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Understanding titration processes is fundamental in analytical chemistry, especially when dealing with acid-base reactions. In this comprehensive guide, we will explore the detailed steps to determine the pH after titrating a 100.0 mL sample of 0.10 M ammonia (NH_3) with 0.10 M nitric acid (HNO_3). This scenario involves concepts such as acid-base equilibria, molarity calculations, and the use of Henderson-Hasselbalch equation, providing a thorough understanding suitable for students, educators, and professionals alike.

Introduction to Acid-Base Titration and Relevant Concepts

What is Titration?

Titration is a laboratory technique used to determine the concentration of an unknown solution by reacting it with a solution of known concentration. It involves slowly adding a titrant (the solution of known concentration) to the analyte until the reaction reaches the equivalence point, where the amount of titrant added is stoichiometrically equivalent to the analyte.

Understanding NH_3 and HNO_3

- Ammonia (NH_3): A weak base that reacts with acids to form ammonium salts. Its base dissociation constant (K_b) is approximately 1.8×10^{-5}.
- Nitric Acid (HNO_3): A strong acid that dissociates completely in aqueous solution, providing H^+ ions readily.

Significance of pH Calculation in Titration

Determining the pH after certain volumes of titrant are added helps in:
- Identifying the pH at various points during titration (initial, halfway, equivalence point, and beyond).
- Understanding the buffer regions.

- Calculating the exact point where neutralization occurs.

Step-by-Step Calculation of pH During Titration

To accurately determine the pH after titrant addition, it’s essential to analyze the progress of the titration in stages:

1. Initial pH (before titrant addition)
2. pH after adding some volume of titrant (before equivalence point)
3. At the equivalence point
4. Beyond the equivalence point

In this scenario, we focus on the pH after a certain volume of HNO_3 has been added, though the specific volume is not provided. For illustration, we will examine multiple points during titration.

Initial Conditions: pH Before Titration

Calculating Initial pH of the NH_3 Solution

Given:
- Volume of NH_3 solution: 100.0 mL = 0.100 L
- Concentration of NH_3: 0.10 M

Number of moles of NH_3:
$$ \text{moles NH}_3 = 0.10\, \text{M} \times 0.100\, \text{L} = 0.010\, \text{mol} $$

Since NH_3 is a weak base, it reacts with water:
$$ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- $$

The base dissociation constant:
$$ K_b = 1.8 \times 10^{-5} $$

Using the initial concentration:
$$ \text{Initial concentration} = 0.10\, \text{M} $$

Set up an ICE table to find $[OH^-]$:
Let x = $[OH^-]$ at equilibrium.

$$ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} $$

Assuming x is small compared to initial concentration:

$$ K_b = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} $$

$$ x^2 = K_b \times 0.10 = 1.8 \times 10^{-5} \times 0.10 = 1.8 \times 10^{-6} $$

$$ x = \sqrt{1.8 \times 10^{-6}} \approx 1.34 \times 10^{-3}\, \text{M} $$

pOH:
$$ \text{pOH} = -\log [\text{OH}^-] = -\log (1.34 \times 10^{-3}) \approx 2.87 $$

pH:
$$ \text{pH} = 14 - \text{pOH} \approx 14 - 2.87 = 11.13 $$

Initial pH ≈ 11.13

Calculating pH After Partial Titration

Suppose a certain volume of HNO_3 has been added; for example, 50.0 mL of 0.10 M HNO_3. Let's analyze this case.

Volume and Moles of Titrant Added

- Volume of HNO_3 added:
$$ V_{HNO_3} = 50.0\, \text{mL} = 0.050\, \text{L} $$
- Moles of HNO_3 added:
$$ \text{moles HNO}_3 = 0.10\, \text{M} \times 0.050\, \text{L} = 0.005\, \text{mol} $$

Reaction Between NH_3 and HNO_3

The reaction is:
$$ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- $$

Since moles of NH_3 initially are 0.010 mol:
- Moles of NH_3 remaining:
$$ 0.010\, \text{mol} - 0.005\, \text{mol} = 0.005\, \text{mol} $$
- Moles of NH_4^+ formed:
$$ 0.005\, \text{mol} $$

Total volume of solution:
$$ V_{total} = 100.0\, \text{mL} + 50.0\, \text{mL} = 150.0\, \text{mL} = 0.150\, \text{L} $$

Concentrations:
- $[\text{NH}_3] = \frac{0.005\, \text{mol}}{0.150\, \text{L}} \approx 0.0333\, \text{M}$
- $[\text{NH}_4^+] = \frac{0.005\, \text{mol}}{0.150\, \text{L}} \approx 0.0333\, \text{M}$

Buffer Solution and pH Calculation

The solution now contains a mixture of weak base (NH_3) and its conjugate acid (NH_4^+). This forms a buffer system.

Use the Henderson-Hasselbalch equation:
$$ \text{pH} = pK_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right) $$

First, find pK_a:
$$ pK_a = 14 - pK_b $$
$$ pK_b = -\log K_b = -\log (1.8 \times 10^{-5}) \approx 4.74 $$
$$ pK_a = 14 - 4.74 = 9.26 $$

Calculate pH:
$$ \text{pH} = 9.26 + \log \left(\frac{0.0333}{0.0333} \right) = 9.26 + \log 1 = 9.26 $$

pH after adding 50 mL of HNO_3 ≈ 9.26

At the Equivalence Point

The equivalence point occurs when all the NH_3 has been neutralized by HNO_3.

- Moles of NH_3 initially: 0.010 mol
- Moles of HNO_3 added to reach equivalence:
$$ 0.010\, \text{mol} $$
- Volume of HNO_3 required:
$$ V_{eq} = \frac{0.010\, \text{mol}}{0.10\, \text{M}} = 0.100\, \text{L} = 100\, \text{mL} $$

Total volume at equivalence:
$$ 100\, \text{mL} + 100\, \text{mL} = 200\, \text{mL} $$

At this point, the solution contains only ammonium nitrate (NH_4NO_3), which is a neutral salt, but ammonium ion (NH_4^+) is a weak acid.