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Titration is a fundamental technique in analytical chemistry used to determine the concentration of an unknown solution by reacting it with a standard solution of known concentration. In this scenario, a 50.0-ml sample of nitrous acid (HNO_2), a weak acid, is titrated with sodium hydroxide (NaOH), a strong base. A key point of interest is determining the pH after 25.0 ml of NaOH has been added—a process that involves understanding acid-base reactions, calculating moles, and applying equilibrium principles. This article walks you through the step-by-step process of calculating the pH at this specific point in the titration, providing insights into titration calculations, the behavior of weak acids, and the importance of pH in analytical chemistry.

Understanding the Components of the Titration

1. The Acid: Nitrous Acid (HNO_2)

- Properties: HNO_2 is a weak acid with a known acid dissociation constant (Ka).
- Concentration and Volume: 0.10 M, 50.0 mL.
- Role in Titration: The acid reacts with NaOH, a strong base, in a proton transfer reaction.

2. The Base: Sodium Hydroxide (NaOH)

- Properties: NaOH is a strong base that fully dissociates in water.
- Concentration and Volume: 0.14 M, volume added: 25.0 mL.
- Role in Titration: Reacts with HNO_2 to form its conjugate base, NO_2^-.

Calculating the Moles of Reactants

1. Initial Moles of HNO_2

- Calculation:

$$
\text{Moles of HNO}_2 = \text{Concentration} \times \text{Volume}
$$

$$
= 0.10\, \text{mol/L} \times 0.0500\, \text{L} = 0.00500\, \text{mol}
$$

2. Moles of NaOH Added

- Calculation:

$$
\text{Moles of NaOH} = 0.14\, \text{mol/L} \times 0.0250\, \text{L} = 0.00350\, \text{mol}
$$

3. Moles Remaining of HNO_2 After Reaction

- Since NaOH is a strong base and HNO_2 is a weak acid, they react in a 1:1 molar ratio:

$$
\text{HNO}_2 + \text{OH}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}
$$

- Remaining HNO_2:

$$
0.00500\, \text{mol} - 0.00350\, \text{mol} = 0.00150\, \text{mol}
$$

- Produced NO_2^- (conjugate base):

$$
0.00350\, \text{mol}
$$

Determining the pH After 25.0 mL of NaOH Has Been Added

At this point in the titration, the solution contains:
- Remaining weak acid (HNO_2) with 0.00150 mol.
- Conjugate base (NO_2^-) with 0.00350 mol.
- Total volume of the solution:

$$
50.0\, \text{mL} + 25.0\, \text{mL} = 75.0\, \text{mL} = 0.0750\, \text{L}
$$

1. Calculating the Concentrations of Acid and Base

- Concentration of HNO_2:

$$
\frac{0.00150\, \text{mol}}{0.0750\, \text{L}} = 0.0200\, \text{M}
$$

- Concentration of NO_2^-:

$$
\frac{0.00350\, \text{mol}}{0.0750\, \text{L}} = 0.0467\, \text{M}
$$

2. Using the Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation relates the pH to the concentrations of the weak acid and its conjugate base:

$$
\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)
$$

Where:
- A^- is the conjugate base (NO_2^-)
- HA is the weak acid (HNO_2)
- K_a is the acid dissociation constant

3. Finding the K_a of HNO_2

- Given K_a for HNO_2: Approximately 4.5×10^{-4}

- Calculating pKa:

$$
\text{p}K_a = -\log K_a = -\log (4.5 \times 10^{-4}) \approx 3.35
$$

4. Calculating the pH

- Plugging into the Henderson-Hasselbalch equation:

$$
\text{pH} = 3.35 + \log \left(\frac{0.0467}{0.0200} \right)
$$

$$
\text{pH} = 3.35 + \log (2.335)
$$

$$
\text{pH} = 3.35 + 0.368 \approx 3.72
$$

Therefore, the pH after adding 25.0 mL of NaOH is approximately 3.72.

Additional Insights Into Titration Calculations and Acid-Base Equilibria

Understanding Acid-Base Equilibria in Titration

1. The Role of Weak Acids and Their Conjugates

Weak acids like HNO_2 do not dissociate completely; instead, they establish an equilibrium:

$$
\text{HNO}_2 \leftrightarrow \text{H}^+ + \text{NO}_2^-
$$

The conjugate base, NO_2^-, can accept protons, which influences the pH depending on the ratio of acid to conjugate base.

2. Buffer Regions in Titration

At the point where equal moles of acid and conjugate base are present, the solution acts as a buffer, maintaining a relatively stable pH. The pH at this point is close to the pKa of the weak acid.

3. Equivalence Point and Beyond

- When all the acid has reacted (at the equivalence point), the solution contains only the conjugate base, which will hydrolyze to produce OH^-, making the solution basic.
- Before the equivalence point, the pH is less than 7; after, it becomes greater than 7.

Practical Applications of Titration Data

1. Determining Unknown Concentrations

By understanding the titration curve and calculations like those above, chemists can determine the concentration of unknown acids or bases accurately.

2. Buffer Solution Preparation

Knowledge of the pKa and the ratio of acid to conjugate base enables the preparation of buffer solutions with desired pH levels.

3. Environmental and Industrial Chemistry

Titration data is essential for analyzing water quality, pharmaceutical formulations, and chemical manufacturing processes.

Conclusion

The titration of a weak acid like HNO_2 with a strong base such as NaOH involves understanding the stoichiometry of acid-base reactions and applying equilibrium principles to determine the pH at various stages. After adding 25.0 mL of NaOH to a 50.0-mL sample of 0.10 M HNO_2, the solution contains a mixture of remaining acid and newly formed conjugate base, resulting in a buffered solution with an approximate pH of 3.72. This calculation highlights the importance of concepts like molarity, moles, the Henderson-Hasselbalch equation, and acid dissociation constants in analytical chemistry. Mastery of these principles allows chemists to perform precise titrations, analyze unknown solutions, and develop applications across scientific fields.

Frequently Asked Questions

What is the initial pH of the 0.10 M HNO2 solution before titration?

The initial pH can be calculated using the acid dissociation constant (Ka) for HNO2. First, find the Ka (approximately 4.5×10^{-4}). Then, set up the expression for weak acid dissociation and solve for [H+], resulting in an initial pH around 3.4.

How do I determine the amount of NaOH added to reach the equivalence point?

Calculate the moles of HNO2: 0.10 M × 0.050 L = 0.005 mol. Since NaOH is 0.14 M, the volume needed to neutralize this is 0.005 mol / 0.14 M ≈ 0.0357 L or 35.7 mL. Since only 25.0 mL is added, the titration is incomplete, and the solution is still acidic.

What is the pH after adding 25.0 mL of NaOH during the titration?

At 25.0 mL of NaOH added, the moles of NaOH are 0.14 M × 0.025 L = 0.0035 mol. The initial moles of HNO2 are 0.005 mol, so after neutralization, remaining HNO2 is 0.005 - 0.0035 = 0.0015 mol, and the moles of $NO2^-$ formed are 0.0035 mol. The solution contains a mixture of weak acid and its conjugate base, so the pH can be calculated using the Henderson-Hasselbalch equation.

How do I calculate the pH at this point using the Henderson-Hasselbalch equation?

Use pH = pKa + log([A−]/[HA]). Here, [A−] = 0.0035 mol / (0.050 L + 0.025 L) ≈ 0.0035 / 0.075 L ≈ 0.0467 M, and [HA] = 0.0015 / 0.075 L ≈ 0.02 M. With pKa ≈ 3.34 for HNO2, pH ≈ 3.34 + log(0.0467/0.02) ≈ 3.34 + 0.37 ≈ 3.71.

What is the significance of the pH value after adding 25.0 mL of NaOH in the titration process?

The pH indicates the solution is in the buffer region, where both the weak acid (HNO2) and its conjugate base (NO2−) coexist. This pH value helps to understand the progress of titration and how close the solution is to the equivalence point, which occurs at approximately 35.7 mL of NaOH added.

Additional Resources

Titration of HNO_2 with NaOH: An In-Depth Analytical Chemistry Review

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Introduction

Titration is a fundamental technique in analytical chemistry, used extensively to determine the concentration of an unknown solution by reacting it with a standard solution of known concentration. In this article, we delve into a specific titration scenario involving nitrous acid (HNO_2) and sodium hydroxide (NaOH).

Imagine a laboratory setting where a 50.0-mL sample of 0.10 M HNO_2 is titrated with 0.14 M NaOH. After adding 25.0 mL of NaOH, what is the pH of the solution? This question encapsulates core concepts in acid-base chemistry, including the behavior of weak acids and their conjugate bases, the calculation of pH during titration, and the application of equilibrium principles.

Our goal is to not only compute the pH at this specific point but also to provide a comprehensive understanding of the underlying chemistry, step-by-step calculations, and relevant theoretical considerations.

Background Concepts and Chemical Principles

Before diving into the calculations, it’s essential to understand the key principles involved:

1. Acid-Base Equilibria

- Weak acids like HNO_2 partially dissociate in water:

$HNO_2 \rightleftharpoons H^+ + NO_2^-$

- The degree of dissociation depends on the acid's dissociation constant, Ka.

- The conjugate base, NO_2^-, can undergo hydrolysis, affecting the pH.

2. Titration Dynamics

- When titrating a weak acid with a strong base, the pH changes gradually, especially before the equivalence point.

- The titration curve has characteristic regions:
- Initial pH (before any base added)
- Buffer region (when both weak acid and conjugate base are present)
- Equivalence point (all weak acid neutralized)
- Post-equivalence (excess strong base)

3. Calculating pH at a Given Titrant Volume

- Quantify initial moles of acid and base.
- Determine the reaction extent (how much acid has reacted).
- Use equilibrium expressions (for weak acids or hydrolysis) to find the pH.

Step-by-Step Calculation: Determining the pH After 25.0 mL of NaOH Is Added

Step 1: Determine Initial Moles of HNO_2

Given data:

- Volume of HNO_2 solution, V_1 = 50.0 mL = 0.0500 L
- Concentration of HNO_2, M_1 = 0.10 M

Calculate initial moles of HNO_2:

$$
n_{HNO_2} = M_1 \times V_1 = 0.10\, \text{mol/L} \times 0.0500\, \text{L} = 0.00500\, \text{mol}
$$

Step 2: Determine Moles of NaOH Added

Given:

- Volume of NaOH added, V_2 = 25.0 mL = 0.0250 L
- Concentration of NaOH, M_2 = 0.14 M

Calculate moles of NaOH added:

$$
n_{NaOH} = M_2 \times V_2 = 0.14\, \text{mol/L} \times 0.0250\, \text{L} = 0.00350\, \text{mol}
$$

Step 3: Reaction Between HNO_2 and NaOH

Since NaOH is a strong base and HNO_2 is a weak acid:

- The NaOH will react completely with HNO_2 to form NO_2^- and water:

$$
HNO_2 + OH^- \rightarrow NO_2^- + H_2O
$$

- The reaction consumes an equal number of moles of HNO_2 and NaOH, producing NO_2^-.

Determine the limiting reagent:

- Initial moles of HNO_2 = 0.00500 mol
- Moles of NaOH added = 0.00350 mol

Since NaOH is less than initial acid, it will react completely with an equivalent amount:

- Moles of HNO_2 reacted = 0.00350 mol
- Moles of HNO_2 remaining = 0.00500 mol - 0.00350 mol = 0.00150 mol
- Moles of NO_2^- formed = 0.00350 mol

Step 4: Final Concentrations After Reaction

Total volume of solution:

$$
V_{total} = V_1 + V_2 = 50.0\, \text{mL} + 25.0\, \text{mL} = 75.0\, \text{mL} = 0.0750\, \text{L}
$$

Determine concentrations:

- Remaining HNO_2:

$$
[\text{HNO}_2] = \frac{0.00150\, \text{mol}}{0.0750\, \text{L}} = 0.0200\, \text{M}
$$

- Formed NO_2^-:

$$
[\text{NO}_2^-] = \frac{0.00350\, \text{mol}}{0.0750\, \text{L}} \approx 0.0467\, \text{M}
$$

Analyzing the Buffer System

At this point, the solution contains a mixture of weak acid (HNO_2) and its conjugate base (NO_2^-), making it a buffer system. The pH can be calculated using the Henderson-Hasselbalch equation:

$$
\boxed{
\text{pH} = pK_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)
}
$$

Where:

- $[\text{A}^-]$ = concentration of conjugate base (NO_2^-)
- $[\text{HA}]$ = concentration of weak acid (HNO_2)
- pK_a = negative log of the acid dissociation constant for HNO_2

Step 5: Find the pK_a of HNO_2

The K_a for HNO_2 is typically around 4.5×10^{-4}. Therefore:

$$
pK_a = -\log(4.5 \times 10^{-4}) \approx 3.35
$$

Final pH Calculation

Using the concentrations:

$$
[\text{HNO}_2] = 0.0200\, \text{M}
$$
$$
[\text{NO}_2^-] = 0.0467\, \text{M}
$$

Apply the Henderson-Hasselbalch equation:

$$
\text{pH} = 3.35 + \log \left(\frac{0.0467}{0.0200} \right)
$$

Calculate the ratio:

$$
\frac{0.0467}{0.0200} = 2.335
$$

Calculate the logarithm:

$$
\log(2.335) \approx 0.368
$$

Finally, determine the pH:

$$
\text{pH} = 3.35 + 0.368 = \boxed{3.72}
$$

Additional Considerations

1. Validity of the Approximation

The Henderson-Hasselbalch equation is valid here because:

- Both HA and A^- are present in significant concentrations.
- The solution is within the buffer region, away from the equivalence point.

2. Near the Buffer Region

- If more NaOH were added, the pH would increase towards the equivalence point, eventually surpassing the buffer capacity.

3. Effect of K_a Variations

- Slight changes in the K_a value of HNO_2 would influence the pH calculation. Accurate literature values should be used for precise lab work.

Broader Implications and Practical Applications

Understanding this titration scenario is essential in various contexts:

- Environmental Chemistry: Monitoring nitrous acid levels in water treatment.
- Pharmaceuticals: Buffer formulation involving weak acids and bases.
- Industrial Processes: pH control during chemical manufacturing.

The principles demonstrated here — stoichiometric calculations, equilibrium analysis, buffer pH determination — are foundational skills for chemists and lab technicians.

Summary of Key Steps

- Calculated initial moles of HNO_2.
- Determined moles of NaOH added and reacted.
- Established remaining concentrations of HNO_2 and formed NO_2^-.
- Used the Henderson-Hasselbalch equation with known pK_a to find the pH.
- Resulted in a pH of approximately 3.72 after adding 25.0 mL of NaOH.

Final Thoughts

This detailed analysis underscores the importance of understanding acid-base equilibria, titration mechanics, and the use of mathematical tools like the Henderson-Hasselbalch equation. Mastery of these concepts allows chemists to accurately determine solution properties and control chemical processes effectively. Whether in research, industrial applications, or quality control, such calculations are indispensable tools in the chemist’s repertoire

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