

# Sections 17.3 – 17.6

## Acid-Base Equilibria

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# Acid-Base Equilibria

In these sections...

- a. Relative acid-base strength
- b. Determining  $K_a$  and  $K_b$  experimentally
- c. Estimating pH of solutions
- d. Acid-Base Properties of Salts
- e. Molecular control of acid-base strength

# Acid-Base Equilibria

Bronsted Acid:  $\text{H}^+$  (proton) donor

Bronsted Base:  $\text{H}^+$  acceptor

Acid-Base reactions:  $\text{H}^+$  transfer reaction

## Conjugate Acid-Base Pairs:

*acid*

HF

$\text{NH}_4^+$

*conjugate base*

$\text{F}^-$

$\text{NH}_3$

# Strong vs. Weak Acids

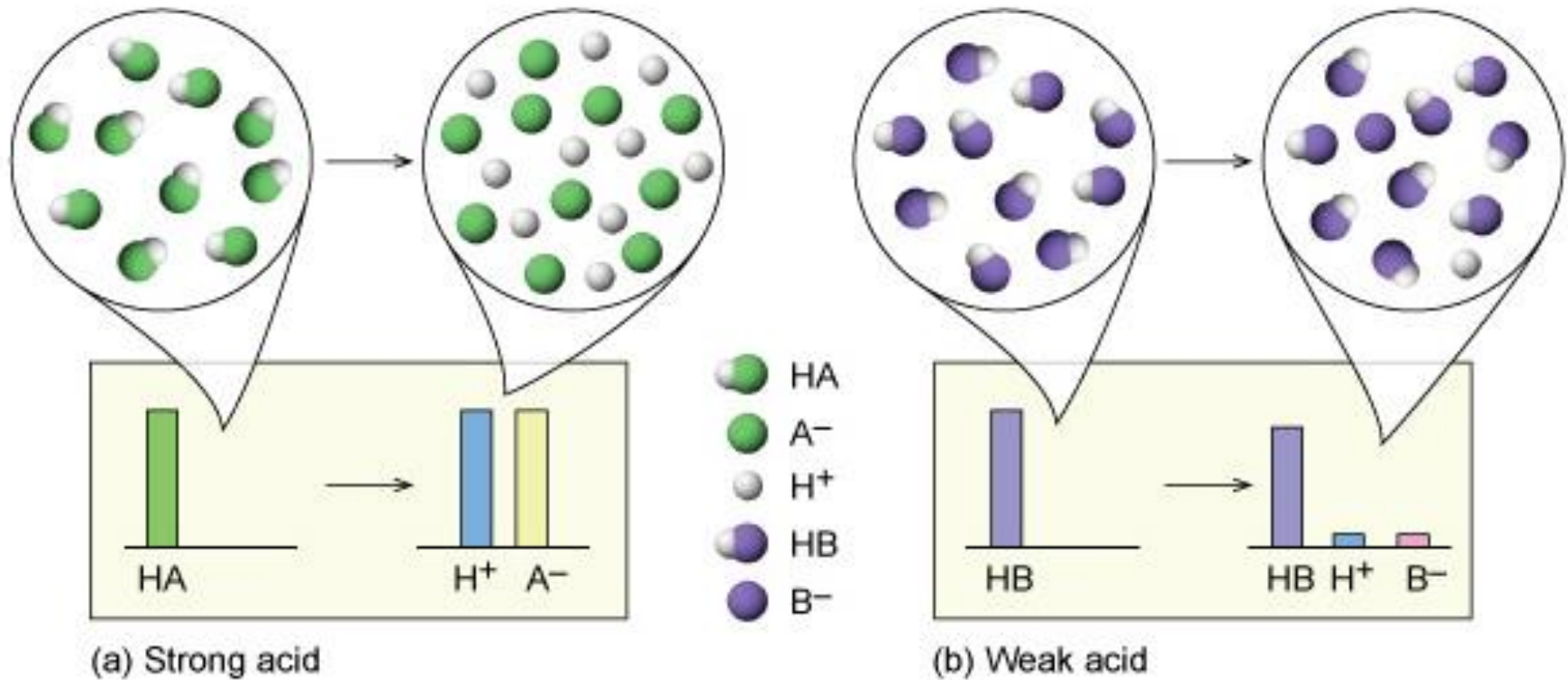
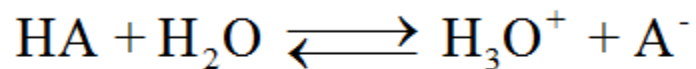


Figure 16.3.1: Molecular view of (a) strong and (b) weak acids

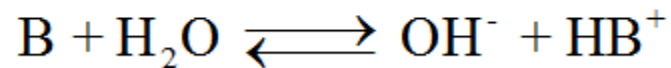
# Weak Acid-Base Strength Varies Greatly Depending on the Equilibrium Constant

## Acid Equilibria in Water



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

## Base Equilibria in Water



$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]}$$

### K<sub>a</sub> and K<sub>b</sub> Values

Name of Acid	Acid	K <sub>a</sub>	Name of Base	Base	K <sub>b</sub>
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	large	hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	very small
Hydrochloric acid	HCl	large	chloride ion	Cl <sup>-</sup>	very small
Nitric acid	HNO <sub>3</sub>	large	nitrate ion	NO <sub>3</sub> <sup>-</sup>	very small
Hydronium ion	H <sub>3</sub> O <sup>+</sup>	1.0	water	H <sub>2</sub> O	1.0 × 10 <sup>-14</sup>
Hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	1.2 × 10 <sup>-2</sup>	sulfate ion	SO <sub>4</sub> <sup>2-</sup>	8.3 × 10 <sup>-13</sup>
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	7.5 × 10 <sup>-3</sup>	dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	1.3 × 10 <sup>-12</sup>
Hexaaquairon(III) ion	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	6.3 × 10 <sup>-3</sup>	pentaaquahydroxoiron(III) ion	Fe(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	1.6 × 10 <sup>-12</sup>
Hydrofluoric acid	HF	7.4 × 10 <sup>-4</sup>	fluoride ion	F <sup>-</sup>	1.4 × 10 <sup>-11</sup>
Formic acid	HCO <sub>2</sub> H	1.8 × 10 <sup>-4</sup>	formate ion	HCO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-11</sup>
Benzoic acid	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	6.3 × 10 <sup>-5</sup>	benzoate ion	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	1.6 × 10 <sup>-10</sup>
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	1.8 × 10 <sup>-5</sup>	acetate ion	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-10</sup>
Hexaaquaaluminum ion	Al(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	7.9 × 10 <sup>-6</sup>	pentaaquahydroxoaluminum ion	Al(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	1.3 × 10 <sup>-9</sup>
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	4.2 × 10 <sup>-7</sup>	hydrogen carbonate ion	HCO <sub>3</sub> <sup>-</sup>	2.4 × 10 <sup>-8</sup>
Hydrogen sulfide	H <sub>2</sub> S	1 × 10 <sup>-7</sup>	hydrogen sulfide ion	HS <sup>-</sup>	1 × 10 <sup>-7</sup>
Dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6.2 × 10 <sup>-8</sup>	hydrogen phosphate ion	HPO <sub>4</sub> <sup>2-</sup>	1.6 × 10 <sup>-7</sup>
Hypochlorous acid	HOCl	3.5 × 10 <sup>-8</sup>	hypochlorite ion	OCl <sup>-</sup>	2.9 × 10 <sup>-7</sup>
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	5.6 × 10 <sup>-10</sup>	ammonia	NH <sub>3</sub>	1.8 × 10 <sup>-5</sup>
Hydrocyanic acid	HCN	4.0 × 10 <sup>-10</sup>	cyanide ion	CN <sup>-</sup>	2.5 × 10 <sup>-5</sup>
Hexaaquairon(II) ion	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	3.2 × 10 <sup>-10</sup>	pentaaquahydroxoiron(II) ion	Fe(H <sub>2</sub> O) <sub>5</sub> OH <sup>+</sup>	3.1 × 10 <sup>-5</sup>
Hydrogen carbonate ion	HCO <sub>3</sub> <sup>-</sup>	4.8 × 10 <sup>-11</sup>	carbonate ion	CO <sub>3</sub> <sup>2-</sup>	2.1 × 10 <sup>-4</sup>
Hydrogen phosphate ion	HPO <sub>4</sub> <sup>2-</sup>	3.6 × 10 <sup>-13</sup>	phosphate ion	PO <sub>4</sub> <sup>3-</sup>	2.8 × 10 <sup>-2</sup>
Water	H <sub>2</sub> O	1.0 × 10 <sup>-14</sup>	hydroxide ion	OH <sup>-</sup>	1.0
Hydrogen sulfide ion	HS <sup>-</sup>	1 × 10 <sup>-19</sup>	sulfide ion	S <sup>2-</sup>	1 × 10 <sup>5</sup>

**Strong Acids:** HCl, HBr, HI, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>

**Strong Bases:** NaOH, KOH, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>

# Trends in relative acid/base strength for conjugate pairs.

K <sub>a</sub> and K <sub>b</sub> Values					
Name of Acid	Acid	K <sub>a</sub>	Name of Base	Base	K <sub>b</sub>
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	large	hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	very small
Hydrochloric acid	HCl	large	chloride ion	Cl <sup>-</sup>	very small
Nitric acid	HNO <sub>3</sub>	large	nitrate ion	NO <sub>3</sub> <sup>-</sup>	very small
Hydronium ion	H <sub>3</sub> O <sup>+</sup>	1.0	water	H <sub>2</sub> O	1.0 × 10 <sup>-14</sup>
Hydrogen sulfate ion	HSO <sub>4</sub> <sup>-</sup>	1.2 × 10 <sup>-2</sup>	sulfate ion	SO <sub>4</sub> <sup>2-</sup>	8.3 × 10 <sup>-13</sup>
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	7.5 × 10 <sup>-3</sup>	dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	1.3 × 10 <sup>-12</sup>
Hexaaquairon(III) ion	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	6.3 × 10 <sup>-3</sup>	pentaaquahydroxoiron(III) ion	Fe(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	1.6 × 10 <sup>-12</sup>
Hydrofluoric acid	HF	7.4 × 10 <sup>-4</sup>	fluoride ion	F <sup>-</sup>	1.4 × 10 <sup>-11</sup>
Formic acid	HCO <sub>2</sub> H	1.8 × 10 <sup>-4</sup>	formate ion	HCO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-11</sup>
Benzoic acid	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	6.3 × 10 <sup>-5</sup>	benzoate ion	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	1.6 × 10 <sup>-10</sup>
Acetic acid	CH <sub>3</sub> CO <sub>2</sub> H	1.8 × 10 <sup>-5</sup>	acetate ion	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	5.6 × 10 <sup>-10</sup>
Hexaaquaaluminum ion	Al(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	7.9 × 10 <sup>-6</sup>	pentaaquahydroxoaluminum ion	Al(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	1.3 × 10 <sup>-9</sup>
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	4.2 × 10 <sup>-7</sup>	hydrogen carbonate ion	HCO <sub>3</sub> <sup>-</sup>	2.4 × 10 <sup>-8</sup>
Hydrogen sulfide	H <sub>2</sub> S	1 × 10 <sup>-7</sup>	hydrogen sulfide ion	HS <sup>-</sup>	1 × 10 <sup>-7</sup>
Dihydrogen phosphate ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6.2 × 10 <sup>-8</sup>	hydrogen phosphate ion	HPO <sub>4</sub> <sup>2-</sup>	1.6 × 10 <sup>-7</sup>
Hypochlorous acid	HClO	3.5 × 10 <sup>-8</sup>	hypochlorite ion	ClO <sup>-</sup>	2.9 × 10 <sup>-7</sup>
Ammonium ion	NH <sub>4</sub> <sup>+</sup>	5.6 × 10 <sup>-10</sup>	ammonia	NH <sub>3</sub>	1.8 × 10 <sup>-5</sup>
Hydrocyanic acid	HCN	4.0 × 10 <sup>-10</sup>	cyanide ion	CN <sup>-</sup>	2.5 × 10 <sup>-5</sup>
Hexaaquairon(II) ion	Fe(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	3.2 × 10 <sup>-10</sup>	pentaaquahydroxoiron(II) ion	Fe(H <sub>2</sub> O) <sub>5</sub> OH <sup>+</sup>	3.1 × 10 <sup>-5</sup>
Hydrogen carbonate ion	HCO <sub>3</sub> <sup>-</sup>	4.8 × 10 <sup>-11</sup>	carbonate ion	CO <sub>3</sub> <sup>2-</sup>	2.1 × 10 <sup>-4</sup>
Hydrogen phosphate ion	HPO <sub>4</sub> <sup>2-</sup>	3.6 × 10 <sup>-13</sup>	phosphate ion	PO <sub>4</sub> <sup>3-</sup>	2.8 × 10 <sup>-2</sup>
Water	H <sub>2</sub> O	1.0 × 10 <sup>-14</sup>	hydroxide ion	OH <sup>-</sup>	1.0
Hydrogen sulfide ion	HS <sup>-</sup>	1 × 10 <sup>-19</sup>	sulfide ion	S <sup>2-</sup>	1 × 10 <sup>5</sup>

**Strong Acids:** HCl, HBr, HI, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>

**Strong Bases:** NaOH, KOH, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>

# Relationship Between $K_a$ and $K_b$ for an Acid-Base Conjugate Pair

$$K_a \times K_b = 1.0 \times 10^{-14}$$

Ammonia is a base with  $K_b = 1.8 \times 10^{-5}$ . What is the conjugate acid, and what is its  $K_a$  value?



## Determining the $K_a$ Value Experimentally

Measure pH for a solution of known concentration.

pH  $\rightarrow$   $[H_3O^+]$   $\rightarrow$  x in an ICE table  $\rightarrow$  all [ ]'s  $\rightarrow$   $K_a$

What is the value of  $K_a$  for an acid, HA, for which a 0.240 M solution has a pH of 3.28?

Determining  $K_b$ :

A 0.300 M solution of a weak base has a pH of 9.20.

What is  $K_b$ ?

Estimating the pH when [HA] and  $K_a$  are known

Set up ICE Table  $\rightarrow x = [\text{H}_3\text{O}^+] \rightarrow \text{pH}$

What is the pH of a 0.150 M solution of HF?

Estimate when  $[HA]_o > 100 \times K_a$

What is the pH of a 0.150 M solution of HCN?

## Estimating pH of weak base solutions

What is the pH of a 0.150 M solution of  $\text{NH}_3$ ?

# Acid-Base Properties of Salts

Look at acid-base properties of each ion.

Ions that are conjugates from strong acids or strong bases are pH neutral.

Anions that are conjugates of weak acids are usually weak bases.

**$K_a$  and  $K_b$  Values**

Name of Acid	Acid	$K_a$	Name of Base	Base	$K_b$
Sulfuric acid	$H_2SO_4$	large	hydrogen sulfate ion	$HSO_4^-$	very small
Hydrochloric acid	HCl	large	chloride ion	$Cl^-$	very small
Nitric acid	$HNO_3$	large	nitrate ion	$NO_3^-$	very small
Phosphoric acid	$H_3PO_4$	$7.5 \times 10^{-3}$	dihydrogen phosphate ion	$H_2PO_4^-$	$1.3 \times 10^{-12}$
Hydrofluoric acid	HF	$7.4 \times 10^{-4}$	fluoride ion	$F^-$	$1.4 \times 10^{-11}$
Formic acid	$HCO_2H$	$1.8 \times 10^{-4}$	formate ion	$HCO_2^-$	$5.6 \times 10^{-11}$
Benzoic acid	$C_6H_5CO_2H$	$6.3 \times 10^{-5}$	benzoate ion	$C_6H_5CO_2^-$	$1.6 \times 10^{-10}$
Acetic acid	$CH_3CO_2H$	$1.8 \times 10^{-5}$	acetate ion	$CH_3CO_2^-$	$5.6 \times 10^{-10}$
Carbonic acid	$H_2CO_3$	$4.2 \times 10^{-7}$	hydrogen carbonate ion	$HCO_3^-$	$2.4 \times 10^{-8}$
Hydrogen sulfide	$H_2S$	$1 \times 10^{-7}$	hydrogen sulfide ion	$HS^-$	$1 \times 10^{-7}$
Dihydrogen phosphate ion	$H_2PO_4^-$	$6.2 \times 10^{-8}$	hydrogen phosphate ion	$HPO_4^{2-}$	$1.6 \times 10^{-7}$
Hypochlorous acid	HClO	$3.5 \times 10^{-8}$	hypochlorite ion	$ClO^-$	$2.9 \times 10^{-7}$
Ammonium ion	$NH_4^+$	$5.6 \times 10^{-10}$	ammonia	$NH_3$	$1.8 \times 10^{-5}$
Hydrocyanic acid	HCN	$4.0 \times 10^{-10}$	cyanide ion	$CN^-$	$2.5 \times 10^{-5}$
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	$3.2 \times 10^{-10}$	pentaquahydroxoiron(II) ion	$Fe(H_2O)_5OH^+$	$3.1 \times 10^{-5}$
Hydrogen carbonate ion	$HCO_3^-$	$4.8 \times 10^{-11}$	carbonate ion	$CO_3^{2-}$	$2.1 \times 10^{-4}$
Hydrogen phosphate ion	$HPO_4^{2-}$	$3.6 \times 10^{-13}$	phosphate ion	$PO_4^{3-}$	$2.8 \times 10^{-2}$
Water	$H_2O$	$1.0 \times 10^{-14}$	hydroxide ion	$OH^-$	1.0
Hydrogen sulfide ion	$HS^-$	$1 \times 10^{-19}$	sulfide ion	$S^{2-}$	$1 \times 10^5$

Examples:

NaCN

KNO<sub>3</sub>

NH<sub>4</sub>Cl

NaHCO<sub>2</sub>

Na<sub>2</sub>CO<sub>3</sub>

KHSO<sub>4</sub>

NH<sub>4</sub>CN

Strong Acids: HCl, HBr, HI,  $H_2SO_4$ ,  $HNO_3$ ,  $HClO_4$

Strong Bases: NaOH, KOH,  $Ca(OH)_2$ ,  $Ba(OH)_2$

# Molecular Structure and Acid Strength

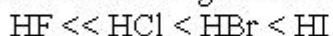
## 1. H-A Bond Strength and Acid Strength

As bond strength increases, acid strength decreases.

Table 16.4 Bond Energies and  $K_a$  values for the H—X acids

H—X	Bond Energy	$K_a$
H—F	569 kJ/mol	$\sim 7 \times 10^{-4}$
H—Cl	431 kJ/mol	$\sim 10^7$
H—Br	368 kJ/mol	$\sim 10^9$
H—I	297 kJ/mol	$\sim 10^{10}$

The order of acid strength for this series



## 2. H-A, Electronegativity of A and Acid Strength

As electronegativity increases, acid strength increases.

