Chapter 16

ACIDS AND BASES

(Part I)

16.1

Brønsted Acids and Bases

- A **Brønsted acid** is a species that donates a proton. (a proton donor).

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

| acid | | hydronium ion | conjugate base |

A *Conjugate base* is what remains of the acid after the donation of a proton.

- A **Brønsted base** is a species that accepts a proton. (a proton acceptor).

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

| base | | conjugate acid | |

A *Conjugate acid* is a newly formed protonated species.

Brønsted Acids and Bases

16.1

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

loses a proton
gains a proton

acid   base   conjugate acid   conjugate base

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

gains a proton
loses a proton

base   acid   conjugate acid   conjugate base

Any reaction, using the Brønsted theory, involves both an *acid* and a *base*.

Water is an **amphoteric species** which can act as a Brønsted *acid* or as a Brønsted *base*.

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Brønsted Acids and Bases

16.1

TABLE 16.1	Conjugate Bases of Some Common Species
Species	**Conjugate Base**
CH_3COOH	CH_3COO^-
H_2O	OH^-
NH_3	NH_2^-
H_2SO_4	HSO_4^-

TABLE 16.2	Conjugate Acids of Some Common Species
Species	**Conjugate Acid**
NH_3	NH_4^+
H_2O	H_3O^+
OH^-	H_2O
H_2NCONH_2 (urea)	$H_2NCONH_3^+$

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16.1

Brønsted Acids and Bases

- Exercise:

  Identify acids, conjugate acids, bases and conjugate bases in the reactions below:

  (a) $H_2SO_4(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + H_3O^+(aq)$

  | acid | base | conjugate base | conjugate acid |

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

  | acid | base | conjugate acid | conjugate base |

- Exercise:

  What is the conjugate base of $H_2PO_4^-$?

  $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

  conjugate base

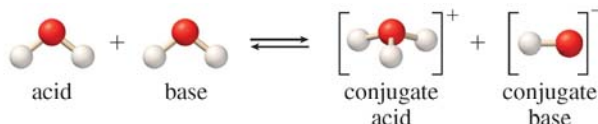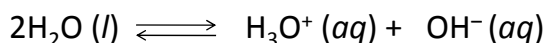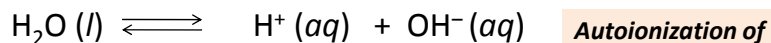*Dr. Al-Saadi*   5

16.2

The Acid-Base Properties of Water

- Water is a very weak electrolyte. It undergoes ionization to a very small extent.

  $H_2O\ (l) \rightleftharpoons H^+(aq) + OH^-(aq)$ *Autoionization of water*

  $2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

  acid   base   conjugate acid   conjugate base

- The equilibrium expression of water autoionization is:

  $K_w = [H^+][OH^-]$ or $K_w = [H_3O^+][OH^-]$

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Equilibrium Constant of Water Autoionization Reaction

$$K_w = [H^+] [OH^-] \quad \text{or} \quad K_w = [H_3O^+] [OH^-]$$
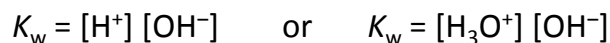
- At 25°C for pure water:

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \ M.$$

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- One can influence the concentrations of $[H_3O^+]$ or $[OH^-]$ by adding an acid or base to pure water. However, at 25°C, the product of the hydronium ion and hydroxide ion concentrations is always constant.

- For example, if you add an acid to pure water, $[H_3O^+]$ increases and $[OH^-]$ decreases (*a new equilibrium position*), yet K_w remains constant.

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Equilibrium Constant in Aqueous Solutions

- For any aqueous solution:

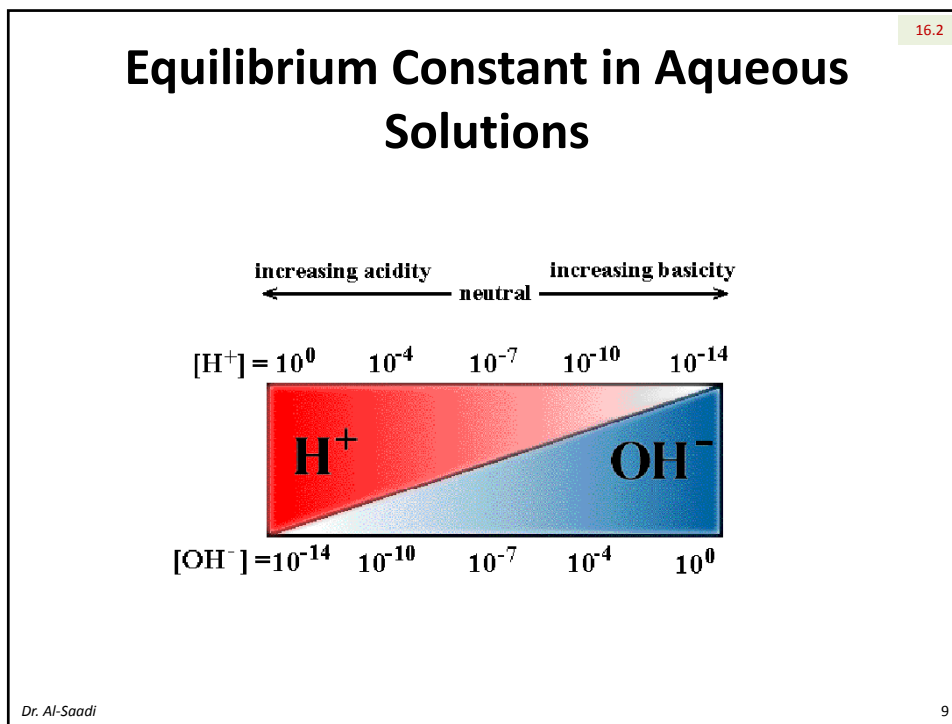$$K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14} \qquad \text{at 25°C}$$

- Remember that K_w is always constant at a given temperature.

   However, there can be infinite possibilities of the equilibrium positions for aqueous solution.

   o When $[H_3O^+] = [OH^-]$; the solution is *neutral*.

   o When $[H_3O^+] > [OH^-]$; the solution is *acidic*.

   o When $[H_3O^+] < [OH^-]$; the solution is *basic*.

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Equilibrium Constant in Aqueous Solutions

16.2

increasing acidity   increasing basicity
              neutral

$[H^+] = 10^0$ 10^{-4} 10^{-7} 10^{-10} 10^{-14}

H^+ OH^-

$[OH^-] = 10^{-14}$ 10^{-10} 10^{-7} 10^{-4} 10^0

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Equilibrium Constant in Aqueous Solutions

16.2

- Exercise:

  Calculate [OH⁻] in a solution in which the concentration of protons is 0.0012 *M* at 25°C. Is the solution acidic, basic or neutral?

  At 25°C, K_w is always equal to 1×10^{-14} .

  K_w =   [H₃O⁺]   [OH⁻]

  1×10^{-14} = (0.0012) [OH⁻]

  [OH⁻] = 1×10^{-14} / 0.0012 = 8.3×10^{-12} *M*

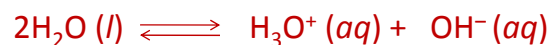 The solution is acidic.

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Equilibrium Constant in Aqueous Solutions

- Exercise:

  At 60°C, the value of K_w is 1×10^{-13} .

  (a) Predict whether the reaction:

  $$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

  is exothermic or endothermic.

  Since K_w increases with temperature, the reaction must be *endothermic*.

  (b) Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 60°C.

  At 60°C, $K_w = [H^+][OH^-] = 1 \times 10^{-13}$; and $[H^+] = [OH^-]$

  $$1 \times 10^{-13} = [H^+]\ [H^+]$$

  $$[H^+] = (1 \times 10^{-13})^{1/2} = 3 \times 10^{-7}$$

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11

The pH Scale

- The **pH scale** is a convenient way to express the *acidity* and *basicity* of a solution (the concentration of H_3O^+ ions).

  The pH of a solution is defined as:

  $$pH = -\log [H_3O^+] \text{ or } pH = -\log [H^+]$$

- Example:

  Two solutions with hydronium ion concentrations of 1.0×10^{-4} *M* and 5.0×10^{-9} *M*. Find their pH values.

  2 sig. fig.

  The first solution;   pH = - log (1.0×10^{-4}) = 4.00

  The second solution;   pH = - log (5.0×10^{-9}) = 8.30

  2 decimal places

  The number of sig. fig in the log is equal to the number of decimal places in the answer
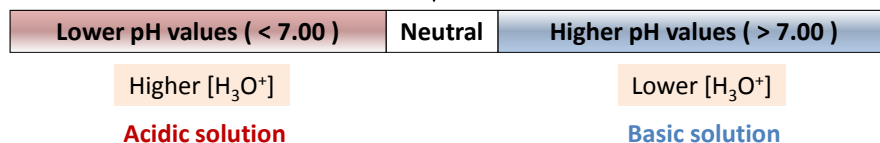
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12

6

The pH Scale

▪ Exercise:

Find the pH of a neutral solution.

A neutral solution has $[H_3O^+] = [OH^-]$.

Since $K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14}$

then $[H_3O^+] = 1.0 \times 10^{-7}$

$pH = - \log (1.0 \times 10^{-7}) = 7.00$

↓

Lower pH values (< 7.00)	Neutral	Higher pH values (> 7.00)
Higher $[H_3O^+]$		Lower $[H_3O^+]$
Acidic solution		**Basic solution**

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The pH Values vs. Hydronium Ion Concentrations

TABLE 16.3	Benchmark pH Values for a Range of Hydronium Ion Concentrations at 25°C		
$[H_3O^+](M)$	$-\log [H_3O^+]$	pH	
0.10	$-\log (1.0 \times 10^{-1})$	1.00	
0.010	$-\log (1.0 \times 10^{-2})$	2.00	
1.0×10^{-3}	$-\log (1.0 \times 10^{-3})$	3.00	
1.0×10^{-4}	$-\log (1.0 \times 10^{-4})$	4.00	
1.0×10^{-5}	$-\log (1.0 \times 10^{-5})$	5.00	
1.0×10^{-6}	$-\log (1.0 \times 10^{-6})$	6.00	Acidic
1.0×10^{-7}	$-\log (1.0 \times 10^{-7})$	7.00	Neutral
1.0×10^{-8}	$-\log (1.0 \times 10^{-8})$	8.00	Basic
1.0×10^{-9}	$-\log (1.0 \times 10^{-9})$	9.00	
1.0×10^{-10}	$-\log (1.0 \times 10^{-10})$	10.00	
1.0×10^{-11}	$-\log (1.0 \times 10^{-11})$	11.00	
1.0×10^{-12}	$-\log (1.0 \times 10^{-12})$	12.00	
1.0×10^{-13}	$-\log (1.0 \times 10^{-13})$	13.00	
1.0×10^{-14}	$-\log (1.0 \times 10^{-14})$	14.00	

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The pH Meter

- A pH meter is commonly used in laboratories to determine the pH of solutions.
- The pH meter is an electrical device with a probe that measures the proton concentration in a solution and displays the pH value.

The pH Scale

TABLE 16.4	pH Values of Some Common Fluids		
Fluid	**pH**	**Fluid**	**pH**
Stomach acid	1.0	Saliva	6.4−6.9
Lemon juice	2.0	Milk	6.5
Vinegar	3.0	Pure water	7.0
Grapefruit juice	3.2	Blood	7.35−7.45
Orange juice	3.5	Tears	7.4
Urine	4.8−7.5	Milk of magnesia	10.6
Rainwater (in clean air)	5.5	Household ammonia	11.5

Since   pH = -log $[H_3O^+]$
then

$$[H_3O^+] = 10^{-pH}$$

A measured pH is a convenient way to determine the concentration of hydronium ions in solutions

16.3

The pH Scale

- Exercise:

  What is the pH of a solution that has a hydronium ion concentration of 6.5 x $10^{-5}M$?

- Exercise:

  What is the hydronium ion concentration of a solution with pH 3.65?

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17

16.3

The pOH Scale

- A **pOH scale** is analogous to the pH scale. It is defined as:

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

  Also,

  $$[OH^-] = 10^{-pOH}$$

$[OH^-]$ (M)	pOH	
0.10	1.00	
1×10^{-3}	3.00	
1×10^{-5}	5.00	Basic
1×10^{-7}	7.00	Neutral
1×10^{-9}	9.00	Acidic
1×10^{-11}	11.00	
1×10^{-13}	13.00	

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18

The pOH Scale

- Recall that at 25°C:

$$K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

$$-\log([H_3O^+][OH^-]) = -\log(1.0 \times 10^{-14})$$

$$-\log[H_3O^+] - \log[OH^-] = 14.00$$

$$\text{pH} + \text{pOH} = 14.00$$

[OH⁻] (M)	pOH	pH	
0.10	1.00	13.00	↑
1×10^{-3}	3.00	11.00	
1×10^{-5}	5.00	9.00	Basic
1×10^{-7}	7.00	7.00	Neutral
1×10^{-9}	9.00	5.00	Acidic
1×10^{-11}	11.00	4.00	
1×10^{-13}	13.00	1.00	↓

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The pOH Scale

- Exercise:
  What is the pOH of a solution that has a hydroxide ion concentration of 4.3×10^{-2} M?

- Exercise:
  What is the hydroxide ion concentration of a solution with pOH 8.35?

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The pH and pOH Scale

▪ Exercise:

What is the hydroxide ion concentration and the pOH of a solution that has pH 9.45 at 25°C?

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Strong Acids and Bases

▪ Strong acids and strong bases are *completely* ionized when dissolved in water.

TABLE 4.1	The Strong Acids
Acid	**Ionization Equation**
Hydrochloric acid	$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$
Hydrobromic acid	$HBr(aq) \longrightarrow H^+(aq) + Br^-(aq)$
Hydroiodic acid	$HI(aq) \longrightarrow H^+(aq) + I^-(aq)$
Nitric acid	$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$
Chloric acid	$HClO_3(aq) \longrightarrow H^+(aq) + ClO_3^-(aq)$
Perchloric acid	$HClO_4(aq) \longrightarrow H^+(aq) + ClO_4^-(aq)$
Sulfuric acid*	$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$

*Note that although each sulfuric acid molecule has two ionizable hydrogen atoms, it only undergoes the first ionization completely, effectively producing one H⁺ ion and one HSO₄⁻ ion per H₂SO₄ molecule. The second ionization happens only to a very small extent.

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Strong Acids

- Because strong acids are completely ionized in aqueous solutions, it is easy to determine the pH of that solution.

$$[H_3O^+]_{eq} = [\text{strong acid}]_{initial}$$

- Exercise:

  Calculate the concentration of HNO_3 and the pH of an aqueous solution that is 6.7×10^{-5} M in HNO_3 at 25°C.

Strong Bases

- Strong bases are also *completely* ionized in aqueous solutions. They are:

  - the hydroxides of the alkaline metals (Li, Na, K, Rb and Cs), and

    Group 1A $\text{LiOH}\,(aq) \longrightarrow \text{Li}^+(aq) + \text{OH}^-(aq)$

  - the hydroxides of the heaviest earth alkaline metals (Ca, Sr and Ba).

    Group 2A $\text{Ca(OH)}_2\,(aq) \longrightarrow \text{Ca}^{2+}(aq) + \textbf{2}\text{OH}^-(aq)$

  $$[OH^-]_{eq} = [\text{strong base}]_{initial}$$

- The pH of solutions containing a strong base can be easily calculated.

pH of Strong Bases

- Exercise:

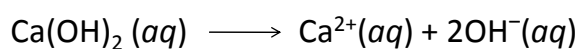 A 10.00-L solution contains 0.72 mol of NaOH at 25°C. Find its pH?

pH of Strong Bases

- Exercise:

  At 25°C, what is the pH of a solution that is 0.034 M in $Ca(OH)_2$?

  $Ca(OH)_2$ completely ionizes, and the $[OH^-]$ is equal to twice the initial concentration of $Ca(OH)_2$.

  $$Ca(OH)_2 \ (aq) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

  $$[OH^-] = 0.034 \ M \ Ca(OH)_2 \times \frac{2 \ mol \ OH^-}{1 \ mol \ Ca(OH)_2} = 0.068 \ M$$

  $pOH = -\log(0.068) = 1.17$

  At 25°C ; pH + pOH = 14.00

  pH = 14.00 − 1.17 = 12.83

Weak Acids

Molar concentrations

- Most of the acids are weak acids.

- Weak acids are NOT completely ionized in water. They are ionized in water *only to a limited extent*.

- The degree of dissociation of a weak acid depends on:
  o acid concentration.
  o equilibrium constant.

Before dissociation

After dissociation, at equilibrium

HA

H^+ A^-

Strong acids

HA

HA

Weak acids

H^+ A^-

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27

The Acid Ionization Constant

- For a weak *monoprotic* acid HA:

$$HA(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

or:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

the equilibrium expression is:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

- K_a is called the ***acid ionization constant***. Its magnitude indicates how strong a weak acid is.
  o Large K_a values indicates a stronger acid.
  o Smaller K_a values indicates a weaker acid.

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28

14

The Acid Ionization Constant

TABLE 16.6	Ionization Constants of Some Weak Acids at 25°C		
Name of Acid	Formula	Structure	K_a
Hydrofluoric acid	HF	H—F	7.1×10^{-4}
Nitrous acid	HNO_2	O=N—O—H	4.5×10^{-4}
Formic acid	HCOOH	$H—\overset{\overset{O}{\|\|}}{C}—O—H$	1.7×10^{-4}
Benzoic acid	C_6H_5COOH	⬡—$\overset{\overset{O}{\|\|}}{C}$—O—H	6.5×10^{-5}
Acetic acid	CH_3COOH	$CH_3—\overset{\overset{O}{\|\|}}{C}—O—H$	1.8×10^{-5}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}
Phenol	C_6H_5OH	⬡—O—H	1.3×10^{-10}

The larger the K_a value, the stronger the acid is.

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29

Calculating pH from K_a

- Exercise:

  Calculate the pH at 25°C of a 0.18 M solution of a weak acid that has K_a = 9.2 x 10^{-6}.

$$K_a = \frac{[H^+] \, [A^-]}{[HA]} = 9.2 \text{ x } 10^{-6}$$

We use the same method we studied in the previous chapter.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	HA	H^+	A^-
Initial concentration (M):	0.18	0	0
Change in concentration (M):	$-x$	$+x$	$+x$
Equilibrium concentration (M):	$0.18 - x$	x	x

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Continue on the next slide ⟶ 30

15

$$K_a = \frac{[H^+] [A^-]}{[HA]} = 9.2 \times 10^{-6} = \frac{(x)(x)}{0.18 - x} = \frac{x^2}{0.18 - x}$$

Since K_a is very small compared to the initial acid concentration, we can make use of a useful approximation instead of solving the problem using a quadratic equation.

The 5% rule $\dfrac{x^2}{0.18 - x} \approx \dfrac{x^2}{0.18} = 9.2 \times 10^{-6}$

Solving for x:

$$x = 1.3 \times 10^{-3} \ M$$

The above approximation is valid only when x is significantly smaller than the $[HA]_{initial}$.

(x must be less than 5% of $[HA]_{initial}$ in order for the above approximation to be valid).

$$pH = -\log [H^+]$$
$$= -\log (1.3 \times 10^{-3})$$
$$= 2.89$$

Check the validity => $\dfrac{1.3 \times 10^{-3}}{0.18}$ X 100% = 0.72%   < 5%   ✓ OK

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Calculating pH from K_a

- Exercise:

  Try the previous example again with a 0.018 *M* solution at 25°C.

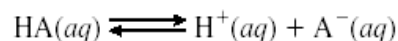*Dr. Al-Saadi*   32

Calculating K_a from pH

- **Exercise:**

  An aqueous solution that is 0.25 M in a monoprotic weak acid has a pH of 3.47 at 25°C. Find its K_a.

  $[HA]_{initial}$ = 0.25 M
  $[H^+]_{eq}$ = $10^{-3.47}$ = 3.39 x 10^{-4} M

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	HA	H⁺	A⁻
Initial concentration (M):	0.25	0	0
Change in concentration (M):	−3.39 x 10^{-4}	+3.39 x 10^{-4}	+3.39 x 10^{-4}
Equilibrium concentration (M):	0.2497	3.39 x 10^{-4}	3.39 x 10^{-4}

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{(3.39 \times 10^{-4})^2}{0.2497} = 4.6 \times 10^{-7}$$

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Weak Bases

- Most of the bases are weak bases. Weak bases are not ionized completely when dissolved in water.

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

weak base conjugate acid conjugate base

  The equilibrium expression for the ionization of a weak base is:

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

- K_b is called the ***base ionization constant***. Its magnitude indicates how strong a weak base is.

  o Large K_b values indicates a stronger base.

  o Smaller K_b values indicates a weaker base.

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17

Weak Bases

16.6

TABLE 16.7	Ionization Constants of Some Weak Bases at 25°C		
Name of Base	**Formula**	**Structure**	K_b
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{..}{N}-H$	5.6×10^{-4}
Methylamine	CH_3NH_2	$CH_3-\overset{..}{N}-H$	4.4×10^{-4}
Ammonia	NH_3	$H-\overset{..}{N}-H$	1.8×10^{-5}
Pyridine	C_5H_5N	(ring)$\overset{..}{N}$:	1.7×10^{-9}
Aniline	$C_6H_5NH_2$	(ring)$-\overset{..}{N}-H$	3.8×10^{-10}
Urea	H_2NCONH_2	$H-\overset{..}{N}-\overset{O}{C}-\overset{..}{N}-H$	1.5×10^{-14}

The larger the K_b value, the stronger the base is.

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Weak Bases

16.6

TABLE 16.7	Ionization Constants of Some Weak Bases at 25°C	
Name of Base	**Formula**	**Structure**
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{..}{N}-H$
Methylamine	CH_3NH_2	$CH_3-\overset{..}{N}-H$
Ammonia	NH_3	$H-\overset{..}{N}-H$
Pyridine	C_5H_5N	(ring)$\overset{..}{N}$:
Aniline	$C_6H_5NH_2$	(ring)$-\overset{..}{N}-H$
Urea	H_2NCONH_2	$H-\overset{..}{N}-\overset{O}{C}-\overset{..}{N}-H$

- **What does make these weak bases able to accept H+?**

The lone pair of electrons on the N atom enables these weak bases to grab H+ ions from Brønsted acids.

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16.6

Solving Problems Involving Weak Bases

- Solving problems involving weak bases requires the same approach used for weak acids.

  Make sure you notice that solving for *x* in a weak-base problem gives the hydroxide ion concentration rather than the hydronium ion concentration.

16.6

Solving Problems Involving Weak Bases

- Exercise:

  Determine the K_b of a weak base if a 0.50 *M* solution of the base has a pH of 9.59 at 25°C.

  At 25°C:
  pOH = 14.00 − pH = 14.00 − 9.59 = 4.41
  $[OH^-] = 10^{-4.41} = 3.89 \times 10^{-5}$ *M*.

	B(aq) +	H$_2$O(l) $\rightleftharpoons$	BH$^+$(aq) +	OH$^-$(aq)
Initial concentration (*M*):	0.50		0	0
Change in concentration (*M*):	-3.89×10^{-5}		$+3.89 \times 10^{-5}$	$+3.89 \times 10^{-5}$
Equilibrium concentration (*M*):	0.49996		3.89×10^{-5}	3.89×10^{-5}

16.6

Solving Problems Involving Weak Bases

- Exercise (*Continue*):

  Determine the K_b of a weak base if a 0.50 M solution of the base has a pH of 9.59 at 25°C.

  $$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(3.89 \times 10^{-5})^2}{0.49996}$$

  $$K_b = 3.0 \times 10^{-9}$$

Dr. Al-Saadi 39