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Understanding titration processes is fundamental in analytical chemistry, especially when determining the concentration of unknown solutions, analyzing acid-base reactions, and calculating pH changes during titration. In this detailed article, we explore the titration of ammonia (NH_3), a weak base, with hydrochloric acid (HCl), a strong acid. Specifically, we focus on calculating the pH at the equivalence point in this titration. This example is pertinent for students and professionals seeking to deepen their understanding of acid-base titrations, buffer solutions, and pH calculations.

Introduction to Acid-Base Titration

Titration is a laboratory technique used to determine the concentration of an unknown solution by adding a titrant of known concentration until a reaction reaches its equivalence point. The equivalence point signifies the exact moment when the amount of titrant added is chemically equivalent to the analyte in the solution.

In our case, ammonia (NH_3) is a weak base, and hydrochloric acid (HCl) is a strong acid. When titrating NH_3 with HCl, the reaction proceeds as follows:

Reaction Equation

\[\mathrm{NH_3 (aq) + HCl (aq) \rightarrow NH_4^+ (aq) + Cl^- (aq)} \]

The equivalence point occurs when all NH_3 has reacted to form ammonium ions (NH_4^+). Because HCl is a strong acid, it fully dissociates, and the resulting solution at the equivalence point contains only ammonium ions and chloride ions.

Understanding the Components of the Titration

Before calculating the pH at the equivalence point, we need to understand the initial concentrations, volumes, and the nature of the species involved.

Initial Conditions

- Volume of ammonia solution (V_1): 25.0 mL = 0.025 L
- Concentration of ammonia (C_1): 0.400 M
- Concentration of HCl (C_2): 0.400 M

Since both solutions have the same molarity, the volume of HCl required to reach the equivalence point can be calculated based on molar relationships.

Calculating the Volume of HCl Needed at the Equivalence Point

The reaction involves a 1:1 molar ratio between NH_3 and HCl. Therefore:

$$ \text{Moles of NH}_3 = C_1 \times V_1 $$

$$ \text{Moles of HCl needed} = \text{Moles of NH}_3 $$

Calculations:

$$ \text{Moles of NH}_3 = 0.400\, \mathrm{mol/L} \times 0.025\, \mathrm{L} = 0.010\, \mathrm{mol} $$

Since HCl is 0.400 M:

$$ V_{HCl} = \frac{\text{moles of HCl}}{C_2} = \frac{0.010\, \mathrm{mol}}{0.400\, \mathrm{mol/L}} = 0.025\, \mathrm{L} = 25.0\, \mathrm{mL} $$

Thus, 25.0 mL of HCl of 0.400 M concentration will be required to reach the equivalence point.

What Happens at the Equivalence Point?

At the equivalence point:
- All NH_3 has been converted into NH_4^+.
- The solution contains only ammonium ions (NH_4^+) and chloride ions (Cl^-).
- The pH is determined by the hydrolysis of NH_4^+, which acts as a weak acid.

Because HCl is a strong acid, it completely neutralizes NH_3, leading to a solution of ammonium ions, which influence the pH.

Calculating the pH at the Equivalence Point

Since the solution contains only ammonium ions, which are weak acids, the pH at this point depends on the acid dissociation of NH_4^+.

Step 1: Determine the Concentration of NH_4^+

Total volume after titration:

$$ V_{total} = V_{initial} + V_{added} = 25.0\, \mathrm{mL} + 25.0\, \mathrm{mL} = 50.0\, \mathrm{mL} = 0.050\, \mathrm{L} $$

Concentration of NH_4^+:

$$ C_{NH_4^+} = \frac{\text{moles of NH}_4^+}{V_{total}} $$

Since all NH_3 has reacted:

$$ \text{Moles of NH}_4^+ = \text{initial moles of NH}_3 = 0.010\, \mathrm{mol} $$

Thus:

$$ C_{NH_4^+} = \frac{0.010\, \mathrm{mol}}{0.050\, \mathrm{L}} = 0.200\, \mathrm{M} $$

Step 2: Write the Hydrolysis Reaction of NH_4^+

Ammonium ion hydrolysis:

$$ \mathrm{NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_3 (aq) + H_3O^+ (aq)} $$

This equilibrium is characterized by the acid dissociation constant K_a of NH_4^+, which is related to the base dissociation constant K_b of NH_3:

$$ K_a \times K_b = K_w $$

Where:

- K_b for NH_3 = 1.8×10^{-5}

- K_w = 1.0×10^{-14}

Calculating K_a:

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

Step 3: Set Up the Expression for Hydrolysis

Let x be the concentration of H_3O^+ produced at equilibrium:

$$\mathrm{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+}$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Assuming initial concentration of NH_4^+ = 0.200 M, and change of x:

$$K_a = \frac{x \times x}{0.200 - x} \approx \frac{x^2}{0.200}$$

Since K_a is small, x is much less than 0.200 M, so the approximation:

$$K_a \approx \frac{x^2}{0.200}$$

Solve for x:

$$x^2 = K_a \times 0.200 = 5.56 \times 10^{-10} \times 0.200 = 1.11 \times 10^{-10}$$

$$x = \sqrt{1.11 \times 10^{-10}} \approx 1.05 \times 10^{-5} \, \mathrm{M}$$

This represents the concentration of H_3O^+.

Calculating the pH

The pH is given by:

$$\text{pH} = -\log [H_3O^+]$$

$$\text{pH} = -\log (1.05 \times 10^{-5})$$

$$\text{pH} \approx 4.98$$

Final Answer:

The pH at the equivalence point of titrating 25.0 mL of 0.400 M NH_3 with 0.400 M HCl is approximately 4.98.

Additional Considerations and Related Topics

Understanding this titration process opens the door to a variety of related concepts:

- Buffer Solutions: The solution at the half-equivalence point contains equal concentrations of NH_3 and NH_4^+, acting as a buffer with a pH close to the pKa of NH_4^+ (~9.25), which can be useful in buffer preparation.
- Titration Curves: Plotting pH versus volume of titrant provides visual insight into the titration process, including the equivalence point, buffer region, and initial pH.
- Effect of Molarity and Volume: Changing concentrations of titrant or initial solutions will affect the volume needed to reach equivalence and the pH at that point.
- Applications in Industry and Medicine: Acid-base titrations are essential in

Frequently Asked Questions

What is the pH at the equivalence point when titrating 25.0 mL of 0.400 M NH_3 with 0.400 M HCl?

The pH at the equivalence point is approximately 5.5 because the titration involves a weak base (NH_3) and a strong acid (HCl), resulting in a slightly acidic solution at equivalence.

How do you determine the pH at the equivalence point in the titration of a weak base with a strong acid?

At the equivalence point, the weak base has been fully neutralized to form its conjugate acid, which then dictates the pH. You calculate the concentration of the conjugate acid and use its K_a to find the pH.

What is the relevant chemical reaction when titrating NH_3 with HCl?

The reaction is $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$. At the equivalence point, all NH_3 has been converted to NH_4^+, which affects the pH.

How do you calculate the amount of NH_3 in moles in the sample?

Using the concentration and volume: moles of NH_3 = 0.400 mol/L × 0.025 L = 0.010 mol.

What is the volume of HCl needed to reach the equivalence point?

Since both solutions are 0.400 M, the volume of HCl required is equal to the moles of NH_3 divided by the HCl concentration: 0.010 mol / 0.400 mol/L = 0.025 L or 25.0 mL.

How does the conjugate acid NH_4^+ influence the pH at the

equivalence point?

NH_4^+ is a weak acid, and its hydrolysis in water produces H_3O^+ ions, making the solution slightly acidic with a pH less than 7.

What is the approximate pK_a of NH_4^+, and how does it relate to the pH at the equivalence point?

The pK_a of NH_4^+ is about 9.25. Since pH = 14 - pK_b, and pK_b of NH_3 is around 4.75, the pH at equivalence is roughly 5.5, reflecting the hydrolysis of NH_4^+.

Why is the pH at the equivalence point less than 7 in this titration?

Because the conjugate acid NH_4^+ hydrolyzes to produce H_3O^+ ions, making the solution slightly acidic at the equivalence point.

Can the pH at the equivalence point be exactly calculated? If yes, how?

Yes, by calculating the concentration of NH_4^+ after titration and using its K_a to find the pH via hydrolysis equations.

What is the significance of knowing the pH at the equivalence point in titrations?

It helps determine the nature of the titration, the strength of the acid or base involved, and is essential for accurate pH calculations in analytical chemistry.

Additional Resources

Titration: Unlocking the pH at Equivalence for Ammonia and Hydrochloric Acid

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Introduction

In the realm of analytical chemistry, titration stands as a fundamental technique for determining the concentration of unknown solutions. It involves the gradual addition of a titrant to a analyte until a reaction reaches completion, often indicated by a color change or a specific pH. Among the many titrations, the acid-base titration of ammonia (NH_3) with hydrochloric acid (HCl) is a classic example that illuminates core principles of chemical equilibria, buffer solutions, and pH calculations.

In this article, we delve into a specific scenario: A 25.0 mL sample of 0.400 M NH_3 is titrated with 0.400 M HCl. Our goal is to determine the pH at the equivalence point — a pivotal point in titration where the amount of acid equals the amount of base, and the reaction is complete. This in-depth analysis not only demonstrates the calculations involved but also provides insight into the underlying chemistry and practical implications.

Understanding the Chemistry: The Ammonia-HCl Titration

Before embarking on calculations, it's essential to understand the chemical reactions at play.

The Acid-Base Reaction

Ammonia (NH_3) is a weak base, and hydrochloric acid (HCl) is a strong acid. When they react, the following reaction occurs:

$$ \text{NH}_3 (aq) + \text{HCl} (aq) \rightarrow \text{NH}_4^+ (aq) + \text{Cl}^- (aq) $$

At the equivalence point, all the ammonia has been converted into ammonium ions (NH_4^+).

Significance of the Equivalence Point

- Complete Reaction: All the NH_3 has reacted with HCl.
- Nature of the Solution: The solution contains only ammonium ions and chloride ions.
- pH Determination: The pH at this point depends on the hydrolysis of ammonium ions, as HCl is a strong acid and is fully reacted.

Step 1: Calculating the Moles of NH_3 in the Sample

Given data:

- Volume of NH_3 solution, $V_{NH_3} = 25.0\, \text{mL} = 0.025\, \text{L}$
- Concentration of NH_3, $M_{NH_3} = 0.400\, \text{M}$

$$ \text{Moles of NH}_3 = M_{NH_3} \times V_{NH_3} = 0.400\, \text{mol/L} \times 0.025\, \text{L} = 0.010\, \text{mol} $$

Step 2: Determining the Volume of HCl Needed to Reach Equivalence

Since HCl is also 0.400 M, the moles needed to neutralize all NH_3 are:

$$ \text{Moles of HCl} = \text{Moles of NH}_3 = 0.010\, \text{mol} $$

The volume of HCl required:

$$ V_{HCl} = \frac{\text{Moles of HCl}}{M_{HCl}} = \frac{0.010\, \text{mol}}{0.400\, \text{mol/L}} = 0.025\, \text{L} = 25.0\, \text{mL} $$

Interpretation: To reach equivalence, 25.0 mL of 0.400 M HCl must be added to the ammonia solution.

Step 3: pH at the Equivalence Point

Since HCl is a strong acid and NH_3 is a weak base, the titration's equivalence point is not neutral but slightly acidic. This is due to the hydrolysis of the ammonium ion (NH_4^+).

Hydrolysis of Ammonium Ion

The ammonium ion can act as a weak acid:

$$ \text{NH}_4^+ (aq) + \text{H}_2\text{O} (l) \leftrightarrow \text{NH}_3 (aq) + \text{H}_3\text{O}^+ $$

The equilibrium constant for this hydrolysis is derived from the acid dissociation constant of ammonium, K_a.

Step 4: Determining the Acid Dissociation Constant of Ammonium

The relationship between the base dissociation constant (K_b) of ammonia and the acid dissociation constant (K_a) of ammonium is:

$$ K_a \times K_b = K_w $$

Where:

- K_b for NH_3 = 1.8×10^{-5} (at 25°C)
- $K_w = 1.0 \times 10^{-14}$

Calculating K_a:

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

This small K_a indicates ammonium is a weak acid.

Step 5: Concentration of Ammonium at Equivalence

At the equivalence point, the total moles of ammonium:

$$ \text{Moles of } \text{NH}_4^+ = 0.010\, \text{mol} $$

and the total volume:

$$ V_{total} = V_{initial} + V_{HCl} = 25.0\, \text{mL} + 25.0\, \text{mL} = 50.0\, \text{mL} = 0.050\, \text{L} $$

Concentration of ammonium:

$$ [\text{NH}_4^+] = \frac{0.010\, \text{mol}}{0.050\, \text{L}} = 0.200\, \text{M} $$

Step 6: Calculating the pH at the Equivalence Point

The key step involves calculating the hydrolysis of ammonium ions:

$$ \text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 + \text{H}_3\text{O}^+ $$

Using the expression for hydrolysis:

$$ K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} $$

Assuming:

- $x = [\text{H}_3\text{O}^+]$, the concentration of hydronium ions generated.
- $[\text{NH}_4^+]$ decreases by x but for small x, initial concentration approximations are valid.

Set up the expression:

$$ K_a = \frac{x \times x}{0.200 - x} \approx \frac{x^2}{0.200} $$

Given $K_a = 5.56 \times 10^{-10}$, solving for x:

$$ x^2 = K_a \times 0.200 = 5.56 \times 10^{-10} \times 0.200 = 1.11 \times 10^{-10} $$

$$ x = \sqrt{1.11 \times 10^{-10}} \approx 1.05 \times 10^{-5} \, \text{M} $$

This x is the concentration of H_3O^+.

Now, calculate pH:

$$ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.05 \times 10^{-5}) \approx 4.98 $$

Final Result: pH at the Equivalence Point ≈ 4.98

This value reflects a solution that is slightly acidic, which aligns with the chemical nature of the ammonium ion resulting from the titration of a weak base with a strong acid. The pH is just below 5, confirming the expected acidity at the equivalence point.

Summary and Practical Insights

- The amount of HCl required to reach the equivalence point for the given ammonia solution is 25.0

mL.
- The pH at the equivalence point is approximately 4.98, indicating a slightly acidic solution.
- This titration exemplifies the principles of weak base-strong acid reactions, hydrolysis, and pH calculations at the equivalence point.

Additional Considerations

- Buffer Region: Before reaching the equivalence point, the pH gradually drops, and the solution acts as a buffer due to the presence of both NH_3 and NH_4^+.
- Beyond Equivalence: Adding excess HCl would rapidly decrease the pH, approaching that of the strong acid.
- Experimental Validation: Theoretical calculations align with typical titration curves, where the pH at equivalence for weak base-strong acid titrations is slightly

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