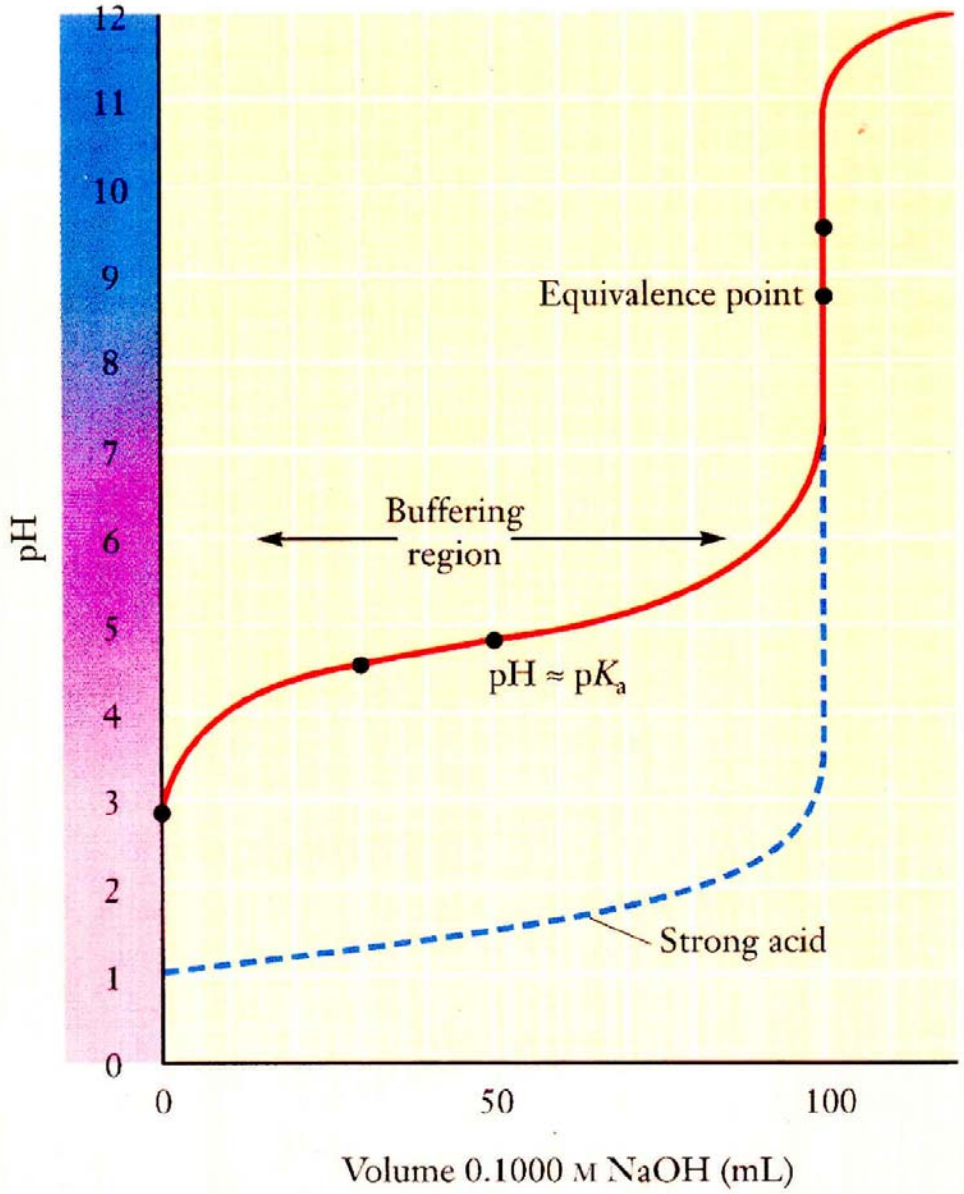


FIGURE 10.14 A titration curve for the titration of a weak acid by a strong base. The curve shown in red is for 100.0 mL of 0.1000 M CH_3COOH titrated with 0.1000 M NaOH. For comparison, the dashed blue line shows the titration curve for a strong acid of the same amount and concentration as presented in Figure 10.13.

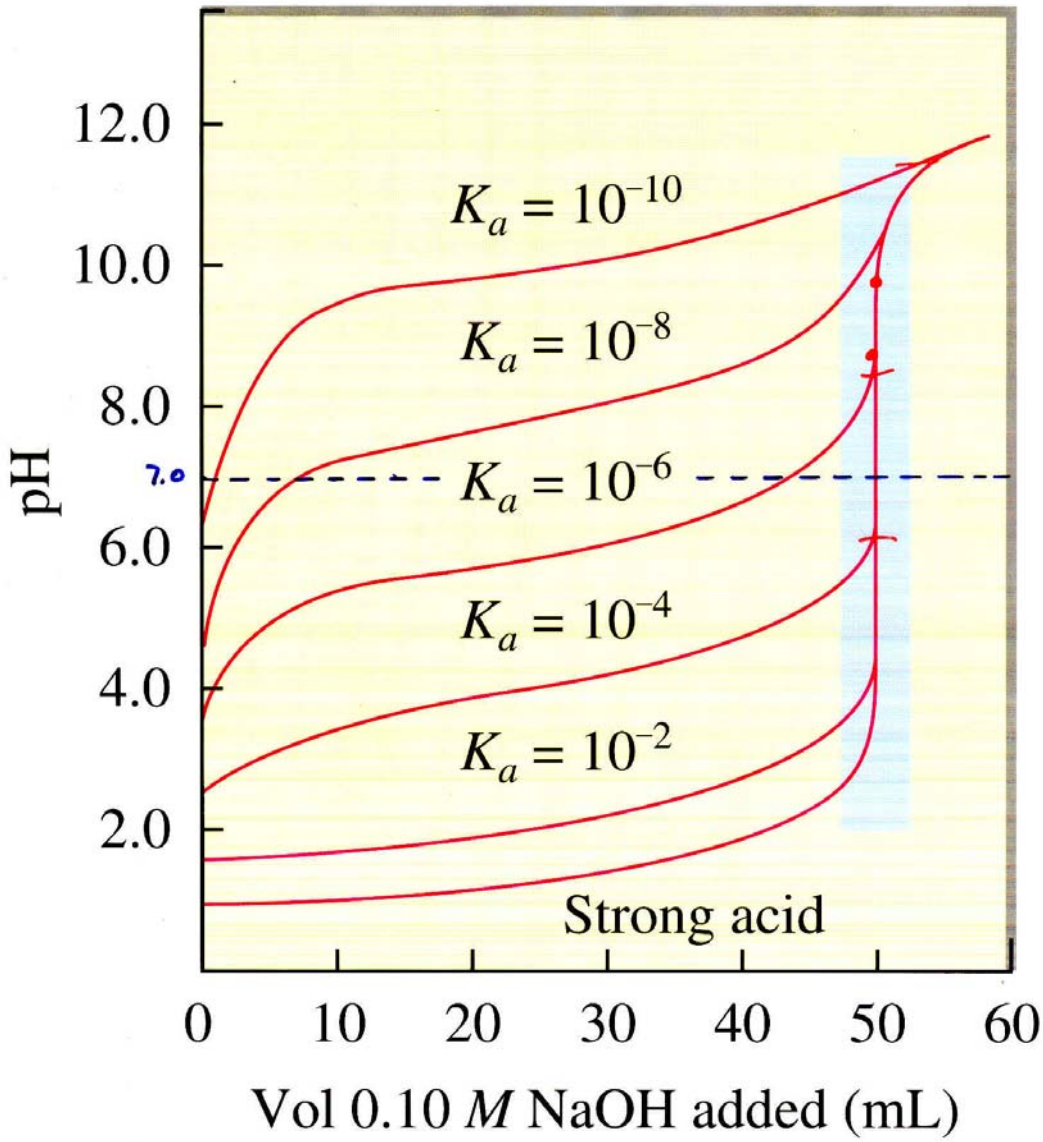
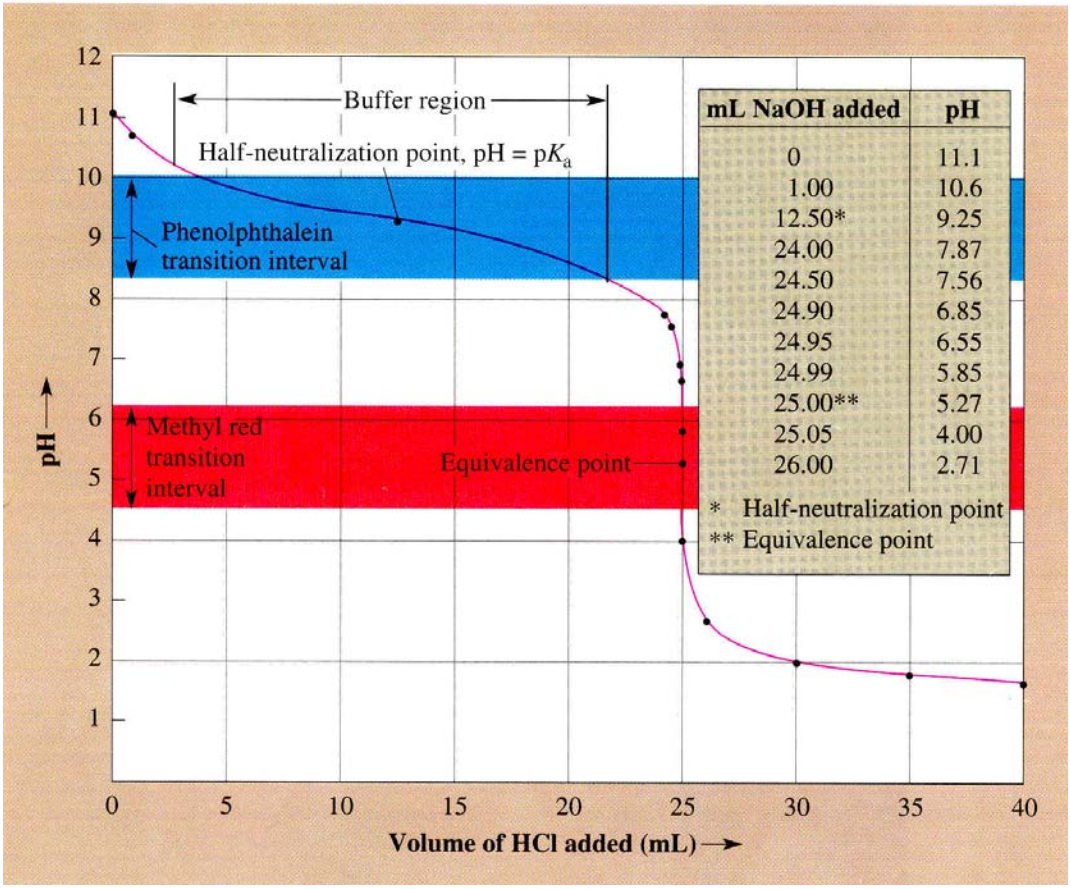


Figure 15.4
The shape of the titration curve as a function of K_a

A Weak Base–Strong Acid Titration Curve



mL NaOH added	pH
0	11.1
1.00	10.6
12.50*	9.25
24.00	7.87
24.50	7.56
24.90	6.85
24.95	6.55
24.99	5.85
25.00**	5.27
25.05	4.00
26.00	2.71

* Half-neutralization point
** Equivalence point

Curve for Titration of a Weak Acid with a Weak Base

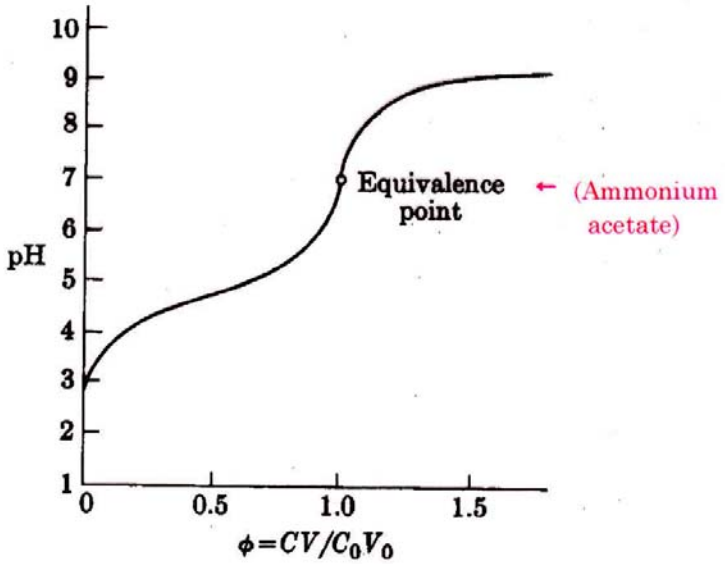


FIG. 5–15. Titration curve. pH as a function of fraction titrated in the titration of 0.10 molar acetic acid with 0.10 molar ammonia. The equivalence point coincides with the inflection point of the titration curve.

For the titration of a weak acid with a strong base or of a weak base with a strong acid, the solution at the equivalence point consists of a salt of the conjugate base of the weak acid (*e.g.*, sodium acetate), for which pH > 7, or of the conjugate acid of the weak base (*e.g.*, ammonium chloride), for which pH < 7. Prior to reaching the equivalence point, the solution consists of a buffer (*e.g.*, acetic acid + acetate ions).

However, in the titration of a weak acid with a weak base (*e.g.*, acetic acid with ammonia), the solution at the equivalence point consists of a buffer (ammonium acetate), and the pH is determined by the K_a and K_b of the weak acid and weak base, respectively:

$$pH = -\log [H_3O^+] = -\log \sqrt{K_w \frac{K_a}{K_b}}$$

If $K_a = K_b$ (as in ammonium acetate), then pH = 7.

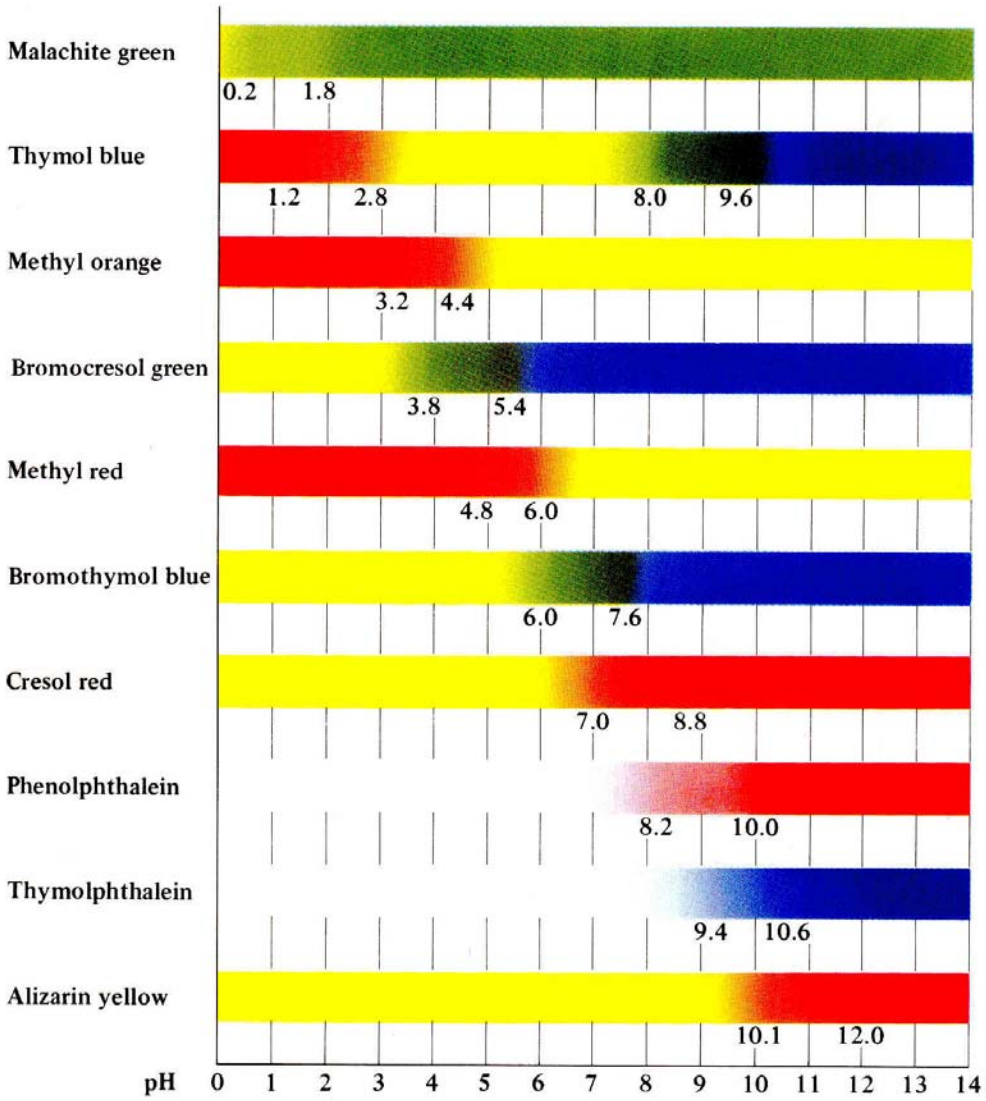
Acid-Base Indicators

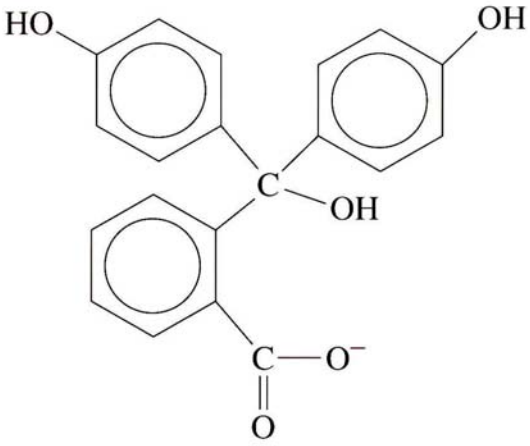
Weak acids that have one color in their acidic form (HIn) and a different color in their basic form (In^-).

pH at color change varies widely for different indicators. Selected to be within ~ 1 pH unit of equivalence point.

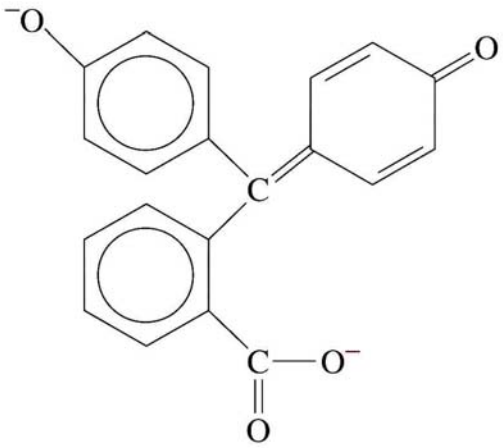
Indicator	pK_{In}	pH range of color change	Color of acid form		Color of base form
thymol blue	1.7	1.2 to 2.8	red		yellow
methyl orange	3.4	3.2 to 4.4	red		yellow
bromophenol blue	3.9	3.0 to 4.6	yellow		blue
bromocresol green	4.7	3.8 to 5.4	yellow		blue
methyl red	5.0	4.8 to 6.0	red		yellow
litmus	6.5	5.0 to 8.0	red		blue
bromothymol blue	7.1	6.0 to 7.6	yellow		blue
phenol red	7.9	6.6 to 8.0	yellow		red
thymol blue	8.9	8.0 to 9.6	yellow		blue
phenolphthalein	9.4	8.2 to 10.0	colorless		pink
alizarin yellow R	11.2	10.1 to 12.0	yellow		red
alizarin	11.7	11.0 to 12.4	red		purple

*The colors of the acid and base forms are only a symbolic representation of the actual colors.


Malachite green
0.2
1.8
Thymol blue
1.2
2.8
8.0
9.6
Methyl orange
3.2
4.4
Bromocresol green
3.8
5.4
Methyl red
4.8
6.0
Bromothymol blue
6.0
7.6
Cresol red
7.0
8.8
Phenolphthalein
8.2
10.0
Thymolphthalein
9.4
10.6
Alizarin yellow
10.1
12.0
pH
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14



(Colorless acid form, HIn)



(Pink base form, In^-)

Figure 15.6
The acid and base forms of phenolphthalein

Matrix of 96 vials containing solutions buffered at 12 different pH values, ranging from acidic on the left (pH = 1) to alkaline on the right (pH = 12), and containing one of 8 different indicators (A - H) (see key to indicators below picture):

A Thymol blue
B Thymolphthalein
C Congo red
D Cabbage extract
E Bromothymol blue
F Phenolphthalein
G Indigo carmine
H Universal indicator, a mix of a few different indicators including some of the above

Diprotic Acids:

TABLE 25.1

DICARBOXYLIC ACIDS AND DERIVATIVES

Name	Formula	M.p., °C	Solub., g/100 g H_2O at 20°	K_1	K_2
Oxalic	HOOC—COOH	189	9	3500×10^{-5}	4.0×10^{-5}
Malonic	$HOOCCH_2COOH$	136	74	140	0.22
Succinic	$HOOC(CH_2)_2COOH$	185	6	6.4	.25
Glutaric	$HOOC(CH_2)_3COOH$	98	64	4.5	.38
Adipic	$HOOC(CH_2)_4COOH$	151	2	3.7	.24
Pimelic	$HOOC(CH_2)_5COOH$	105	5	3.4	.26
Suberic	$HOOC(CH_2)_6COOH$	144	0.2	2.6	.25
Azelaic	$HOOC(CH_2)_7COOH$	106	0.3	2.9	.28
Sebacic	$HOOC(CH_2)_8COOH$	134	0.1	2.6	.26
Maleic	*cis*-HOOCCH=CHCOOH	130.5	79	1200	.026
Fumaric	*trans*-HOOCCH=CHCOOH	302	0.7	93	2.9
Phthalic	$1,2\text{-}C_6H_4(COOH)_2$	231	0.7	120	0.3
Isophthalic	$1,3\text{-}C_6H_4(COOH)_2$	348.5	0.01	29	2.7
Terephthalic	$1,4\text{-}C_6H_4(COOH)_2$	300subl	0.002	15	
Hemimellitic	$1,2,3\text{-}C_6H_3(COOH)_3$	190d	3	160	6.3
Trimellitic	$1,2,4\text{-}C_6H_3(COOH)_3$	238	sol.	300	14
Trimesic	$1,3,5\text{-}C_6H_3(COOH)_3$	380	2	76	13
Succinic anhydride		120			
Maleic anhydride		60			
Phthalic anhydride		131			
Succinimide		126	23	3×10^{-11}	
Phthalimide		238	0.6	5×10^{-9}	

Oxalic Acid:

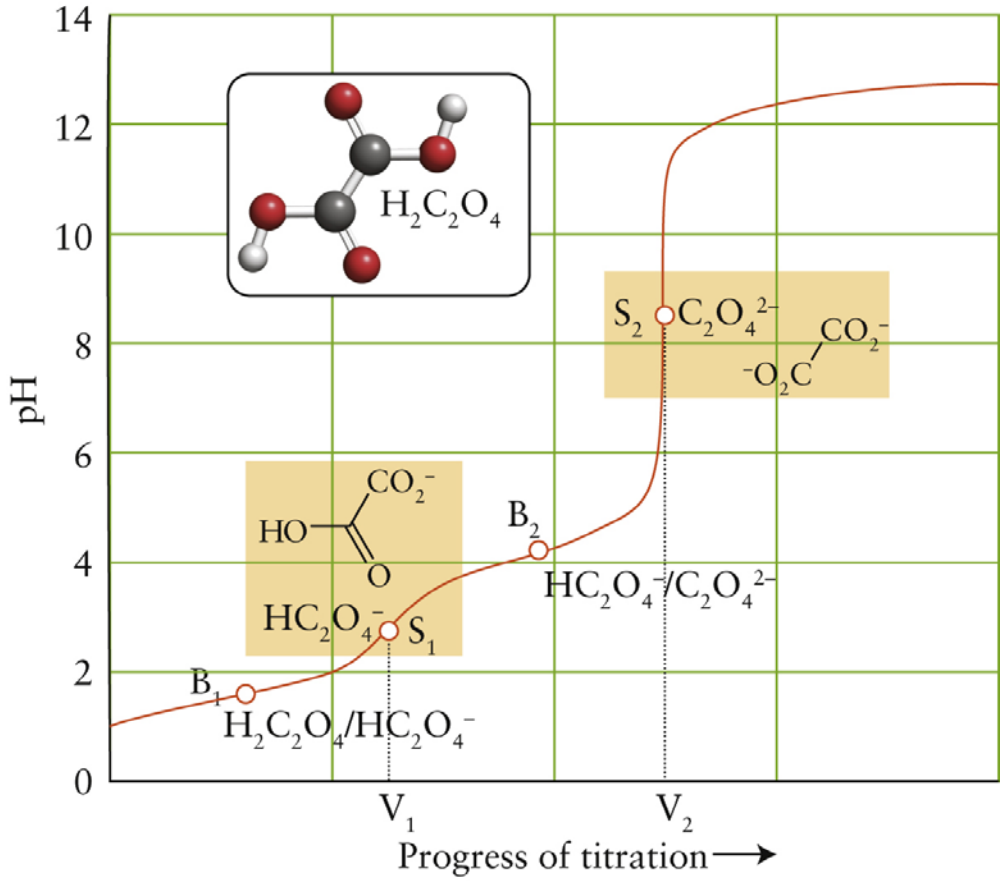


Figure 6H.11
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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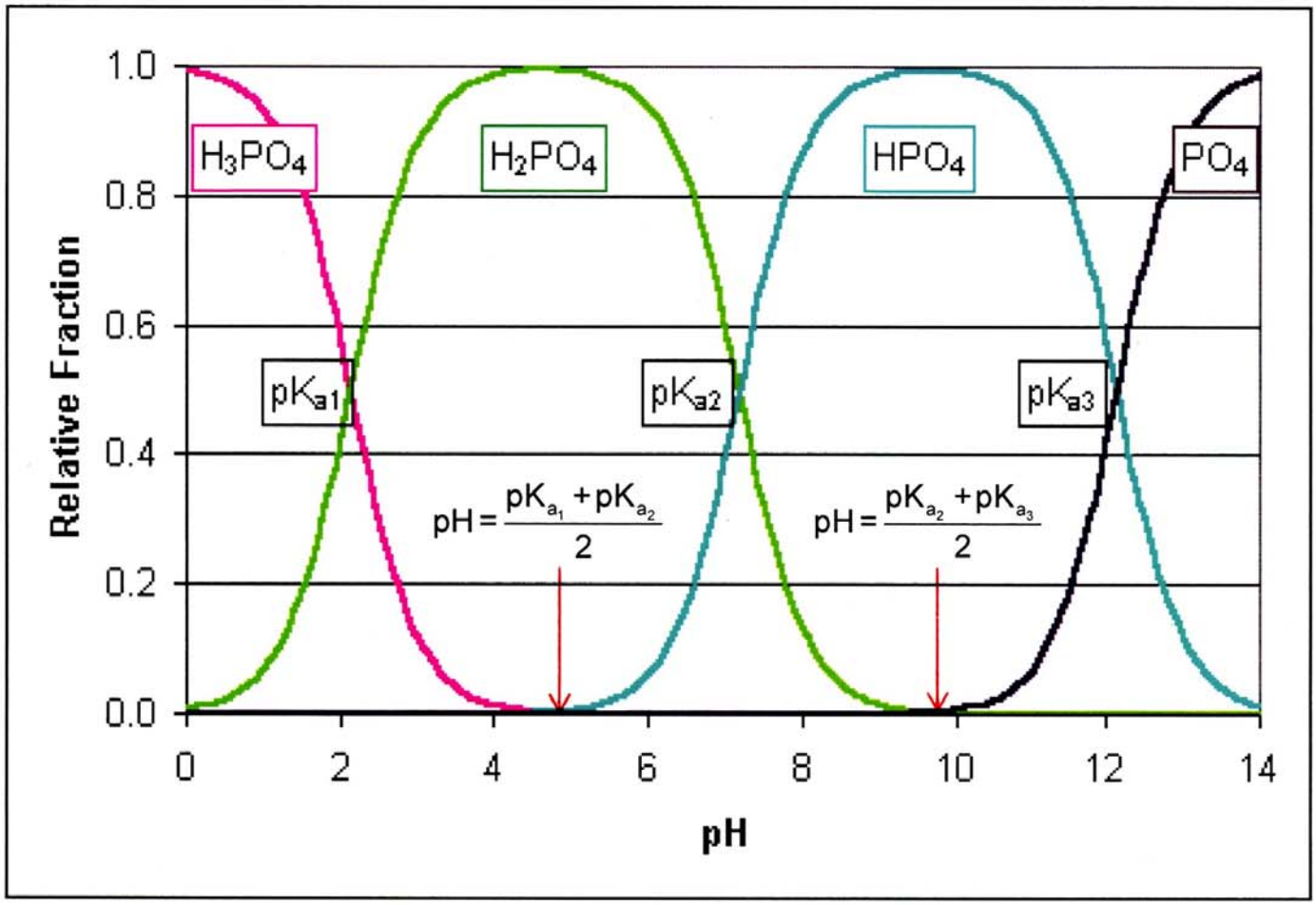
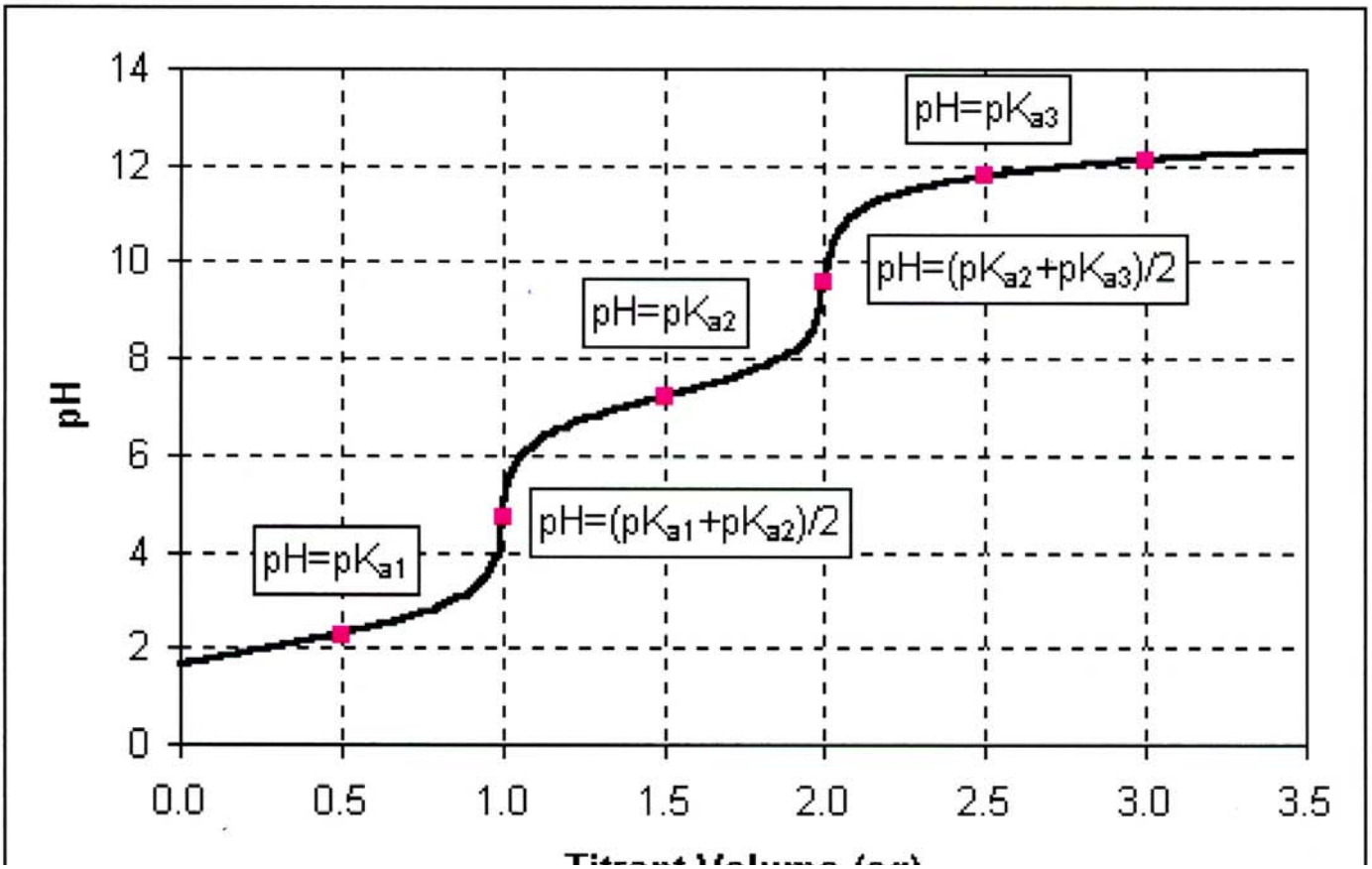
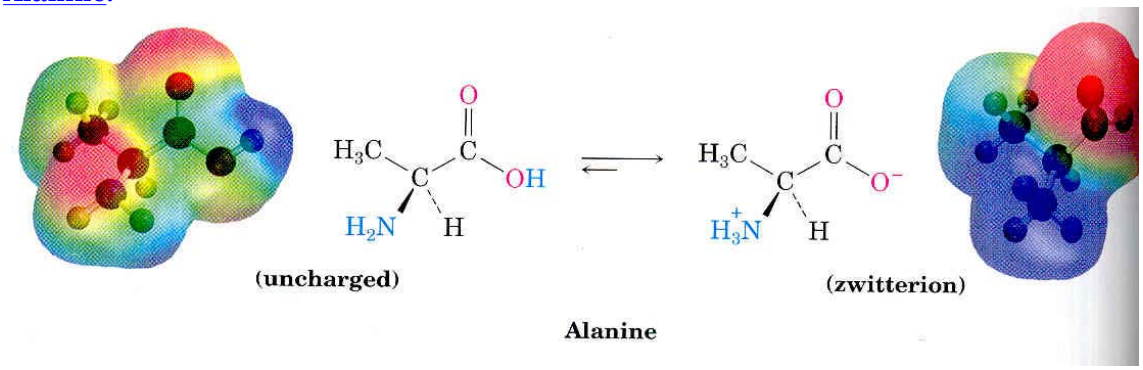
Phosphoric Acid: (H_3PO_4)

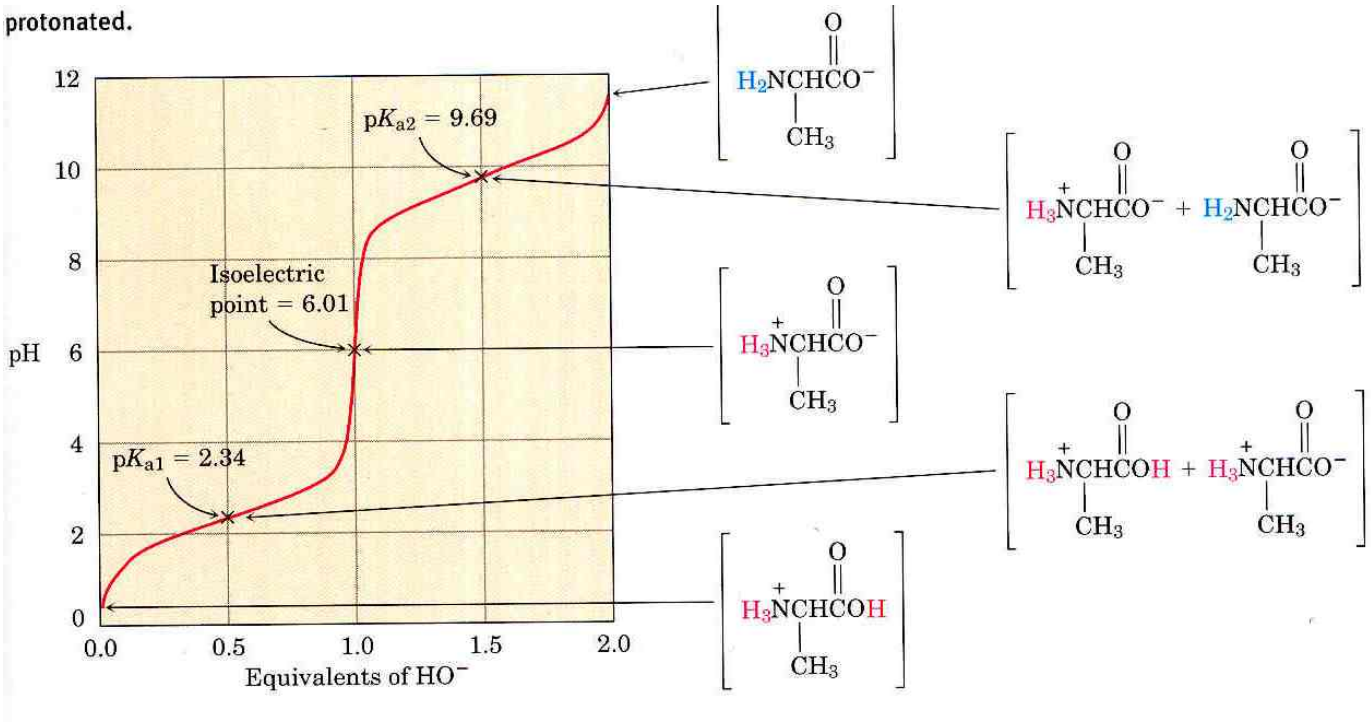

H3PO4
H2PO4
HPO4
PO4
pKa1
pKa2
pKa3
pH = (pKa1 + pKa2)/2
pH = (pKa2 + pKa3)/2
Relative Fraction
pH
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14


pH=pKa3
pH=(pKa2+pKa3)/2
pH=pKa2
pH=(pKa1+pKa2)/2
pH=pKa1
pH
14
12
10
8
6
4
2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

Amino Acids:

Alanine:





Histidine:

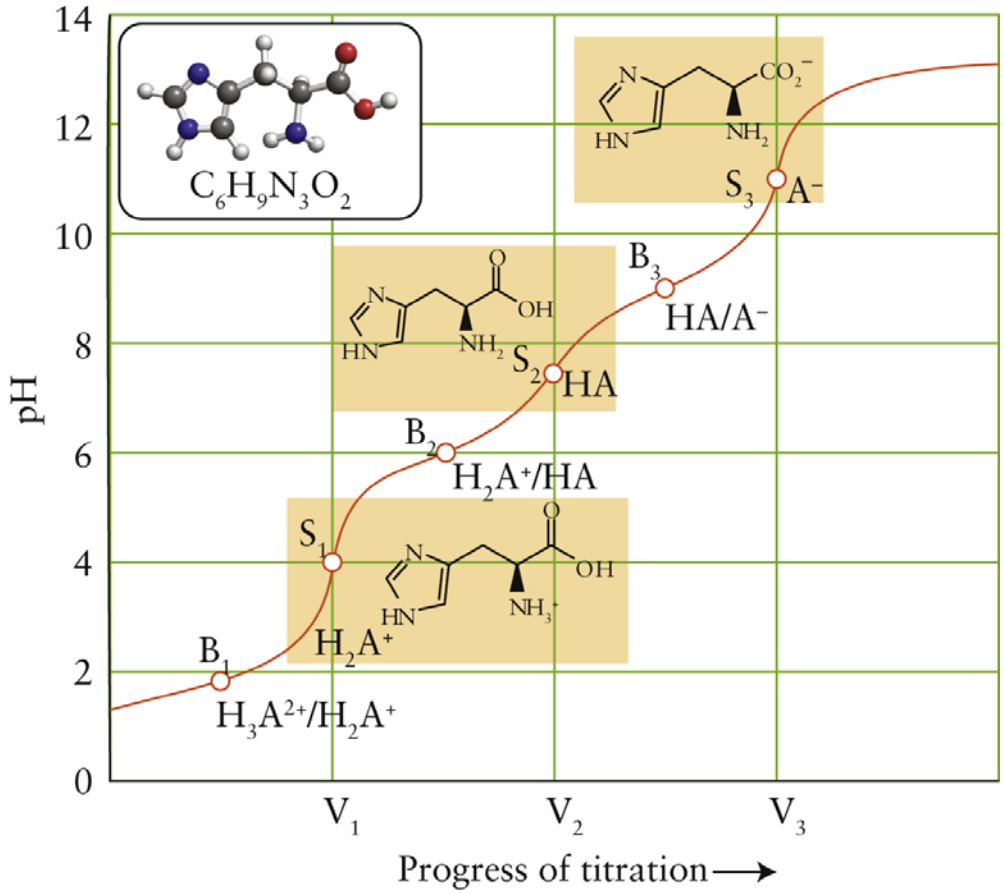


Figure 6H.10
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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