Acid and Base Titrations

AP Chemistry

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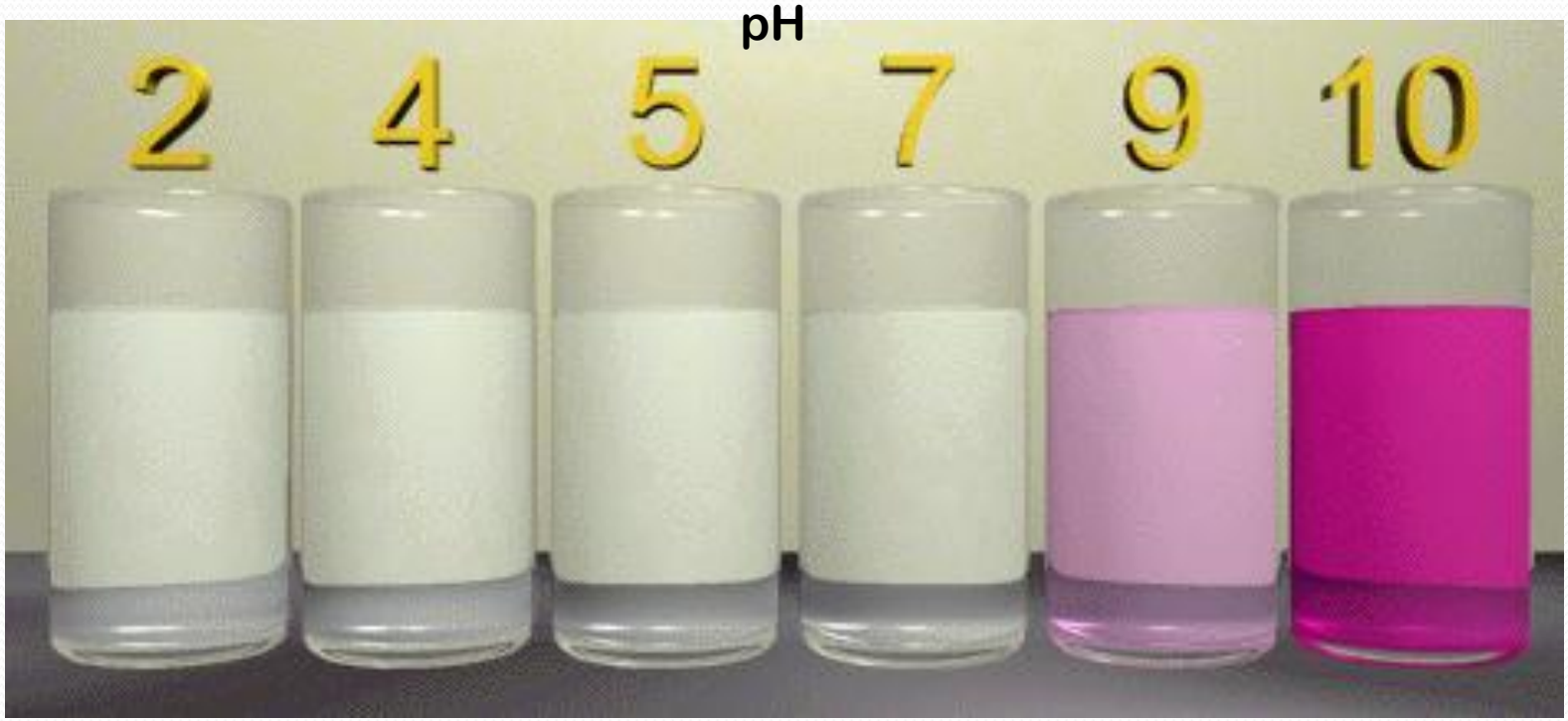
What is a Titration?

- It is a procedure that is commonly used to determine amount of acid or base in solution
  - Solution of known concentration (titrant) is delivered to a solution being analyzed (analyte)
- Acid-base indicators can be used to signal the **equivalence point** of a titration
  - At this point, moles of acid = moles of base
    - Determined by stoichiometry ONLY!

Acid-Base Indicator Examples

- Acid-base indicators are weak acids that undergo a color change at a known pH

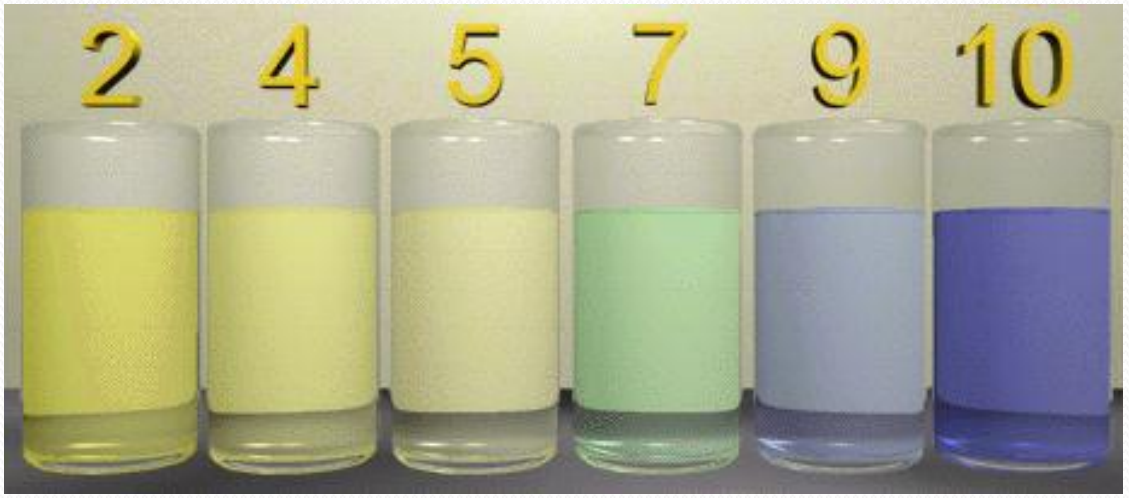


Phenolphthalein

Acid-Base Indicator Examples

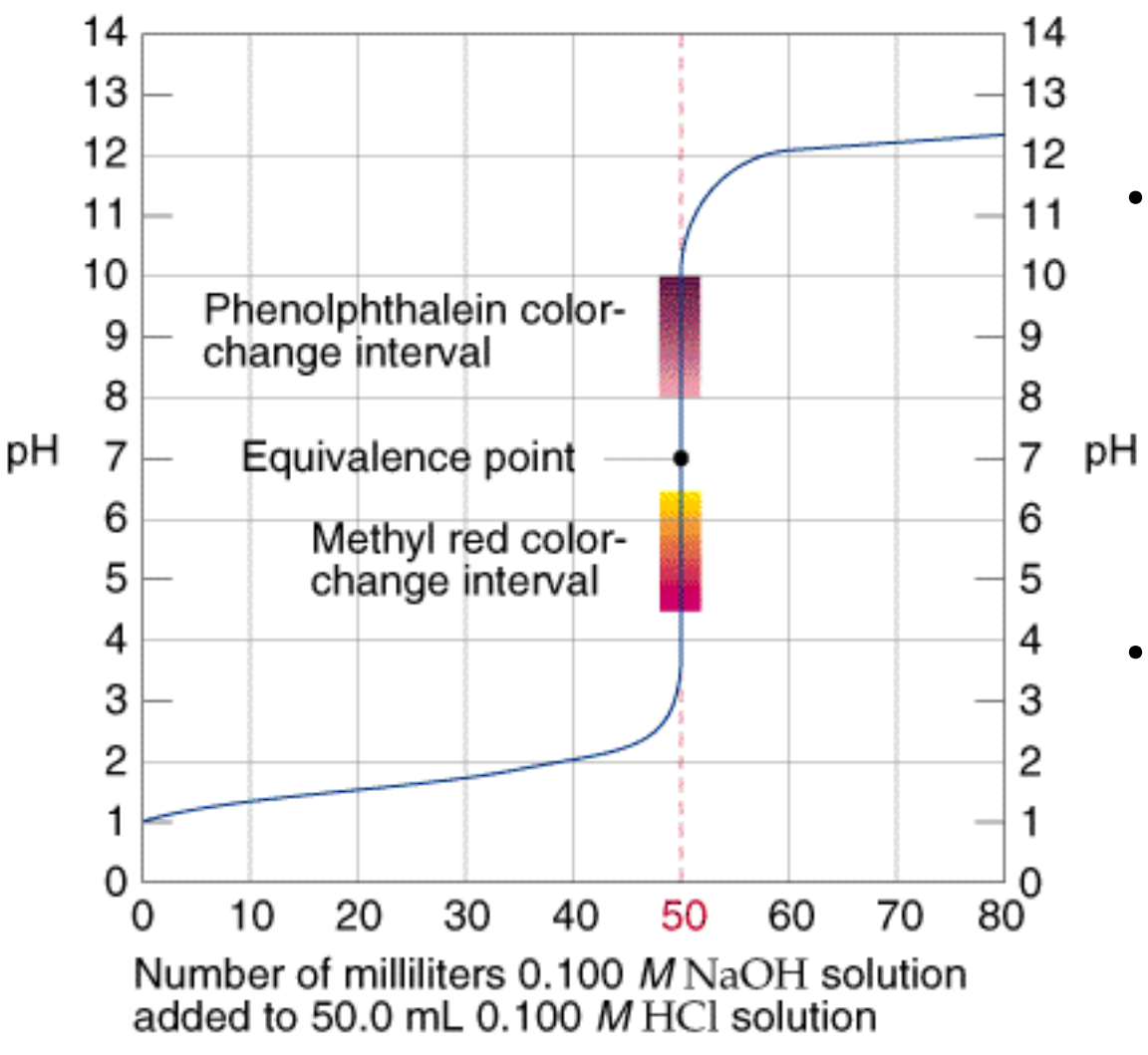
- Select the indicator that undergoes a color change closest to the pH at the equivalence point

Bromthymol blue



Methyl red

Titration Curves



- The plot of pH versus volume during a titration is a <u>titration curve</u>
- The shape of the titration curve makes it possible to determine the equivalence point, K_a, or K_b
- pH at the equivalence point is determined by the acid-base properties of the CONJUGATE present at the equivalence point

Types of Titrations

- There are three major types of titrations:
  - Strong Acid – Strong Base
    - Example – $NaOH\ (aq) + HCl\ (aq)$
  - Strong Base – Weak Acid
    - Example – $NaOH\ (aq) + HC_2H_3O_2\ (aq)$
  - Strong Acid – Weak Base
    - Example – $HCl\ (aq) + NH_3\ (aq)$

Strong Acid-Strong Base Titrations

Calculating pH of Strong Acid-Strong Base Titrations

- Before any base is added, the pH is given by the strong acid solution so pH < 7
  - pH =- log $[H^+]$
- When base is added (before the equivalence point is reached), the pH is given by the amount of strong acid in excess
  - Use BCA table to determine moles of H^+ still present after the reaction:

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

- At equivalence point, the amount of base added is stoichiometrically equivalent to the amount of acid originally present
  - Therefore, the pH is determined by the salt solution
    - Because the salt produced is neutral, pH = 7

Detecting the Equivalence Point in a Strong Acid-Strong Base Titration

- To detect the equivalence point, we use an indicator that changes color somewhere near 7.00
- Usually, we use phenolphthalein that changes color between pH 8.3 to 10.0
  - In an acidic solution, phenolphthalein is colorless
  - As NaOH is added, there is a slight pink color at the addition point
  - When the flask is swirled and the reagents mixed, the pink color disappears
  - At the **end point**, the solution is light pink
  - If more base is added, the solution turns darker pink

What's the Difference Between the Equivalence Point and the End Point in a Titration?

- The *equivalence point* in a titration is the point at which the acid and base are present in stoichiometric quantities
- The *end point* in a titration is the ***observed*** point
- The difference between equivalence point and end point is called the **titration error**

Strong Acid-Strong Base Titrations – Beyond the Equivalence Point

- In this region, all of your strong acid has reacted and you have an excess of strong base
- Use BCA table to determine [OH-] after reaction occurs assuming volumes are additive

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

- Calculate pH from pOH

Visualizing a Strong Acid-Strong Base Titration

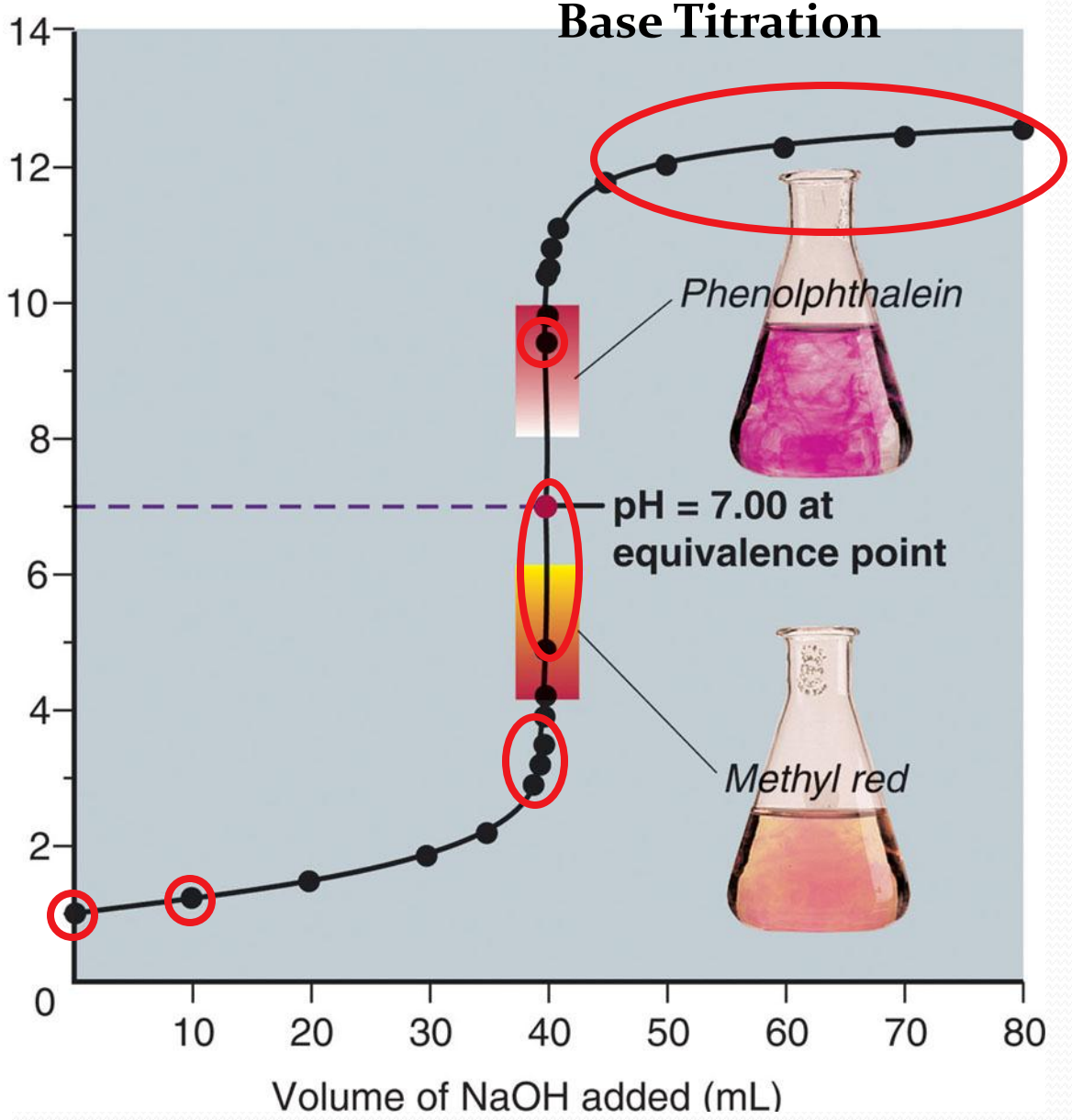


Strong Acid-Strong Base Titration Summary

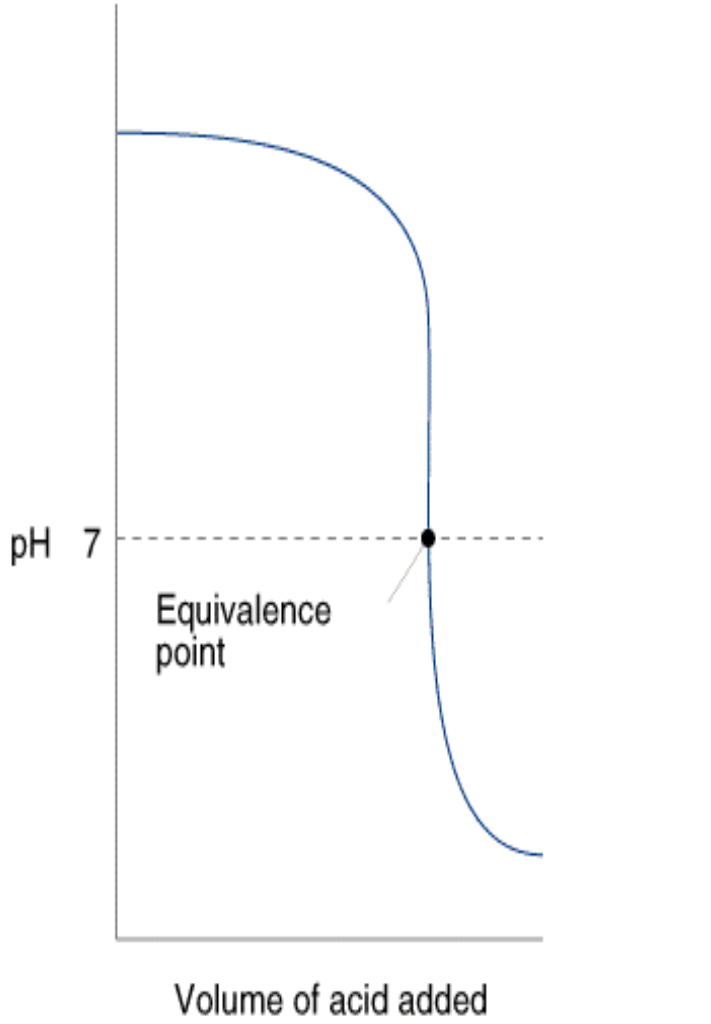
- pH is low initially
- As base is added, the pH increases slowly
- The pH rises steeply when the moles of OH- nearly equals the moles of H_3O^+
  - pH = 7 at equivalence point
- The additional drop of base neutralizes the tiny excess acid and introduces a tiny excess of base
- Then, pH increases smoothly as more base is added
  - Sharp "S" shape titration curve
- There are no buffered regions!

Figure 19.7 Curve for a Strong acid-Strong Base Titration

Volume of NaOH added (mL)	pH
00.00	1
10.00	1
20.00	1
30.00	1
35.00	2
39.00	2
39.50	3
39.75	3
39.90	3
39.95	4
39.99	4
40.00	7
40.01	9
40.05	9
40.10	10
40.25	10
40.50	10
41.00	11
45.00	11
50.00	12
60.00	12
70.00	12
80.00	12



Strong Base-Strong Acid Titration Curve



- The shape of a strong base-strong acid titration curve is very similar to a strong acid-strong base titration curve
  - Initially, the strong base is in excess, so the pH > 7
  - As acid is added, the pH decreases but is still greater than 7
  - At equivalence point, the pH is given by the salt solution (i.e. pH = 7)
  - After equivalence point, the pH is given by the strong acid in excess, so pH < 7

Practice!

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Weak Acid-Strong Base Titrations

Weak Acid-Strong Base Titrations – Initial Conditions

- Consider the titration of acetic acid, $HC_2H_3O_2$ and NaOH
- Before any base is added, the solution contains only weak acid
  - pH is given by the equilibrium system (ICE table)
- As strong base is added, the strong base consumes a stoichiometric quantity of weak acid:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$$

  - The acid is being neutralized and its conjugate base is being formed

Weak Acid-Strong Base Titrations – Before the Equivalence Point

- Thus, the solution contains a mixture of acid and conjugate base before the equivalence point
  - Buffer!
- The pH is given by the buffer calculation
  - First the amount of $C_2H_3O_2^-$ generated is calculated, as well as the amount of $HC_2H_3O_2$ consumed
    - BCA table using the neutralization reaction between the weak acid and strong base
  - Calculate new [HA] and [A-] assuming volumes are additive
  - Then, the pH is calculated using equilibrium conditions
    - ICE table or Henderson-Hasselbalch

Weak Acid-Strong Base Titrations – At the Equivalence Point

- At the equivalence point, all the acetic acid has been consumed and all the NaOH has been consumed
  - However, $C_2H_3O_2^-$ has been generated which is a weak base whose reaction with water cannot be neglected
- Therefore, the pH is given by the $C_2H_3O_2^-$ reacting with water
  - Hydrolysis reaction of conjugate base with water!

$$A^-(aq) + H_2O\ (l) \leftrightarrow HA(aq) + OH^-(aq)$$

- This means pH > 7 for weak acid-strong base titration
- More importantly, pH ≠ 7 for a weak acid-strong base titration

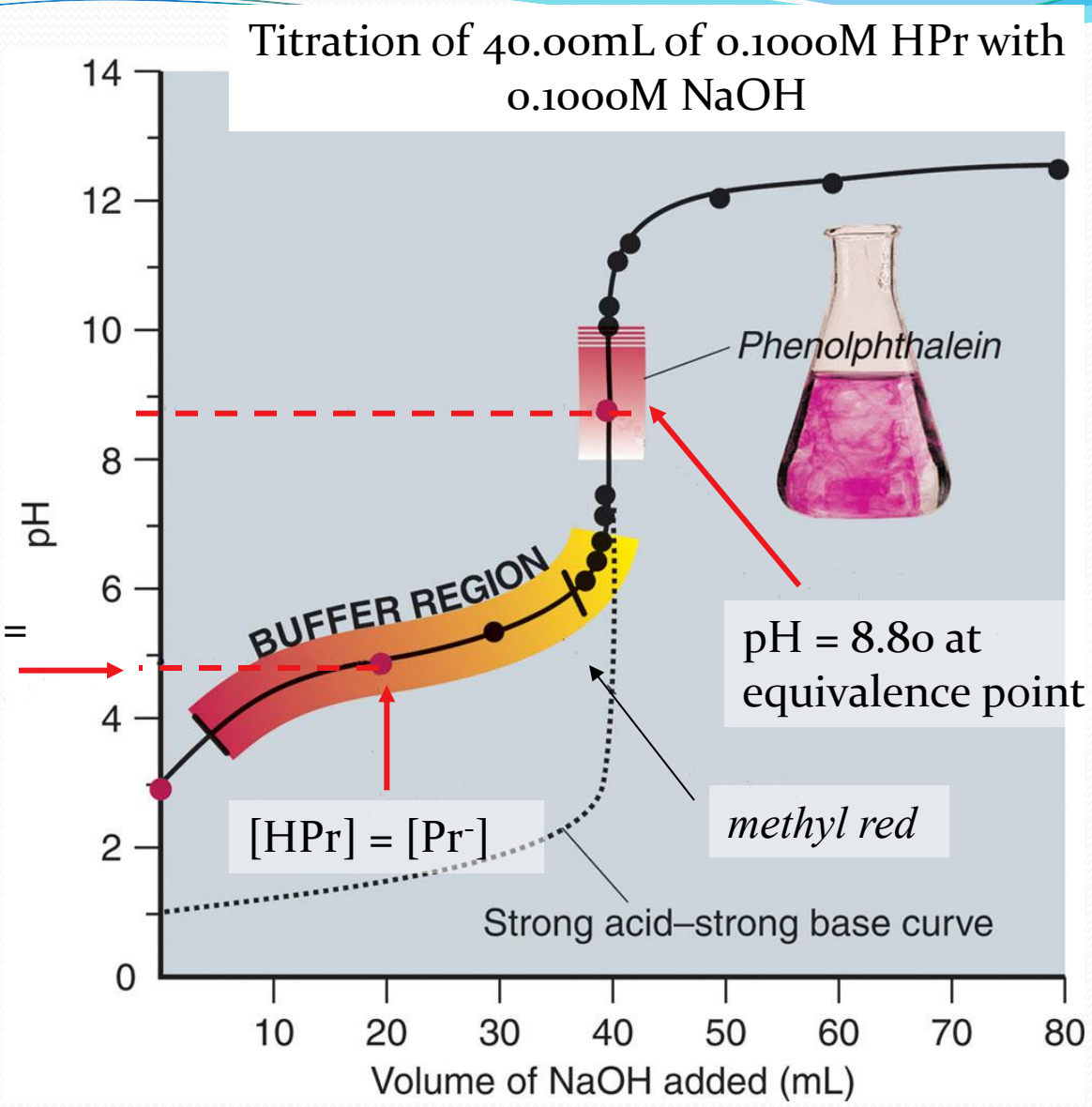
Weak Acid-Strong Base Titrations – Beyond the Equivalence Point

- In this region, all of your weak acid has reacted and you have an excess of strong base
  - You also have the conjugate base present
- Since OH- is a stronger base than A-, use BCA table to determine [OH-] after reaction occurs assuming volumes are additive
- Calculate pH from pOH

A Summary of a Weak Acid-Strong Base Titration

- Initial pH is high as weak acid dissociates slightly
- A buffer region is present!
  - A gradual rising portion of the curve appearing before the equivalence point
  - At midpoint of the buffer region, pH=pKa
- pH at equivalence point is > 7 due to conjugate base!
- Beyond equivalence point, pH increases slowly as excess OH- is added
  - Weak "S" shape titration curve

Curve for a Weak Acid-Strong Base Titration



pK_a of HPr = 4.89

Weak Acid-Strong Base Animation

Particle View of Weak Acid-Strong Base Titration

Steps to Solve Weak Acid-Strong Base Titration Problems

- When only HA is in the beginning, use ICE table calculate H^+ and pH like a weak acid type calculation
- As strong base is added, you must write a "Before Reaction" – "Change" – "After Reaction" table using MOLES ONLY using the reaction below:

$$OH^- + HA \rightarrow H_2O + A^-$$

  - This will help with stoichiometry calculations to determine new concentrations for H-H equation using K_a value of weak acid

Steps to Solve Weak Acid-Strong Base Titration Problems

- At equivalence point (OH- = HA), pH >7 due to presence of A- only!
  - pH of solution will be determined by the reaction of A- with water
  - Set up an ICE table to determine equilibrium concentrations using the reaction:

$$A^- + H_2O \leftrightarrow HA + OH^-$$

  - Find K_b from K_a and substitute into equilibrium expression to solve for "x"
  - Calculate [OH-] using new volume, pOH, then pH
- Beyond the equivalence point , set up a "BCA" table using MOLES ONLY using the reaction below:

$$OH^- + HA \rightarrow H_2O + A^-$$

  - Although there are two bases present (OH- and A-), OH- is stronger so pH is governed by the presence of OH- only!
    - Calculate pOH then pH using new volume!

Weak Acid-Strong Base Calculation Tutorial

Interactive Tutorial

Practice

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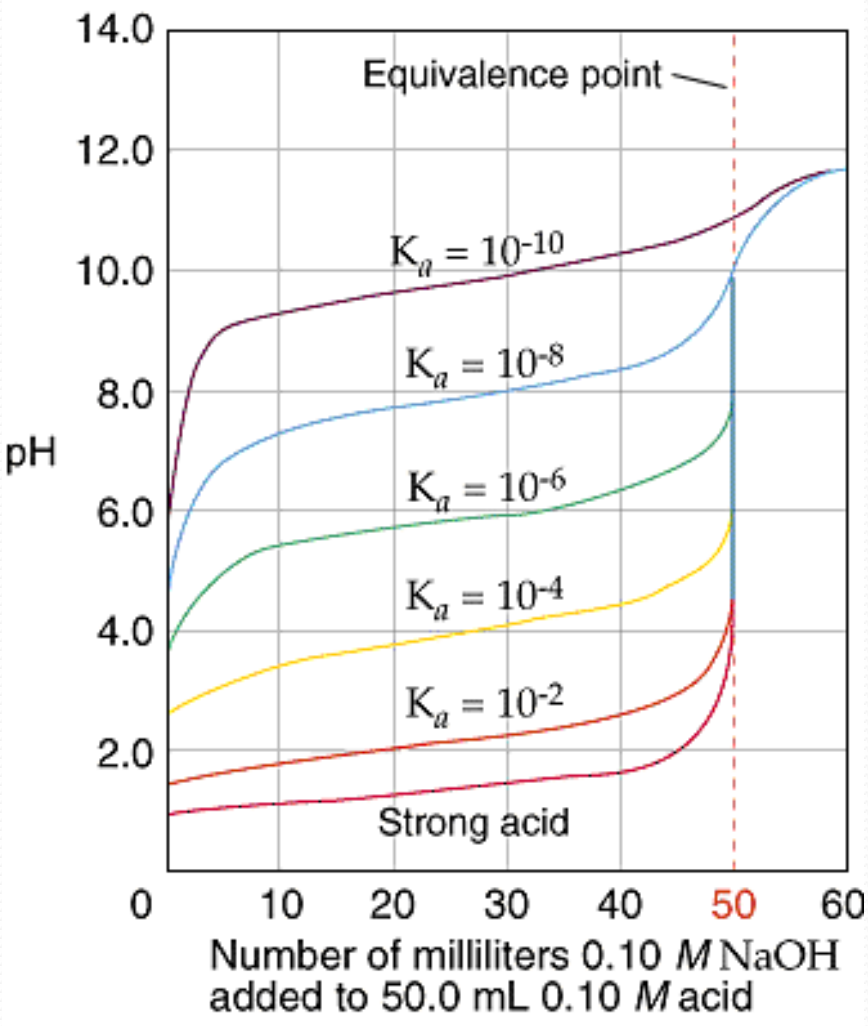
Comparing Different Titration Curves

- For a strong acid-strong base titration, the pH begins at less than 7 and gradually increases as base is added
  - Near the equivalence point, the pH increases dramatically
- For a weak acid-strong base titration, the initial pH rise is more steep than the strong acid-strong base case
  - However, there is a leveling off due to buffer effects
  - The inflection point is not as steep for a weak acid-strong base titration
- The shape of the two curves after equivalence point is the same because pH is determined by the strong base in excess
- Two features of titration curves are affected by the strength of the acid:
  - The amount of the initial rise in pH, and
  - The length of the inflection point at equivalence

Comparing Different Titration Curves

- The weaker the acid, the smaller the equivalence point inflection
- For very weak acids, it is impossible to detect the equivalence point

Weak Acid-Strong Base Titration Curves

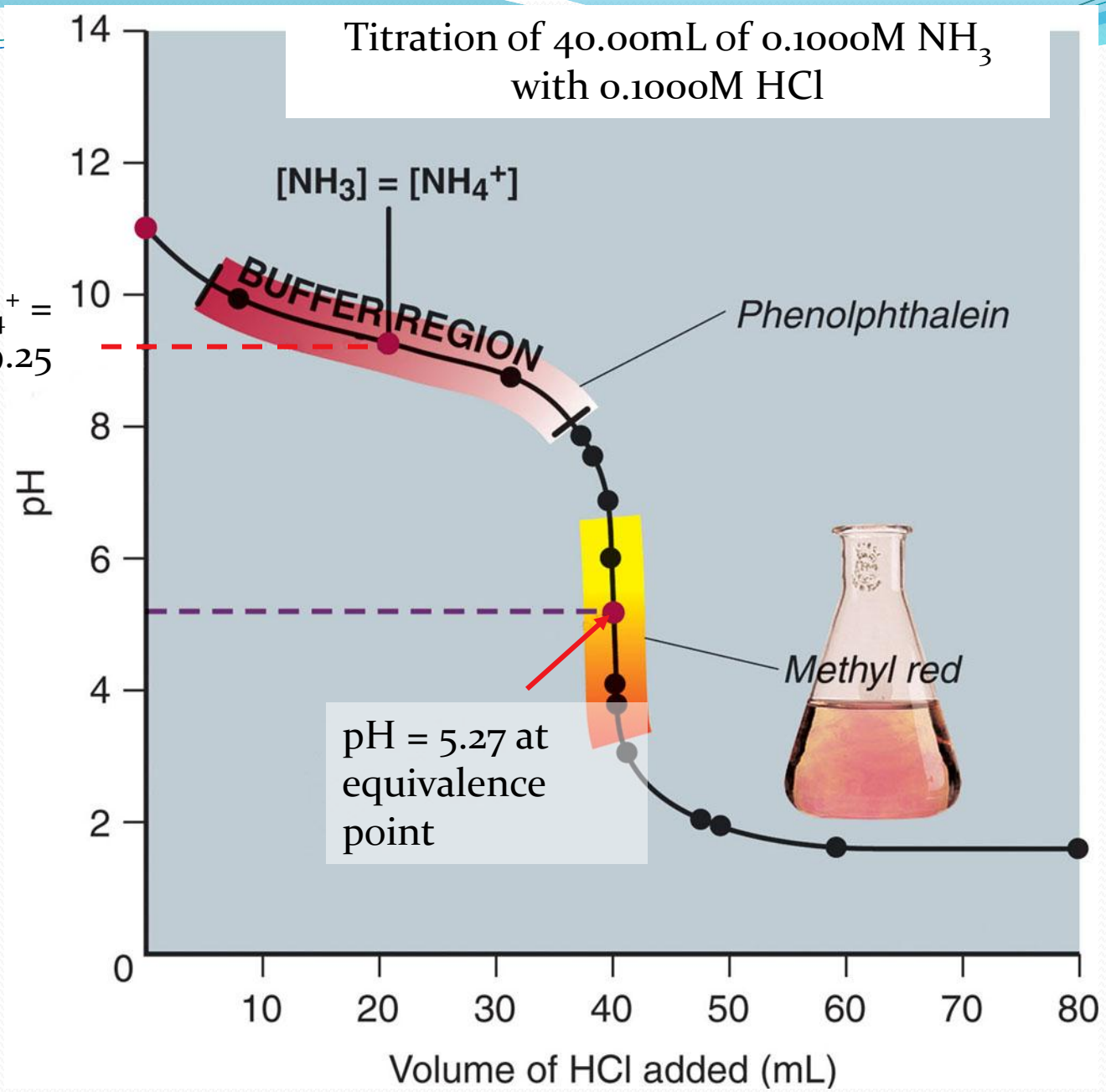


Weak Base-Strong Acid Titrations

Features of a Weak Base –Strong Acid Titration Curve

- Titration of weak bases with strong acids have similar features to a weak acid-strong base titration
  - Same "S" shape curve as WA vs SB , but inverted
    - Initially, pH above 7 as it is a weak base
    - pH decreases in buffer region
      - At midpoint of buffer region, pH=pKa
    - After buffer region, curve drops vertically to equivalence point
    - pH at equivalence point is below 7
    - Beyond equivalence point, pH decreases slowly as more acid is added

Curve for a weak base-strong acid titration



Steps to Solve Weak Base-Strong Acid Titration Problems

- When only B is present in the beginning, use ICE table calculate OH-, pOH and pH like a weak base type calculation
- As strong acid is added, you must write a "Before Reaction" – "Change" – "After Reaction" table using MOLES ONLY using the reaction below:

$$H^+ + B \rightarrow BH^+$$

  - This will help with stoichiometry calculations to determine new concentrations for H-H equation using K_b value of weak base

$$pOH = pK_b + \log\left(\frac{[BH^+]}{[B]}\right)$$

Steps to Solve Weak Base-Strong Acid Titration Problems

- At equivalence point ($H^+ = B$), pH < 7 due to presence of BH^+ only!
  - pH of solution will be determined by the reaction of BH^+ with water
  - Set up an ICE table to determine equilibrium concentrations using the reaction:

$$BH^+ + H_2O \leftrightarrow B + H_3O^+$$

  - Find K_a from K_b and substitute into equilibrium expression to solve for "x"
  - With $[H_3O^+]$, calculate pH
- Beyond the equivalence point, all of your weak base has reacted and you have an excess of strong acid
  - You also have the conjugate acid present
- Set up a "After Reaction" table using MOLES ONLY using the reaction below:

$$H^+ + B \rightarrow BH^+$$

  - Although there are two acids present (H^+ and BH^+), H^+ is stronger so pH is governed by the presence of H^+ only!
    - Calculate pH using new volume!

Practice

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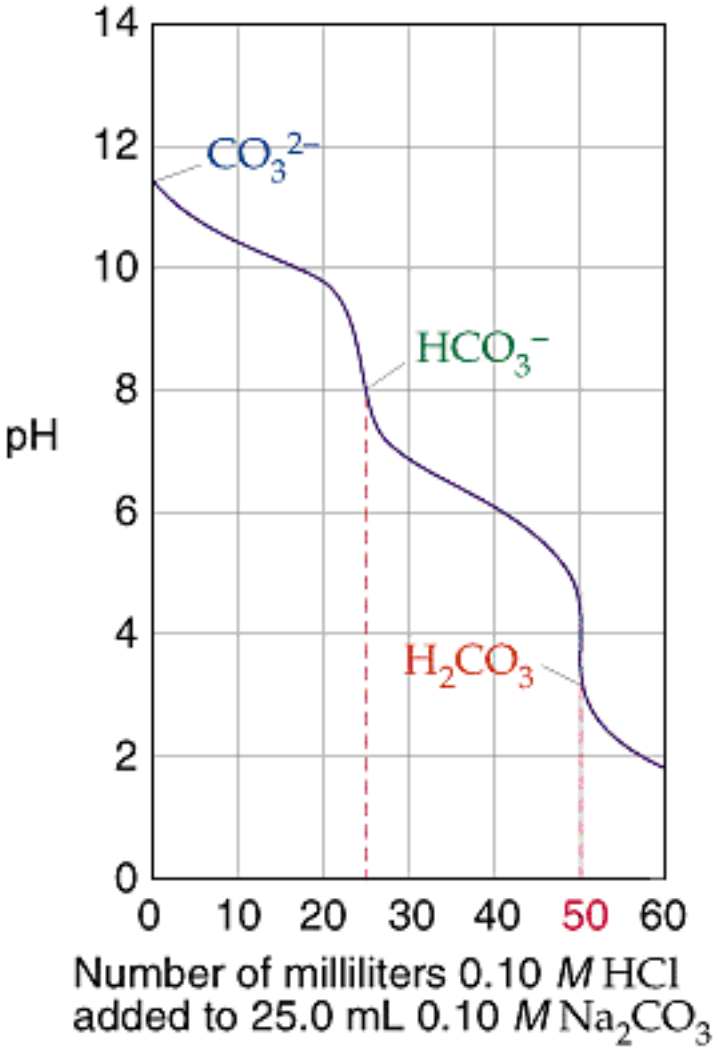
Titrations with Polyprotic Acids

What is a Polyprotic Acid?

- In polyprotic acids, each ionizable proton dissociates in steps
- Therefore in a titration, there are *n* equivalence points corresponding to each ionizable proton
- For example in the titration of Na_2CO_3 with HCl, there are two equivalence points:
  - One for the formation of HCO_3^-
  - One for the formation of H_2CO_3

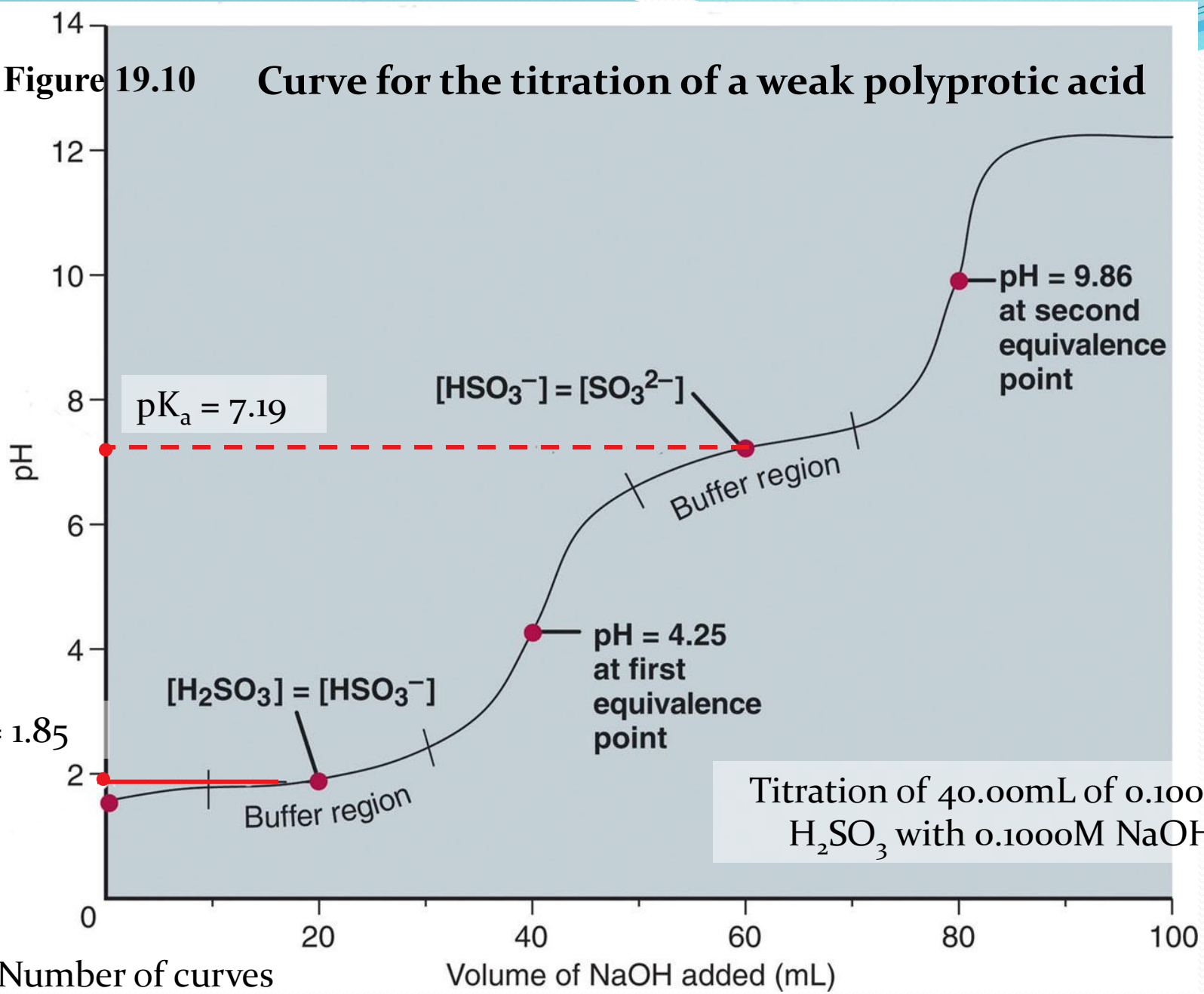
Titrations with Polyprotic Acids



Titration of a Polyprotic Acid

Titration Animation

Figure 19.10 **Curve for the titration of a weak polyprotic acid**



pK$_a$ = 1.85

- Number of curves =Number of H+ ions

Demystifying Titration Curves

- Follow along with the accompanying notes:

Demystifying Titration Curves on the AP Exam