

Consider The Titration Of 100.0 ML Of 0.100 M H₂NNH₂ (K_b 3.0 X 10⁻⁶) By 0.200 M HNO₃. Calculate The PH

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Titration is a fundamental laboratory technique used in chemistry to determine the concentration of an unknown solution by reacting it with a solution of known concentration. In this detailed guide, we will explore the titration process involving hydrazine (H₂NNH₂), a weak base, reacting with a strong acid, nitric acid (HNO₃). Specifically, we will analyze the titration of 100.0 mL of 0.100 M hydrazine with 0.200 M nitric acid and calculate the resulting pH at various stages of the titration, focusing on the equivalence point. This comprehensive explanation aims to deepen your understanding of acid-base titrations, dissociation constants, and pH calculations, optimized for both students and educators seeking clarity on this chemical process.

Understanding the Key Components of the Titration

Before delving into the calculations, it is essential to familiarize ourselves with the chemical species involved, their properties, and the key concepts underpinning the titration process.

Hydrazine (H₂NNH₂)

- Hydrazine is a weak base with the chemical formula H₂NNH₂.
- It reacts with acids to form hydrazinium salts.
- The base dissociation constant (K_b) for hydrazine is given as 3.0×10^{-6} .

Nitric Acid (HNO₃)

- Nitric acid is a strong acid, fully dissociating in aqueous solution.
- It reacts with hydrazine in a typical acid-base titration.

Key Concepts

- Titration: The controlled addition of a titrant (HNO₃) to an analyte solution (H₂NNH₂) until the reaction reaches the equivalence point.
- Equivalence Point: The point during titration where equivalents of acid have completely reacted with the base.
- pH Calculation: Determining the acidity or alkalinity of the solution at different stages, especially at the equivalence point.

Initial Conditions and Data

Let's summarize the initial data for this titration:

- Volume of hydrazine solution, $V_1 = 100.0 \text{ mL} = 0.100 \text{ L}$
- Concentration of hydrazine, $C_1 = 0.100 \text{ M}$
- Concentration of nitric acid, $C_2 = 0.200 \text{ M}$
- K_b of hydrazine $= 3.0 \times 10^{-6}$

The number of moles of hydrazine initially present:

$$n_{\text{base}} = C_1 \times V_1 = 0.100 \text{ mol/L} \times 0.100 \text{ L} = 0.0100 \text{ mol}$$

The titrant, HNO_3 , will be added gradually in increments, and calculations will be performed at key points: initial, half-equivalence, equivalence point, and beyond.

Step 1: Calculating the Initial pH of Hydrazine Solution

Hydrazine, being a weak base, undergoes hydrolysis:



The base dissociation constant (K_b) relates to the concentration of hydroxide ions:

$$K_b = \frac{[\text{N}_2\text{H}_4][\text{OH}^-]}{[\text{H}_2\text{NNH}_2]}$$

Assuming x is the concentration of OH^- at equilibrium:

$$K_b = \frac{x^2}{C_1 - x} \approx \frac{x^2}{C_1}$$

since x is small compared to C_1 :

$$x^2 = K_b \times C_1 = 3.0 \times 10^{-6} \times 0.100 = 3.0 \times 10^{-7}$$

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$$x = \sqrt{3.0 \times 10^{-7}} \approx 5.48 \times 10^{-4}, \text{M}$$

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The initial pOH:

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$$\text{pOH} = -\log [\text{OH}^-] = -\log (5.48 \times 10^{-4}) \approx 3.26$$

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Thus, the initial pH:

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$$\text{pH} = 14 - \text{pOH} = 14 - 3.26 = 10.74$$

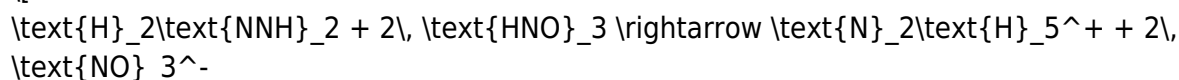
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Initial pH of the hydrazine solution is approximately 10.74.

Step 2: Determining the Moles of Acid Needed to Reach the Equivalence Point

At the equivalence point, all hydrazine has reacted with nitric acid:

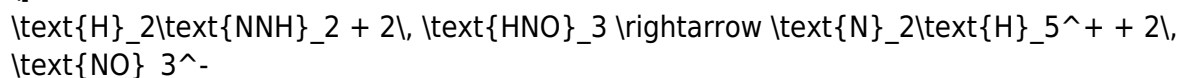
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However, since hydrazine is a weak base and nitric acid is strong, the neutralization reaction is:

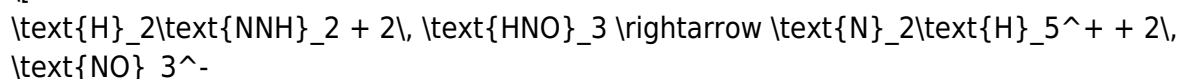
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But in practice, the reaction simplifies to:

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The key point here is that hydrazine reacts with nitric acid in a 1:2 molar ratio.

Calculating the moles of nitric acid needed:

$$n_{\text{acid}} = 2 \times n_{\text{base}} = 2 \times 0.0100 \text{ mol} = 0.0200 \text{ mol}$$

Corresponding volume of HNO_3 :

$$V_{\text{acid}} = \frac{n_{\text{acid}}}{C_2} = \frac{0.0200 \text{ mol}}{0.200 \text{ mol/L}} = 0.100 \text{ L} = 100.0 \text{ mL}$$

Thus, the equivalence point occurs after adding 100 mL of 0.200 M HNO_3 .

Step 3: Calculating pH at Various Titration Stages

To fully understand the titration, we analyze the solution's pH at different points:

1. Initial (before any acid is added)
2. Halfway to equivalence
3. At the equivalence point
4. Beyond the equivalence point

Initial pH (No acid added)

Already calculated: $\text{pH} \approx 10.74$

2. pH at Half-Equivalence Point

At half the equivalence point, half of hydrazine has reacted to form hydrazinium ions (N_2H_5^+). For weak base titrations, the pH at half-equivalence corresponds to the pK_a of the conjugate acid.

- Hydrazine's conjugate acid: hydrazinium ion (N_2H_5^+)
- Relation:

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

Given:

$$pK_b = -\log K_b = -\log 3.0 \times 10^{-6} \approx 5.52$$

Thus,

$$pK_a = 14 - 5.52 = 8.48$$

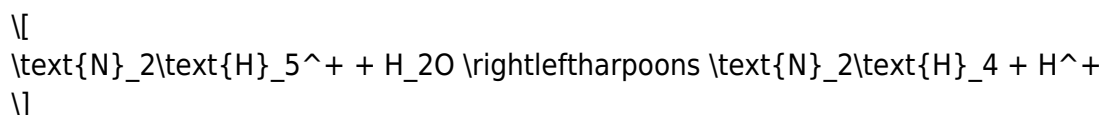
At half-equivalence:

$$pH = pK_a \approx 8.48$$

pH at half-equivalence point: approximately 8.48.

3. pH at the Equivalence Point

At the equivalence point, all hydrazine has been converted to hydrazinium ions ($N_2H_5^+$). Since hydrazinium is a weak acid, it can hydrolyze:



The hydrolysis constant (K_a) relates to K_b :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-6}} \approx 3.33 \times 10^{-9}$$

Using the hydrolysis expression:

$$K_a = \frac{[H^+][N_2H_4]}{[N_2H_5^+]}$$

Assuming the initial

Frequently Asked Questions

What is the initial concentration of hydrazine (H_2NNH_2) in the titration?

The initial concentration of hydrazine is 0.100 M in 100.0 mL of solution.

What is the molarity and volume of the titrant used in the titration?

The titrant, nitric acid (HNO_3), has a concentration of 0.200 M, and the volume used can be determined from the titration process.

How do you determine the pH at the equivalence point of titrating hydrazine with nitric acid?

At the equivalence point, all hydrazine has reacted to form its conjugate acid, and the pH is determined by the hydrolysis of the resulting hydrazinium ion (N_2H_5^+).

What is the K_b of hydrazine, and how does it affect the titration calculation?

The K_b of hydrazine is 3.0×10^{-6} , which indicates its weak basic nature and helps in calculating the pH of the solution at various stages.

How do you calculate the pH of the solution before the equivalence point in this titration?

Before the equivalence point, the pH is determined by the remaining hydrazine and its partial hydrolysis, using the K_b and initial concentrations.

What is the significance of the pK_a value in this titration, and how is it related to K_b ?

The pK_a is related to the K_b by the relation $pK_a + pK_b = 14.0$ at 25°C , and it helps determine the pH of the conjugate acid formed during titration.

Can you outline the steps to calculate the pH at the equivalence point of this titration?

Yes, first determine the moles of hydrazine reacted, find the concentration of the hydrazinium ion at equivalence, then use hydrolysis equations and the K_b to calculate the pH.

Additional Resources

Titration of Hydrazine (H₂NNH₂) with Nitric Acid (HNO₃): A Comprehensive Analysis of pH Calculation

Introduction

In the realm of analytical chemistry, titration remains a cornerstone technique for quantifying the concentration of unknown solutions and understanding acid-base interactions. Today, we delve into a nuanced titration scenario involving hydrazine (H₂NNH₂), a notable weak base, and nitric acid (HNO₃), a strong acid. This case is particularly intriguing because it combines fundamental principles of chemical equilibria, stoichiometry, and pH calculation, all within a practical context.

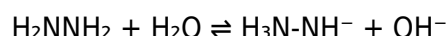
Our objective is to analyze and compute the pH of a solution following the titration of 100.0 mL of 0.100 M hydrazine with 0.200 M nitric acid. The process involves understanding the acid-base reactions, the nature of hydrazine, and applying relevant equilibrium expressions to arrive at an accurate pH value.

Understanding the Components

Hydrazine (H₂NNH₂): The Weak Base

Hydrazine is a potent, yet weak, base with a known base dissociation constant (K_b) of 3.0×10^{-6} . Its chemical structure features two nitrogen atoms connected by a single bond, with each nitrogen bearing a lone pair capable of accepting protons:

- Chemical Equation for Hydrazine's Base Dissociation:

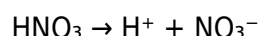


- Significance of K_b: The magnitude of K_b indicates hydrazine's relative strength as a base. A K_b of 3.0×10^{-6} suggests moderate basicity, warranting careful equilibrium calculations to determine pH after titration.

Nitric Acid (HNO₃): The Strong Acid

Nitric acid is a strong acid, fully dissociating in aqueous solution:

- Dissociation Equation:



- Implication: When titrating hydrazine with HNO₃, the acid will rapidly react with hydrazine's lone pairs, converting it into its conjugate acid form.

The Titration Scenario

Initial Conditions:

- Volume of hydrazine solution: 100.0 mL (0.100 L)
- Concentration of hydrazine: 0.100 M
- Concentration of nitric acid: 0.200 M

Goal:

Calculate the pH after a specific volume of nitric acid has been added or, alternatively, determine the pH at the equivalence point.

Step 1: Establishing the Titration Progress and Stoichiometry

Given the initial data, let's analyze the titration:

- Moles of hydrazine initially:

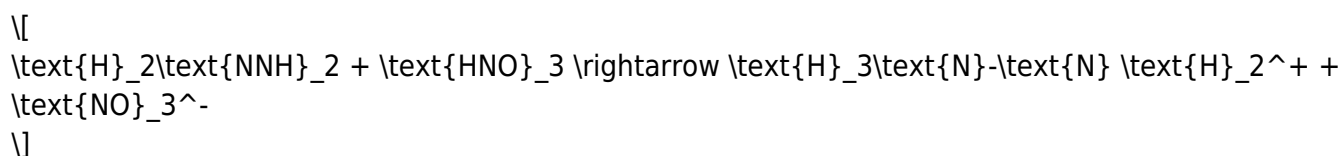
$$n_{\text{moles}} = M \times V = 0.100 \, \text{mol/L} \times 0.100 \, \text{L} = 0.0100 \, \text{mol}$$

- Moles of nitric acid added:

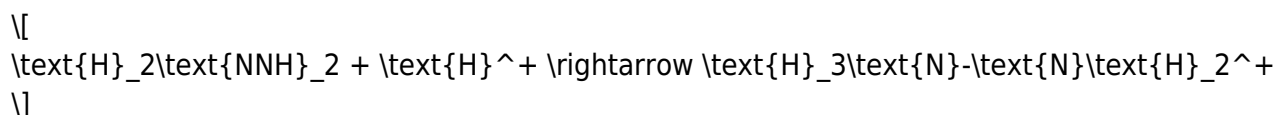
For a given volume V_{HNO_3} , the moles are:

$$n_{\text{moles}} = 0.200 \, \text{mol/L} \times V_{\text{HNO}_3}$$

The reaction between hydrazine and nitric acid is:



However, more precisely, hydrazine reacts with strong acids via protonation:



This indicates a 1:1 molar ratio for the neutralization reaction.

Step 2: Determining the Volume of Acid Required to Reach Equivalence

To reach the equivalence point:

$$n_{\text{moles of acid}} = n_{\text{moles of hydrazine}} = 0.0100 \, \text{mol}$$

- Volume of HNO₃ needed:

$$V_{\text{eq}} = \frac{0.0100 \text{ mol}}{0.200 \text{ mol/L}} = 0.0500 \text{ L} = 50.0 \text{ mL}$$

Thus, adding 50.0 mL of 0.200 M HNO₃ to the initial 100.0 mL hydrazine solution will reach the equivalence point.

Step 3: pH at Various Stages of Titration

The pH depends heavily on the extent of the titration:

- Before the equivalence point: Excess hydrazine dominates.
- At the equivalence point: Hydrazine is fully converted into its conjugate acid.
- After the equivalence point: Excess nitric acid determines the pH.

Step 4: Calculating pH at the Equivalence Point

At equivalence, all hydrazine has been protonated to form hydrazinium ions ($\text{H}_3\text{N-NH}_2^+$). These conjugate acids are weak acids and will hydrolyze in water, affecting the pH.

Step-by-step:

1. Calculate moles of hydrazinium ions:

$$\text{moles} = 0.0100 \text{ mol}$$

2. Total volume after addition:

$$V_{\text{total}} = 100.0 \text{ mL} + 50.0 \text{ mL} = 150.0 \text{ mL} = 0.150 \text{ L}$$

3. Concentration of hydrazinium ion:

$$[\text{H}_3\text{N-NH}_2^+] = \frac{0.0100 \text{ mol}}{0.150 \text{ L}} = 0.0667 \text{ M}$$

4. Determine the hydrolysis of hydrazinium ion:

Hydrazinium ion is a weak acid with an acid dissociation constant (K_a), related to (K_b) of hydrazine:

$$K_a = \frac{K_w}{K_b}$$

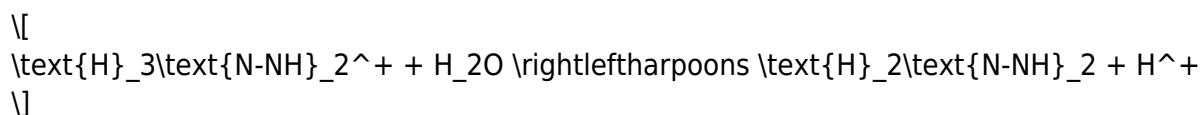
Where:

- $K_w = 1.0 \times 10^{-14}$
- $K_b = 3.0 \times 10^{-6}$

Calculating K_a :

$$K_a = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-6}} = 3.33 \times 10^{-9}$$

5. Set up hydrolysis equilibrium:



- Initial concentration: 0.0667 M
- Change: $(-x)$
- Equilibrium concentration of (H^+) : (x)

6. Expression for K_a :

$$K_a = \frac{x^2}{[\text{H}_3\text{N-NH}_2^+] - x} \approx \frac{x^2}{0.0667}$$

(Assuming (x) is small relative to initial concentration)

7. Solve for (x) :

$$x^2 = K_a \times 0.0667 = 3.33 \times 10^{-9} \times 0.0667 \approx 2.22 \times 10^{-10}$$

$$x = \sqrt{2.22 \times 10^{-10}} \approx 1.49 \times 10^{-5} \text{ M}$$

8. Calculate pH:

$$\text{pH} = -\log [\text{H}^+] = -\log (1.49 \times 10^{-5}) \approx 4.83$$

Therefore, the pH at the equivalence point is approximately 4.83.

Stage-Specific pH Calculations

1. Before equivalence (excess hydrazine):

- Calculate moles of hydrazine remaining after partial titration.
- Use the base dissociation constant (K_b) to find the concentration of OH^- .
- pOH from hydrolysis, then convert to pH.

2. After equivalence (excess nitric acid):

- Excess HNO_3 dictates pH.
- Calculate molarity of excess H^+ , then pH directly.

Additional Considerations:

- Hydrazine's K_b value suggests it is a weak base, making equilibrium calculations vital.
- The conjugate acid's hydrolysis significantly influences pH at the equivalence point.

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