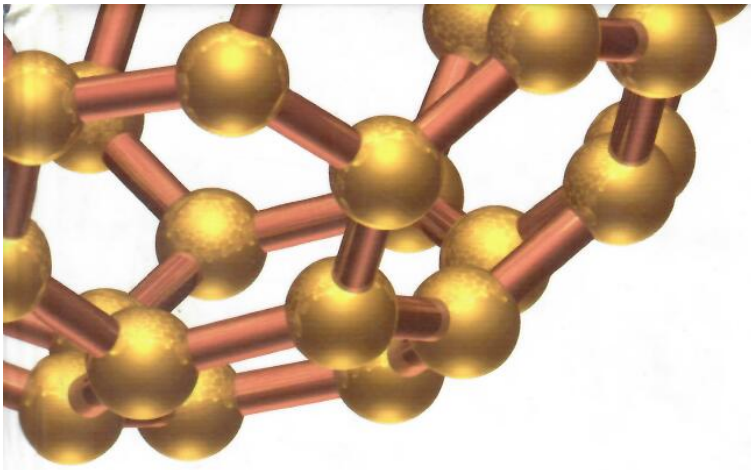

For Advanced High School Chemistry

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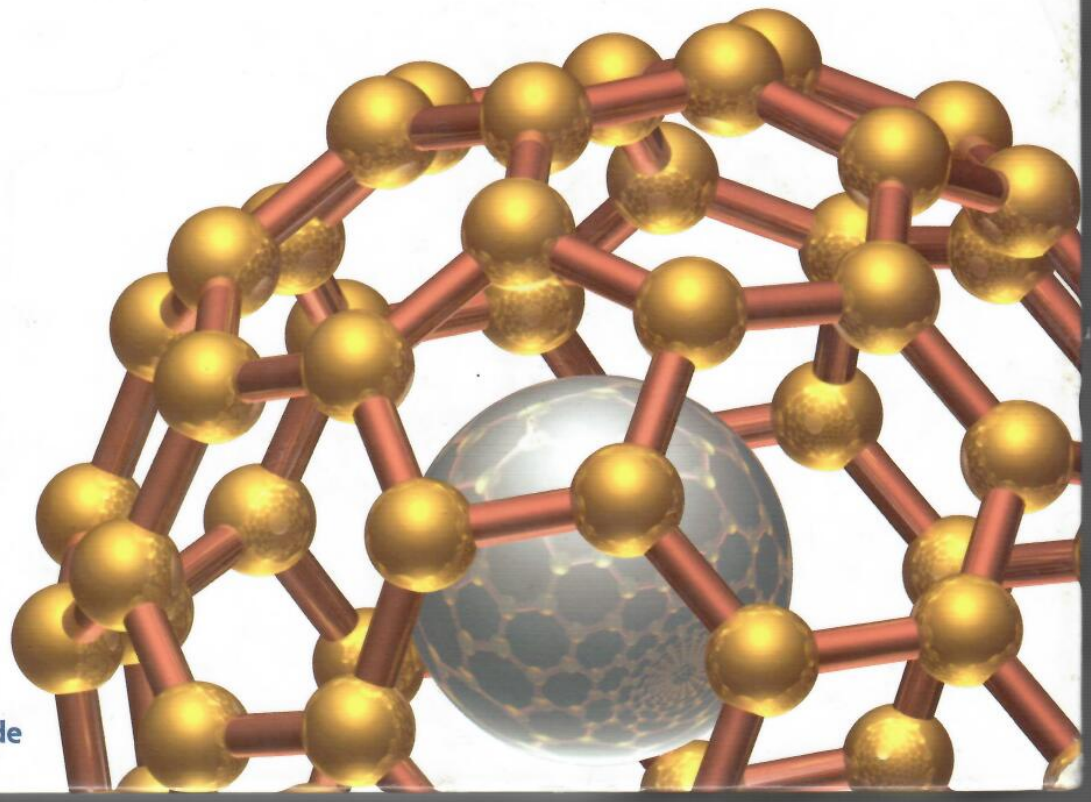

CD-ROM Inside

Chemistry

The Central Science

Eighth Revised Edition

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

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\ M$$

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

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

If we were asked to solve for $[CO_3^{2-}]$, we would need to use K_{a2}. Let's illustrate that calculation. Using the values of $[HCO_3^-]$ and $[H^+]$ calculated above, and setting $[CO_3^{2-}] = y$, we have the following initial and equilibrium concentration values:

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

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

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

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\ M = [CO_3^{2-}]$$

The value calculated for y is indeed very small in comparison to 4.0×10^{-5}, showing that our assumption was justified. It also shows that the ionization of HCO_3^- is negligible in comparison to that of H_2CO_3 as far as production of H^+ is concerned. However, it is the *only* source of 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 CO_2 is in the form of CO_2 or H_2CO_3, a small fraction ionizes to form H^+ and HCO_3^-, and an even smaller fraction ionizes to give CO_3^{2-}.

PRACTICE EXERCISE

Calculate the pH and concentration of oxalate ion, $[C_2O_4^{2-}]$, in a 0.020 M solution of oxalic acid, $H_2C_2O_4$ (see Table 16.3). ***Answers:*** pH = 1.80; $[C_2O_4^{2-}] = 6.4 \times 10^{-5}\ M$

16.7 Weak Bases

Many substances behave as weak bases in water. Such substances react with water, removing protons from H_2O, thereby forming the conjugate acid of the base and OH^- ions:

$$\text{Weak base} + H_2O \rightleftharpoons \text{conjugate acid} + OH^- \qquad [16.30]$$

The most commonly encountered weak base is ammonia:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [16.31]$$

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

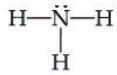
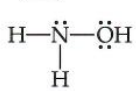
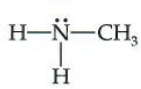
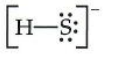
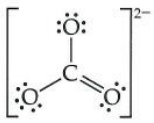
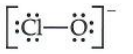
$$K = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]} \qquad [16.32]$$

Because the concentration of water is essentially constant, the $[H_2O]$ term is incorporated into the equilibrium constant, giving

$$K_b = K[H_2O] = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad [16.33]$$

The constant K_b is called the **base-dissociation constant**, by analogy with the acid-dissociation constant, K_a, for weak acids. *The constant K_b always refers to the equi-*

TABLE 16.4 Some Weak Bases and Their Aqueous Solution Equilibria

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)		NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)		H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)		$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)		$HClO$	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

librium in which a base reacts with H_2O to form the conjugate acid and 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 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 OH^- in a 0.15 *M* solution of 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:

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

We then tabulate the equilibrium concentrations involved in the equilibrium:

	$NH_3(aq)$ +	$H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial	0.15 *M*	—	0	0
Change	$-x$ *M*	—	$+x$ *M*	$+x$ *M*
Equilibrium	$(0.15 - x)$ *M*	—	x *M*	x *M*

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