

8.6 At equilibrium,  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$[\text{H}^+] = [\text{A}^-] = (0.135)(0.040\text{ M}) = 5.40 \times 10^{-3}\text{ M}$$

$$[\text{HA}] = (1 - 0.135)(0.040\text{ M}) = 3.46 \times 10^{-2}\text{ M}$$

The dissociation constant,  $K_a$ , of the acid is therefore

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(5.40 \times 10^{-3})^2}{3.46 \times 10^{-2}} = 8.4 \times 10^{-4}$$

8.8 The dissociation constant of a monoprotic acid at 298 K is  $1.47 \times 10^{-3}$ . Calculate the degree of dissociation by (a) assuming ideal behavior and (b) using a mean activity coefficient  $\gamma_{\pm} = 0.93$ . The concentration of the acid is 0.010 M.

Let  $\alpha$  be the degree of dissociation of the monoprotic acid. The corresponding concentrations of all species are

	HA	$\rightleftharpoons$	H <sup>+</sup>	+	A <sup>-</sup>	
Initial	0.010		0		0	M
At equilibrium	0.010 (1 - $\alpha$ )		0.010 $\alpha$		0.010 $\alpha$	M

(a)

$$K_a = 1.47 \times 10^{-3} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.010\alpha)^2}{0.010(1 - \alpha)}$$

$$1.0 \times 10^{-4}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$

$$\alpha = 0.32$$

Therefore, assuming ideal behavior, the acid is 32% dissociated.

(b)

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

Since HA is an uncharged species and the solution is dilute,  $\gamma_{\text{HA}}$  is approximately 1. Furthermore,  $\gamma_+\gamma_- = \gamma_{\pm}^2$ . The  $K_a$  expression becomes

$$K_a = 1.47 \times 10^{-3} = \frac{[\text{H}^+][\text{A}^-]\gamma_{\pm}^2}{[\text{HA}]} = \frac{(0.010\alpha)^2(0.93)^2}{0.010(1 - \alpha)}$$

$$8.65 \times 10^{-5}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$

$$\alpha = 0.34$$

Therefore, accounting for non-ideality, the acid is 34% dissociated.

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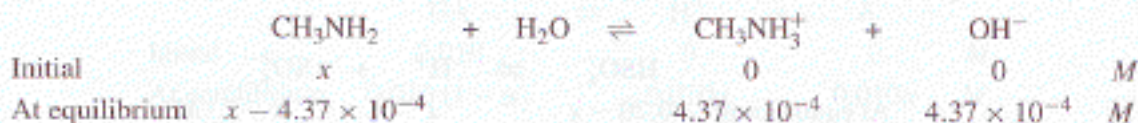
**8.16** A solution of methylamine ( $\text{CH}_3\text{NH}_2$ ) has a pH of 10.64. How many grams of methylamine are in 100.0 mL of the solution?

Methylamine is a base. It ionizes to give equal concentrations of  $\text{CH}_3\text{NH}_3^+$  and  $\text{OH}^-$ , which can be calculated from the pH of the solution.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.64 = 3.36$$

$$[\text{OH}^-] = 10^{-3.36} = 4.37 \times 10^{-4} \text{ M}$$

Let  $x \text{ M}$  of methylamine be present initially. The equilibrium concentration is then  $x - 4.37 \times 10^{-4} \text{ M}$ . The concentrations of various species are written below the chemical equation.



$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(4.37 \times 10^{-4})^2}{x - 4.37 \times 10^{-4}}$$

$$x = 8.73 \times 10^{-4}$$

where  $x$  represents the initial concentration of  $\text{CH}_3\text{NH}_2$  in solution.

The mass of methylamine can now be calculated.

$$\text{Number of moles of methylamine} = (8.73 \times 10^{-4} \text{ M})(0.100 \text{ L}) = 8.73 \times 10^{-5} \text{ mol}$$

$$\text{Mass of methylamine} = (8.73 \times 10^{-5} \text{ mol})(31.06 \text{ g mol}^{-1}) = 2.7 \times 10^{-3} \text{ g}$$

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**HW7** (a) Calculate the percent ionization of a 0.20 *M* solution of the monoprotic acetylsalicylic acid (aspirin,  $C_9H_8O_4$ ) for which  $K_a = 3.0 \times 10^{-4}$ . (b) The pH of gastric juice in the stomach of a certain individual is 1.00. After a few aspirin tablets have been swallowed, the concentration of acetylsalicylic acid in the stomach is 0.20 *M*. Calculate the percent ionization of the acid under these conditions.

(a) The ionization reaction is

	$C_9H_8O_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_9H_7O_4^-(aq)$	
Initial	0.20		0		0	<i>M</i>
At equilibrium	$0.20 - x$		$x$		$x$	<i>M</i>

$$K_a = 3.0 \times 10^{-4} = \frac{x^2}{0.20 - x}$$

$$x^2 + 3.0 \times 10^{-4}x - 6.0 \times 10^{-5} = 0$$

$$x = 7.60 \times 10^{-3}$$

Therefore, the percent ionization is

$$\frac{x}{0.20} \times 100\% = 3.8\%$$

(b) At pH 1.00 the concentration of  $H^+$  is 0.10 *M*. According to Le Chatelier's principle, this will suppress the ionization of acetylsalicylic acid. The  $H^+$  contribution from the ionization of the acetylsalicylic acid is negligible compared with the  $H^+$  concentration in gastric juice, and to two-significant-figure accuracy, this contribution is ignored. The percent ionization of the acid can be obtained using the equilibrium expression:

$$K_a = \frac{[H^+][C_9H_7O_4^-]}{[C_9H_8O_4]}$$

$$\% \text{ ionization} = \frac{[C_9H_7O_4^-]}{[C_9H_8O_4]} \times 100\% = \frac{K_a}{[H^+]} = \frac{3.0 \times 10^{-4}}{0.1} \times 100\% = 0.30\%$$

Although the acetylsalicylic acid has negligible effect on the pH of the gastric juices, the high acidity of the gastric juices appears to enhance the rate of absorption of nonionized aspirin molecules through the stomach lining. In some cases this can irritate these tissues and cause bleeding.