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Understanding the titration of nitrous acid with lithium hydroxide is fundamental in analytical chemistry, particularly in acid-base reactions. When a weak acid such as nitrous acid (HNO_2) is titrated with a strong base like lithium hydroxide (LiOH), the progression of the reaction provides valuable insights into the solution's pH at various stages. This article offers a comprehensive guide to calculating the pH during such titrations, emphasizing the concepts, calculations, and practical considerations involved.

Introduction to Acid-Base Titration

Titration is a laboratory technique used to determine the concentration of an unknown solution by reacting it with a solution of known concentration. In acid-base titrations, an acid reacts with a base, and the point at which the reaction is complete is called the equivalence point. The pH at various points during titration reflects the relative strengths of the acid and base involved.

Key Concepts:

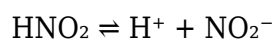
- Weak Acid (Nitrous Acid, HNO_2): Partially dissociates in water.
- Strong Base (Lithium Hydroxide, LiOH): Completely dissociates in water.
- Equivalence Point: The point where moles of acid equal moles of base.

Understanding the Components of the Titration

Before delving into calculations, it's essential to understand the initial conditions and the chemistry involved.

1. Nitrous Acid (HNO_2)

- Concentration: 0.150 M
- Volume: 15.0 mL
- Dissociation in Water:



- Acid Dissociation Constant (K_a): Approximately 4.5×10^{-14}

2. Lithium Hydroxide (LiOH)

- Concentration: 0.150 M

- Volume: Variable during titration

3. Moles of Nitrous Acid

Calculating initial moles:

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$\text{Moles of HNO}_2 = M \times V = 0.150 \, \text{mol/L} \times 0.015 \, \text{L} = 2.25 \times 10^{-3} \, \text{mol}$

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Step-by-Step Titration Process and pH Calculation

The titration involves adding LiOH to the nitrous acid solution gradually. The pH at any point depends on the amount of acid and base present.

1. Initial pH (Before Titration)

At the start, only nitrous acid is present.

Calculating initial pH:

- Use the expression for weak acid dissociation:

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

- Assuming initial concentration of HNO_2 is 0.150 M, and x is $[H^+]$:

$$K_a = \frac{x^2}{[HNO_2] - x} \approx \frac{x^2}{0.150}$$

- Solve for x :

$$x = \sqrt{K_a \times 0.150}$$

$$x = \sqrt{4.5 \times 10^{-14} \times 0.150} \approx \sqrt{6.75 \times 10^{-15}} \approx 8.22 \times 10^{-8} \, \text{M}$$

- Initial pH:

$$\text{pH} = -\log [H^+] = -\log (8.22 \times 10^{-8}) \approx 7.08$$

Thus, the initial pH is approximately 7.08, slightly above neutral due to the weak acid.

Calculating pH at Various Stages of Titration

The pH at any point during titration depends on the amount of titrant added, specifically:

- Before the equivalence point
- At the equivalence point
- After the equivalence point

1. Before the Equivalence Point

This is when the moles of LiOH added are less than the initial moles of HNO₂.

Key points:

- The solution contains unreacted nitrous acid and some formed nitrite ions (NO₂⁻).
- The pH is governed by the weak acid and its conjugate base equilibrium.

Calculating pH at a given volume:

Suppose you add (V_{LiOH}) mL of LiOH:

- Moles of LiOH added:

$$n_{\text{LiOH}} = 0.150 \, \text{mol/L} \times V_{\text{LiOH}}$$

- Moles of HNO₂ remaining after reaction:

$$n_{\text{HNO}_2} = 2.25 \times 10^{-3} - n_{\text{LiOH}}$$

- Moles of NO₂⁻ formed:

$$n_{\text{NO}_2^-} = n_{\text{LiOH}}$$

- Total volume:

$$V_{\text{total}} = 15.0 \, \text{mL} + V_{\text{LiOH}}$$

- Concentrations:

$$[\text{HNO}_2] = \frac{n_{\text{HNO}_2}}{V_{\text{total}}}$$

$$[\text{NO}_2^-] = \frac{n_{\text{NO}_2^-}}{V_{\text{total}}}$$

Using the Henderson-Hasselbalch Equation:

The mixture contains a weak acid and its conjugate base:

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \right)$$

$$- \text{ } (\text{p}K_a = -\log K_a \approx 13.35)$$

2. At the Equivalence Point

This occurs when:

$$n_{\text{LiOH}} = n_{\text{HNO}_2} = 2.25 \times 10^{-3} \text{ mol}$$

Volume of LiOH required:

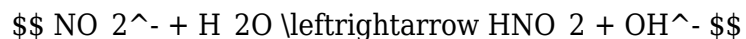
$$V_{\text{eq}} = \frac{n_{\text{HNO}_2}}{0.150 \text{ mol/L}} = \frac{2.25 \times 10^{-3}}{0.150} = 0.015 \text{ L} = 15.0 \text{ mL}$$

At this point:

- All nitrous acid has been neutralized to nitrite ions.
- The solution contains only NO_2^- , which is a conjugate base of a weak acid.

Calculating pH at the equivalence point:

- The solution is basic due to hydrolysis of NO_2^- :



- The hydrolysis constant:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} \approx 0.222$$

- Moles of NO_2^- after titration:

$$2.25 \times 10^{-3} \text{ mol}$$

- Concentration of NO_2^- :

$$[\text{NO}_2^-] = \frac{2.25 \times 10^{-3}}{15.0 \text{ mL} + 15.0 \text{ mL} = 30 \text{ mL}} = 0.030 \text{ M}$$

$$[\text{NO}_2^-] = \frac{2.25 \times 10^{-3}}{0.030} = 0.075 \text{ M}$$

- Set up hydrolysis expression:

$$x = [\text{OH}^-]$$

$$K_b = \frac{x^2}{[\text{NO}_2^-] - x} \approx \frac{x^2}{0.075}$$

$$x = \sqrt{K_b \times 0.075} = \sqrt{0.222 \times 0.075} \approx \sqrt{0.01665} \approx 0.129 \text{ M}$$

- Compute pOH:

$$\text{pOH} = -\log x = -\log 0.129 \approx 0.89$$

- pH:

$$\text{pH} = 14 - \text{pOH} = 14 - 0.89 = 13.11$$

Result: The pH at the equivalence point is approximately 13.11, strongly basic due to hydrolysis.

3. After the Equivalence Point

When excess LiOH is added beyond the equivalence point:

- The solution contains excess OH⁻ ions.
- pH can be calculated directly from the excess hydroxide concentration.

Suppose (V_{excess}) mL of LiOH is added:

- Excess moles:

$$n_{\text{OH}^-} = 0.150 \times (V$$

Frequently Asked Questions

How do you determine the pH during the titration of nitrous acid with LiOH at the equivalence point?

At the equivalence point, all nitrous acid has reacted with LiOH to form its conjugate base, leading to a solution of nitrite ions. The pH is determined by the hydrolysis of these ions, which typically results in a pH slightly above 7 due to their basic nature.

What is the initial pH of the 0.150 M nitrous acid solution before titration?

The initial pH can be calculated using the acid dissociation constant (K_a) of nitrous acid. Using the formula $\text{pH} = 0.5 (\text{pK}_a - \log [\text{HA}])$, the initial pH is approximately 2.14, indicating a weak acid solution.

At what point during the titration does the pH rapidly change, and why?

The pH rapidly changes near the equivalence point because a small addition of base completely neutralizes the acid, shifting the solution from acidic to basic conditions. This is characteristic of titrations involving weak acids and strong bases.

How do you calculate the volume of LiOH needed to reach the equivalence point in this titration?

Since both solutions are 0.150 M and the acid volume is 15.0 mL, the volume of LiOH required is equal to the acid's moles divided by the base's molarity: $(0.150 \text{ mol/L} \times 0.015 \text{ L}) / 0.150 \text{ mol/L} = 0.015 \text{ L}$ or 15.0 mL.

What is the expected pH after adding half the volume of LiOH needed to reach the equivalence point?

At half the equivalence point, half of the nitrous acid has been neutralized, and the pH is determined by the buffer solution of weak acid and its conjugate base. The pH can be calculated using the Henderson-Hasselbalch equation and is approximately equal to the pKa of nitrous acid, around 3.37.

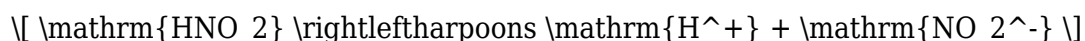
Additional Resources

A 15.0 mL sample of 0.150 M nitrous acid is titrated with a 0.150 M LiOH solution. This scenario presents a classic acid-base titration involving a weak acid, nitrous acid (HNO_2), and a strong base, lithium hydroxide (LiOH). Such titrations are fundamental in analytical chemistry for determining unknown concentrations, understanding acid-base equilibria, and practicing quantitative analysis. In this comprehensive review, we will explore the principles behind this titration, step-by-step calculations to find the pH at various stages, and discuss the significance of such experiments in laboratory settings.

Understanding the Components of the Titration

Nitrous Acid (HNO_2)

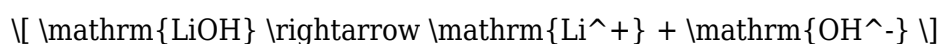
Nitrous acid is a weak, monoprotic acid with the chemical formula HNO_2 . It exists in equilibrium with its conjugate base, nitrite ion (NO_2^-), as shown:



The acid dissociation constant (K_a) for nitrous acid is approximately 4.5×10^{-4} , indicating moderate acidity. Its pKa is around 3.35, which influences how its pH changes during titration with a strong base.

Lithium Hydroxide (LiOH)

LiOH is a strong base that dissociates completely in aqueous solution:



This complete dissociation simplifies calculations, as the hydroxide ion concentration directly correlates with the amount of LiOH added.

Initial Conditions and Calculations

Determining Initial Moles of Nitrous Acid

Given:

- Volume of nitrous acid sample: 15.0 mL = 0.015 L
- Concentration of nitrous acid: 0.150 M

Calculate moles:

$$\text{Moles of HNO}_2 = 0.150 \, \text{mol/L} \times 0.015 \, \text{L} = 0.00225 \, \text{mol}$$

This initial amount sets the stage for the titration process.

Calculating the Equivalence Point

Since both solutions have the same molarity (0.150 M), the volume of LiOH needed to reach the equivalence point is equal to the volume of the acid solution:

$$V_{\text{equiv}} = \frac{\text{moles of HNO}_2}{\text{molarity of LiOH}} = \frac{0.00225 \, \text{mol}}{0.150 \, \text{mol/L}} = 0.015 \, \text{L} = 15.0 \, \text{mL}$$

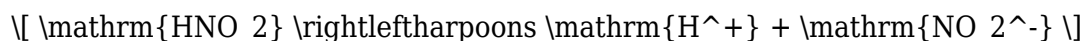
At this point, all the nitrous acid has been neutralized to form nitrite ions.

pH Calculations During the Titration

The titration curve involves several key points: initial pH, various intermediate points, the equivalence point, and the post-equivalence region.

Initial pH (Before Titration)

Using the acid dissociation of nitrous acid:



The expression for K_a :

$$K_a = \frac{[\mathrm{H}^+][\mathrm{NO}_2^-]}{[\mathrm{HNO}_2]}$$

Assuming initial concentrations and negligible ionization:

$$[\mathrm{H}^+] = \sqrt{K_a \times C_{\mathrm{HNO}_2}}$$

$$[\mathrm{H}^+] = \sqrt{4.5 \times 10^{-4} \times 0.150} \approx \sqrt{6.75 \times 10^{-5}} \approx 8.22 \times 10^{-3}$$

pH:

$$\mathrm{pH} = -\log(8.22 \times 10^{-3}) \approx 2.085$$

This initial pH reflects a solution that is mildly acidic.

pH at the Half-Equivalence Point

At half the equivalence volume (7.5 mL of LiOH added), the amount of acid and conjugate base are equal, and the pH equals the pKa:

$$\mathrm{pH} = \mathrm{p}K_a = 3.35$$

This point is important because it indicates the buffer region where the pH change is relatively gradual.

pH at the Equivalence Point

When all the acid has been neutralized, the solution contains only nitrite ions (NO_2^-). Since NO_2^- is the conjugate base of a weak acid, it will hydrolyze in water:



The hydrolysis constant (K_b):

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} \approx 2.22 \times 10^{-11}$$

Concentration of NO_2^- at equivalence:

$$[\mathrm{NO}_2^-] = \frac{\text{moles}}{\text{volume at equivalence}} = \frac{0.00225 \text{ mol}}{0.030 \text{ L}} = 0.075 \text{ M}$$

Hydrolysis of NO_2^- :

$$K_b = \frac{[\mathrm{OH}^-]^2}{[\mathrm{NO}_2^-]}$$

$$[\mathrm{OH}^-] = \sqrt{K_b \times [\mathrm{NO}_2^-]} = \sqrt{2.22 \times 10^{-11} \times 0.075} \approx 1.29 \times 10^{-6} \text{ M}$$

pOH:

$$\mathrm{pOH} = -\log(1.29 \times 10^{-6}) \approx 5.89$$

pH:

$$\mathrm{pH} = 14 - 5.89 \approx 8.11$$

Thus, the equivalence point is slightly basic, as expected for a weak acid-strong base titration.

Post-Equivalence pH (After Excess LiOH)

Adding more LiOH beyond the equivalence point results in excess hydroxide ions. The pH increases sharply, and the calculation simplifies:

$$\text{Excess } \mathrm{OH}^- = \frac{\text{additional moles of LiOH}}{\text{total volume}}$$

for example, if an additional 0.001 mol of LiOH is added:

Total volume:

$$15 \, \mathrm{mL} + (\text{additional volume})$$

Total moles of OH^- :

$$0.001 \, \mathrm{mol}$$

Concentration:

$$[\mathrm{OH}^-] = \frac{0.001 \, \mathrm{mol}}{0.015 \, \mathrm{L} + \text{additional volume}}$$

which leads to a pOH and pH calculation.

Significance and Applications of Such Titrations

Educational Importance

Performing titrations like this helps students understand acid-base equilibria, buffer regions, and the concept of equivalence points. It reinforces theoretical knowledge through practical application.

Industrial and Laboratory Uses

Accurate titration techniques are essential in quality control, environmental testing, and

pharmaceutical formulation. Understanding the properties of weak acids and their titration curves enable chemists to determine concentrations precisely.

Features and Pros/Cons

Features:

- Clear visualization of titration curve
- Demonstrates buffer regions and equivalence point
- Allows calculation of unknown concentrations

Pros:

- Fundamental for analytical chemistry
- Teaches precision and careful measurement
- Helps understand weak acid/base behavior

Cons:

- Sensitive to titrant and analyte purity
- Requires careful endpoint detection
- Slight inaccuracies in volume measurement can affect results

Conclusion

The titration of a 15.0 mL sample of 0.150 M nitrous acid with a 0.150 M LiOH solution exemplifies core principles of acid-base chemistry. By understanding the initial conditions, calculating pH at various points, and recognizing the significance of buffer regions and hydrolysis reactions, chemists can accurately determine the pH at any stage of the titration. This process not only deepens conceptual understanding but also enhances practical skills vital for laboratory analysis and research. Whether for academic purposes or industrial applications, mastering such titrations is fundamental in the chemist's toolkit.

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