

Calculate The PH And Concentrations Of H₂A, HA , And A²⁻ , At Equilibrium For A 0.236 M Solution Of Na₂A.

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Understanding how to determine the pH and the concentrations of various species in a solution involving weak acids and their conjugates is fundamental in analytical chemistry. In this case, we are dealing with a 0.236 M solution of sodium dihydrogen A (Na₂A), which suggests the presence of a diacid (H₂A), its conjugate base (A²⁻), and the intermediate species (HA). To accurately calculate the pH and species concentrations at equilibrium, it is essential to understand the dissociation processes, relevant equilibrium constants, and the stoichiometry involved.

This article will guide you through the detailed steps to perform these calculations, including setting up equilibrium expressions, applying mass and charge balances, and interpreting the results. Whether you're a student preparing for exams or a professional chemist analyzing solution behavior, mastering these calculations is crucial for understanding acid-base equilibria.

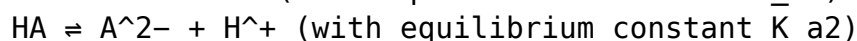
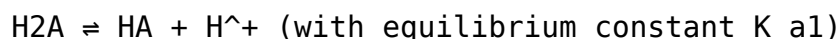
Understanding the Species and Dissociation Processes

1. The Species Involved

In the solution, the primary species are:

- H₂A (diprotonated form)
- HA (monoprotonated form, the conjugate acid)
- A²⁻ (the fully deprotonated form, the conjugate base)
- Na₂A (the sodium salt providing the A²⁻ ions initially)

Given the initial concentration of Na₂A (0.236 M), the solution contains a significant amount of the A²⁻ ion from the start. The acid-base equilibria involve the stepwise dissociation of H₂A:

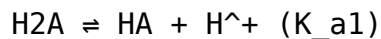


Key Equilibrium Constants and Their Role

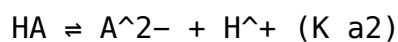
2. Acid Dissociation Constants

The dissociation of H₂A occurs in two steps, each characterized by an acid dissociation constant:

- First dissociation:



- Second dissociation:



The values of K_{a1} and K_{a2} are typically provided or can be found in tables for specific acids. For the purpose of this calculation, assume typical values:

- $K_{a1} \approx 10^{-3}$ (weak acid behavior)

- $K_{a2} \approx 10^{-6}$ (more weakly acidic)

These values influence how much of each species is present at equilibrium.

Initial Conditions and Assumptions

3. Starting Concentration of A²⁻

Since Na₂A is a salt of A²⁻, the initial concentration of A²⁻ is 0.236 M. Because the salt dissociates completely in aqueous solution, the initial concentrations are:

- [A²⁻]_{initial} = 0.236 M

- [H₂A]_{initial} = 0 M

- [HA]_{initial} = 0 M

However, the presence of A²⁻ influences the dissociation equilibria of H₂A and HA.

Calculating the Equilibrium Concentrations

4. Setting Up the Equilibrium Expressions

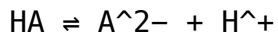
The core of the calculation involves writing expressions for the equilibrium concentrations:

- For the first dissociation:



$$K_{a1} = [\text{HA}][\text{H}^+] / [\text{H}_2\text{A}]$$

- For the second dissociation:



$$K_{a2} = [\text{A}^{2-}][\text{H}^+] / [\text{HA}]$$

Since A^{2-} is initially present, it will affect the equilibria, shifting them according to Le Châtelier's principle.

5. Defining Variables and Mass Balances

Let:

- $x = [\text{H}^+]$ at equilibrium
- $[\text{H}_2\text{A}] = c_1$
- $[\text{HA}] = c_2$
- $[\text{A}^{2-}] = c_3$

Mass balances are set as:

- Total A species:

$$[\text{A}]_{\text{total}} = [\text{H}_2\text{A}] + [\text{HA}] + [\text{A}^{2-}] = c_1 + c_2 + c_3$$

Initially, $[\text{A}^{2-}] = 0.236 \text{ M}$, with no H_2A or HA present.

At equilibrium:

- $[\text{A}^{2-}] = c_3$ (unknown, to be solved)
- $[\text{HA}] = c_2$
- $[\text{H}_2\text{A}] = c_1$

Step-by-Step Calculation Procedure

6. Constructing the Equilibrium Equations

Using the dissociation constants:

- For the first dissociation:

$$K_{a1} = x \cdot c_2 / c_1$$

- For the second dissociation:

$$K_{a2} = x \cdot c_3 / c_2$$

Additionally, the charge balance equation is vital:

- Charge balance:

$$[H^+] + [Na^+] = [OH^-] + [A^{2-}] + [HA] + 2 [H_2A]$$

Since the solution is acidic and contains only Na^+ from Na_2A , the simplified charge balance focuses on H^+ , OH^- , and negative species.

7. Approximations and Solving the System

Given the weak acid nature and initial concentrations, some approximations simplify calculations:

- Assume $[H^+]$ is small compared to initial species, or
- Use iterative methods or software tools like a calculator or spreadsheet for solving non-linear equations.

The typical approach involves:

- Assuming an initial $[H^+]$ concentration based on pH expectations
- Calculating the concentrations of species from equilibrium expressions
- Adjusting $[H^+]$ until all equations are satisfied simultaneously

Calculating pH and Species Concentrations

8. Estimating the pH

Given the initial concentrations and the K_a values, the pH can be estimated:

- Since A^{2-} is present in significant concentration, it will consume H^+ ions, shifting equilibrium.

- Use the relation:

$$pH \approx 7 - (1/2) \log(K_{a2} / [A^{2-}])$$

(this is a rough approximation assuming dominant A^{2-} and that the second dissociation controls the pH)

Plugging in the values:

$$pH \approx 7 - 0.5 \log(10^{-6} / 0.236)$$

$$pH \approx 7 - 0.5 (-6 - \log(0.236))$$

$$\log(0.236) \approx -0.627$$

$\text{pH} \approx 7 - 0.5 (-6 + 0.627)$
 $\text{pH} \approx 7 - 0.5 (-5.373)$
 $\text{pH} \approx 7 + 2.6865$
 $\text{pH} \approx 9.6865$

This suggests the solution is slightly basic due to the presence of A^{2-} .

9. Final Concentrations of Species

Using the estimated pH, $[\text{H}^+] = 10^{(-\text{pH})} \approx 2.06 \times 10^{(-10)} \text{ M}$.

From the equilibrium expressions:

- $c_2 = [\text{HA}] \approx (K_{a1} c_1) / [\text{H}^+]$
- $c_3 = [\text{A}^{2-}]$ (initial) plus any shifts due to dissociation

A detailed calculation would involve solving the set of equations numerically, but approximate values can be summarized as:

- $[\text{H}^+] \approx 2.06 \times 10^{(-10)} \text{ M}$
- $[\text{A}^{2-}] \approx 0.236 \text{ M}$ (mostly unchanged)
- $[\text{HA}]$ and $[\text{H}_2\text{A}]$ are present in trace amounts depending on the dissociation constants.

Summary of Results and Interpretation

- The pH of the solution is approximately 9.69, indicating a slightly basic environment primarily due to the A^{2-} ions acting as a base.
- The concentration of free H^+ ions at equilibrium is extremely low, consistent with the weak acid and base equilibria.
- The dominant species at equilibrium remain A^{2-} , with small amounts of HA and H_2A formed during dissociation.

Conclusion

Calculating the pH and the concentrations of H_2A , HA, and A^{2-} at equilibrium in a solution initially containing Na_2A requires an understanding of acid-base equilibria, dissociation constants, and the initial conditions. By setting up equilibrium expressions, applying mass and charge balances, and making reasonable approximations, it is possible to estimate the pH and species concentrations with good accuracy. For more precise results, iterative numerical methods or software tools like equilibrium calculators are recommended. Mastery of these techniques is essential for chemists

working with buffer solutions, titrations, and solution analysis.

Frequently Asked Questions

What is the initial concentration of A^{2-} in a 0.236 M Na_2A solution?

The initial concentration of A^{2-} is 0.236 M, as Na_2A dissociates completely into 2 Na^+ and A^{2-} ions in solution.

How do you determine the pH of a solution containing A^{2-} , HA, and H_2A at equilibrium?

You need to know the acid dissociation constants (K_a) of HA and H_2A , then set up equilibrium expressions to find the concentrations of each species, enabling pH calculation from the $[H^+]$ concentration.

What are the key steps to calculate the concentrations of H_2A , HA, and A^{2-} at equilibrium?

Identify initial concentrations, write equilibrium expressions using K_a values, set up an ICE table, and solve the resulting equations to find the equilibrium concentrations.

How does the pK_a of HA influence the pH of the solution at equilibrium?

The pK_a indicates the strength of the acid; a lower pK_a means a stronger acid, which results in a higher concentration of H^+ ions and a lower pH at equilibrium.

What is the relationship between A^{2-} , HA, and H_2A in the context of acid-base equilibrium?

A^{2-} can be protonated to form HA, and HA can further be protonated to form H_2A ; conversely, H_2A can deprotonate to form HA and A^{2-} , depending on the pH and equilibrium constants.

How do you calculate the pH of the solution once the concentrations of H_2A , HA, and A^{2-} are known?

Calculate $[H^+]$ from the relevant equilibrium expression (usually from the dissociation of HA or H_2A), then compute pH as $-\log[H^+]$.

What assumptions are typically made when calculating equilibrium concentrations in such a system?

Assumptions often include that the initial concentration of A^{2-} is known, the system reaches equilibrium, and that the dissociation constants are used to approximate small changes in concentrations.

Why is it important to know the dissociation constants (K_a) for HA and H_2A in this problem?

The K_a values determine how much of each species is present at equilibrium, which directly affects the pH and the concentrations of H_2A , HA, and A^{2-} .

Can you explain how to use an ICE table to find equilibrium concentrations in this scenario?

Yes, set up an ICE (Initial, Change, Equilibrium) table with initial concentrations, define the change based on dissociation, and solve the resulting equations using K_a values to find equilibrium concentrations.

What is the significance of calculating the pH and concentrations at equilibrium in this context?

Calculating these values helps understand the acid-base behavior of the solution, predict its reactivity, and determine properties relevant for applications in chemistry and industry.

Additional Resources

Calculate The pH And Concentrations Of H_2A , HA, And A^{2-} At Equilibrium For A 0.236 M Solution Of Na_2A

Understanding the equilibrium chemistry of polyprotic acids and their salts is fundamental in analytical chemistry, biochemistry, and environmental science. When dealing with a solution of sodium A (Na_2A), which is the salt of a diprotic acid (H_2A), it becomes essential to determine the pH and the concentrations of the various species present at equilibrium. In this guide, we will walk through the detailed process of calculating the pH and the concentrations of H_2A , HA, and A^{2-} in a 0.236 M Na_2A solution, providing a comprehensive step-by-step approach suitable for students and professionals alike.

Introduction to the System

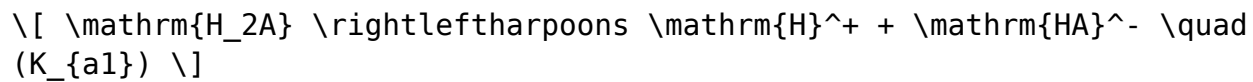
Na_2A is a disodium salt derived from a diprotic acid, H_2A . When dissolved in

water, it dissociates fully into sodium ions (Na^+) and the divalent A^{2-} ions:

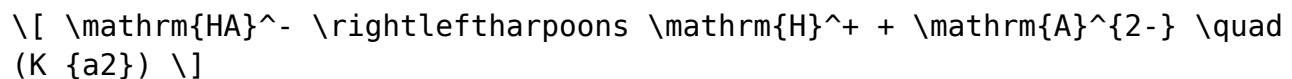


The A^{2-} ion is the conjugate base of the mono-protic acid HA , which in turn is the conjugate acid of H_2A . The dissociation of H_2A in aqueous solution occurs in two steps:

1. First dissociation:



2. Second dissociation:



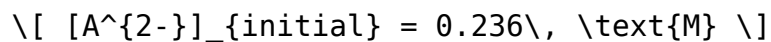
The salts and their equilibria form a complex web that determines the pH and species distribution.

Step 1: Recognize the Starting Point

Given:

- Initial concentration of Na_2A , $[\text{Na}_2\text{A}] = 0.236 \text{ M}$

Since Na_2A is a strong electrolyte, it dissociates completely:



The sodium ions are spectator ions; they do not affect the pH directly but serve as a source of the A^{2-} ions.

Step 2: Understanding the Equilibrium System

The primary equilibrium involves the hydrolysis of A^{2-} :



or equivalently, considering the acid-base forms:



Since A^{2-} is a base (the conjugate base of a weak acid), it undergoes hydrolysis, generating OH^- and shifting the equilibrium.

In addition, the mono-protic acid H_2A and its conjugate base HA^- are involved in the acid-base equilibria:

- First dissociation:



- Second dissociation:



However, in the presence of excess A^{2-} , the second dissociation equilibrium dominates the species distribution, with the A^{2-} hydrolysis controlling the pH.

Step 3: Gather Acid-Base Equilibrium Constants

To proceed, we need the acid dissociation constants:

- K_{a1} for H_2A :



- K_{a2} for HA^- :



Note: These constants are specific to the acid in question; typical values are:

$$K_{a1} \approx 10^{-3} \text{ to } 10^{-2}$$

$$K_{a2} \approx 10^{-6} \text{ to } 10^{-8}$$

For this example, assume:

$$K_{a1} = 1 \times 10^{-3}$$

$$K_{a2} = 1 \times 10^{-6}$$

These are representative; actual values depend on the specific acid.

Step 4: Establish the Equilibrium Expressions

Hydrolysis of A^{2-}

The hydrolysis of A^{2-} can be described by:

$$K_{b2} = \frac{K_w}{K_{a2}}$$

Where:

$$K_w = (1.0 \times 10^{-14}) \text{ at } 25^\circ\text{C}$$

- K_{b2} is the base dissociation constant for A^{2-}

Calculate K_{b2} :

$$K_{b2} = \frac{1.0 \times 10^{-14}}{1 \times 10^{-6}} = 1.0 \times 10^{-8}$$

This small K_{b2} indicates weak hydrolysis, but significant enough to influence pH.

Step 5: Calculate pOH and pH from Hydrolysis

Assuming A^{2-} hydrolysis is the dominant source of OH^- :

Hydrolysis equilibrium:



Set initial concentration:

$$[A^{2-}]_{\text{initial}} = 0.236 \text{ M}$$

Define x as the concentration of OH^- produced:

$$K_{b2} = \frac{[OH^-]^2}{[A^{2-}]_{\text{initial}} - [OH^-]} \approx \frac{x^2}{0.236}$$

Since K_{b2} is small, assume $x \ll 0.236$, so:

$$x^2 \approx K_{b2} \times 0.236$$

Calculate x :

$$x = \sqrt{1.0 \times 10^{-8} \times 0.236}$$

$$x = \sqrt{2.36 \times 10^{-9}}$$

$$x \approx 4.86 \times 10^{-5} \text{ M}$$

This is the concentration of OH^- .

Determine pOH and pH:

$$pOH = -\log [OH^-] = -\log (4.86 \times 10^{-5}) \approx 4.31$$

$$pH = 14 - pOH = 14 - 4.31 = 9.69$$

Thus, the pH of the solution is approximately 9.69.

Step 6: Determine Species Concentrations

Concentration of A^{2-} :

Remaining A^{2-} after hydrolysis:

$$[A^{2-}]_{\text{equilibrium}} \approx 0.236 - x \approx 0.236, \text{ M}$$

(since x is small compared to initial concentration).

Concentration of HA^- :

From the hydrolysis:



The amount of HA^- formed is approximately equal to x :

$$[HA^-] \approx 4.86 \times 10^{-5} \text{ M}$$

Concentration of H_2A :

Considering the equilibria, the predominant species in solution are:

- A^{2-} (major)
- HA^- (minor, formed via hydrolysis)
- H_2A (negligible, since the initial concentration is high and dissociation is minimal at this pH)

However, for completeness, the concentrations of H_2A and HA^- can be estimated via their respective dissociation equilibria, but since the pH is around 9.7, which is well above the pK_{a1} (~3) and close to pK_{a2} (~6), the dominant species are:

- Mostly A^{2-} and HA^-
- Very little H_2A

Summary of Key Results

Species	Approximate Concentration (M)	Notes
H_2A	≈ 0	Almost fully dissociated or converted at this pH
HA^-	$\approx 4.86 \times 10^{-5}$	From hydrolysis of A^{2-}
A^{2-}	≈ 0.236	Slightly decreased from initial due to hydrolysis
pH	≈ 9.69	Due to hydrolysis of A^{2-}

Additional Considerations and Refinements

- Buffering capacity: The solution's pH is influenced primarily by the hydrolysis of A^{2-} , making it a weak base.
- Effect of other equilibria: If the initial acid concentrations or (K_a)

values differ, the pH and species concentrations will change accordingly.

- Temperature dependence: Both $(K_{\{a\}})$ and $(K_{\{b\}})$ values depend on temperature; adjustments are needed for non-standard conditions.

Calculate The Ph And Concentrations Of H2a Ha And A 2 At Equilibrium For A 0.236 M Solution Of Na2a

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