Chapter 18b

- Ionic Equilibria: Acids and Bases

Acid-Base Properties of Salts

- Soluble salts (ionic compounds) dissolve in water to produce ions.
  - In particular, salts that contain group IA metals, NO_3^-, and NH_4^+ ions usually dissolve to produce ions.
- Some salts dissolve to produce ions that do not change the pH of water.
  - These are salts that produce neutral solution.
- Some salts dissolve that produce strong conjugates of acids or bases.
  - These are salts that produce either basic or acidic solution.

Acid-Base Properties of Salts

- Examples of salts that produce neutral solutions:
  - $NaCl$ (aq) → Na^+ (aq) + **Cl^-** (aq)
  - KNO_3 (aq) → K^+ (aq) + **NO_3^-**(aq)
  - Na_2SO_4 (aq) → 2 Na^+ (aq) + **SO_4^{2-}** (aq)
  - $LiClO_4$ (aq) → Li^+ (aq) + **ClO_4^-** (aq)
  - KBr (aq) → K^+ (aq) + **Br^-** (aq)
- Weak conjugates bases of strong acids are produced and do not upset the balance of H_3O^+ & OH^- in neutral water.

Acid-Base Properties of Salts

- Examples of salts that produce basic or acidic solutions:
  - Na_2CO_3 (aq) → $2Na^+$ (aq) + **CO_3^{2-}** (aq)
  - KF (aq) → K^+ (aq) + **F^-** (aq)
  - $NaCH_3COO$ (aq) → 2 Na^+ (aq) + **CH_3COO^-** (aq)
  - NH_4Cl (aq) → **NH_4^+** (aq) + Cl^- (aq)
  - NH_4CH_3COO (aq) → **NH^+** (aq) + **CH_3COO^-** (aq)
- Strong conjugate bases of weak acids, strong conjugate acids of weak bases or both are produced.
- These strong conjugates react with water and do upset the balance of H_3O^+ & OH^- in neutral water.

Solvolysis

This reaction process is the most difficult concept in this chapter.

- Solvolysis is the reaction of a substance with the solvent in which it is dissolved.
- Hydrolysis refers to the ***reaction of a substance with water*** or its ions.
- Combination of the anion of a weak acid with H_3O^+ ions from water to form <u>nonionized</u> weak acid molecules.

Solvolysis

- The combination of a weak acid's anion with H_3O^+ ions, from water, to form <u>nonionized</u> weak acid molecules is a form of hydrolysis.

$$A^- + H_3O^+ \rightleftharpoons HA + H_2O$$

$$\text{recall } H_2O + H_2O \rightleftharpoons H_3O + OH^-$$

Solvolysis

- The reaction of the anion of a weak monoprotic acid with water is commonly represented as:

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

Solvolysis

- Recall that at 25ºC
- in **neutral** solutions:

  $[H_3O^+] = 1.0 \times 10^{-7}\ M = [OH^-]$
- in **basic** solutions:

  $[H_3O^+] < 1.0 \times 10^{-7}\ M$ and $[OH^-] > 1.0 \times 10^{-7}\ M$
- in **acidic** solutions:

  $[OH^-] < 1.0 \times 10^{-7}\ M$ and $[H_3O^+] > 1.0 \times 10^{-7}\ M$

Solvolysis

- Remember from Brønsted-Lowry acid-base theory:
  - *The conjugate base of a strong acid is a very weak base.*
  - *The conjugate base of a weak acid is a stronger base.*
- Hydrochloric acid, a typical strong acid, is essentially completely ionized in dilute aqueous solutions.

$$HCl + H_2O \xrightarrow{\sim 100\%} H_3O^+ + Cl^-$$

Solvolysis

- The conjugate base of HCl, the Cl^- ion, is a very weak base.
  - The chloride ion is such a weak base that it will not react with the hydronium ion.

$$Cl^- + H_3O^+ \rightarrow \text{No rxn. in dilute aqueous solutions}$$

- This fact is true for all strong acids and their anions.

Solvolysis

- HF, a weak acid, is only slightly ionized in dilute aqueous solutions.
- Its conjugate base, the F^- ion, is a much stronger base than the Cl^- ion.
- The F^- ions combine with H_3O^+ ions to form nonionized HF.
  - Two competing equilibria are established.

$$HF + H_2O \rightleftarrows H_3O^+ + F^-$$

only slightly

$$H_3O^+ + F^- \rightleftarrows HF + H_2O$$

nearly completely

Solvolysis

- Dilute aqueous solutions of salts can be produced from the following neutralization reactions :

1. Salts of Strong Bases and Strong Acids (neutral solutions)

   $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
2. Salts of Strong Bases and Weak Acids (basic solutions)

   $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$
3. Salts of Weak Bases and Strong Acids (acidic solutions)

   $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$
1. Salts of Weak Bases and Weak Acids (depends upon the K_a and K_b of the individual weal acid and weak base.)

   $NH_3(aq) + HF(aq) \rightarrow NH_4F(aq)$

Salts of Strong Bases and Weak Acids

- Salts made from strong acids and strong soluble bases form ***neutral aqueous solutions***.
- An example is potassium nitrate, KNO_3, made from nitric acid and potassium hydroxide.

$$KNO_{3(s)} \xrightarrow{\sim 100\% \text{ in } H_2O} K^+ + NO_3^-$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+$$

The ions that are in solution $\uparrow_{KOH}$ $\uparrow_{HNO_3}$

The KOH and HNO_3 are present in equal amounts.

There is no reaction to upset $[H_3O^+][OH^-]$

Thus the solution is neutral.

Salts of Strong Bases and Weak Acids

- Salts made from strong soluble bases and weak acids hydrolyze to form ***basic solutions***.
  - Anions of weak acids (strong conjugate bases) react with water to form hydroxide ions.
- An example is sodium hypochlorite, NaClO, made from sodium hydroxide and hypochlorous acid.

$$NaOH\ (aq) + HClO\,(aq) \longrightarrow H_2O\,(l) + NaClO\ (aq)$$

- Since NaClO is a soluble salt (group IA metal):

$$NaClO\ (aq) \xrightarrow{100\%} Na^+\,(aq) + ClO^-\,(aq)$$

Salts of Strong Bases and Weak Acids

$$NaClO_{(s)} \xrightarrow{\sim 100\% \text{ in } H_2O} Na^+ + ClO^-$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+$$

Notice ions in solution $\uparrow_{NaOH}$ $\uparrow_{HClO}$

Which is the stronger acid or base?

The conjugate base of a weak acid is very strong.

Salts of Strong Bases and Weak Acids

$$NaClO_{(s)} \xrightarrow{\sim 100\% \text{ in } H_2O} Na^+ + ClO^-$$

$$H_2O + \cancel{H_2O} \rightleftarrows OH^- + \cancel{H_3O^+}$$

$$ClO^- + \cancel{H_3O^+} \longrightarrow HClO + \cancel{H_2O}$$

- We can combine these last two equations into one single equation that represents the total reaction.

$$ClO^-\,(aq) + H_2O\,(l) \rightleftarrows HClO\,(aq) + OH^-\,(aq)$$

The strong conjugate base reacts with water to produce a basic solution.

Salts of Strong Bases and Weak Acids

- The equilibrium constant for this reaction, called the ***hydrolysis constant***, is written as: Notice that hydrolysis constant is for the ClO^- that reacts with water to produce OH^-.

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

Salts of Strong Bases and Weak Acids

- Which can be used to calculate the *hydrolysis constant* for the hypochlorite ion:

$$K_w = K_a K_b$$

$$K_b = \frac{K_w}{K_{a\ \text{for HClO}}} = \frac{1\times10^{-14}}{3.5\times10^{-8}}$$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = 2.9\times10^{-7}$$

Salts of Strong Bases and Weak Acids

- This same method can be applied to the *anion of any weak monoprotic acid.*

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

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{K_W}{K_{a\ \text{for HA}}}$$

Salts of Strong Bases and Weak Acids

Example 1: Calculate the hydrolysis constants for the following anions of weak acids.

1. The fluoride ion, F^-, the anion of hydrofluoric acid, HF. For HF, K_a=7.2 x 10^{-4}.

$$F^- + H_2O \rightleftarrows HF + OH^-$$

The fluoride ion is acting as a base.

Therefore, we need to determine its ionization constant as a base – its hydrolysis constant.

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{K_w}{K_{a\ \text{for HF}}}$$

$$K_b = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}$$

Salts of Strong Bases and Weak Acids

The cyanide ion, CN^-, the anion of hydrocyanic acid, HCN. For HCN, K_a = 4.0 x 10^{-10}.

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

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{K_w}{K_{a\ \text{for HCN}}}$$

$$K_b = \frac{1.0\times10^{-14}}{4.0\times10^{-10}} = 2.5\times10^{-5}$$

Salts of Strong Bases and Weak Acids

Example 2: Calculate [OH^-], pH and percent hydrolysis for the hypochlorite ion in 0.10 *M* sodium hypochlorite, NaClO, solution. "Clorox", "Purex", etc., are 5% sodium hypochlorite solutions.

$$NaClO_{(s)} \xrightarrow{\sim 100\%\ \text{in}\ H_2O} Na^+ + ClO^-$$

$$0.10M \quad \Rightarrow \quad 0.10M \quad 0.10M$$

Salts of Strong Bases and Weak Acids

- Set up the equation for the hydrolysis and the algebraic representations of the equilibrium concentrations.

	ClO^- $\xrightarrow{H_2O}$	$HClO$ +	OH^-
Initial:	0.10*M*	0*M*	0*M*
Change:	-*xM*	+*xM*	+ *xM*
At equil:	(0.10-*x*)*M*	*xM*	*xM*

Salts of Strong Bases and Weak Acids

- Substitute the algebraic expressions into the hydrolysis constant expression.

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = 2.9\times10^{-7}$$

$$K_b = \frac{(x)(x)}{(0.10-x)} = 2.9\times10^{-7}$$

Salts of Strong Bases and Weak Acids

- Substitute the algebraic expressions into the hydrolysis constant expression.

The simplifying assumption can be made in this case.

x << 0.10 and 0.10-x ≈ 0.10

The equation reduces to $x^2 = 2.9\times10^{-8}$

$$x = 1.7\times10^{-4} M = [ClO^-] = [OH^-]$$

$$pOH = -\log(1.7\times10^{-4})$$

$$pOH = 3.77$$

$$pH = 14.00 - 3.77$$

$$= 10.23$$

Salts of Strong Bases and Weak Acids

- The percent hydrolysis for the hypochlorite ion may be represented as:

$$\%\ hydrolysis = \frac{[ClO^-]_{hydrolyzed}}{[ClO^-]_{original}} \times 100\%$$

$$\%\ hydrolysis = \frac{1.7\times10^{-4} M}{0.10 M} \times 100\% = 0.17\%$$

Salts of Strong Bases and Weak Acids

- If a similar calculation is performed for 0.10 *M* NaF solution and the results from 0.10 *M* sodium fluoride and 0.10 *M* sodium hypochlorite compared, the following table can be constructed.

Solution	K_a	K_b	$[OH^-]$ (*M*)	pH	% hydrolysis
NaF	7.2×10^{-4}	1.4×10^{-11}	1.2×10^{-6}	8.08	0.0012
NaClO	3.5×10^{-8}	2.9×10^{-7}	1.7×10^{-4}	10.23	0.17

Salts of Weak Bases and Strong Acids

- Salts made from weak bases and strong acids form **acidic aqueous solutions**.
- An example is ammonium bromide, NH_4Br, made from ammonia and hydrobromic acid.

$$NH_4Br_{(s)} \xrightarrow{H_2O \sim 100\%} NH_4^+ + Br^-$$

$$H_2O + H_2O \rightleftarrows OH^- + H_3O^+$$

Ions in solution are $\uparrow_{NH_4OH}$ $\uparrow_{HBr}$

Which is the stronger acid or base?

The conjugate acid of a weak base is very strong.

Salts of Weak Bases and Strong Acids

The relatively strong acid, NH_4^+, reacts with the OH^- ion removing it from solution leaving excess H_3O^+

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

generates excess H_3O^+

- The reaction may be more simply represented as:

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

Salts of Weak Bases and Strong Acids

- Or even more simply as:

$$NH_4^+ \rightleftarrows NH_3 + H^+$$

- The hydrolysis constant expression for this process is:

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

or

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Salts of Weak Bases and Strong Acids

- Which we recognize as:

$$K_w = K_a K_b$$

$$K_a = \frac{K_w}{K_{b(NH_3)}}$$

$$K_a = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

Salts of Weak Bases and Strong Acids

- In its simplest form for this hydrolysis:

$$NH_4^+(aq) \underset{}{\overset{H_2O}{\rightleftharpoons}} NH_3(aq) + H_3O^+(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6\times10^{-10}$$

Salts of Weak Bases and Strong Acids

Example 3: Calculate $[H^+]$, pH, and percent hydrolysis for the ammonium ion in 0.10 *M* ammonium bromide, NH_4Br, solution.

1. Write down the hydrolysis reaction and set up the table as we have done before:

	NH_4^+ $\overset{H_2O}{\rightleftharpoons}$	NH_3 +	H_3O^+
Initial:	$0.10M$	$+xM$	$+xM$
Change:	$-xM$	$+xM$	$+xM$
Equilibrium	$(0.10-x)M$	xM	xM

Salts of Weak Bases and Strong Acids

2. Substitute the algebraic expressions into the hydrolysis constant.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6\times10^{-10}$$

$$K_a = \frac{(x)(x)}{(0.10-x)} = 5.6\times10^{-10}$$

The assumption is applicable.

$x << 0.10$ thus $0.10 - x \approx 0.10$

Salts of Weak Bases and Strong Acids

3. Complete the algebra and determine the concentrations and pH.

$$\frac{(x)\ (x)}{0.10-x} = 5.6\times10^{-10}$$

$$x^2 = 5.6\times10^{-11}$$

$$x = 7.5\times10^{-6}M$$

$$[NH_3] = [H_3O^+] = 7.5\times10^{-6}M$$

$$pH = 5.12$$

Salts of Weak Bases and Strong Acids

4. The percent hydrolysis of the ammonium ion in 0.10 *M* NH_4Br solution is:

$$\%\ \text{hydrolysis} = \frac{[NH_4^+]_{hydrolized}}{[NH_4^+]_{original}} \times 100\%$$

$$\%\ \text{hydrolysis} = \frac{7.5\times10^{-6}M}{0.10M} \times 100\%$$

$$\%\ \text{hydrolysis} = 0.0075\%$$

Salts of Weak Bases and Weak Acids

- Salts made from weak acids and weak bases can form ***neutral, acidic*** or ***basic aqueous solutions***.
  - The pH of the solution depends on the relative values of the ionization constant of the weak acids and bases.

1. Salts of weak bases and weak acids for which parent $K_{base} = K_{acid}$ make ***neutral solutions***.

Salts of Weak Bases and Weak Acids

- An example is ammonium acetate, NH_4CH_3COO, made from aqueous ammonia, NH_3,and acetic acid, CH_3COOH.

  K_a for acetic acid = K_b for ammonia = 1.8×10^{-5}.

Salts of Weak Bases and Weak Acids

- The ammonium ion hydrolyzes to produce H^+ ions. Its hydrolysis constant is:

$$NH_4^+ \overset{H_2O}{\rightleftharpoons} NH_3 + H_3O^+$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6\times10^{-10}$$

Salts of Weak Bases and Weak Acids

- The acetate ion hydrolyzes to produce OH^- ions. Its hydrolysis constant is:

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

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.6\times10^{-10}$$

Salts of Weak Bases and Weak Acids

- Because the hydrolysis constants for both ions are equal, their aqueous solutions are neutral.
- Equal numbers of H^+ and OH^- ions are produced.

$$NH_4CH_3COO \xrightarrow{H_2O \sim 100\%} NH_4^+ + CH_3COO^-$$

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

Ions in solution are $\uparrow_{NH_4OH}$ $\uparrow_{CH_3COOH}$

A weak acid and base are formed in solution!

Salts of Weak Bases and Weak Acids

2. Salts of weak bases and weak acids for which parent $K_{base} > K_{acid}$ make ***basic solutions***.
   - An example is ammonium hypochlorite, NH_4ClO, made from aqueous ammonia, NH_3,and hypochlorous acid, HClO.

K_b for $NH_3 = 1.8 \times 10^{-5}$ > K_a for HClO = 3.5×10^{-8}

Salts of Weak Bases and Weak Acids

- The ammonium ion hydrolyzes to produce H+ ions. Its hydrolysis constant is:

$$NH_4^+ \xrightarrow[\longleftarrow]{H_2O} NH_3 + H_3O^+$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6\times10^{-10}$$

Salts of Weak Bases and Weak Acids

- The hypochlorite ion hydrolyzes to produce OH^- ions. Its hydrolysis constant is:

$$ClO^- + H_2O \rightleftarrows HClO + OH^-$$

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = 2.9\times10^{-7}$$

- Because the K_b for ClO^- ions is three orders of magnitude larger than the K_a for NH_4^+ ions, OH^- ions are produced in excess making the ***solution basic***.

Salts of Weak Bases and Weak Acids

3. Salts of weak bases and weak acids for which parent $K_{base} < K_{acid}$ make ***acidic solutions*.**
   - An example is trimethylammonium fluoride,$(CH_3)_3NHF$, made from trimethylamine, $(CH_3)_3N$,and hydrofluoric acid acid, HF.

K_b for $(CH_3)_3N = 7.4 \times 10^{-5}$ < K_a for $HF = 7.2 \times 10^{-4}$

Salts of Weak Bases and Weak Acids

- Both the cation, $(CH_3)_3NH^+$, and the anion, F^-, hydrolyze.

$$[(CH_3)_3NH]^+F^- \xrightarrow{H_2O\sim100\%} [(CH_3)_3NH]^+ + F^-$$

Salts of Weak Bases and Weak Acids

- The trimethylammonium ion hydrolyzes to produce H^+ ions. Its hydrolysis constant is:

$$(CH_3)_3NH^+ \rightleftarrows (CH_3)_3N + H^+$$

$$K_a = \frac{[(CH_3)_3N][H^+]}{[(CH_3)_3NH^+]} = \frac{K_w}{K_{b\ for\ (CH_3)_3N}}$$

$$K_a = \frac{1.0\times10^{-14}}{7.4\times10^{-5}} = 1.4\times10^{-10}$$

Salts of Weak Bases and Weak Acids

- The fluoride ion hydrolyzes to produce OH- ions. Its hydrolysis constant is:

$$F^- + H_2O \rightleftarrows HF + OH^-$$

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{K_w}{K_{a\ for\ HF}}$$

$$K_b = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}$$

- Because the K_a for $(CH_3)_3NH^+$ ions is one order of magnitude larger than the K_b for F^- ions, H^+ ions are produced in excess making the ***solution acidic***.

Salts of Weak Bases and Weak Acids

- ***Summary of the major points of hydrolysis up to now.***
  1. The reactions of anions of weak monoprotic acids (from a salt) with water to form free molecular acids and OH^-.

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

$$K_b = \frac{K_w}{K_{a(HA)}}$$

Salts of Weak Bases and Weak Acids

2. The reactions of anions of weak bases (from a salt) with water to form free molecular bases and H_3O^+.

$$BH^+ + H_2O \rightleftarrows B + H_3O^+$$

$$K_a = \frac{K_w}{K_{b(B)}} \quad (B = \text{weak base})$$

Salts of Weak Bases and Weak Acids

- Aqueous solutions of salts of ***strong acids*** and ***strong bases*** are ***neutral***.
- Aqueous solutions of salts of ***strong bases*** and ***weak acids*** are ***basic***.
- Aqueous solutions of salts of ***weak bases*** and ***strong acids*** are ***acidic***.
- Aqueous solutions of salts of ***weak bases*** and ***weak acids*** can be ***neutral***, ***basic*** or ***acidic***.

The values of K_a and K_b determine the pH.

End of Chapter 18b

- Weak aqueous acid-base mixtures are called buffers. They are the subject of Chapter 19.