Acid – Base Titrations

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Titration Curve

A titration curve is a plot of pH vs. the amount of titrant added. Typically the titrant is a strong (completely) dissociated acid or base. Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

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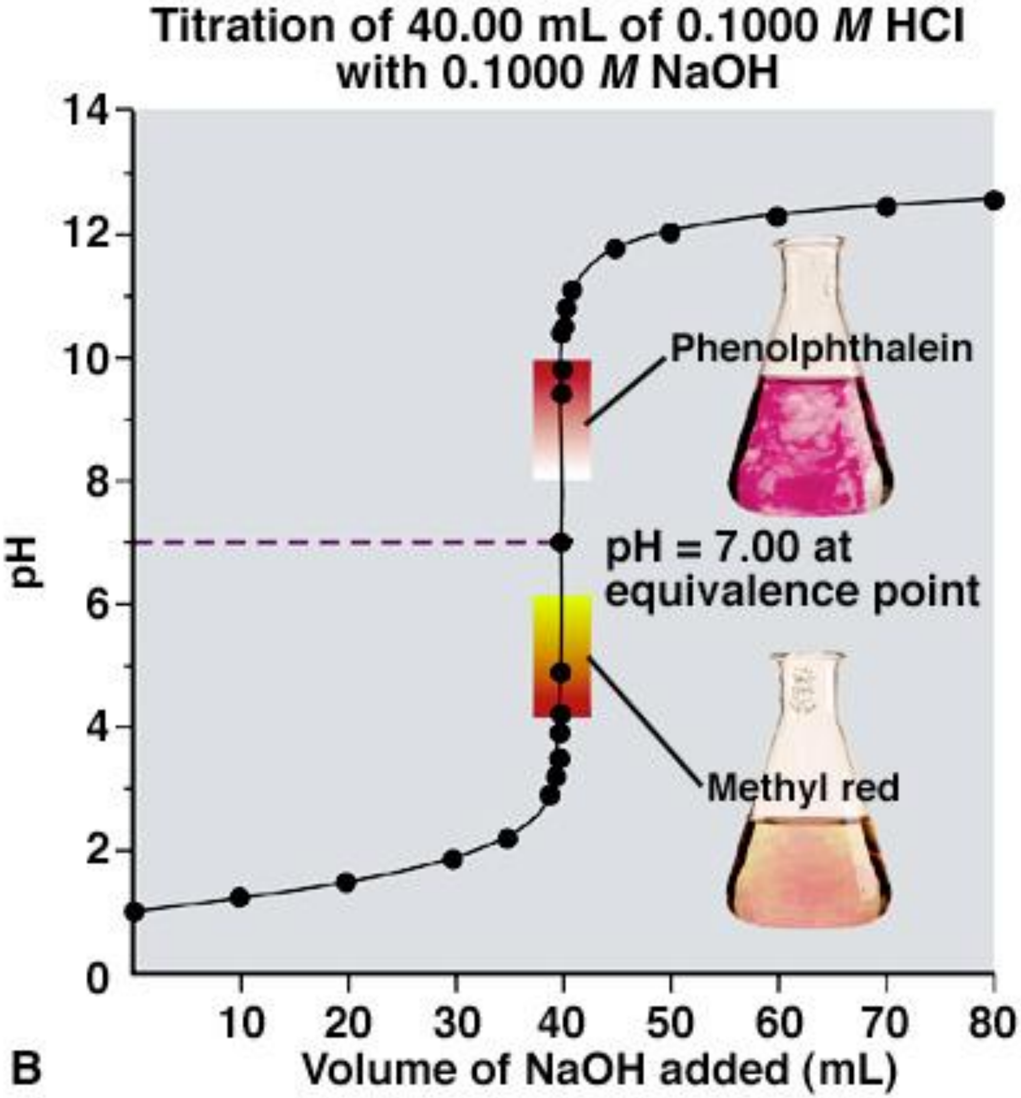


Titration of 40.00 mL of 0.1000 *M* HCl with 0.1000 *M* NaOH

Features of the Strong Acid-Strong Base Titration Curve

1. The pH starts out low, reflecting the high [H_3O^+] of the strong acid and increases gradually as acid is neutralized by the added base.

2. Suddenly the pH rises steeply. This occurs in the immediate vicinity of the equivalence point. For this type of titration the pH is 7.0 at the equivalence point.

3. Beyond this steep portion, the pH increases slowly as more base is added.

Sample Calculation: Strong Acid-Strong Base Titration Curve

Problem 24-1. Consider the titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Region 1. Before the equivalence point, after adding 20.0 mL of 0.100 M NaOH. (Half way to the equivalence point.)

Initial moles of H_3O^+ =

- Moles of OH^- added =

$$[H_3O^+] = \frac{\text{amount (mol) of } H_3O^+ \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

Sample Calculation: Strong Acid-Strong Base Titration Curve (Cont. I)

Region 2. At the equivalence point, after adding 40.0 mL of 0.100 M NaOH.

Initial moles of H_3O^+ = 0.0400 L x 0.100 M = 0.00400 M H_3O^+

- Moles of OH^- added = 0.0400 L x 0.100 M =0.00400 mol OH^-

$$[H_3O^+] = \frac{\text{amount (mol) of } H_3O^+ \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

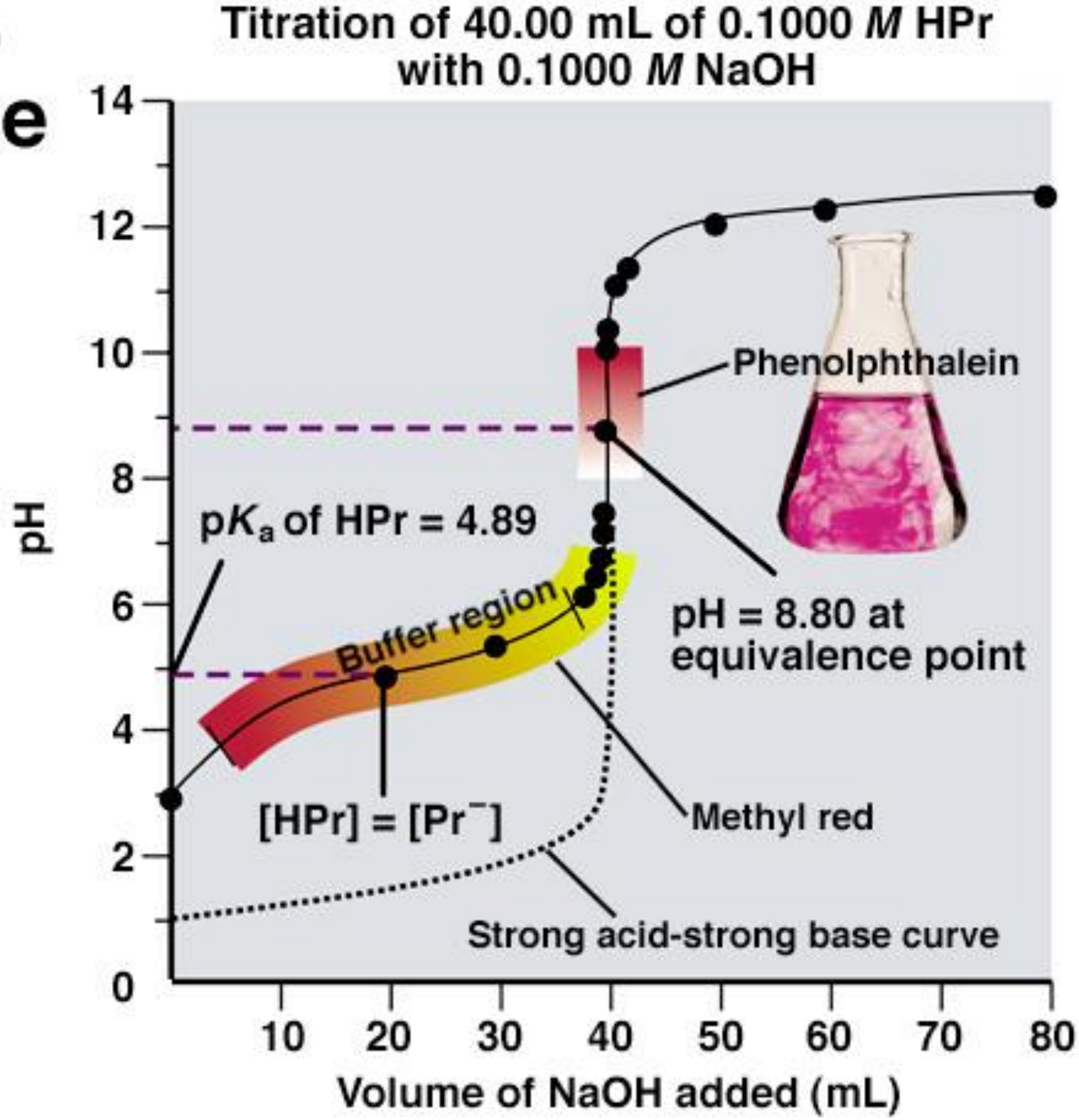
Sample Calculation: Strong Acid-Strong Base Titration Curve (cont. II)

Region 3. After the equivalence point, after adding 50.0 mL of 0.100 M NaOH. (Now calculate excess OH^-)

Total moles of OH^- = 0.0500 L x 0.100 M = 0.00500 mol OH^- -
Moles of H_3O^+ consumed = 0.0400 L x 0.100 M =0.00400 mol

$$[\mathrm{OH}^-] = \frac{\text{amount (mol) of } \mathrm{OH}^- \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

Weak Acid-Strong Base Titration Curve



HPr = Propionic Acid

The four Major Differences Between a Strong Acid-Strong Base Titration Curve and a Weak Acid-Strong Base Titration Curve

1. The initial pH is higher.
2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point.
3. The pH at the equivalence point is greater than 7.00.
4. The steep rise interval is less pronounced.

Sample Calculation: Weak Acid-Strong Base Titration Curve

Problem 24-2. Consider the titration of 40.0 mL of 0.100 M HPr ($K_a = 1.3 \times 10^{-5}$) with 0.100 M NaOH.

Region 1. The solution of weak acid to be titrated, before any base is added.

Solution:

Ans:

Sample Calculation: Weak Acid-Strong Base Titration Curve (Cont.I)

Problem 24-2. Consider the titration of 40.0 mL of 0.100 M HPr (K_a = 1.3 x 10^{-5}) with 0.100 M NaOH.

Region 2. After 30. mL of base (total) has been added. This is clearly in the buffer region of the titration curve.

Solution: Refer to Lecture 23.

Can use the calculator program, ‘Buf’ developed in lecture 23. But first must calculate the nominal amounts of acid and base forms of the weak acid created by addition of the strong base. These are:

$[HA]_0$ =

$[A^-]_0$ =

Ans: From buffer program: **pH =**

Sample Calculation: Weak Acid-Strong Base Titration Curve (Cont.II)

Problem 24-2. Consider the titration of 40.0 mL of 0.100 M HPr (K_a = 1.3 x 10^{-5}) with 0.100 M NaOH.

Region 3. After 40. mL of base (total) has been added. This is clearly at the equivalence point of the titration curve.

Solution: Refer to Lecture 23.

Can use the calculator program developed in lecture 23. But first must calculate the nominal amounts of acid and base forms of the weak acid created by addition of the strong base. These are:

$[HA]_0$ =

$[A^-]_0$ =

Ans: From buffer program: **pH =**

Sample Calculation: Strong Acid-Strong Base Titration Curve (cont. III)

Region 4. After the equivalence point, after adding 50.0 mL of 0.100 M NaOH. (Now calculate excess OH^-)

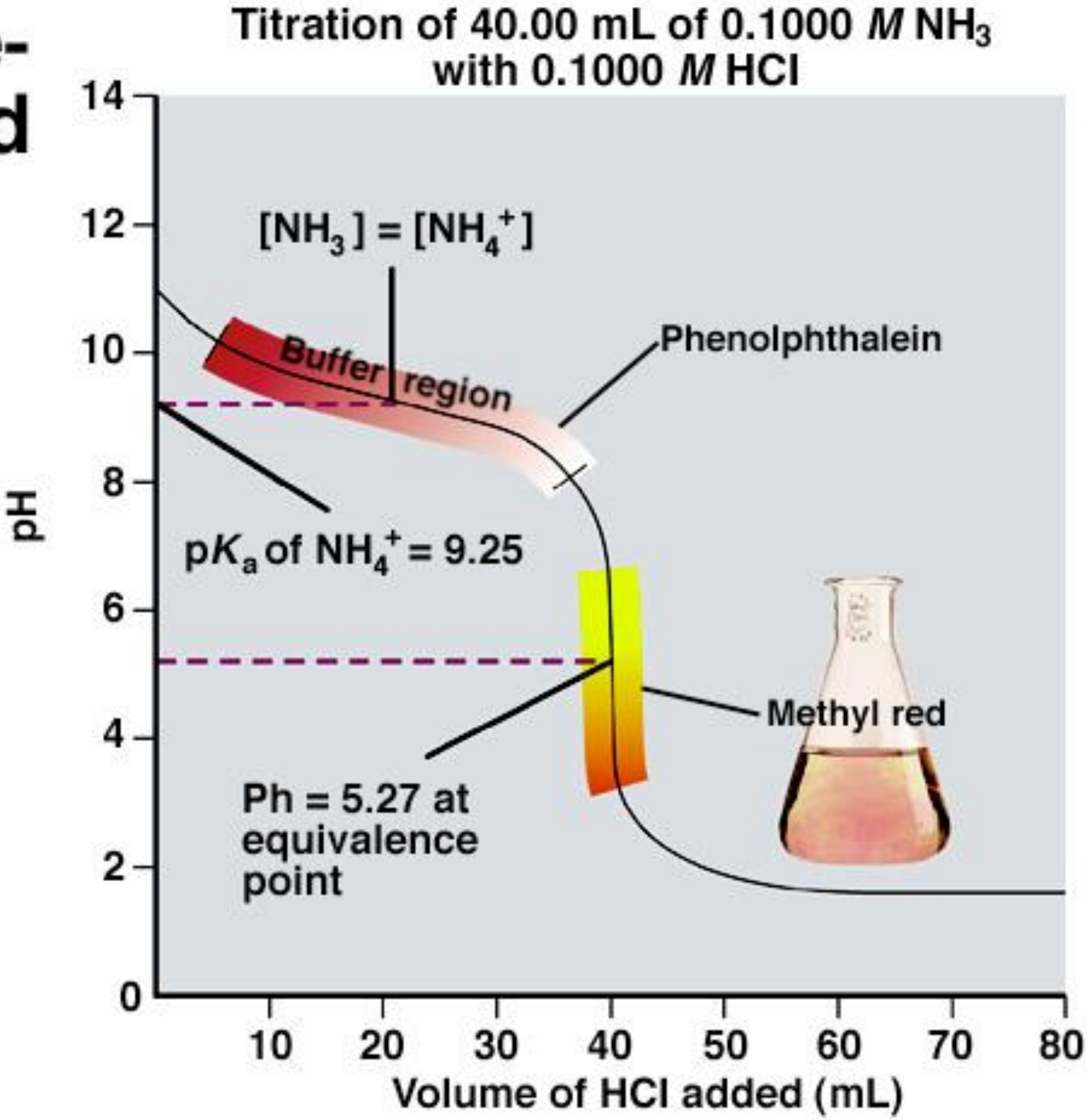
Total moles of OH^- = -

Moles of weak acid consumed =

Moles of OH^- remaining =

$$[OH^-] = \frac{\text{amount (mol) of } OH^- \text{ remaining after neutraliza tin}}{\text{original volume of acid} + \text{volume of added base}}$$

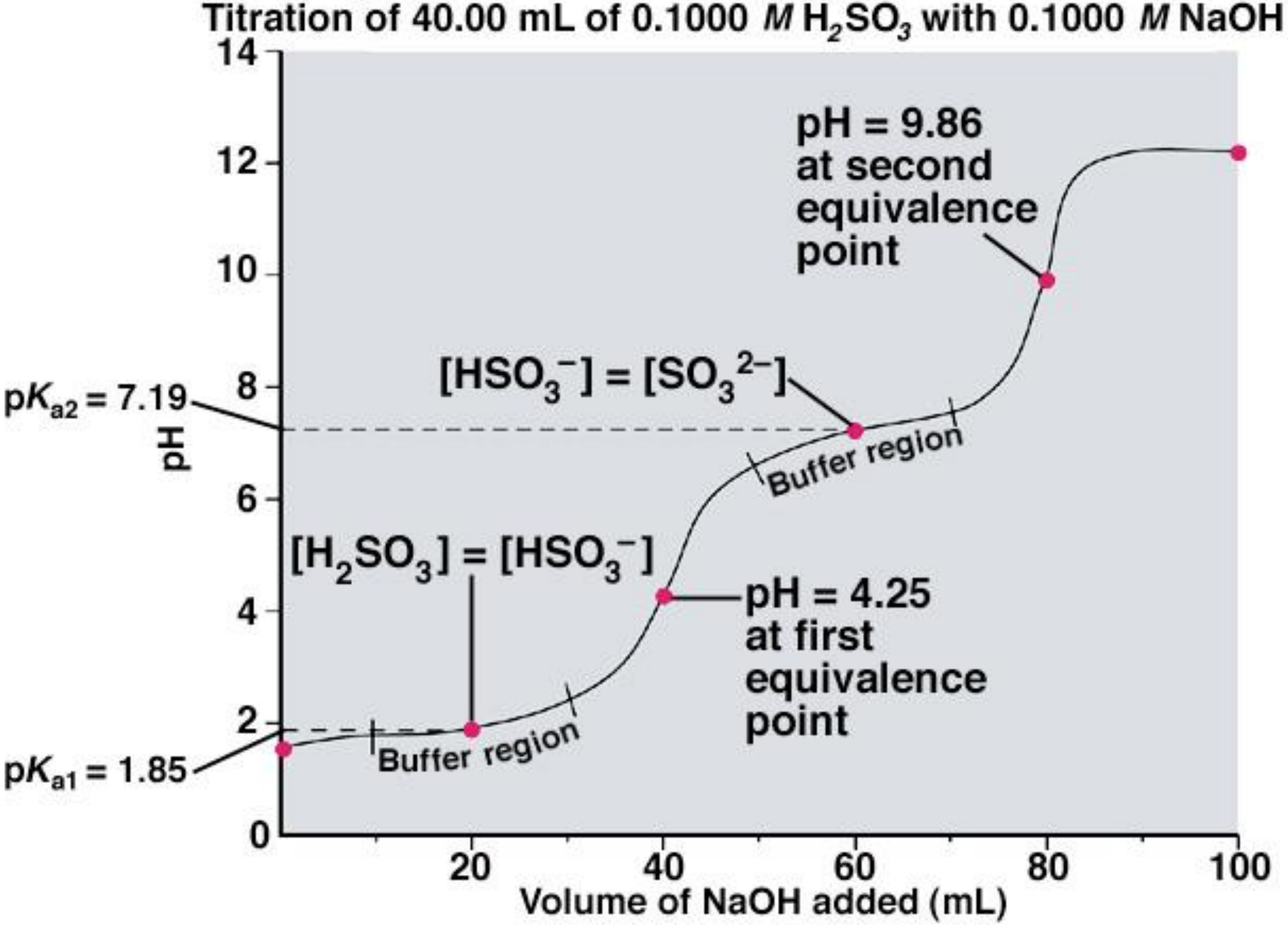
Weak Base-Strong Acid Titration Curve



The four Major Differences Between a Weak Acid-Strong Base Titration Curve and a Weak Base-Strong Acid Titration Curve

1. The initial pH is above 7.00.
2. A gradually decreasing portion of the curve, called the buffer region, appears before a steep fall to the equivalence point.
3. The pH at the equivalence point is less than 7.00.
4. Thereafter, the pH decreases slowly as excess strong acid is added.

Weak Polyprotic Acid Titration Curve



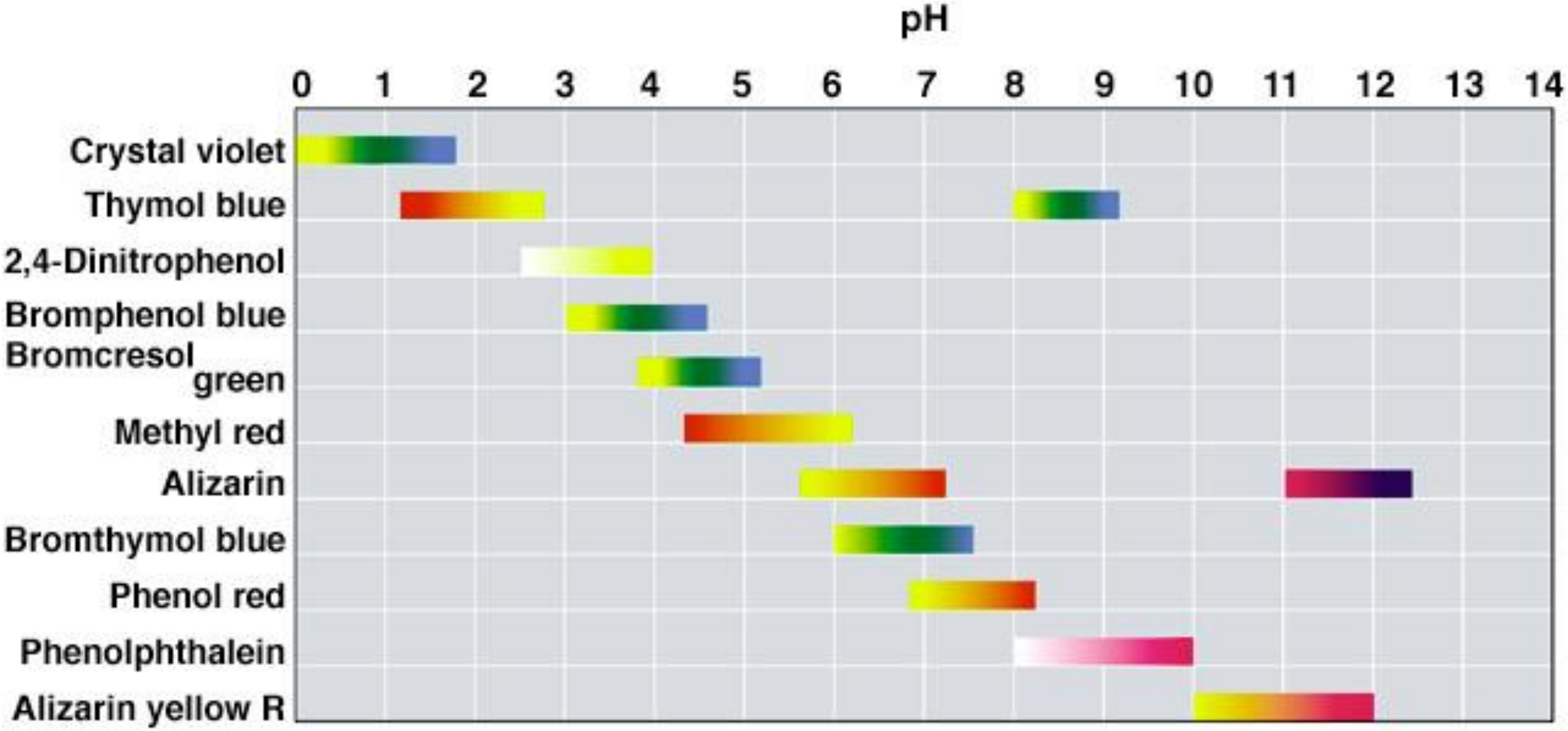
Features of the Titration of a Polyprotic Acid with a Strong Base

1. The loss of each mole of H^+ shows up as separate equivalence point (but only if the two pK_as are separated by more than 3 pK units).

2. The pH at the midpoint of the buffer region is equal to the pK_a of that acid species.

3. The same volume of added base is required to remove each mole of H^+.

pH Range of Acid-Base Indicators



Acid-Base Indicators and the Measurement of pH

- Definition: A weak organic acid, HIn that has a different color than its conjugate base, In^-, with the color change occurring over a specific and relatively narrow pH range.
- Typically, one or both forms are intensely colored, so only a tiny amount of indicator is needed, far too little to perturb the pH of the solution.
- Since the indicator molecule is a weak acid, the ratio of the two forms governed by the $[H_3O^+]$ of the test solution:

$$\mathrm{HIn}(aq) + \mathrm{H_2O}(l) = \mathrm{H_3O^+}(aq) + \mathrm{In^-}(aq) \qquad \mathrm{K_a\ of\ HIn} = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]}$$

$$\text{Therefore :} \qquad \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} = \frac{[\mathrm{H_3O^+}]}{[\mathrm{K_a}]}$$

Let us consider quantitatively, the case of titrating a weak acid with a strong base. If the weak acid has one dissociable proton, then the overall reaction is:

$$HA + OH^- = A^- + H_20$$

We will assume that the strong base NaOH and the weak acid anion NaA are completely dissociated in solution.

Furthermore, we will not neglect the contribution of the dissociation of water.

Our Titration System is Governed by Four Equations

acid - base equilibrium

water hydrolysis

charge balance

material balance

- Such a system has 8 experimentally measurable variables: K_a, K_w, $[HA]_0$ and $[NaOH]_0$
- If we assume that the first four (K_a, K_w, $[HA]_0$ and $[NaOH]_0$) are known, then we are left with 4 equations in 4 unknowns.
- Of the 4 unknowns, the only one we can conveniently measure is $[H^+]$. This suggests that we solve the four equations for $[H^+]$ by successive elimination.

The Exact Solution to the Titration Problem

We now proceed to solve the four equations for [H^+] by successive elimination of variables. The result for [H^+] is

Finding [H^+] requires that we find the three roots of the above cubic equation and then selecting the one root that is consistent with physical reality, i.e. leads to all positive concentrations. Fortunately, in the above case only one root is positive and the other two are negative.

This positive root can be found by the ‘Solver’ function of your calculator. You can make a wild guess that is positive and the calculator will converge to the correct answer.

Answers

1. Region 1, pH = 1.477, Region 2, pH = 7.000, Region 3, pH = 12.046
2. Region 1, pH = 2.95 , Region 2, pH = 5.36 , Region 3,

   pH = 8.79 , Region 4 = 12.05