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: $CN^- + H_2O \rightleftharpoons HCN + OH^-$ (weak acid forms)

In a solution of NH_4Cl: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (weak base forms)

In a solution of NaCl: (no hydrolysis)

In a solution of $NH_4C_2H_3O_2$: (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 NaC2H3O2, where

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_2O_2^-]}$$

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 H^+ gives:

$$K_b = \frac{[HC_2H_3O_2][OH^-]\ \mathbf{[H^+]}}{[C_2H_2O_2^-]\ \mathbf{[H^+]}}$$

$$= \frac{1}{K_a} \cdot K_w$$

Ka is the equilibrium constant for the ionization of $HC_2H_3O_2$ found in tables.
For the hydrolysis reaction given above, we can write:

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_2O_2^-]} = \frac{K_w}{K_a}$$

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 for HCN = 4.0×10^{-10}

K_a for HNO_2 = 4.5×10^{-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_4CN will hydrolyze more than either NH_4Cl or KCN.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

The H_3O^+ 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^-, $H_2PO_4^-$, HCO_3^-, etc) Will the solution of such a salt be acidic due to the reaction:

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad K_{a2} = 4.7 \times 10^{-11}$$

Or will it be basic due to the reaction:

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \qquad K_b = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.4 \times 10^{-8}$$

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. $NaC_2H_3O_2$, NH_4Cl, NaCl, Na_2CO_3, $NH_4C_2H_3O_2$, $NaHSO_4$, $FeCl_3$, NaH_2PO4, $NaHCO_3$. 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 Al^{3+} ION

Mix about 1 g of dry $Al_2(SO_4)_3$ and 1 g of dry $NaHCO_3$. Is there a reaction?____

Add a few milliliters of H_2O. Is there a reaction?_____Write the evidence for the reaction, if there is any.

Report Sheet
Reactions of Salt with Water

Name_____
Last First
Instructor's Initial _____

A. THE EXTENT OF HYDROLYSIS OF CERTAIN SALTS

Measure the pH of distilled H_2O: _____Why is it different from 7?

_____

1. MEASURE THE pH of 0.10 M SALT SOLUTIONS

0.10 M solutions	**pH measured**	**pOH calculated**	**$[H_3O^+]$ calculated**	**$[OH^-]$ calculated**
$NH_4C_2H_3O_2$				
NH_4Cl				
NaCl				
Na_2CO_3				
$NaC_2H_3O_2$				
$NaHSO_4$				
$FeCl_3$				
NaH_2PO_4				
$NaHCO_3$				

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

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0.10 M solutions	**Equations**
$NH_4C_2H_3O_2$	a. b.
NH_4Cl	
$NaCl$	
Na_2CO_3	
$NaC_2H_3O_2$	
$NaHSO_4$	
$FeCl_3$	
NaH_2PO_4	
$NaHCO_3$	

3. CALCULATE PERCENT HYDROLYSIS FROM TABULATED 'K' VALUES AND FROM MEASURED pH VALUES

a. 0.10 M $NaC_2H_3O_2$

1. Write the net ionic equation for the hydrolysis of $NaC_2H_3O_2$.

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 $HC_2H_3O_2 = 1.8 \times 10^{-5}$)

Setup:

4. From the above K_b find the theoretical $[OH^-]$, then calculate the theoretical % hydrolysis.

Equilibrium equation

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

Initial concentration	0.10	0	0
Change in concentration	$-x$	$+x$	$+x$
Equilibrium concentration	$0.10-x$	x	x

K_b = _____

$x = [OH^-]_{(theoretical)}$ = _____M

$$\%\ \text{hydrolysis}_{(theoretical)} = \frac{[OH^-]_{(theoretical)}}{M_{C2H3O2^-\ (initial)}} \times 100$$

= _____ x 100 =

% hydrolysis $_{theoretical}$ = _____%

5. Calculate experimental % hydrolysis using your experimental $[OH^-]$ for the salt solution from page 5.

Setup:

% hydrolysis $_{experimental}$ = _____%

b. <u>0.10 M Na_2CO_3</u>

1. Write the net ionic equation for the hydrolysis of Na_2CO_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_3^- = 4.7×10^{-11})

<u>Setup:</u>

4. From the above K_b find the theoretical $[OH^-]$, then calculate the theoretical % hydrolysis.

Equilibrium equation

$$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

Initial concentration	0.10	0	0
Change in concentration	- *x*	+ *x*	+ *x*
Equilibrium concentration	0.10- *x*	*x*	*x*

K_b = _____

x = $[OH^-]_{\textbf{(theoretical)}}$ =_____M

$$\%\ \text{hydrolysis}_{\textbf{(theoretical)}} = \frac{[OH^-]_{\textbf{(theoretical)}}}{M_{CO3^{2-}\ \textbf{(initial)}}} \times 100$$

= _____x 100 =

$\%\ \text{hydrolysis}_{\textbf{theoretical}}$ = _____%

5. Calculate <u>experimental</u> % hydrolysis using your experimental $[OH^-]$ for the salt solution from page 5.

<u>Setup:</u>

$\%\ \text{hydrolysis}_{\textbf{experimental}}$ = _____%

Summary of part 3:

Copy the theoretical % hydrolysis of 0.10 M $NaC_2H_3O_2$ from section (a) part 4 on page 7. _____ %

Copy the theoretical % hydrolysis of 0.10 M Na_2CO_3 from section (b) part 4 on page 8. _____ %

Which of the above ions hydrolyze more?

_____
($C_2H_3O_2^-$ or CO_3^{2-})

Conclusion:The _____the acid formed, the greater the % hydrolysis.
(weaker,stronger)

4. HYDROLYSIS OF AMMONIUM SALTS

NH_4Cl, $NH_4C_2H_3O_2$, $(NH_4)_2CO_3$

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 **$NH_4C_2H_3O_2$** and **$(NH_4)_2CO_3$** by comparing the K_b values of $C_2H_3O_2^-$ and CO_3^{2-} and their theoretical % hydrolysis.

K_b for $C_2H_3O_2^-$ =_____ , theoretical %hydrolysis on page 7_____%

K_b for CO_3^{2-} =_____ , 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 NH_4^+

_____

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_2O 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_2PO_4 solution. How would you determine theoretically whether it is acidic or basic?

Given: K_{a1} for H_3PO_4= 6.9 x 10^{-3}, K_{a2} for $H_2PO_4^-$ = 6.3 x 10^{-8}

Hint: Write the two possible reactions of $H_2PO_4^-$ with H_2O

a) $H_2PO_4^- + H_2O \rightleftharpoons$ _____ $+ OH^-$ K_b for $H_2PO_4^- = \frac{K_w}{K_{a1} \text{ for } H_3PO_4}$

K_b= _____

b) $H_2PO_4^- + H_2O \rightleftharpoons$ _____ $+ H_3O^+$ K_{a2} for $H_2PO_4^-$ =_____

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_2PO_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.

Compound	**Acidic, basic, or neutral**	**Write an equilibrium equation for any reaction that may occur**
$Zn(HSO_4)_2$		
KNO_2		
Na_2CO_3		
LiBr		
Na_3PO_4		
$Al(NO_3)_3$		
K_2S		
Na_2SO_4		
KNO_3		
$FeCl_3$		
NH_4Cl		
KCl		

3. Apply the following information about the acid ionization constants:
K_{a1} for H_2S is 1.0×10^{-7} and K_{a2} for HS^- is 1.3×10^{-13}
to predict whether 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 HF is 7.2×10^{-4} and K_a for HOCl is 3.5×10^{-8}
Which salt will hydrolyze more, KF (aq) or 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, NH4OCl (aq) or NaOCl (aq)? **Explain** why.

Answer: _____ will hydrolyze more, **because** _____