REACTIONS OF SALTS WITH WATER

Hydrolysis as applied to water solutions of inorganic compounds, can be defined as the reaction of water with one or both ions of a salt to form a weak acid and a OH- or a weak base and H+ ion or both. For example,

In a solution of NaCN: \( \text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^- \) (weak acid forms)

In a solution of NH\(_4\)Cl: \( \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \) (weak base forms)

In a solution of NaCl: \( \) (no hydrolysis)

In a solution of NH\(_4\)C\(_2\)H\(_3\)O\(_2\): \( \) (both, a weak acid and a weak base, form)

THE EQUILIBRIUM CONSTANT FOR HYDROLYSIS REACTION

A quantitative measure of the extent to which a given salt will hydrolyze is given by the equilibrium constant of the hydrolysis reaction. Setting the K-expression in the usual way, we find for NaC\(_2\)H\(_3\)O\(_2\), where

\[ \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 (aq) + \text{OH}^- (aq) \]

\[ K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} \]

Values for \( K_b \) cannot be found in tables. Instead, they can be derived from values of other equilibrium constants that are found in tables. Multiplying both numerator and denominator of the expression shown above by \( \text{H}^+ \) gives:

\[ K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-][\text{H}^+]}{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]} = \frac{1}{K_a} \cdot K_w \]

Ka is the equilibrium constant for the ionization of HC\(_2\)H\(_3\)O\(_2\) found in tables. For the hydrolysis reaction given above, we can write:

\[ K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{K_w}{K_a} \]

The numerical value of \( K_b \) for the above equilibrium, then, is

\[ K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10} \]
THE WEAKER THE ACID OR BASE FORMED THE GREATER THE PERCENT OF HYDROLYSIS

\[ K_a \text{ for HCN} = 4.0 \times 10^{-10} \]
\[ K_a \text{ for HNO}_2 = 4.5 \times 10^{-4} \]

Which would you expect to hydrolyze most, KCN or KNO\(_2\)?

Would the pH of these salts be more than or less than 7?

Which salt would have a pH closer to 7?

SIMULTANEOUS HYDROLYSIS OF CATION AND ANION

If both, cation and anion, undergo hydrolysis, the salt will be more strongly hydrolyzed than it would be for either ion separately. NH\(_4\)CN will hydrolyze more than either NH\(_4\)Cl or KCN.

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]
\[ \text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^- \]

The H\(_3\)O\(^+\) from the hydrolysis of NH\(_4\)\(^+\) combines with the OH\(^-\) from the hydrolysis of CN\(^-\) forming water. The equilibrium of both reactions will shift to the right.

pH OF ACID SALT SOLUTIONS

An acid salt is one that still contains H as part of the anion (HSO\(_4\)\(^-\), H\(_2\)PO\(_4\)\(^-\), HCO\(_3\)\(^-\), etc)

Will the solution of such a salt be acidic due to the reaction:
\[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad K_{a2} = 4.7 \times 10^{-11} \]

Or will it be basic due to the reaction:
\[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad K_b = K_w = 1.0 \times 10^{14} \]
\[ K_{a1} = 4.2 \times 10^{-7} \]
\[ = 2.4 \times 10^{-8} \]

The simplest way to decide which reaction predominates is to compare the values of the two equilibrium constants, \(K_b\) and \(K_{a2}\), above. Since \(K_b\) is larger than \(K_{a2}\) above, the second reaction predominates and the solution is basic.

Today you will look up tabulated values of equilibrium constants to predict for a given salt which reaction will predominate, then check your prediction experimentally.
EXPERIMENT

Check out a pH pen from the stockroom.

A.  THE EXTENT OF HYDROLYSIS OF CERTAIN SALTS

Place the following 0.10 M solutions in separate wells of a spot plate. NaC₂H₃O₂, NH₄Cl, NaCl, Na₂CO₃, NH₄C₂H₃O₂, NaHSO₄, FeCl₃, NaH₂PO₄, NaHCO₃. Use the pH pen to measure the pH of each solution. Remember to rinse the tip of the pH pen with tap water between tests. Record the results. You will use your measured pH values for later calculations.

B.  HYDROLYSIS OF AMMONIUM SALTS
Remove the stoppers and cautiously smell the odor from bottles of solid ammonium chloride, solid ammonium carbonate, and solid ammonium acetate from the Chem 111 shelves.
Which has the strongest odor? __________
Which has the weakest odor? __________

There is enough water adsorbed on the surface of the apparently dry crystals to make hydrolysis possible. Explain the relative odors of the three salts in terms of the extent of hydrolysis of each, and the relative values of $K_a$ or $K_b$ for the hydrolysis reactions.

C.  HYDROLYSIS OF Al³⁺ ION
Mix about 1 g of dry Al₂(SO₄)₃ and 1 g of dry NaHCO₃. Is there a reaction? ____
Add a few milliliters of H₂O. Is there a reaction? _____ Write the evidence for the reaction, if there is any.
A. THE EXTENT OF HYDROLYSIS OF CERTAIN SALTS

Measure the pH of distilled H$_2$O: ______________Why is it different from 7?

1. MEASURE THE pH of 0.10 M SALT SOLUTIONS

<table>
<thead>
<tr>
<th>0.10 M solutions</th>
<th>pH measured</th>
<th>pOH calculated</th>
<th>[H$_3$O$^+$] calculated</th>
<th>[OH$^-$] calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$C$_2$H$_3$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaC$_2$H$_3$O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaHSO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaH$_2$PO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td></td>
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</tr>
</tbody>
</table>
2. **THE HYDROLYSIS REACTIONS**

Write net-ionic equations for the reaction of each salt with water below to illustrate the observed pH given on page 5. If there is no reaction, write N.R.

<table>
<thead>
<tr>
<th>0.10 M solutions</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄C₂H₃O₂</td>
<td>a.</td>
</tr>
<tr>
<td></td>
<td>b.</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td></td>
</tr>
<tr>
<td>NaC₂H₃O₂</td>
<td></td>
</tr>
<tr>
<td>NaHSO₄</td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td></td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td></td>
</tr>
<tr>
<td>NaHCO₃</td>
<td></td>
</tr>
</tbody>
</table>
3. CALCULATE PERCENT HYDROLYSIS FROM TABULATED ‘K’ VALUES AND FROM MEASURED pH VALUES
   a. 0.10 M NaC₂H₃O₂
      1. Write the net ionic equation for the hydrolysis of NaC₂H₃O₂.

      2. Write the $K_b$ expression for the hydrolysis reaction.

      3. Calculate the value of $K_b$ for this salt from tabulated values of equilibrium constants. ($K_a$ for HC₂H₅O₂ = 1.8 x 10⁻⁵)
         Setup:

      4. From the above $K_b$ find the theoretical $[\text{OH}^-]$, then calculate the theoretical % hydrolysis.
         Equilibrium equation
         \[ \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_5\text{O}_2 (aq) + \text{OH}^- (aq) \]
         \[
         \begin{array}{c|c|c|c}
         \text{Initial concentration} & 0.10 & 0 & 0 \\
         \text{Change in concentration} & -x & +x & +x \\
         \text{Equilibrium concentration} & 0.10-x & x & x \\
         \end{array}
         \]
         \[
         K_b = \frac{\text{Product concentration}}{\text{Reactant concentration}}
         \]
         \[
         x = [\text{OH}^-]_{(\text{theoretical})} = \text{_______} \text{M}
         \]
         \[
         \% \text{ hydrolysis}_{(\text{theoretical})} = \frac{[\text{OH}^-]_{(\text{theoretical})}}{\text{M}_{\text{C}_2\text{H}_3\text{O}_2^- \text{initial}}} \times 100
         \]
         \[
         = \text{_______} \times 100 = \text{_______}\%
         \]

      5. Calculate experimental % hydrolysis using your experimental $[\text{OH}^-]$ for the salt solution from page 5.
         Setup:

         \[
         \% \text{ hydrolysis}_{\text{experimental}} = \text{_______}\%
         \]
b. 0.10 M Na\textsubscript{2}CO\textsubscript{3}

1. Write the net ionic equation for the hydrolysis of Na\textsubscript{2}CO\textsubscript{3}.

2. Write the \( K_b \) expression for the hydrolysis reaction.

3. Calculate the value of \( K_b \) for this salt from tabulated values of equilibrium constants. (\( K_{a2} \) for HCO\textsuperscript{3}- = 4.7 \times 10^{-11}\)

   Setup:

   \[
   \begin{array}{c|c|c|c}
   \text{Initial concentration} & 0.10 & 0 & 0 \\
   \text{Change in concentration} & -x & +x & +x \\
   \text{Equilibrium concentration} & 0.10-x & x & x \\
   \end{array}
   \]

   \[
   K_b = \frac{\text{Product Concentration}^2}{\text{Concentration of Starting Material}}
   \]

   \[
   x = [\text{OH}^-]_{\text{theoretical}} = \text{M}
   \]

   \[
   \% \text{ hydrolysis (theoretical)} = \frac{[\text{OH}^-]_{\text{theoretical}}}{M_{\text{CO}_3^{2-} \text{ (initial)}}} \times 100
   \]

   \[
   = \text{M} \times 100 =
   \]

   \[
   \% \text{ hydrolysis theoretical} = \text{%}
   \]

4. From the above \( K_b \) find the theoretical \([\text{OH}^-]\), then calculate the theoretical \% hydrolysis.

   Equilibrium equation

   \[
   \text{CO}_3^{2-} (aq) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- (aq) + \text{OH}^- (aq)
   \]

5. Calculate experimental \% hydrolysis using your experimental \([\text{OH}^-]\) for the salt solution from page 5.

   Setup:

   \[
   \% \text{ hydrolysis experimental} = \text{%}
   \]
Summary of part 3:
Copy the theoretical % hydrolysis of 0.10 M NaC₃H₃O₂ from section (a) part 4 on page 7. ____________ %
Copy the theoretical % hydrolysis of 0.10 M Na₂CO₃ from section (b) part 4 on page 8. ____________ %
Which of the above ions hydrolyze more?
(C₃H₃O₂⁻ or CO₃²⁻)
Conclusion: The ____________the acid formed, the greater the % hydrolysis.
(weaker, stronger)

4. HYDROLYSIS OF AMMONIUM SALTS
NH₄Cl, NH₄C₃H₃O₂, (NH₄)₂CO₃

The salt with the strongest odor of ammonia is: ________________
Write the hydrolysis equation for the:
a) Cation undergoing hydrolysis _______________________________________________________________________
b) Anion undergoing hydrolysis _______________________________________________________________________

The salt with the next strongest odor is ________________
Write the hydrolysis equation for the:
a) Cation undergoing hydrolysis _______________________________________________________________________
b) Anion undergoing hydrolysis _______________________________________________________________________

The salt with the least odor of ammonia is ________________
The one ion undergoing hydrolysis is ________________
Write the hydrolysis equation for that ion: _______________________________________________________________________

Which of the above salts will hydrolyze the least? ________________
Why? _______________________________________________________________________

Compare the extent of hydrolysis of NH₄C₃H₃O₂ and (NH₄)₂CO₃ by comparing the K₉ values of C₃H₃O₂⁻ and CO₃²⁻ and their theoretical % hydrolysis.
K₉ for C₃H₃O₂⁻ = ____________ , theoretical %hydrolysis on page 7 ____________ %
K₉ for CO₃²⁻ = ____________ , theoretical %hydrolysis on page 8 ____________ %

From the theoretical % hydrolysis of the above ions and the odor of their ammonium salts, which would you say undergoing hydrolysis to a higher extent? ________________
Explain the effect of the % hydrolysis of the anion on the extent of hydrolysis of NH₄⁺ _______________________________________________________________________

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C. HYDROLYSIS OF Al\(^{3+}\) ION:

1. Mix dry Al\(_2\)(SO\(_4\))\(_3\) and dry NaHCO\(_3\). Is there a reaction? ____________

2. Add a few ml of H\(_2\)O to the above mixture. Is there a reaction? _______

Give the evidence for the reaction: _______________________

Write a net-ionic equation to show the hydrolysis reaction of Al\(^{3+}\)

Net-ionic equation: _________________________________

Is the solution acidic or basic? ________________

Write a net-ionic equation to show the reaction of the produced H\(^+\) with the added HCO\(_3^-\).

Net-ionic equation:_________________________________

Write an equation to show the formation of the produced gas.

Equation: _________________________________________

Add the three equations above. Drop out terms that appear on both sides, to obtain the net-ionic equation of the overall reaction.

Net-ionic equation: ___________________________________

EXERCISES:

1. You have tested experimentally the pH of 0.10 M NaH\(_2\)PO\(_4\) solution. How would you determine theoretically whether it is acidic or basic?

Given: K\(_{a1}\) for H\(_3\)PO\(_4\) = 6.9 \times 10^{-3}, \quad K_{a2} for H\(_2\)PO\(_4^-\) = 6.3 \times 10^{-8}

Hint: Write the two possible reactions of H\(_2\)PO\(_4^-\) with H\(_2\)O

a) H\(_2\)PO\(_4^-\) + H\(_2\)O \rightleftharpoons \_\_\_\_\_\_\_\_\_\_\_\_\_ + OH\(^-\) \quad K_b for H\(_2\)PO\(_4^-\) = \frac{K_w}{K_{a1} for H\(_3\)PO\(_4\)}

b) H\(_2\)PO\(_4^-\) + H\(_2\)O \rightleftharpoons \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ + H\(_3\)O\(^+\) \quad K_{a2} for H\(_2\)PO\(_4^-\) = _______

Compare the K values for the above equilibrium reactions, hence predict whether the solution is acidic or basic. Answer: ____________________

Check your answer against the measured value of 0.10 M NaH\(_2\)PO\(_4\) on page 5.

The measured pH value is ________; the solution is ________ (acidic, or basic)
2. For each of the salts below, indicate whether its water solution would be acidic, basic or neutral. Write an equilibrium equation for any reaction that may occur in water.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Acidic, basic, or neutral</th>
<th>Write an equilibrium equation for any reaction that may occur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(HSO₄)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(NO₃)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KNO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Apply the following information about the acid ionization constants:
   $K_{a1}$ for $\text{H}_2\text{S}$ is $1.0 \times 10^{-7}$ and $K_{a2}$ for $\text{HS}^-$ is $1.3 \times 10^{-13}$
   to predict whether $\text{NaHS (aq)}$ is acidic, basic, or neutral. You must show the setup.
   **Setup:**
   
   Answer: NaHS is ________ because ______________________________ (acidic, basic, or neutral)

4. Consider the following acid ionization constants:
   $K_a$ for $\text{HF}$ is $7.2 \times 10^{-4}$ and $K_a$ for $\text{HOCl}$ is $3.5 \times 10^{-8}$
   Which salt will hydrolyze more, $\text{KF (aq)}$ or $\text{KOCl (aq)}$?
   **Setup:** Write the equilibrium equations and calculate the $K$ values.
   
   Answer: ______________ will hydrolyze more, because ________________.

5. Which salt is expected to hydrolyze more, $\text{NH}_4\text{OCl (aq)}$ or $\text{NaOCl (aq)}$? **Explain** why.
   
   Answer: ______________ will hydrolyze more, because ______________________________

   __________________________________________________________

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