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Understanding how to determine the pH of a solution after titration is fundamental in chemistry, especially when dealing with weak bases like ammonia (NH₃) and strong acids such as nitric acid (HNO₃). In this article, we will analyze the titration process step-by-step, focusing on a specific example: a 100.0 mL sample of 0.10 M NH₃ titrated with 0.10 M HNO₃. We'll explore how to calculate the pH at various points during the titration, including before the equivalence point, at the equivalence point, and after the equivalence point, providing a comprehensive guide to understanding acid-base titrations involving weak bases and strong acids.

Understanding the Components of the Titration

Before delving into calculations, it is important to understand the fundamentals of the titration process involving ammonia and nitric acid.

Ammonia as a Weak Base

- Ammonia (NH₃) is a weak base that partially dissociates in water:
- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- The base dissociation constant (K_b) for ammonia is approximately 1.8×10^{-5} .

Nitric Acid as a Strong Acid

- Nitric acid (HNO₃) is a strong acid that completely dissociates in water:
- $\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-$
- The complete dissociation means that every mole of HNO₃ provides one mole of H⁺ ions.

What Happens During Titration?

- The HNO_3 reacts with NH_3 to produce NH_4^+ (ammonium ions) and water:
- $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^-$
- The titration continues until all the NH_3 has reacted, reaching the equivalence point where moles of acid equal moles of base.

Calculating Initial Conditions

Let's start by determining the initial moles of NH_3 in the sample.

Initial Moles of NH_3

1. Given volume of NH_3 solution: 100.0 mL (or 0.100 L)
2. Concentration of NH_3 : 0.10 M
3. Calculate moles:

Moles of NH_3 = concentration $\times$ volume = $0.10 \text{ mol/L} \times 0.100 \text{ L} = 0.010 \text{ mol}$

Initial pH of the NH_3 Solution

- Since NH_3 is a weak base, its initial pH can be calculated using the K_b expression.

Calculating the pOH and pH Before Titration

1. Set up the equilibrium expression for NH_3 dissociation:
2. $K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3]$
3. Assuming x is the concentration of OH^- at equilibrium:
4. $K_b = x^2 / (\text{initial concentration of } \text{NH}_3 - x) \approx x^2 / 0.10$ (since x is small)
5. Calculate x :

$$x = \sqrt{K_b \times 0.10} = \sqrt{(1.8 \times 10^{-5}) \times 0.10} \approx \sqrt{1.8 \times 10^{-6}} \approx 1.34 \times 10^{-3} \text{ M}$$

1. Calculate pOH:

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

1. Finally, determine pH:

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

Determining the pH During the Titration

The pH at any point during titration depends on the volume of HNO_3 added. We consider three main regions:

1. Before the equivalence point
2. At the equivalence point
3. After the equivalence point

1. pH Before the Equivalence Point

This is when less than 100 mL of HNO_3 has been added; the solution contains unreacted NH_3 and some NH_4^+ .

Calculations of Moles of HNO_3 Added

- Suppose an arbitrary volume of HNO_3 , V mL, has been added:
- Moles of HNO_3 added: $0.10 \text{ mol/L} \times V/1000 \text{ L} = 0.0001 V \text{ mol}$

Remaining Moles of NH_3

- Moles of NH_3 remaining: initial - reacted = $0.010 \text{ mol} - \text{moles reacted}$
- moles reacted = moles of HNO_3 added = $0.0001 V$

Concentration of Unreacted NH_3

- Remaining volume of solution: $100 \text{ mL} + V \text{ mL} = (100 + V) \text{ mL} = (0.100 + V/1000) \text{ L}$

- Concentration of NH_3 :

$$[\text{NH}_3] = (\text{initial moles} - \text{reacted}) / \text{total volume} = (0.010 - 0.0001 V) / (0.100 + V/1000)$$

Calculating pOH and pH

- Use the same equilibrium approach as initial, but with the remaining NH_3 concentration.
- Additionally, the solution now contains NH_4^+ (from reacted NH_3), which is a weak acid contributing to the hydrogen ion concentration.

Example: After adding 20 mL of HNO_3

1. Moles of HNO_3 added:

$$0.10 \text{ mol/L} \times 20/1000 \text{ L} = 0.002 \text{ mol}$$

1. Moles of NH_3 remaining:

$$0.010 \text{ mol} - 0.002 \text{ mol} = 0.008 \text{ mol}$$

1. Total volume:

$$0.100 \text{ L} + 0.020 \text{ L} = 0.120 \text{ L}$$

1. NH_3 concentration:

$$[\text{NH}_3] = 0.008 \text{ mol} / 0.120 \text{ L} \approx 0.0667 \text{ M}$$

1. NH_4^+ concentration:

$$0.002 \text{ mol} / 0.120 \text{ L} \approx 0.0167 \text{ M}$$

- The presence of NH_4^+ makes the solution slightly acidic, and the pH can be calculated using the acid dissociation constant (K_a) for NH_4^+ , which is related to K_b of NH_3 :

$$K_a = K_w / K_b = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) \approx 5.56 \times 10^{-10}$$

- Set up the equilibrium for NH_4^+ dissociation:



- Using the concentration of NH_4^+ , solve for $[\text{H}^+]$:

$$[\text{H}^+] \approx \sqrt{(K_a \times [\text{NH}_4^+])} \approx \sqrt{(5.56 \times 10^{-10} \times 0.0167)} \approx \sqrt{(9.3 \times 10^{-12})} \approx 9.64 \times 10^{-6} \text{ M}$$

- Calculate pH:

$$\text{pH} = -\log[\text{H}^+] \approx 5.02$$

This illustrates how the pH decreases as more acid is added toward the equivalence point.

2. At the Equivalence Point

The equivalence point occurs when all the NH_3 has reacted with HNO_3 :

- Moles of HNO_3 added = initial moles of NH_3 = 0.010

Frequently Asked Questions

What is the initial pH of the 0.10 M NH_3 solution before titration?

The initial pH can be calculated using the K_b for NH_3 . $K_b = 1.8 \times 10^{-5}$. Using the concentration of NH_3 (0.10 M), $\text{pOH} = 0.5 \times (\text{p}K_b + \log [\text{NH}_3])$ and $\text{pH} = 14 - \text{pOH}$, the initial pH is approximately 11.09.

How do you determine the amount of HNO_3 required to reach the equivalence point?

Since both solutions are 0.10 M and the volume of NH_3 is 100 mL, the moles of NH_3 are 0.01 mol. Therefore, 0.01 mol of HNO_3 (also 0.10 M) is needed, which corresponds to 100 mL of HNO_3 .

What is the pH of the solution after adding 50 mL of HNO_3 during titration?

At 50 mL of HNO_3 added, half the amount needed to reach equivalence has been added. The solution contains a buffer of NH_3 and NH_4^+ , and the pH equals the $\text{p}K_b$ of ammonium, approximately 9.25.

What is the pH of the solution at the equivalence point?

At the equivalence point, all NH_3 has been neutralized to NH_4^+ . The pH is determined by the hydrolysis of NH_4^+ , resulting in a slightly acidic pH around 5.5.

How do you calculate the pH after adding less than the

equivalent volume of HNO₃?

When less than the equivalence volume is added, the solution contains unreacted NH₃ and some NH₄⁺. Use the Henderson-Hasselbalch equation: $\text{pH} = \text{pK}_a + \log([\text{NH}_3]/[\text{NH}_4^+])$ to find the pH.

What is the pH of the solution after adding more than the equivalence point?

Beyond the equivalence point, excess HNO₃ remains in solution, and the pH is dictated by the concentration of excess HNO₃, which is strongly acidic, resulting in a pH less than 7.

How does the buffer region affect the pH during titration of NH₃ with HNO₃?

In the buffer region, typically near half-neutralization, the solution resists pH changes due to the presence of both NH₃ and NH₄⁺, maintaining a relatively stable pH around 9.25.

What is the significance of the titration curve in understanding the pH changes during titration?

The titration curve shows the pH at various points of HNO₃ addition, illustrating the buffer region, the steep rise at the equivalence point, and the post-equivalence acidic pH, helping to visualize the titration process.

How can you experimentally determine the pH after a specific volume of HNO₃ is added?

Using a pH meter, you can measure the pH directly after adding the desired volume of HNO₃. Alternatively, you can calculate it using the concentrations of remaining NH₃, formed NH₄⁺, and excess HNO₃ based on the titration data.

Additional Resources

Titration of Ammonia with Nitric Acid: Determining pH at Various Stages

Understanding the behavior of weak acids and bases during titration processes is fundamental in analytical chemistry. In this article, we will delve into the detailed analysis of a titration scenario involving 0.10 M ammonia (NH₃) and 0.10 M nitric acid (HNO₃). Specifically, we will calculate the pH after various stages of titration of a 100.0 mL sample of ammonia with nitric acid, providing a comprehensive overview of the chemistry involved, including the underlying principles, step-by-step calculations, and practical considerations.

Introduction to Titration of Ammonia with Nitric Acid

Titration is a classic laboratory technique used to determine the concentration of an unknown solution by reacting it with a standard solution of known concentration. When titrating a weak base like ammonia with a strong acid such as nitric acid, the process involves several stages:

- Initial pH before any titrant is added.
- pH after partial neutralization during the titration.
- The equivalence point where the amount of acid equals the amount of base.
- Post-equivalence stage where excess acid is present.

This process is valuable not only for quantitative analysis but also for understanding acid-base equilibria, buffer systems, and the concept of pKa.

Fundamental Concepts and Parameters

Before diving into calculations, let's clarify the key parameters and concepts involved:

- Initial Volume of NH_3 solution: 100.0 mL (or 0.100 L)
- Concentration of NH_3 : 0.10 M
- Concentration of HNO_3 : 0.10 M
- Moles of NH_3 initially present:

$$\text{Moles of NH}_3 = 0.10 \text{ mol/L} \times 0.100 \text{ L} = 0.010 \text{ mol}$$

- Moles of HNO_3 added: Variable, depending on the volume of titrant added.
- Equivalence point: When moles of HNO_3 added = moles of NH_3 initially present (0.010 mol).

Step 1: Calculating pH Before Titration Begins

Initial pH of the ammonia solution

Ammonia (NH_3) is a weak base, and its equilibrium in water is expressed as:



The base dissociation constant (K_b) for ammonia is approximately:

$$K_b = 1.8 \times 10^{-5}$$

Calculating initial pOH and pH:

1. Determine initial concentration: 0.10 M.
2. Set up the equilibrium expression:

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

Assuming $(x = [\mathrm{OH}^-])$ at equilibrium:

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

Since (K_b) is small, $(x \ll 0.10)$, allowing the approximation:

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

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

3. Calculate pOH:

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

4. Calculate pH:

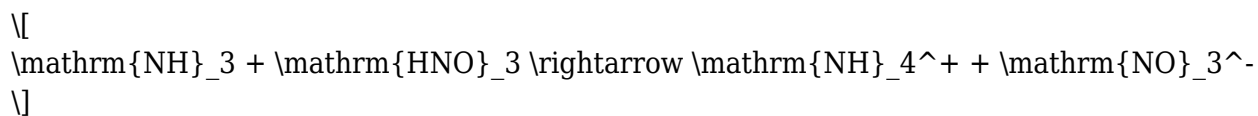
$$\text{pH} = 14 - \text{pOH} = 14 - 2.87 = 11.13$$

Initial pH ≈ 11.13

Step 2: Understanding the Titration Process

As we titrate ammonia with nitric acid, the following reactions and concepts come into play:

- Reaction between NH_3 and HNO_3 :



- Neutralization of NH_3 : Converts weak base into its conjugate acid, NH_4^+ .
- Buffer formation: When partial neutralization occurs, the solution contains both NH_3 and NH_4^+ , forming a buffer system.
- At equivalence point: All NH_3 has been converted into NH_4^+ ; the solution primarily contains NH_4^+ and NO_3^- .
- Beyond equivalence point: Excess HNO_3 determines the pH.

Step 3: Calculating pH at Various Stages of Titration

To fully understand the titration, we will analyze the pH at key points:

- Before any titrant is added.
- After adding a certain volume of HNO_3 (partial neutralization).
- At the equivalence point.
- After surpassing equivalence (excess acid).

3.1: pH Before Titration (0 mL HNO_3 added)

As calculated above, the initial pH is approximately 11.13.

3.2: pH After Adding Part of the Acid (e.g., 5 mL of HNO_3)

Calculating moles of HNO_3 added:

$$\backslash \\ V_{\text{HNO}_3} = 5\text{ mL} = 0.005\text{ L} \\ \backslash$$

$$\backslash \\ \text{Moles of HNO}_3 = 0.10\text{ mol/L} \times 0.005\text{ L} = 0.0005\text{ mol} \\ \backslash$$

Remaining moles of NH_3 :

$$0.010\text{ mol} - 0.0005\text{ mol} = 0.0095\text{ mol}$$

Moles of NH_4^+ formed:

$$0.0005\text{ mol}$$

New concentrations:

- Total volume after addition:

$$V_{\text{total}} = 100\text{ mL} + 5\text{ mL} = 105\text{ mL} = 0.105\text{ L}$$

- Concentration of remaining NH_3 :

$$\frac{0.0095\text{ mol}}{0.105\text{ L}} \approx 0.0905\text{ M}$$

- Concentration of NH_4^+ :

$$\frac{0.0005\text{ mol}}{0.105\text{ L}} \approx 0.00476\text{ M}$$

Buffer system:

The solution now contains a mixture of NH_3 and NH_4^+ , forming a buffer. We can calculate the pH using the Henderson-Hasselbalch equation:

$$\boxed{\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}}$$

Where:

- pK_a of NH_4^+ (conjugate acid of NH_3):

$$\text{pK}_a = 14 - \text{pK}_b$$

Given:

$$pK_b = -\log K_b = -\log(1.8 \times 10^{-5}) \approx 4.74$$

Therefore:

$$pK_a = 14 - 4.74 = 9.26$$

Plugging into the formula:

$$\text{pH} = 9.26 + \log \left(\frac{0.0905}{0.00476} \right)$$

$$\log \left(\frac{0.0905}{0.00476} \right) = \log (19.02) \approx 1.28$$

$$\text{pH} \approx 9.26 + 1.28 = 10.54$$

pH after adding 5 mL of $\text{HNO}_3 \approx 10.54$

3.3: pH at the Equivalence Point

At equivalence point:

- Moles of HNO_3 added = Moles of NH_3 initially present = 0.010 mol.
- Total volume:

$$V_{\text{total}} = 100 \text{ mL}$$

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