

## Chapter 18b

### Ionic Equilibria: Acids and Bases



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## Acid-Base Properties of Salts

- Soluble salts (ionic compounds) dissolve in water to produce ions.
  - In particular, salts that contain group IA metals,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  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.

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## Acid-Base Properties of Salts

- Examples of salts that produce neutral solutions:
  - $\text{NaCl (aq)} \rightarrow \text{Na}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$
  - $\text{KNO}_3 \text{(aq)} \rightarrow \text{K}^+ \text{(aq)} + \text{NO}_3^- \text{(aq)}$
  - $\text{Na}_2\text{SO}_4 \text{(aq)} \rightarrow 2 \text{Na}^+ \text{(aq)} + \text{SO}_4^{2-} \text{(aq)}$
  - $\text{LiClO}_4 \text{(aq)} \rightarrow \text{Li}^+ \text{(aq)} + \text{ClO}_4^- \text{(aq)}$
  - $\text{KBr (aq)} \rightarrow \text{K}^+ \text{(aq)} + \text{Br}^- \text{(aq)}$
- Weak conjugate bases of strong acids are produced and do not upset the balance of  $\text{H}_3\text{O}^+$  &  $\text{OH}^-$  in neutral water.

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## Acid-Base Properties of Salts

- Examples of salts that produce basic or acidic solutions:
  - $\text{Na}_2\text{CO}_3 \text{(aq)} \rightarrow 2\text{Na}^+ \text{(aq)} + \text{CO}_3^{2-} \text{(aq)}$
  - $\text{KF (aq)} \rightarrow \text{K}^+ \text{(aq)} + \text{F}^- \text{(aq)}$
  - $\text{NaCH}_3\text{COO (aq)} \rightarrow 2 \text{Na}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$
  - $\text{NH}_4\text{Cl (aq)} \rightarrow \text{NH}_4^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$
  - $\text{NH}_4\text{CH}_3\text{COO (aq)} \rightarrow \text{NH}_4^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$
- 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  $\text{H}_3\text{O}^+$  &  $\text{OH}^-$  in neutral water.

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## Solvolyis

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  $\text{H}_3\text{O}^+$  ions from water to form nonionized weak acid molecules.

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## Solvolyis

- The combination of a weak acid's anion with  $\text{H}_3\text{O}^+$  ions, from water, to form nonionized weak acid molecules is a form of hydrolysis.



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## Solvolysis

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



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## Solvolysis

- Recall that at 25°C
- 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  $[H_3O^+] > 1.0 \times 10^{-7} M$

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## Solvolysis

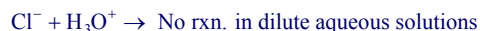
- Remember from Brønsted-Lowry acid-base theory:
  - *The conjugate base of a strong acid is a very weak base.*
  - *The conjugate base of a weak acid is a stronger base.*
- Hydrochloric acid, a typical strong acid, is essentially completely ionized in dilute aqueous solutions.



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## 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.

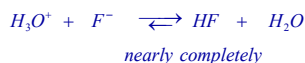
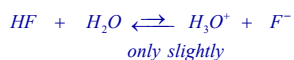


- This fact is true for all strong acids and their anions.

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## 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.



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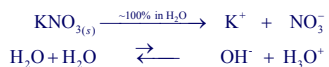
## Solvolysis

- 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 weak acid and weak base.)  
 $NH_3(aq) + HF(aq) \rightarrow NH_4F(aq)$

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### 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,  $\text{KNO}_3$ , made from nitric acid and potassium hydroxide.



The ions that are in solution  $\uparrow_{\text{KOH}}$   $\uparrow_{\text{HNO}_3}$

The KOH and  $\text{HNO}_3$  are present in equal amounts.

There is no reaction to upset  $[\text{H}_3\text{O}^+][\text{OH}^-]$

Thus the solution is neutral.

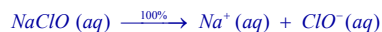
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### Salts of Strong Bases and Weak Acids

- 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,  $\text{NaClO}$ , made from sodium hydroxide and hypochlorous acid.

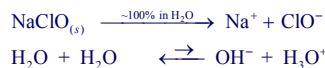


- Since  $\text{NaClO}$  is a soluble salt (group IA metal):



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### Salts of Strong Bases and Weak Acids



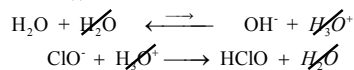
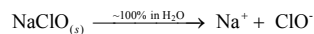
Notice ions in solution  $\uparrow_{\text{NaOH}}$   $\uparrow_{\text{HClO}}$

Which is the stronger acid or base?

The conjugate base of a weak acid is very strong.

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### Salts of Strong Bases and Weak Acids



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



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

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### 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  $\text{ClO}^-$  that reacts with water to produce  $\text{OH}^-$ .

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

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### Salts of Strong Bases and Weak Acids

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

$$K_w = K_a K_b$$

$$K_b = \frac{K_w}{K_{a \text{ for HClO}}} = \frac{1 \times 10^{-14}}{3.5 \times 10^{-8}}$$

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = 2.9 \times 10^{-7}$$

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### Salts of Strong Bases and Weak Acids

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

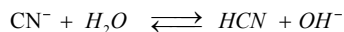


$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a \text{ for HA}}$$

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### Salts of Strong Bases and Weak Acids

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



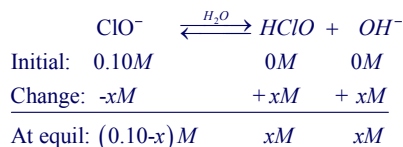
$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = \frac{K_w}{K_a \text{ for HCN}}$$

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

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### Salts of Strong Bases and Weak Acids

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



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### Salts of Strong Bases and Weak Acids

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

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



The fluoride ion is acting as a base.

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

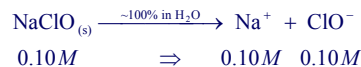
Therefore, we need to determine its ionization constant as a base – its hydrolysis constant.

$$K_b = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

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### 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.



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### Salts of Strong Bases and Weak Acids

- Substitute the algebraic expressions into the hydrolysis constant expression.

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = 2.9 \times 10^{-7}$$

$$K_b = \frac{(x)(x)}{(0.10-x)} = 2.9 \times 10^{-7}$$

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### 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.

$$x \ll 0.10 \text{ and } 0.10 - x \approx 0.10$$

The equation reduces to  $x^2 = 2.9 \times 10^{-8}$

$$x = 1.7 \times 10^{-4} M = [\text{ClO}^-] = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.7 \times 10^{-4})$$

$$\text{pOH} = 3.77$$

$$\text{pH} = 14.00 - 3.77$$

$$= 10.23$$

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### Salts of Strong Bases and Weak Acids

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

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

$$\% \text{ hydrolysis} = \frac{1.7 \times 10^{-4} M}{0.10 M} \times 100\% = 0.17\%$$

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

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### Salts of Weak Bases and Strong Acids

- Salts made from weak bases and strong acids form **acidic aqueous solutions**.
- An example is ammonium bromide,  $\text{NH}_4\text{Br}$ , made from ammonia and hydrobromic acid.



Which is the stronger acid or base?

The conjugate acid of a weak base is very strong.

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### Salts of Weak Bases and Strong Acids

The relatively strong acid,  $\text{NH}_4^+$ , reacts with the  $\text{OH}^-$  ion removing it from solution leaving excess  $\text{H}_3\text{O}^+$



generates excess  $\text{H}_3\text{O}^+$

- The reaction may be more simply represented as:



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### Salts of Weak Bases and Strong Acids

- Or even more simply as:



- The hydrolysis constant expression for this process is:

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

or

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

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### Salts of Weak Bases and Strong Acids

- Which we recognize as:

$$K_w = K_a K_b$$

$$K_a = \frac{K_w}{K_b(\text{NH}_3)}$$

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

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### Salts of Weak Bases and Strong Acids

- In its simplest form for this hydrolysis:



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

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### Salts of Weak Bases and Strong Acids

Example 3: Calculate  $[\text{H}^+]$ , pH, and percent hydrolysis for the ammonium ion in 0.10 M ammonium bromide,  $\text{NH}_4\text{Br}$ , solution.

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

	$\text{NH}_4^+$	$\xrightleftharpoons{H_2O}$	$\text{NH}_3$	$+$	$\text{H}_3\text{O}^+$
Initial:	0.10M		+ xM		+ xM
Change:	-xM		+ xM		+ xM
Equilibrium	(0.10 - x)M		xM		xM

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### Salts of Weak Bases and Strong Acids

- Substitute the algebraic expressions into the hydrolysis constant.

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

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

The assumption is applicable.

$$x \ll 0.10 \text{ thus } 0.10 - x \approx 0.10$$

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### Salts of Weak Bases and Strong Acids

- Complete the algebra and determine the concentrations and pH.

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

$$x^2 = 5.6 \times 10^{-11}$$

$$x = 7.5 \times 10^{-6} M$$

$$[\text{NH}_3] = [\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} M$$

$$\text{pH} = 5.12$$

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### Salts of Weak Bases and Strong Acids

- The percent hydrolysis of the ammonium ion in 0.10 M  $\text{NH}_4\text{Br}$  solution is:

$$\% \text{ hydrolysis} = \frac{[\text{NH}_4^+]_{\text{hydrolyzed}}}{[\text{NH}_4^+]_{\text{original}}} \times 100\%$$

$$\% \text{ hydrolysis} = \frac{7.5 \times 10^{-6} M}{0.10 M} \times 100\%$$

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

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### 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  $K_{\text{base}} = K_{\text{acid}}$  make **neutral solutions**.

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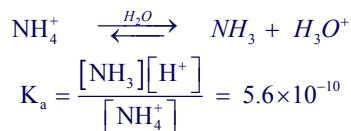
### Salts of Weak Bases and Weak Acids

- An example is ammonium acetate,  $\text{NH}_4\text{CH}_3\text{COO}$ , made from aqueous ammonia,  $\text{NH}_3$ , and acetic acid,  $\text{CH}_3\text{COOH}$ .  
 $K_a$  for acetic acid =  $K_b$  for ammonia =  $1.8 \times 10^{-5}$ .

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### Salts of Weak Bases and Weak Acids

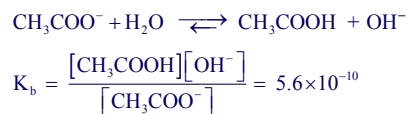
- The ammonium ion hydrolyzes to produce  $\text{H}^+$  ions. Its hydrolysis constant is:



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### Salts of Weak Bases and Weak Acids

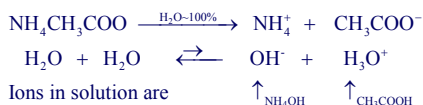
- The acetate ion hydrolyzes to produce  $\text{OH}^-$  ions. Its hydrolysis constant is:



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### Salts of Weak Bases and Weak Acids

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



A weak acid and base are formed in solution!

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### Salts of Weak Bases and Weak Acids

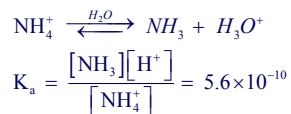
2. Salts of weak bases and weak acids for which parent  $K_{\text{base}} > K_{\text{acid}}$  make **basic solutions**.
- An example is ammonium hypochlorite,  $\text{NH}_4\text{ClO}$ , made from aqueous ammonia,  $\text{NH}_3$ , and hypochlorous acid,  $\text{HClO}$ .

$$K_b \text{ for } \text{NH}_3 = 1.8 \times 10^{-5} > K_a \text{ for } \text{HClO} = 3.5 \times 10^{-8}$$

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### Salts of Weak Bases and Weak Acids

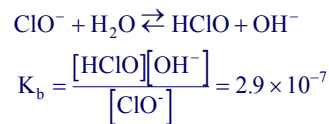
- The ammonium ion hydrolyzes to produce H<sup>+</sup> ions. Its hydrolysis constant is:



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### Salts of Weak Bases and Weak Acids

- The hypochlorite ion hydrolyzes to produce OH<sup>-</sup> ions. Its hydrolysis constant is:



- Because the K<sub>b</sub> for ClO<sup>-</sup> ions is three orders of magnitude larger than the K<sub>a</sub> for NH<sub>4</sub><sup>+</sup> ions, OH<sup>-</sup> ions are produced in excess making the **solution basic**.

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### Salts of Weak Bases and Weak Acids

3. Salts of weak bases and weak acids for which parent K<sub>base</sub> < K<sub>acid</sub> make **acidic solutions**.

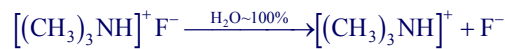
- An example is trimethylammonium fluoride, (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>F<sup>-</sup>, made from trimethylamine, (CH<sub>3</sub>)<sub>3</sub>N, and hydrofluoric acid, HF.

K<sub>b</sub> for (CH<sub>3</sub>)<sub>3</sub>N = 7.4 × 10<sup>-5</sup> < K<sub>a</sub> for HF = 7.2 × 10<sup>-4</sup>

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### Salts of Weak Bases and Weak Acids

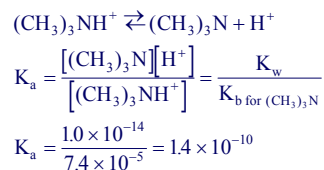
- Both the cation, (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>, and the anion, F<sup>-</sup>, hydrolyze.



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### Salts of Weak Bases and Weak Acids

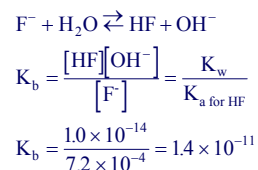
- The trimethylammonium ion hydrolyzes to produce H<sup>+</sup> ions. Its hydrolysis constant is:



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### Salts of Weak Bases and Weak Acids

- The fluoride ion hydrolyzes to produce OH<sup>-</sup> ions. Its hydrolysis constant is:



- Because the K<sub>a</sub> for (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> ions is one order of magnitude larger than the K<sub>b</sub> for F<sup>-</sup> ions, H<sup>+</sup> ions are produced in excess making the **solution acidic**.

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### 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  $\text{OH}^-$ .



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

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### Salts of Weak Bases and Weak Acids

- 2 The reactions of cations of weak bases (from a salt) with water to form free molecular bases and  $\text{H}_3\text{O}^+$ .



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

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### 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.

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### End of Chapter 18b

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

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