



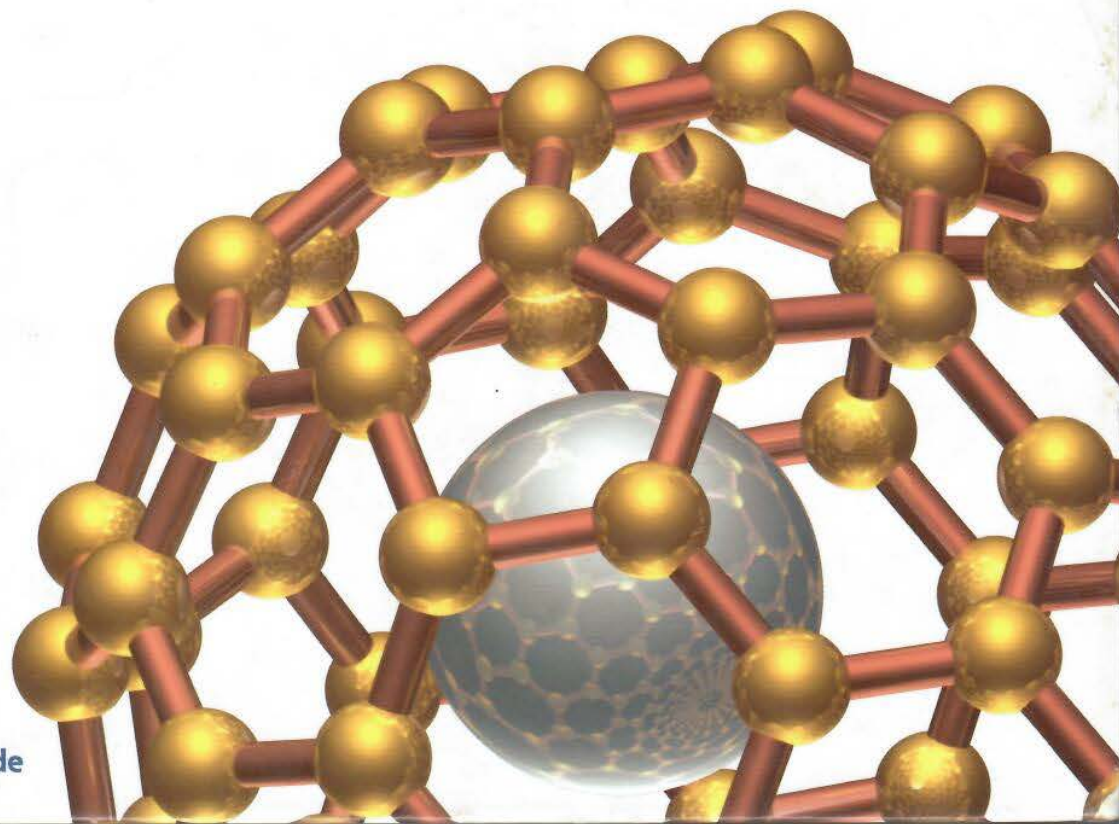
For Advanced  
High School  
Chemistry

Brown LeMay Bursten

# CHEMISTRY

THE CENTRAL SCIENCE

Revised Eighth Edition



# Chemistry

## The Central Science

Eighth Revised Edition

Theodore L. Brown

University of Illinois at Urbana-Champaign

H. Eugene LeMay, Jr.

University of Nevada, Reno

Bruce E. Bursten

The Ohio State University

With contributions by Julia R. Burdge, University of Akron

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Printed in the United States of America  
10 9 8 7 6 5 4 3 2 1

ISBN 0-13-061142-5

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**rotic Acids**

$K_{a3}$

$4.0 \times 10^{-7}$

$4.2 \times 10^{-8}$

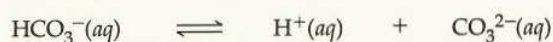
Solving for  $x$ , we have  $x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$

$$x = [\text{H}^+] = [\text{HCO}_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5} \text{ M}$$

The small value of  $x$  indicates that our simplifying assumption was justified. The pH is therefore

$$\text{pH} = -\log [\text{H}^+] = -\log (4.0 \times 10^{-5}) = 4.40$$

If we were asked to solve for  $[\text{CO}_3^{2-}]$ , we would need to use  $K_{a2}$ . Let's illustrate that calculation. Using the values of  $[\text{HCO}_3^-]$  and  $[\text{H}^+]$  calculated above, and setting  $[\text{CO}_3^{2-}] = y$ , we have the following initial and equilibrium concentration values:



Initial	$4.0 \times 10^{-5} \text{ M}$	$4.0 \times 10^{-5} \text{ M}$	0
Change	$-y \text{ M}$	$+y \text{ M}$	$+y \text{ M}$
Equilibrium	$(4.0 \times 10^{-5} - y) \text{ M}$	$(4.0 \times 10^{-5} + y) \text{ M}$	$y \text{ M}$

Assuming that  $y$  is small compared to  $4.0 \times 10^{-5}$ , we have

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11} \text{ M} = [\text{CO}_3^{2-}]$$

The value calculated for  $y$  is indeed very small in comparison to  $4.0 \times 10^{-5}$ , showing that our assumption was justified. It also shows that the ionization of  $\text{HCO}_3^-$  is negligible in comparison to that of  $\text{H}_2\text{CO}_3$  as far as production of  $\text{H}^+$  is concerned. However, it is the *only* source of  $\text{CO}_3^{2-}$ , which has a very low concentration in the solution.

Our calculations thus tell us that in a solution of carbon dioxide in water most of the  $\text{CO}_2$  is in the form of  $\text{CO}_2$  or  $\text{H}_2\text{CO}_3$ , a small fraction ionizes to form  $\text{H}^+$  and  $\text{HCO}_3^-$ , and an even smaller fraction ionizes to give  $\text{CO}_3^{2-}$ .

**PRACTICE EXERCISE**

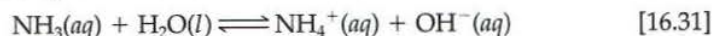
Calculate the pH and concentration of oxalate ion,  $[\text{C}_2\text{O}_4^{2-}]$ , in a 0.020 M solution of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$  (see Table 16.3). **Answers:** pH = 1.80;  $[\text{C}_2\text{O}_4^{2-}] = 6.4 \times 10^{-5} \text{ M}$

## 16.7 Weak Bases

Many substances behave as weak bases in water. Such substances react with water, removing protons from  $\text{H}_2\text{O}$ , thereby forming the conjugate acid of the base and  $\text{OH}^-$  ions:



The most commonly encountered weak base is ammonia:



The equilibrium-constant expression for this reaction can be written as

$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \quad [16.32]$$

Because the concentration of water is essentially constant, the  $[\text{H}_2\text{O}]$  term is incorporated into the equilibrium constant, giving

$$K_b = K[\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad [16.33]$$

The constant  $K_b$  is called the **base-dissociation constant**, by analogy with the

TABLE 16.4 Some Weak Bases and Their Aqueous Solution Equilibria

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	$K_b$
Ammonia ( $\text{NH}_3$ )		$\text{NH}_4^+$	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$
Pyridine ( $\text{C}_5\text{H}_5\text{N}$ )		$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	$1.7 \times 10^{-9}$
Hydroxylamine ( $\text{H}_2\text{NOH}$ )		$\text{H}_3\text{NOH}^+$	$\text{H}_2\text{NOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{NOH}^+ + \text{OH}^-$	$1.1 \times 10^{-6}$
Methylamine ( $\text{NH}_2\text{CH}_3$ )		$\text{NH}_3\text{CH}_3^+$	$\text{NH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{CH}_3^+ + \text{OH}^-$	$4.4 \times 10^{-4}$
Hydrosulfide ion ( $\text{HS}^-$ )		$\text{H}_2\text{S}$	$\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{OH}^-$	$1.8 \times 10^{-7}$
Carbonate ion ( $\text{CO}_3^{2-}$ )		$\text{HCO}_3^-$	$\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$	$1.8 \times 10^{-4}$
Hypochlorite ion ( $\text{ClO}^-$ )		$\text{HClO}$	$\text{ClO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{OH}^-$	$3.3 \times 10^{-7}$

(Notice the equilibrium-constant expression)

Because  $K_b$  compared to 0.15 M. The

Notice that 0.15 M. The

**PRACTICE**  
Which of the following is a weak base: pyridine

### Types of V

How can we determine if a substance is a weak base? We can use the first category of electrophilic substitution reactions. These substances are amines. In the case of  $\text{NH}_3$  with  $\text{CH}_3\text{NH}_2$ , forming an

equilibrium in which a base reacts with  $\text{H}_2\text{O}$  to form the conjugate acid and  $\text{OH}^-$ . Table 16.4 lists the names, formulas, Lewis structures, equilibrium reactions, and values of  $K_b$  for several weak bases in water. Appendix D includes a more extensive list. Notice that these bases contain one or more lone pairs of electrons. A lone pair is necessary to form the bond with  $\text{H}^+$ . Notice also that in the neutral molecules the lone pairs are on nitrogen atoms and that the other bases are anions derived from weak acids.

#### SAMPLE EXERCISE 16.14

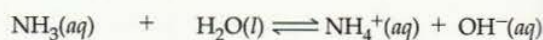
Calculate the concentration of  $\text{OH}^-$  in a 0.15 M solution of  $\text{NH}_3$ .

**Solution** We use essentially the same procedure here as used in solving problems involving the ionization of weak acids. The first step is to write the ionization reaction and the corresponding equilibrium-constant ( $K_b$ ) expression:



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

We then tabulate the equilibrium concentrations involved in the equilibrium:



Initial	0.15 M	—	0	0
Change	$-x$ M	—	$+x$ M	$+x$ M
Equilibrium	$(0.15 - x)$ M	—	$x$ M	$x$ M

H—i  
I

The chemical  $\text{CH}_3\text{NH}_3^+$ .

The second weak acid is hypochlorite,  $\text{NaClO}$ . The hypochlorite ion is always present, the

$\text{ClO}^-$

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