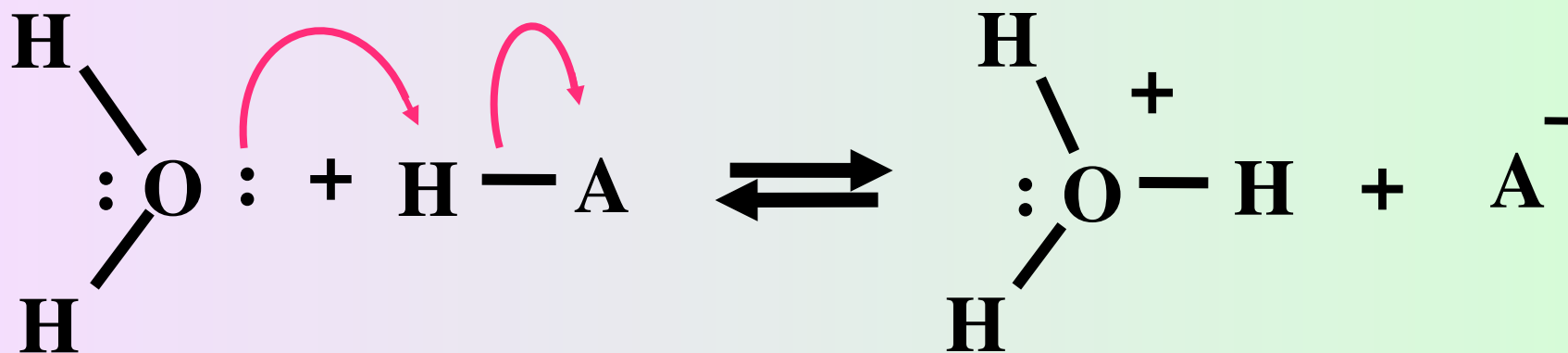


# **Weak Acids and Acid Ionization Constants**

**Acid ionization constants are a particular kind of equilibrium constant**

# Equilibrium constant for proton transfer



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

**Acid ionization constant**

# **Ionization Constants of Some Weak Acids at 25°C**

# Hydrofluoric Acid



$$K_a = 1.71 \times 10^{-4}$$



conjugate base

$$K_b = 1.4 \times 10^{-11}$$

# Hydrocyanic Acid

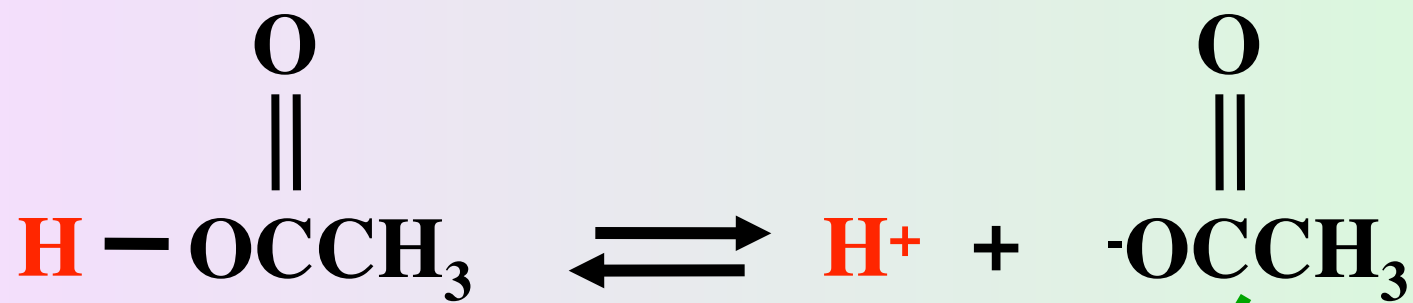


$$K_a = 4.9 \times 10^{-10}$$

conjugate base

$$K_b = 2 \times 10^{-4}$$

# Acetic Acid



$$K_a = 1.8 \times 10^{-5}$$

conjugate base

$$K_b = 5.6 \times 10^{-10}$$

# Practice Exercise

What is the pH of a 0.122 M solution of a weak monoprotic acid HA that has  $K_a = 5.7 \times 10^{-4}$



**Init:**      0.122 M                              0.00M              0.00 M

**final:**      - x                                      + x                      +x

---

0.122 - x                                      + x                      +x

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)^2}{(0.122 - x)} = 5.7 \times 10^{-4}$$

$$\frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)^2}{(0.122 - x)} = 5.7 \times 10^{-4}$$

Small  $K_a$

Approximation  $0.122 - x \cong 0.122$

$$\frac{x^2}{0.122} = 5.7 \times 10^{-4}$$

$$x = [\text{H}^+] = .008 \text{ M}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log (.008)$$

$$\text{pH} = 2.1$$



# Percent Ionization



$$\text{percent ionization} = \frac{[\text{A}^-] \text{ (at equilibrium)}}{[\text{HA}] \text{ (original)}} \times 100$$

# Percent Ionization

consider 1.00 M HOAc

$$K_a = 1.8 \times 10^{-5}$$



**Init:**      1.00 M                      0.00M      0.00 M

**final:**      - x                              + x      +x

---

                 1 - x                              + x      +x

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HOAc}]} = \frac{(x)^2}{(1.00 - x)} = 1.8 \times 10^{-5}$$

$$\frac{(x)^2}{(1.00 - x)} = 1.8 \times 10^{-5}$$

$$x = 0.0042 \text{ M}$$

$$\% \text{ ionization} = 100 \times \frac{[\text{AcO}^-]}{[\text{HOAc}]_0}$$

$$[\text{AcO}^-] = 0.0042 \text{ M}$$

$$[\text{HOAc}]_0 = 1.00$$

$$\% \text{ ionization} = 100 (0.0042) / 1.0 )$$

$$\% \text{ ionization} = 0.42\%$$

# Percent Ionization

Is greater in more dilute solution

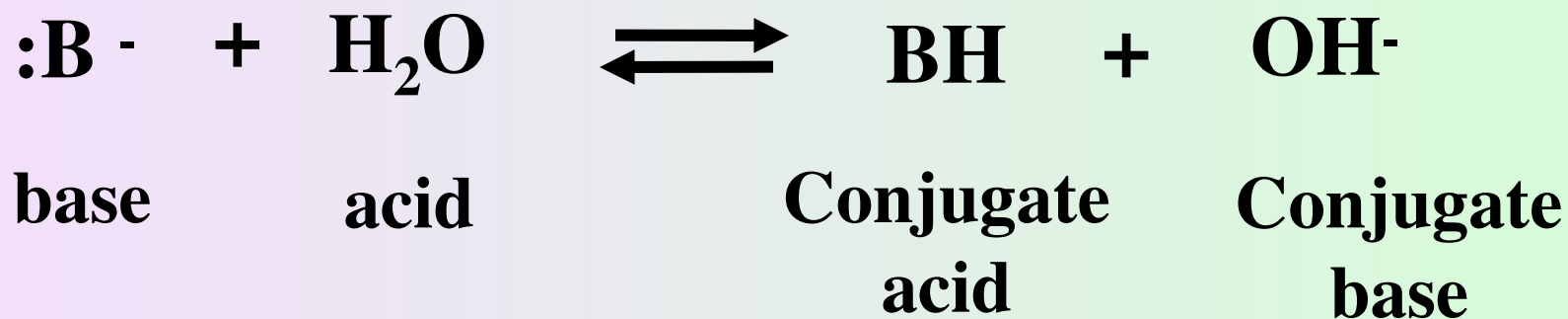
acetic acid:  $K_a = 1.8 \times 10^{-5}$

[acetic acid ]	[ H <sup>+</sup> ]	%dissoc
1.00 M	0.0042 M	0.42%
0.100 M	0.0013 M	1.3%

# **Weak Bases and Base Ionization Constants**

# The Base Ionization Constant $K_b$

Negatively charged base

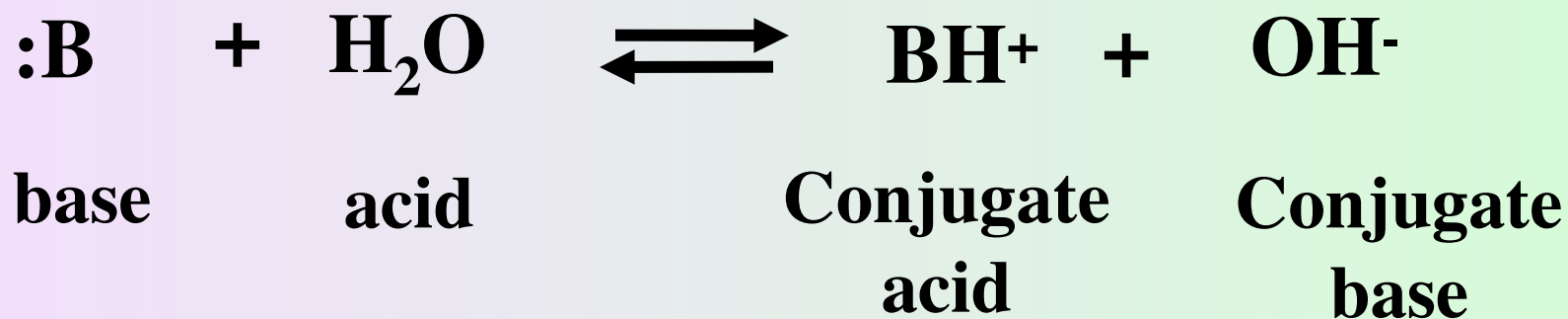


$$K_b = \frac{[\text{BH}] [\text{OH}^-]}{[\text{:B}^-]}$$

base ionization constant

# The Base Ionization Constant $K_b$

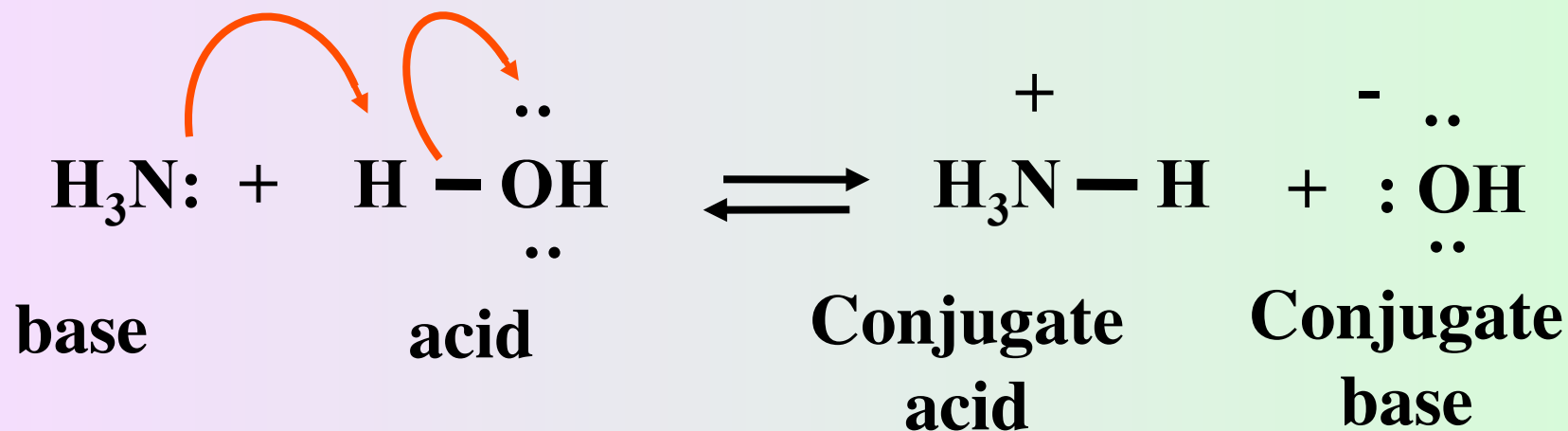
neutral base



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

base ionization constant

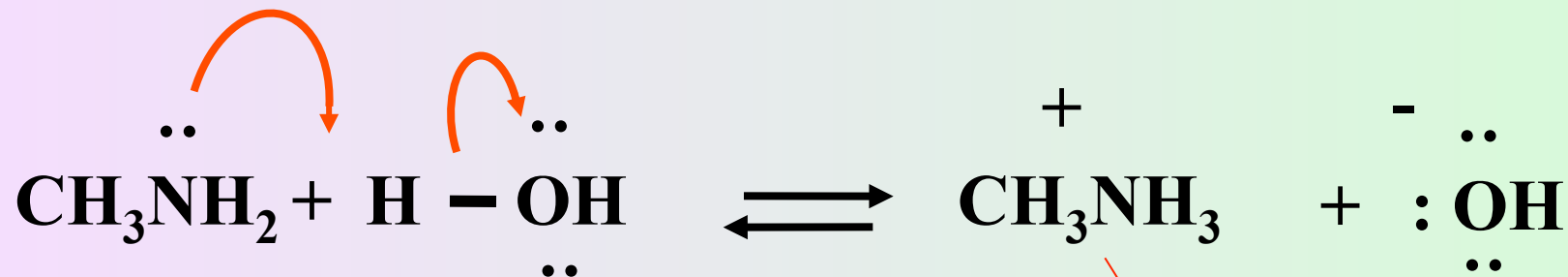
# Ammonia is an example of a neutral molecule that is a weak base



$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{H}_3\text{N}]} = 1.8 \times 10^{-5}$$



# Example: Methylamine

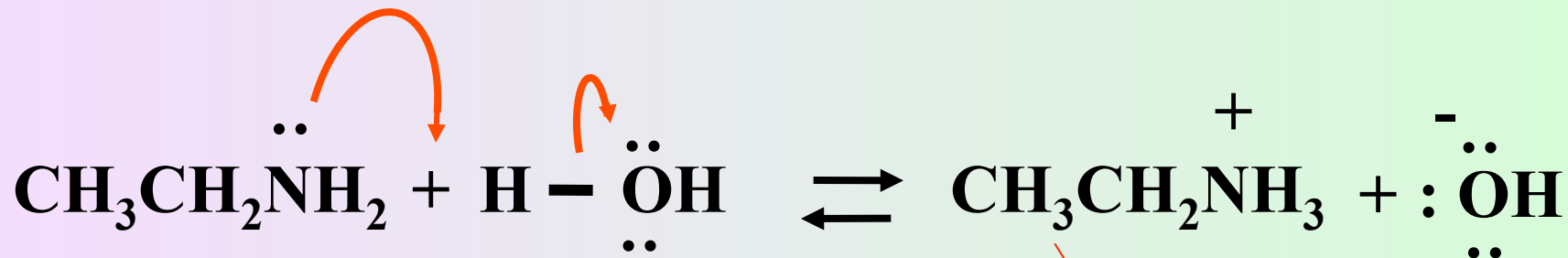


$$K_b = 4.4 \times 10^{-4}$$

Conjugate  
acid

$$K_a = 2.3 \times 10^{-11}$$

# Example: Ethylamine



$$K_b = 5.6 \times 10^{-4}$$

Conjugate  
acid

$$K_a = 1.8 \times 10^{-11}$$

# Practice Exercise

What is the pH of a 0.400 M ammonia solution

$$K_b = 1.8 \times 10^{-5}$$



**Init:**      0.400 M                              0.00M              0.00 M

**final:**      - x                                      + x              +x

---

0.400 - x                                      + x              +x

$$K_b = \frac{[\text{NH}_4^+][\text{HO}^-]}{[\text{NH}_3]} = \frac{(x)^2}{(0.400 - x)} = 1.8 \times 10^{-5}$$

$$K_a = \frac{[\text{NH}_4^+][\text{HO}^-]}{[\text{NH}_3]} = \frac{(x)^2}{(0.400 - x)} = 1.8 \times 10^{-5}$$

Approximation  $.400 - x \cong .400$

$$\frac{x^2}{0.400} = 1.8 \times 10^{-5}$$

$$x = [\text{HO}^-] = 2.7 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

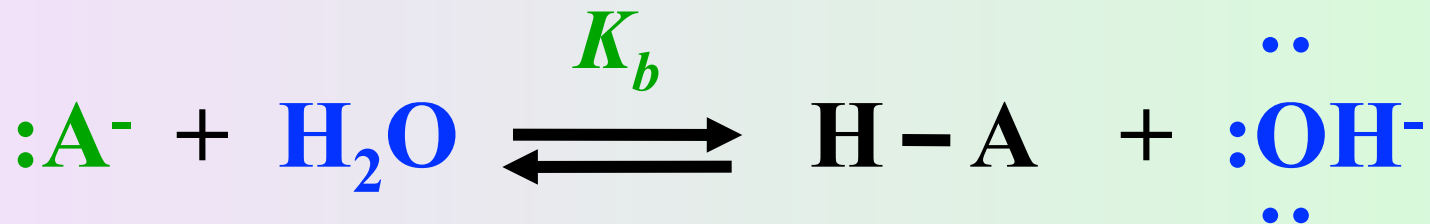
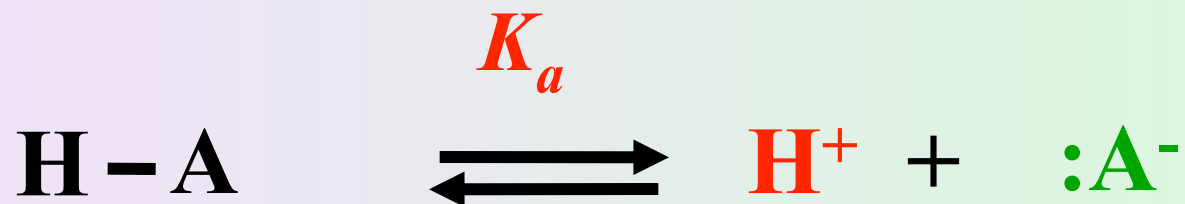
$$\text{pOH} = 2.57$$

$$\text{pH} = 14.00 - 2.57$$

$$\text{pH} = 11.43$$

# **The Relationship Between Conjugate Acid-Base Equilibrium Constants**

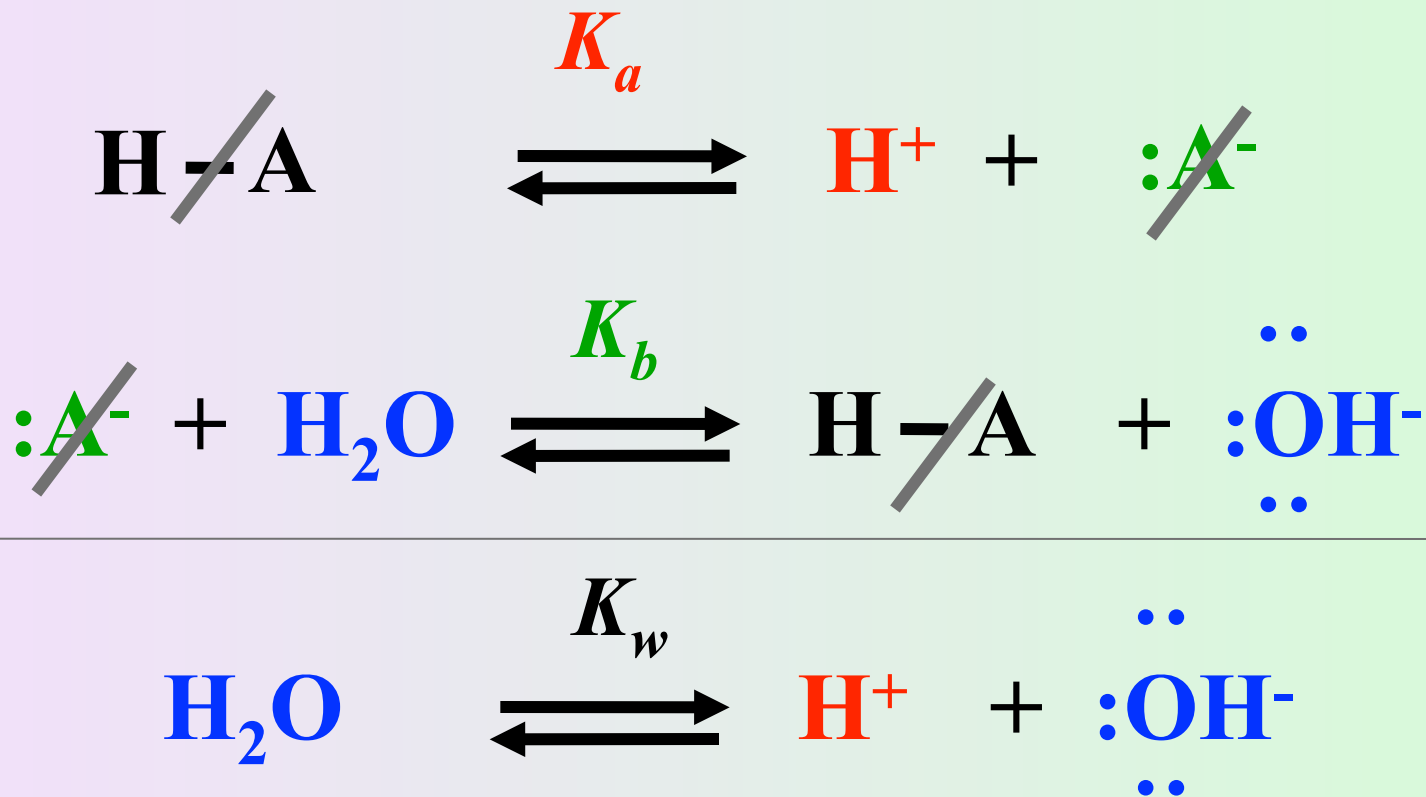
For the two equilibria that involve a conjugate acid-base pair in aqueous solution:



$$K_a K_b = K_w$$

$$\text{At } 25^\circ \text{C} \quad K_a K_b = 1.0 \times 10^{-14}$$

For the two equilibria that involve a conjugate acid-base pair in aqueous solution:



Recall: when adding two equilibria, multiply their equilibrium constants.

$$K_a K_b = K_w$$

If  $K_a$  is small;  $K_b$  is large and vice versa

**the stronger the acid, the weaker its conjugate base**

**the stronger the base, the weaker its conjugate acid**



# Relationships between $K_a$ and $K_b$

Acid	$K_a$	Conjugate base	$K_b$
HF	$7.1 \times 10^{-4}$	F <sup>-</sup>	$1.4 \times 10^{-11}$
CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$	CH <sub>3</sub> COO <sup>-</sup>	$5.6 \times 10^{-10}$
HCN	$4.9 \times 10^{-10}$	CN <sup>-</sup>	$2.0 \times 10^{-5}$
Conjugate acid		Base	
NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$	NH <sub>3</sub>	$1.8 \times 10^{-5}$

# $K_a$ and $K_b$

TABLE 16.5 • Some Conjugate Acid–Base Pairs

Acid	$K_a$	Base	$K_b$
HNO <sub>3</sub>	(Strong acid)	NO <sub>3</sub> <sup>-</sup>	(Negligible basicity)
HF	$6.8 \times 10^{-4}$	F <sup>-</sup>	$1.5 \times 10^{-11}$
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	$1.8 \times 10^{-5}$	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	$5.6 \times 10^{-10}$
H <sub>2</sub> CO <sub>3</sub>	$4.3 \times 10^{-7}$	HCO <sub>3</sub> <sup>-</sup>	$2.3 \times 10^{-8}$
NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$	NH <sub>3</sub>	$1.8 \times 10^{-5}$
HCO <sub>3</sub> <sup>-</sup>	$5.6 \times 10^{-11}$	CO <sub>3</sub> <sup>2-</sup>	$1.8 \times 10^{-4}$
OH <sup>-</sup>	(Negligible acidity)	O <sup>2-</sup>	(Strong base)

© 2012 Pearson Education, Inc.

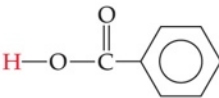
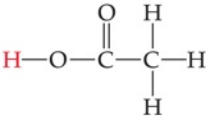
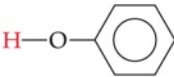
$K_a$  and  $K_b$  are related in this way:

$$K_a \times K_b = K_w$$

Therefore, if you know one of them, you can calculate the other.

# Dissociation Constants

TABLE 16.2 • Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	$K_a$
Chlorous (HClO <sub>2</sub> )	$\text{H}-\text{O}-\text{Cl}-\text{O}$	$\text{ClO}_2^-$	$1.0 \times 10^{-2}$
Hydrofluoric (HF)	$\text{H}-\text{F}$	$\text{F}^-$	$6.8 \times 10^{-4}$
Nitrous (HNO <sub>2</sub> )	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{NO}_2^-$	$4.5 \times 10^{-4}$
Benzoic (C <sub>6</sub> H <sub>5</sub> COOH)		$\text{C}_6\text{H}_5\text{COO}^-$	$6.3 \times 10^{-5}$
Acetic (CH <sub>3</sub> COOH)		$\text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$
Hypochlorous (HOCl)	$\text{H}-\text{O}-\text{Cl}$	$\text{OCl}^-$	$3.0 \times 10^{-5}$
Hydrocyanic (HCN)	$\text{H}-\text{C}\equiv\text{N}$	$\text{CN}^-$	$4.9 \times 10^{-10}$
Phenol (HOC <sub>6</sub> H <sub>5</sub> )		$\text{C}_6\text{H}_5\text{O}^-$	$1.3 \times 10^{-10}$

\*The proton that ionizes is shown in red.

© 2012 Pearson Education, Inc.

The greater the value of  $K_a$ , the stronger is the acid.

# Weak Bases

$K_b$  can be used to find  $[\text{OH}^-]$  and, through it, pH.

TABLE 16.4 • Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	$K_b$
Ammonia ( $\text{NH}_3$ )		$\text{NH}_4^+$	$1.8 \times 10^{-5}$
Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )		$\text{C}_5\text{H}_5\text{NH}^+$	$1.7 \times 10^{-9}$
Hydroxylamine ( $\text{HONH}_2$ )		$\text{HONH}_3^+$	$1.1 \times 10^{-8}$
Methylamine ( $\text{CH}_3\text{NH}_2$ )		$\text{CH}_3\text{NH}_3^+$	$4.4 \times 10^{-4}$
Hydrosulfide ion ( $\text{HS}^-$ )		$\text{H}_2\text{S}$	$1.8 \times 10^{-7}$
Carbonate ion ( $\text{CO}_3^{2-}$ )		$\text{HCO}_3^-$	$1.8 \times 10^{-4}$
Hypochlorite ion ( $\text{ClO}^-$ )		$\text{HClO}$	$3.3 \times 10^{-7}$

\*The atom that accepts the proton is shown in blue.

© 2012 Pearson Education, Inc.