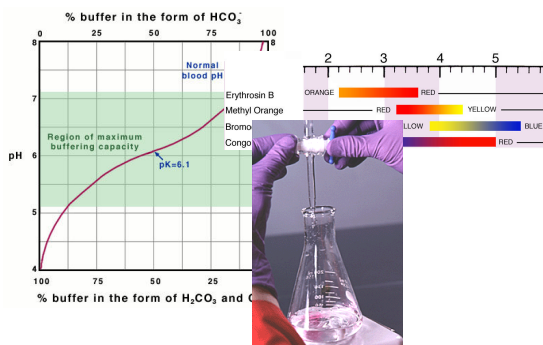


Buffers and Titrations



Buffers

Highly resistant to changes in pH brought about by addition of strong acid or strong base

Made from:
A weak acid and a salt containing its conjugate base

A weak base and a salt containing its conjugate acid

The presence of the salt "suppresses" the dissociation of the weak acid further (related to Le Chatelier's Principle)(see next slide for example)

Best range of buffering ability occurs when the pH to be buffered is close to the pK_a of the weak acid being used.

The most important pH buffer system in the blood involves carbonic acid (a weak acid formed from the carbon dioxide dissolved in blood) and bicarbonate ions (the corresponding conjugate base)

Example: (Suppression of Acid Dissociation)

Calculate the hydronium ion concentration and pH for:

- A solution containing only .200M acetic acid.
- A solution containing .200M acetic acid and 0.100M sodium acetate. Na^+ is a spectator ion.

The K_a for acetic acid is 1.8×10^{-5}

Answer:

$$\text{a) } 1.8 \times 10^{-5} = \frac{(x)(x)}{(.200M-x)} \quad (\text{H}^+)(\text{C}_2\text{H}_3\text{O}_2^-)/(\text{HC}_2\text{H}_3\text{O}_2)$$

$$x = 1.89 \times 10^{-3} \quad \text{pH} = 2.72$$

$$\text{b) } 1.8 \times 10^{-5} = \frac{(x)(x+.100)}{(.200M-x)}$$

$$x = 3.60 \times 10^{-5} \quad \text{pH} = 4.44$$

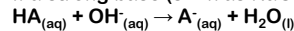
Note that there is much less hydronium (x) in this solution

How Conjugate Acid-Base Pairs Work as Buffers

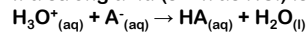
Given a weak acid (HA) and a salt containing its conjugate base (A^-)

Example: acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) and sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$)

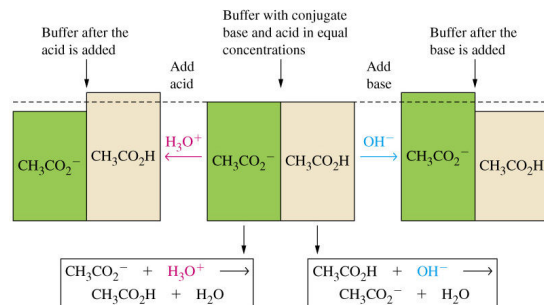
If a strong base (such as NaOH) is added:



If a strong acid (such as HCl) is added:



Visual Interpretation of Buffer Systems (Using acetic acid / acetate)



"Exhausting" a Buffer:

When making a buffer solution, the molarity of the conjugate acid-base pair must be high enough to buffer the anticipated strong acid / strong base that might be added

If a buffer component runs out, the pH will change drastically.

IMPORTANT NOTE: Buffers do not keep the pH of solutions from changing when strong acids or bases are added. They only "minimize" the effect of the acid or base.

Buffers and the Henderson-Hasselbalch Equation

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Why is it best to use a weak acid with a pK_a close to the pH? Can you see why from the Henderson-Hasselbalch equation.

$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch Equation

Steps for producing a buffer solution

Select a weak acid with a pK_a close to the desired pH.

Calculate the necessary ratio $\frac{[\text{conjugate base}]}{[\text{acid}]}$ to give the desired pH.

Calculate the necessary concentrations of conjugate base and acid.

Example:

A student wants to prepare a buffer for a solution at pH = 3.2. Which of the following combinations would be best to use?

HClO; LiClO $K_a = 2.8 \times 10^{-8}$

HSO₄; K₂SO₄ $K_a = 1.0 \times 10^{-2}$

HF; NaF $K_a = 6.9 \times 10^{-4}$

HC₂H₃O₂; NaC₂H₃O₂ $K_a = 1.8 \times 10^{-5}$

Answer: The HF; NaF combination has a pK_a (= 3.16) that is closest to the solution pH and would therefore be best.

Example:

Determine the pH of a buffer solution that is .115M in sodium acetate and .100M in acetic acid ($K_a = 1.8 \times 10^{-5}$)

Is this solution better at buffering acids or bases?

Answer:

$$pH = pK_a + \log \left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \right)$$

$$pH = 4.74 + \log(.115/.100)$$

$$pH = 4.80$$

Since the buffer has a higher concentration in acetate ion (the conjugate base), it will be **better at buffering acids**.

A 500.mL volume of a solution is 0.500M in both formic acid and potassium formate. Calculate the before and after pH of the solution if 40.0mL of .500M HCl is added to the solution. K_a for formic acid (HCHO₂) is 1.9×10^{-4}

Answer:

$$pK_a = -\log(1.9 \times 10^{-4}) = 3.72$$

$$\text{Before: } pH = 3.72 + \log(.500/.500) = 3.72$$

After:

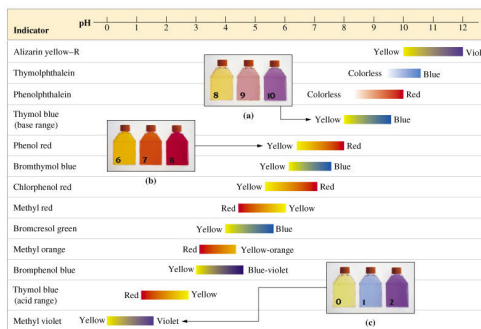
$$\text{Mol HCl} = (.0400L)(.500M) = .0200 \text{ mol HCl}$$

$$\text{Mol formic acid} = (.500L)(0.500M) - .0200 = .27 \text{ mol}$$

$$\text{Mol formate} = (.500L)(0.500M) - .0200 = .23 \text{ mol}$$

$$pH = 3.72 + \log(.23/.27) = 3.65$$

Acid-Base Indicators



Substances (usually weak organic acids or bases) that change color at different pH levels. Useful for identifying specific pH values in solution.

Acid-Base Titrations

Titration: Quantitatively determining the concentration of a solution by reacting it with another solution of precisely known concentration.

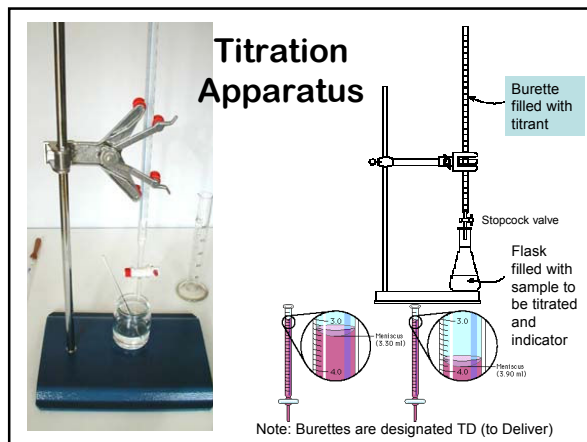
Terminology

Titrant: The solution of known concentration used to titrate a volume of the solution of unknown concentration.

Standardized (standard) solution: Solution of precisely known concentration

Equivalence point: The point at which stoichiometrically equivalent amounts of reactants have reacted

Endpoint: The point where an indicator (such as pH) changes color.



Titration Involving Strong Acids and Strong Bases

The pH at the equivalence point is 7 (neutral)

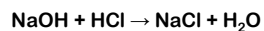
The salt formed in the neutralization has no strength as a conjugate acid or base

Moles of acid vs. base are calculated using stoichiometry and the balanced chemical equation for the neutralization

Example:

In a titration, a 15.0mL sample of an unknown molarity hydrochloric acid is titrated with .0150M NaOH to the equivalence point. If 30.0mL of the base was used, what is the molarity of the HCl?

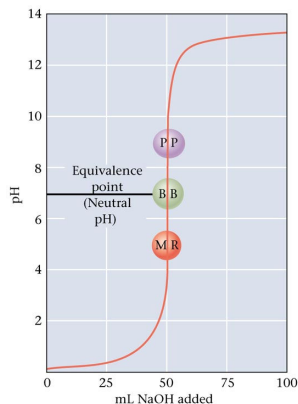
Answer:



Moles of base used:
 $(.0150\text{M})(.0300\text{L}) = 4.50 \times 10^{-4}\text{mol}$

Since the ratio is 1:1, there were $4.50 \times 10^{-4}\text{mol}$ of acid titrated

The molarity of the acid is
 $4.50 \times 10^{-4}\text{mol} / .0150\text{L} = .0300\text{M}$



Titration curve for strong acid titrated with a strong base

Note: The colored spheres denote indicator endpoints

PP = phenolphthalein

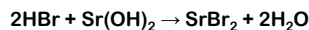
BB = bromthymol blue

MR = methyl red

Example:

A 60.0mL sample of strontium hydroxide is titrated with .200M hydrobromic acid. If 43.5mL is used in the titration, what is the molarity of the strontium hydroxide?

Answer:



Moles acid used: $(.0435\text{L})(.200\text{M}) = 8.70 \times 10^{-3}\text{mol}$

Moles of $\text{Sr}(\text{OH})_2$ titrated = $(8.70 \times 10^{-3}) / (1/2) = 4.35 \times 10^{-3}\text{mol}$

Molarity = $4.35 \times 10^{-3}\text{mol} / .0600\text{L} = .0725\text{M}$

Example:

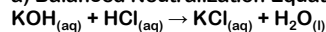
In making a solution for a titration lab, a teacher dissolves a certain amount of potassium hydroxide into enough water to make 700.mL of solution. The teacher forgets how much potassium hydroxide they put in and asks a student to titrate a 15.0mL sample with a .0125M standardized hydrochloric acid solution. The phenolphthalein indicator reaches its endpoint after 35.5mL of the titrant is delivered.

a) What is the molarity of the potassium hydroxide solution?

b) How many grams of potassium hydroxide were contained in the original 700.mL of solution?

Answer:

a) **Balanced Neutralization Equation:**



Moles of HCl used in titration:

$$(.0125\text{M})(.0355\text{L}) = 4.44 \times 10^{-4} \text{mol HCl}$$

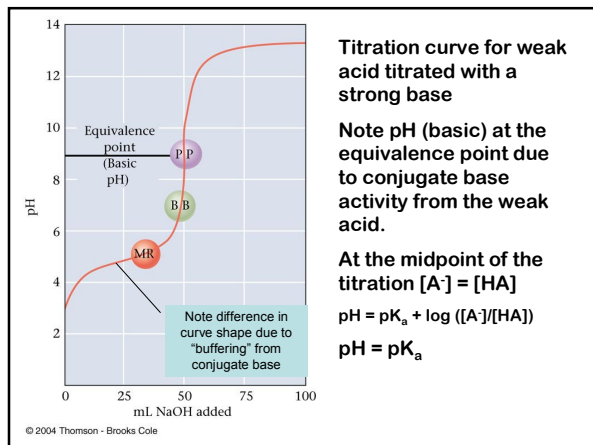
Moles of KOH titrated:

$$4.44 \times 10^{-4} \text{mol HCl} (1 \text{mol KOH}/1 \text{mol HCl}) = 4.44 \times 10^{-4} \text{mol KOH}$$

$$\text{Molarity of KOH} = (4.44 \times 10^{-4} \text{mol}) / (.0150\text{L}) = .0296\text{M}$$

b) **Grams of KOH in 700.mL**

$$(.0296 \text{mol/L})(.700\text{L})(56.11 \text{g/mol}) = 1.16\text{g KOH}$$



Example:

In a titration experiment, a 20.0mL sample of nitrous acid ($K_a = 6.00 \times 10^{-4}$) was titrated using sodium hydroxide

a) What is the pH of the solution at the halfway point in the titration?

b) If the endpoint is achieved using 18.2mL of .100M sodium hydroxide, what is the final pH of the solution?

c) What is the name of the salt that is formed in this neutralization?

d) Which of the three indicators listed in your textbook (p387 table 14.2) would be best for this titration; methyl red, bromthymol blue or phenolphthalein?

Answer:

a) pH at halfway point is given by $\text{pH} = \text{p}K_a$

$$\text{pH} = -\log(6.00 \times 10^{-4}) = 3.22$$

b) Mol NaOH used = $(.0182\text{L})(.100\text{M}) = .00182\text{mol}$

This equals moles of NO_2^- (1:1 mole ratio)

molarity of nitrite ion = $(.00182\text{mol}) / (.0382\text{L}) = .0476\text{M}$

$$K_b(\text{nitrite ion}) = 1.00 \times 10^{-14} / 6.00 \times 10^{-4} = 1.67 \times 10^{-11}$$

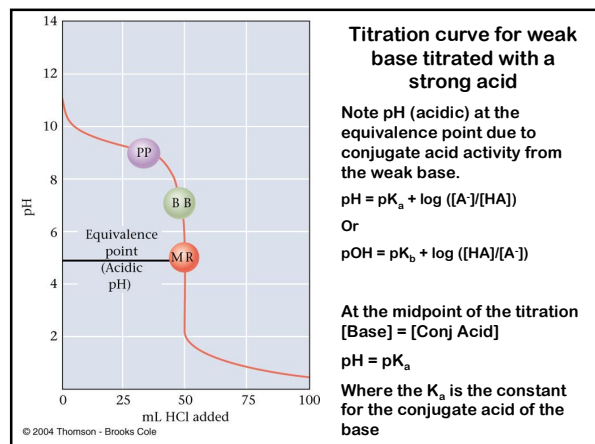
$$1.67 \times 10^{-11} = (x)(x) / (.0476 - x) \quad x = [\text{OH}^-] = 8.91 \times 10^{-7}$$

$$\text{pOH} = -\log(8.91 \times 10^{-7}) = 6.05$$

$$\text{pH} = 14.00 - 6.05 = 7.95$$

c) Sodium nitrite

d) Bromthymol blue (endpoint pH = 7) would be best, but phenolphthalein (endpoint pH = 9) could be used as well.



Example:

A 100.mL sample of .200M ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with .200M hydrobromic acid. Calculate the pH:

- After 20.0mL of acid has been added
- At the midpoint of the titration
- Of the salt solution (ammonium bromide) at the equivalence point.

Answer:

a. Moles of acid added: $(.200M)(.0200L) = .004\text{mol}$
 (This is also moles of conjugate acid produced)
 Moles of base remaining: $(.100L)(.200M) - .004\text{mol} = .016\text{mol}$
 K_a of conjugate acid (NH_4^+) = $1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

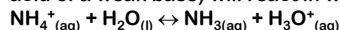
$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{Base}]}{[\text{Conj acid}]} \right)$$

$$= 9.26 + \log (.016/.004) = 9.857 = \mathbf{9.9}$$

b. At the midpoint, $\text{pH} = \text{p}K_a$ of the conjugate acid:
 $\text{pH} = -\log(5.6 \times 10^{-10}) = 9.26 = \mathbf{9.3}$

c. Since the molarities of acid and base are the same, it will take 100.mL of the hydrobromic acid to titrate all of the base. Since the total volume will be 200.mL, the components of the salt (ammonium and bromide) will both be $\frac{1}{2}$ their original molarities or .100M NH_4Br .

The bromine is a spectator ion (conjugate base of a very strong acid). The ammonium ion (the conjugate acid of a weak base) will react in water:

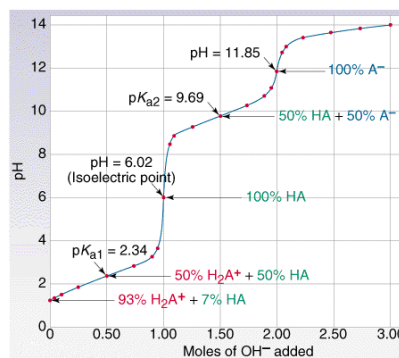


$$5.6 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{(.100-x)} \quad x = 7.0 \times 10^{-6}$$

$$\text{pH} = -\log(7.0 \times 10^{-6}) = 5.15 = \mathbf{5.2}$$

Titration Curves for Polyprotic Acids



This shows the titration curve for a diprotic acid.

Note that there is a separate equivalence point for each titrated hydrogen on the polyprotic acid.

Extra Practice Problems

The pH of blood plasma is 7.40. Assuming the principal buffer system is $\text{HCO}_3^-/\text{H}_2\text{CO}_3$, calculate the ratio $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$. Is this buffer more effective against an added acid or an added base? (K_a for $\text{H}_2\text{CO}_3 = 4.4 \times 10^{-7}$)

Answer:

$$K_a \text{ of } \text{H}_2\text{CO}_3 = 4.4 \times 10^{-7} \quad \text{p}K_a = 6.36$$

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$7.40 = 6.36 + \log \left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$1.04 = \log \left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)$$

$$10^{1.04} = \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10.96:1$$

11:1

Since it is higher in bicarbonate concentration it is somewhat better at buffering against acids.

A 5.00g quantity of a diprotic acid was dissolved in water to make 250.mL of solution. Calculate the molar mass of the acid if 25.0mL of this solution required 11.1mL of 1.00M KOH for neutralization. Assume both protons were titrated.

Answer:

$$\text{Moles KOH used: } (.0111L)(1.00M) = .0111\text{mol KOH}$$

$$\text{Moles H}^+ \text{ titrated: } 1:1 = .0111\text{mol H}^+$$

$$\text{Moles of acid: } .0111\text{mol H}^+ (1\text{mol acid} / 2\text{mol H}^+) = .00555\text{mol acid}$$

$$\text{Molarity of acid: } (.00555\text{mol}) / (.0250L) = .222M$$

$$\text{Moles acid in 250.mL: } (.222M)(.250L) = .0555\text{mol acid}$$

$$\text{Molar Mass (g/mol) } = (5.00\text{g}) / (.0555\text{mol}) = \mathbf{90.1\text{g/mol}}$$