Lecture IV

pH Calculations for the Hydrolysis of Salts

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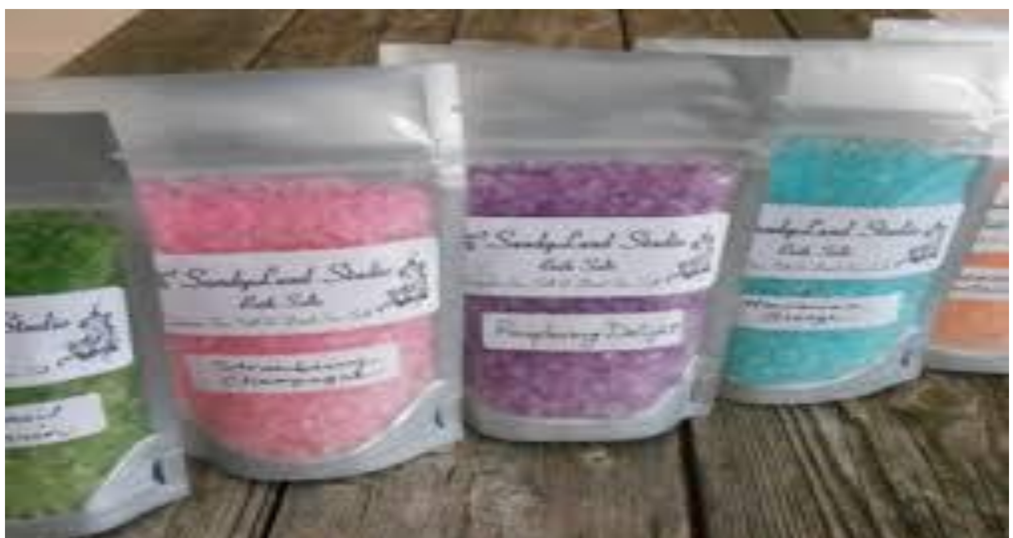


Definitions

Arrehenius

only in water

- Acids – produce H^+
- Bases - produce OH^-

Bronsted-Lowry

any solvent

- Acids – donate H^+
- Bases – accept H^+

Lewis

used in organic chemistry, wider range of substances

- Acids – accept e^- pair
- Bases – donate e^- pair

The Bronsted-Lowry Concept

Conjugate pairs

HCl Cl^-

CH_3COOH CH_3COO^-

NH_4^+ NH_3

HNO_3 NO_3^-

How does a conjugate pair differ?

H^+ transfer

- Conjugate acid- compound formed when an base gains a hydrogen ion.

- Conjugate base – compound formed when an acid loses a hydrogen ion.

Acids and bases come in pairs

- General equation is:

$$HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

- Acid + Base $\leftrightarrow$ Conjugate acid + Conjugate base
- $NH_3 + H_2O \leftrightarrow NH_4^{1+} + OH^{1-}$

  base acid c.a. c.b.
- $HCl + H_2O \leftrightarrow H_3O^{1+} + Cl^{1-}$

  acid base c.a. c.b.
- <u>Amphoteric</u> – a substance that can <u>act as both</u> an acid and base- as water shows

Conjugate Acid-Base Pairs

- The conjugate base of a strong acid, is an example of a ***weak conjugate base.***
- The conjugate base of a weak acid, is an example of a ***strong conjugate base.***
- Conversely, a strong base has a ***weak conjugate acid*** and a weak base has a ***strong conjugate acid.***

Relationship Between pK_a of an Acid and pK_b of its Conjugate Base

$CH_3CO_2H_{(aq)}$ + $H_2O_{(l)}$ ←→ $H_3O^+_{(aq)}$ + $CH_3CO_2^-{}_{(aq)}$

acetic acid *acetate*

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8\times10^{-5}$$

But let us also consider the hydrolysis reaction of acetate,

where acetate acts as a base:

$CH_3CO_2^-{}_{(aq)}$ + $H_2O_{(l)}$ ←→ $OH^-_{(aq)}$ + $CH_3CO_2H_{(aq)}$

acetate *acetic acid*

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = 5.6\times10^{-10}$$

$$K_aK_b = \frac{\cancel{[CH_3CO_2^-]}[H_3O^+]}{\cancel{[CH_3CO_2H]}} \times \frac{\cancel{[CH_3CO_2H]}[OH^-]}{\cancel{[CH_3CO_2^-]}}$$

$$K_aK_b = [H_3O^+] \times [OH^-]$$

$$K_aK_b = K_w$$

$$pK_a + pK_b = pK_w \qquad \text{OR} \qquad pK_a + pK_b = 14 \text{ at } 25\ ^\circ\text{C}$$

This is a general result, the K_a of an acid and the K_b of it's conjugate base are related. From this we can write three equivalent statements…

The higher the K_a of an acid, the lower the K_b of its conjugate base.

The lower the pK_a of an acid, the higher the pK_b of its conjugate base.

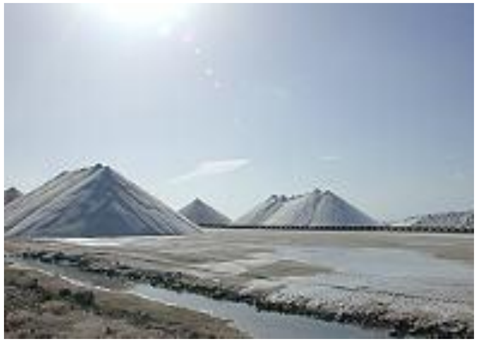
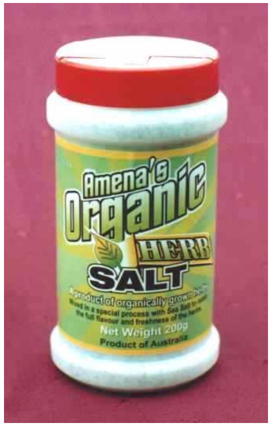
The stronger an acid is, the weaker is it's conjugate base!

Salts

- Ionic compounds that dissolve ~ 100 % in water

What is a SALT?

- Composed of the negative ion of an acid and the positive ion of a base.
- One of the products of a Neutralization Reaction
- Examples: KCl, NaCl, $MgSO_4$, Na_3PO_4

Neutralization

In general: Acid + Base → Salt + Water

All neutralization reactions are <u>double displacement</u> reactions.

$HCl + NaOH \rightarrow NaCl + HOH$

$HCl + Mg(OH)_2 \rightarrow$

$H_2SO_4 + NaHCO_3 \rightarrow$

Salt Solutions

- When salts dissolve, their ions can recombine with water

Salt Solutions

$$A^- + H_2O \leftrightarrow HA + OH^-$$

$$B^+ + H_2O \leftrightarrow H^+ + BOH$$

Salt Hydrolysis

To determine if a salt will form an acidic or basic solution, remember the following rules:

Strong acid + **Strong base** $\longrightarrow$ Neutral solution

Strong acid + Weak base $\longrightarrow$ **Acidic** solution

Weak acid + **Strong base** $\longrightarrow$ **Basic** solution

Acid-Base Properties of Salt Solutions

- Salt solutions are affected by ***salt hydrolysis,*** in which ions produced by the dissociation of a salt react with water to produce either hydroxide ions or hydronium ions—thus impacting pH.
- ***Basic salt solutions*** - an anion that is the strong conjugate base of a weak acid reacts with water to produce hydroxide ion.

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

- ***Neutral salt solutions***
  - A salt composed of the cation of a strong base and the anion of a strong acid produces a neutral solution.
  - These ions do not hydrolyze in water.

For example:

$NaCl$ or KNO_3

- ***Acidic salt solutions***
  - When the cation of a salt is the strong conjugate acid of a weak base, a solution of the salt will be acidic.

For example:

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

Salts That Produce Neutral Solutions

Salts of strong acids/strong bases

Example – solution of $MgBr_2$, salt of strong acid + strong base

$2HBr_{(aq)} + Mg(OH)_{2\,(aq)} \rightarrow 2\,H_2O_{(l)} + MgBr_{2\,(aq)}$ *formation*

$MgBr_{2\,(aq)} \rightarrow Mg^{2+}_{(aq)} + 2\,Br^-_{(aq)}$ *dissolution*

Weak conjugate acid of strong base → $Mg^{+2}_{(aq)} + \cancel{H_2O} \rightarrow$ No *reaction*

Weak conjugate base of strong acid → $Br^-_{(aq)} + \cancel{H_2O} \rightarrow$ No *reaction*

Weak conjugate acid and base do not hydrolyze (do not react with water) $\Rightarrow$ pH = 7

Hydrolysis of Salts

Salts can be acidic, basic, or neutral.

1. Neutral Salts

Consider NaCl

The **neutralization equation** used to produce **NaCl** will tell us what kind of salt it is.

HCl + NaOH → NaCl + HOH

strong acid **strong base** **neutral salt**

When the **acid** and **base** parents are both **strong** the salt is always **neutral**.

-

A neutral salt will dissociate in water.

$$\mathbf{NaCl} \rightarrow \cancel{\mathbf{Na^+}} + \cancel{\mathbf{Cl^-}}$$

no ions to hydrolyze- neutral

Cross off the **both ions** that come from **strong parents** as they do not hydrolyze or react further with water- they are **neutral**.

Salts That Produce Basic Solutions

Salt of Strong Acid/Weak Base

Salts of strong acids/weak bases

Example **– aqueous solution of NH_4NO_3,**

which is salt of strong acid (HNO_3) and weak base (NH_3):

$$HNO_{3(aq)} + NH_{3\,(aq)} \rightarrow NH_4NO_{3\,(aq)}$$ *formation*

$$NH_4NO_{3\,(aq)} \rightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$$ *dissolution*

Weak conjugate base of strong acid → $NO_3^-{}_{(aq)} + \cancel{H_2O} \rightarrow$ No *reaction*

Strong conjugate acid of weak base → $NH_4^+{}_{(aq)} + H_2O \rightarrow H_3O^+{}_{(aq)} + NH_{3\,(aq)}$ *reaction!*

Conjugate acid of the weak base is strong thus it will hydrolyze $\Rightarrow$ pH < 7

Hydrolysis of Salts

Salts can be acidic, basic, or neutral.

2. Basic Salts

Consider NaCN

$$HCN + NaOH \rightarrow NaCN + HOH$$

weak acid — **strong base** — **basic salt**

A basic salt will **first dissociate** in water

$NaCN \rightarrow \cancel{Na^+} + CN^-$ **negative ion left- basic**

Cross off the **Na^+** because it has a strong parent and does **not hydrolyze**- it is **neutral**

Then the **CN^- ion**, from the **weak parent**, will **hydrolyze** (react with water) as a **Bronsted base**.

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

Salt of Weak Acid/Weak Base

Salts of weak acids/weak bases

-conjugate base of the weak acid will hydrolyze, as will the conjugate acid of the weak base. One must look at the pK_a and pK_b to predict the pH of solution.

Example – solution of $C_2H_5NH_3C_7H_5O_2$,(ethylammonium benzoate), salt of weak acid + weak base

$C_7H_5O_2H_{(aq)} + C_2H_5NH_{2\,(aq)} \rightarrow C_2H_5NH_3C_7H_5O_{2\,(aq)}$ *formation*

$C_2H_5NH_3C_7H_5O_{2\,(aq)} \rightarrow C_2H_5NH_3^+{}_{(aq)} + C_7H_5O_2^-{}_{(aq)}$ *dissolution*

Strong conjugate acid of weak base

$C_2H_5NH_3^+{}_{(aq)} + H_2O \rightarrow H_3O^+{}_{(aq)} + C_2H_5NH_{2\,(aq)}$ *reaction!*

Strong conjugate base of weak acid

$C_7H_5O_2^-{}_{(aq)} + H_2O \rightleftarrows C_7H_5O_2H_{(aq)} + OH^-{}_{(aq)}$ *reaction!*

How do we predict which wins out in this competition?

But there's a fourth option!

- If the K_a value for the acidic ion is larger than the K_b value for the basic ion, the solution will be acidic.
- If the K_b value is larger than the K_a value, the solution will be basic.
- Equal K_a and K_b values result in a neutral solution.

Acid-Base Properties of Salt Solutions

- some solutions of salts affect the pH of an aqueous solution
- any acidic or basic property of aqueous salt solutions results from the reaction between water and the dissociated ions of the salt

1. **Salts that dissolve and form Neutral solutions**

- the salt of a strong acid/strong base dissolves in water to form neutral solutions
- Cations from strong bases (Group 1 and 2 ions (except Be^{2+}))
- Anions from strong monoprotic acids (Cl, Br, I, NO_3, ClO_4)
- The solution has a pH of 7
- Ex: NaCl (**Na**OH is strong base, H**Cl** is strong acid)

Acid-Base Properties of Salt Solutions

2. Salts that dissolve and form Acidic solutions

- salts of weak bases (cation) and strong acids (anion) dissolve in water and form acidic solutions (solution pH < 7)
- cation reacts with water
- Ex. NH_4Cl

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$

3. Salts that dissolve and form basic solutions

- salts of strong bases (cation) and weak acids (anion) dissolve in water and form basic solutions (solution pH > 7)
- anion reacts with water
- Ex. $NaCH_3COO$

$$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$$

Acid-Base Properties of Salt Solutions

4. Salts of weak bases and weak acids

- both ions react with water
- If $K_a > K_b$, the solution is acidic
- If $K_a < K_b$, the solution is basic
- Ex. NH_4CN
  - Since K_b of CN^- is much larger than K_a of NH_4^+, an aqueous solution of ammonium cyanide will be basic

- The reaction of an ion with **water** to produce an acidic or basic solution is called **hydrolysis**

Summary

Behavior of Salts in Water

Table 18.8 The Behavior of Salts in Water

Salt Solution (Examples)	pH	Nature of Ions	Ion That Reacts with Water	
Neutral [$NaCl$, KBr, $Ba(NO_3)_2$]	7.0	Cation of strong base Anion of strong acid	None	
Acidic [NH_4Cl, NH_4NO_3, CH_3NH_3Br]	<7.0	Cation of weak base Anion of strong acid	Cation	
Acidic [$Al(NO_3)_3$, $CrCl_3$, $FeBr_3$]	<7.0	Small, highly charged cation Anion of strong acid	Cation	
Basic [CH_3COONa, KF, Na_2CO_3]	>7.0	Cation of strong base Anion of weak acid	Anion	

Hydrolysis of	**Result**
Anions	Raise pH
Cations	Lower pH

Non-Hyrolyzed Ions (a few)

7 Anions, **not** hydrolyzed

Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_3^-, ClO_4^-

10 Cations, **not** hydrolyzed

Li^+, Na^+, K^+, Rb^+, Sc^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Ag^+

Predict whether 0.10 *M* solutions of the following are acidic, basic or nearly neutral.

a) $\mathbf{(CH_3)_3NHCl}$

b) KF

a) **Salts that contain ions that come from a weak acid or base.**

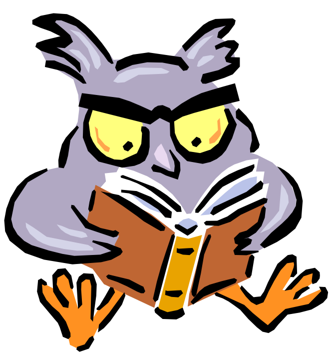
Weak Base: $(CH_3)_3N$ trimethylamine

A salt containing the cation of the weak base and the anion from a strong acid.

$(CH_3)_3NHCl$ trimethylammonium chloride

Add water: $(CH_3)_3NHCl\ (s) + H_2O \rightarrow (CH_3)_3NH^+ + Cl^- + H_2O$

Hydrolysis: $(CH_3)_3NH^+ + H_2O \leftrightarrow (CH_3)_3NHOH + H^+$



An acidic solution.

b) KF

$$F^{-}(aq) + H_2O(l) \longrightarrow HF(aq) + OH^{-}(aq)$$

A basic solution

Hydrolysing salt (Brönsted base)

$$\left[OH^-\right] = \sqrt{K_b C_{salt}}$$

$$\left[OH^-\right] = \sqrt{\frac{K_w}{K_a} C_{salt}}$$

Hydrolysing salt (Brönsted acid)

$$\left[H^+\right] = \sqrt{K_a C_{salt}}$$

$$\left[H^+\right] = \sqrt{\frac{K_w}{K_b} C_{salt}}$$

Example problem:

Suppose a 0.1 mole solution sodium acetate is dissolved in 1 liter of water. What is the pH of the solution?

$$CH_3CO_2^{-} + H_2O \leftrightarrow CH_3CO_2H + OH^{-}$$

	$CH_3CO_2^{-}$	H_2O	CH_3CO_2H	OH^{-}
	base	**acid**	**acid**	**base**
Init. conc.	**0.1M**		**0**	**~0**
Δ conc.	**- y**		**+ y**	**+ y**
Equil. conc.	**0.1– y**		**y**	**y**

1. Find K_b
2. Find $[OH^-]$
3. Find $[H^+]$
4. Find pH

1. Find K_b
2. Find $[OH^-]$
3. Find $[H^+]$
4. Find pH

Example problem:

What is the pH of the solution?

$$CH_3CO_2^- + H_2O \leftrightarrow CH_3CO_2H + OH^-$$

	$CH_3CO_2^-$	CH_3CO_2H	OH^-
Init. conc.	**0.1M**	**0**	**~0**
Δ conc.	**- y**	**+ y**	**+ y**
Equil. conc.	**0.1– y**	**y**	**y**

$$K_a \times K_b = K_w$$

EXAMPLE 1

What is the pH of a 0.10 *M* NaClO solution if K_a for HClO is 3.0×10^{-8}?

SOLUTION: The salt NaClO exists as Na^+ and ClO^-. The Na^+ ions are spectator ions, but ClO^- ions undergo hydrolysis to form the weak acid HClO. Let x equal the equilibrium concentration of HClO (and OH^-):

$$\begin{array}{lcl} ClO^-(aq) + H_2O(l) & \rightleftharpoons & HClO(aq) + OH^-(aq) \\ (0.10 - x)\,M & & xM \qquad\quad xM \end{array}$$

The value of K_b for the reaction is $(1.0 \times 10^{-14})/(3.0 \times 10^{-8}) = 3.3 \times 10^{-7}$. Because K_b is so small, we can neglect x in comparison with 0.10 and thus $0.10 - x \simeq 0.10$.

$$\frac{[HClO][OH^-]}{[ClO^-]} = K_b$$

$$\frac{x^2}{0.10} = 3.3 \times 10^{-7}$$

$$x^2 = 3.3 \times 10^{-8}$$

$$x = 1.8 \times 10^{-4}\,M$$

$$pOH = 3.74$$

$$\text{and } pH = 14 - 3.74 = 10.26$$

Calculate the pH of a 0.10 M KNO_2 solution. $K_a(HNO_2) = 4.5\ 10^{-4}$.

CHEMISTRY: $KNO_2(s) \rightarrow K^+ + NO_2^-$

More Chemistry: $NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$

Equilibrium:		NO_2^-	H_2O	HNO_2	OH^-
	I	0.10	N/A	0	0
	C	-X	N/A	+X	+X
	E	0.10-X	N/A	+X	+X

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$K_aK_b = 1.0 \times 10^{-14}$

$$2.22 \times 10^{-11} = \frac{[x][x]}{[0.10 - x]}$$

Try dropping

$pOH = -\log[OH^-] = 5.83$

$x = 1.49 \times 10^{-6} = [OH^-]$

$pH = 14 - 5.83 = 8.17$

Calculate the pH of a 0.10 $(CH_3)_3NHCl$ solution. $K_b((CH_3)_3NHCl) = 7.4\ 10^{-5}$.

CHEMISTRY: $(CH_3)_3NHCl(s) + H_2O \rightarrow (CH_3)_3NH^+ + Cl^- + H_2O$

More Chemistry: $(CH_3)_3NH^+ + H_2O \leftrightarrow (CH_3)_3NHOH^- + H^+$

Equilibrium:					
	I	0.10	N/A	0	0
	C	-x	N/A	+x	+x
	E	0.10-x	N/A	+x	+x

$$K_a = \frac{[(CH)_3NHOH^-][H^+]}{[(CH)_3NH^+]}$$

$K_aK_b = 1.0 \times 10^{-14}$

Try dropping

$$1.35 \times 10^{-10} = \frac{[x][x]}{[0.10 - x]}$$

pH = $-\log[H^+] = 5.43$

$x = 3.68 \times 10^{-6} = [H^+]$