

17. ACID-BASE EQUILIBRIA

■ Solutions to Exercises

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 17.1 Abbreviate the formula of lactic acid as HL. To solve, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	HL + H ₂ O		H ₃ O ⁺ + L ⁻
Starting	0.025		0 0
Change	-x		+x +x
Equilibrium	0.025 - x		x x

Substituting into the equilibrium-constant equation gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} = \frac{(x)^2}{(0.025 - x)}$$

The value of x equals the value of the molarity of the H₃O⁺ ion, which can be obtained from the pH:

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2.75) = 0.00178 \text{ M}$$

(continued)


Substitute this value for x into the equation to get

$$K_a = \frac{(x)^2}{(0.025 - x)} = \frac{(0.00178)^2}{(0.025 - 0.00178)} = 1.36 \times 10^{-4} = 1.4 \times 10^{-4}$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.00178}{0.025} = 0.071$$

- 17.2 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HAc as the symbol for acetic acid.

Conc. (M)	HAc + H ₂ O		H ₃ O ⁺ + Ac ⁻
Starting	0.10		0 0
Change	-x		+x +x
Equilibrium	0.10 - x		x x

Now, substitute these concentrations and the value of K_a into the equilibrium-constant equation for acid ionization:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-5}$$

Solve the equation for x , assuming x is much smaller than 0.10, so $(0.10 - x) \cong 0.10$.

$$\frac{(x)^2}{(0.10)} \cong 1.7 \times 10^{-5}$$

$$x^2 = 1.7 \times 10^{-5} \times 0.10 = 1.7 \times 10^{-6}$$

$$x = 0.00130 \text{ M}$$

Check to make sure the assumption that $(0.10 - x) \cong 0.10$ is valid:

$$0.10 - 0.00130 = 0.0987, \cong 0.10 \quad (\text{to two significant figures})$$

The concentrations of hydronium ion and acetate ion are

$$[\text{H}_3\text{O}^+] = [\text{Ac}^-] = x = 0.0013 = 1.3 \times 10^{-3} \text{ M}$$

(continued)

The pH of the solution is

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.00130) = 2.884 = 2.88$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.00130}{0.10} = 0.0130 = 0.013$$

- 17.3 Abbreviate the formula for pyruvic acid as HPy. To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	HPy + H ₂ O	H ₃ O ⁺ + Py ⁻
Starting	0.0030	0
Change	-x	+x
Equilibrium	0.0030 - x	x

Substitute the equilibrium concentrations and the value of K_a into the equilibrium-constant equation to get

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Py}^-]}{[\text{HPy}]} = \frac{(x)^2}{(0.0030 - x)} = 1.4 \times 10^{-4}$$

Note that the concentration of acid divided by K_a is $0.0030/1.4 \times 10^{-4} = 21$, which is considerably smaller than 100. Thus, you can expect that x cannot be ignored compared with 0.0030. The quadratic formula must be used. Rearrange the preceding equation to put it into the form $ax^2 + bx + c = 0$.

$$x^2 + 1.4 \times 10^{-4}x - 4.20 \times 10^{-7} = 0$$

Substitute into the quadratic formula to get

$$\begin{aligned} x &= \frac{-1.4 \times 10^{-4} \pm \sqrt{(1.4 \times 10^{-4})^2 + 4(4.20 \times 10^{-7})}}{2} \\ &= \frac{-1.4 \times 10^{-4} \pm 1.303 \times 10^{-3}}{2} \end{aligned}$$

Using the positive root: $x = [\text{H}_3\text{O}^+] = 5.81 \times 10^{-4} \text{ M}$. Now you can calculate the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.81 \times 10^{-4}) = 3.2350 = 3.24$$

- 17.4 To solve, note that $K_{a1} = 1.3 \times 10^{-2} > K_{a2} = 6.3 \times 10^{-8}$, and hence the second ionization and K_{a2} can be ignored. Assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	$\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+ + \text{HSO}_3^-$
Starting	0.25		0 0
Change	-x		+x +x
Equilibrium	0.25 - x		x x

Substitute into the equilibrium-constant equation for the first ionization.

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = \frac{(x)^2}{(0.25 - x)} = 1.3 \times 10^{-2} = 0.013$$

This gives $x^2 + 0.013x - 0.00325 = 0$

Note that the concentration of acid divided by K_a is $0.25/0.013 = 19$, which is considerably smaller than 100. Thus, you can expect that x cannot be ignored compared with 0.25. Reorganize the above equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x = \frac{-0.013 \pm \sqrt{(0.013)^2 + 4(0.00325)}}{2}$$

$$= \frac{-0.013 \pm 0.1147}{2}$$

Using the positive root, $x = [\text{H}_3\text{O}^+] = 0.05087 \text{ M}$.

$$\text{pH} = -\log(0.05087) = 1.293$$

To calculate $[\text{SO}_3^{2-}]$, which will be represented by y , use the second ionization. Assume the starting concentrations of H_3O^+ and HSO_3^- are those from the first equilibrium.

Conc. (M)	$\text{HSO}_3^- + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+ + \text{SO}_3^{2-}$
Starting	0.05087		0 0
Change	-y		+y +y
Equilibrium	0.05087 - y		0.05087 + y y

(continued)

Now, substituting into the K_{a2} expression for the second ionization.

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = \frac{(0.0508 + y)(y)}{(0.0508 - y)} = 6.3 \times 10^{-8}$$

Assuming y is much smaller than 0.0508, note that the $(0.0508 + y)$ cancels the $(0.0508 - y)$ term leaving $y \cong K_{a2}$, or


$$y = [\text{SO}_3^{2-}] \cong 6.3 \times 10^{-8} \text{ M}$$

17.5 First, convert the pH to pOH, and then to $[\text{OH}^-]$:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.84 = 4.16$$

$$[\text{OH}^-] = \text{antilog}(-4.16) = 6.92 \times 10^{-5} \text{ M}$$

Using the symbol Qu for quinine, assemble a table of starting, change, and equilibrium concentrations.


Conc. (M)	Qu + H ₂ O		HQu ⁺ + OH ⁻
Starting	0.0015		0 0
Change	-x		+x +x
Equilibrium	0.0015 - x		x x

Note $x = 6.92 \times 10^{-5}$. Substitute into the equilibrium-constant equation to get

$$K_b = \frac{[\text{HQ}^+][\text{OH}^-]}{[\text{Qu}]} = \frac{(x)^2}{(0.0015 - x)} = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 6.92 \times 10^{-5})}$$

$$= 3.346 \times 10^{-6} = 3.3 \times 10^{-6}$$

17.6 Assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	NH ₃ + H ₂ O		NH ₄ ⁺ + OH ⁻
Starting	0.20		0 0
Change	-x		+x +x
Equilibrium	0.20 - x		x x

(continued)

Assume x is small enough to ignore compared with 0.20. Substitute into the equilibrium-constant equation to get :

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)^2}{(0.20 - x)} \cong \frac{(x)^2}{(0.20)} = 1.8 \times 10^{-5}$$

Solving for x gives

$$x^2 = (0.20) \times 1.8 \times 10^{-5} = 3.6 \times 10^{-6}$$

$$x = [\text{OH}^-] \cong 1.89 \times 10^{-3} \text{ M (Note } x \text{ is negligible compared to 0.20.)}$$

Now calculate the hydronium ion concentration.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-3}} = 5.29 \times 10^{-12} = 5.3 \times 10^{-12} \text{ M}$$

- 17.7 a. Acidic. NH_4NO_3 is the salt of a weak base (NH_4OH) and a strong acid (HNO_3), so a solution of NH_4NO_3 is acidic because of the hydrolysis of NH_4^+ .
- b. Neutral. KNO_3 is the salt of a strong base (KOH) and a strong acid (HNO_3), so a solution of NH_4NO_3 is neutral because none of the ions hydrolyze.
- c. Acidic. $\text{Al}(\text{NO}_3)_3$ is the salt of a weak base $[\text{Al}(\text{OH})_3]$ and a strong acid (HNO_3), so a solution of $\text{Al}(\text{NO}_3)_3$ is acidic because of the hydrolysis of Al^{3+} .

- 17.8 a. Calculate K_b of the F^- ion from the K_a of its conjugate acid, HF :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11} = 1.5 \times 10^{-11}$$

- b. Calculate K_a of $\text{C}_6\text{H}_5\text{NH}_3^+$ from K_b of its conjugate base, $\text{C}_6\text{H}_5\text{NH}_2$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^{-5} = 2.4 \times 10^{-5}$$

- 17.9 Assemble the usual table, writing HBen for benzoic acid and Ben⁻ for the benzoate ion. Let 0.015 - x equal the equilibrium concentration of the benzoate anion.

Conc. (M)	Ben ⁻ + H ₂ O	HBen + OH ⁻
Starting	0.015	0
Change	-x	+x
Equilibrium	0.015 - x	x

Calculate K_b for the Benzoate ion from K_a for HBen.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.58 \times 10^{-10}$$

Substitute into the equilibrium-constant equation. Assume x is much smaller than 0.015.

$$K_b = \frac{[\text{HBen}][\text{OH}^-]}{[\text{Ben}^-]} = \frac{(x)^2}{(0.015 - x)} \cong \frac{(x)^2}{(0.015)} = 1.58 \times 10^{-10}$$

$$x = [\text{HBen}] = [\text{OH}^-] \cong 1.539 \times 10^{-6} \text{ M} \quad (x \text{ is negligible compared to } 0.015.)$$

Thus, the concentration of benzoic acid in the solution is $1.5 \times 10^{-6} \text{ M}$. The pH is

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.539 \times 10^{-6}) = 5.812$$

$$\text{pH} = 14.00 - 5.812 = 8.188 = 8.19$$

- 17.10 Assemble the usual table, using starting [H₃O⁺] = 0.20 M from 0.20 M HCl and letting HFo symbolize HCHO₂.

Conc. (M)	HFo + H ₂ O	H ₃ O ⁺ + Fo ⁻
Starting	0.10	0.20
Change	-x	+x
Equilibrium	0.10 - x	0.20 + x

(continued)

Assume x is negligible compared to 0.10 M and 0.20 M, and substitute into the equilibrium-constant equation to get

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFO}]} = \frac{(0.20 + x)(x)}{(0.10 - x)} \cong \frac{(0.20)(x)}{(0.10)} = 1.7 \times 10^{-4}$$

$$x = [\text{Fo}^-] = 8.50 \times 10^{-5} = 8.5 \times 10^{-5} \text{ M}$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{8.50 \times 10^{-5}}{0.10} = 8.50 \times 10^{-4} = 8.5 \times 10^{-4}$$

- 17.11 Assemble the usual table, using a starting $[\text{CHO}_2^-]$ of 0.018 M from 0.018 M NaCHO_2 and symbolizing HCHO_2 as HFO and the CHO_2^- anion as Fo^- .

Conc. (M)	$\text{HFO} + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+ + \text{Fo}^-$
Starting	0.025		0 0.018
Change	-x		+x +x
Equilibrium	$0.025 - x$		x $0.018 + x$

Substitute into the equilibrium-constant equation. Assume x is negligible compared to 0.025 M and 0.018 M.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFO}]} = \frac{(0.018 + x)(x)}{(0.025 - x)} \cong \frac{(0.018)(x)}{(0.025)} = 1.7 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] \cong 2.36 \times 10^{-4} \text{ M}$$

The pH can now be calculated.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.36 \times 10^{-4}) = 3.627 = 3.63$$

- 17.12 Let HOAc represent $\text{HC}_2\text{H}_3\text{O}_2$ and OAc^- represent $\text{C}_2\text{H}_3\text{O}_2^-$. The total volume of the buffer is

$$\text{Total volume} = 30.0 \text{ mL} + 70.0 \text{ mL} = 100.0 \text{ mL} = 0.1000 \text{ L}$$

The moles of HOAc and OAc^- in the buffer are

$$\text{mol HOAc} = 0.15 \text{ M} \times 0.0300 \text{ L} = 0.00450 \text{ mol}$$

$$\text{mol OAc}^- = 0.0700 \text{ M} \times 0.0700 \text{ L} = 0.0140 \text{ mol}$$

(continued)

The concentrations of HOAc and OAc⁻ in the buffer are

$$[\text{HOAc}] = \frac{0.00450 \text{ mol}}{0.1000 \text{ L}} = 0.0450 \text{ M}$$

$$[\text{OAc}^-] = \frac{0.0140 \text{ mol}}{0.1000 \text{ L}} = 0.140 \text{ M}$$

Now, substitute these starting concentrations into a table.

Conc. (M)	HOAc + H ₂ O ⇌	H ₃ O ⁺ + OAc ⁻
Starting	0.0450	0 0.140
Change	-x	+x +x
Equilibrium	0.0450 - x	x 0.140 + x

Substitute the equilibrium concentrations into the equilibrium-constant expression; then assume x is negligible compared to the starting concentrations of both HOAc and OAc⁻.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]} = \frac{(0.140 + x)(x)}{(0.0450 - x)} \cong \frac{(0.140)(x)}{(0.0450)} = 1.7 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] \cong 5.46 \times 10^{-6} \text{ M}$$

You can now calculate the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.46 \times 10^{-6}) = 5.262 = 5.26$$

- 17.13 First, do the stoichiometric calculation. From Exercise 17.11, [HFO] = 0.025 M and [Fo⁻] = 0.018 M. In one liter of buffer, there are 0.025 mol HFO and 0.018 mol Fo⁻. The moles of OH⁻ (equal to moles NaOH) added are

$$(0.10 \text{ M}) \times 0.0500 \text{ L} = 0.00500 \text{ mol OH}^-$$

The total volume of solution is

$$\text{Total volume} = 1 \text{ L} + 0.0500 \text{ L} = 1.0500 \text{ L}$$

After reaction with the OH⁻, the moles of HFO and Fo⁻ remaining in the solution are:

$$\text{Mol HFO} = (0.025 - 0.00500) \text{ mol} = 0.0200 \text{ mol}$$

$$\text{Mol Fo}^- = (0.018 + 0.00500) \text{ mol} = 0.0230 \text{ mol}$$

(continued)

The concentrations are

$$[\text{HFO}] = \frac{0.0200 \text{ mol}}{1.0500 \text{ L}} = 0.0190 \text{ M}$$

$$[\text{FO}^-] = \frac{0.0230 \text{ mol}}{1.0500 \text{ L}} = 0.0219 \text{ M}$$

Now account for the ionization of HFO to FO^- at equilibrium by assembling the usual table.

Conc. (M)	HFO + H ₂ O	\rightleftharpoons	H ₃ O ⁺ + FO ⁻
Starting	0.0190		0 0.0219
Change	-x		+x +x
Equilibrium	0.0190 - x		x 0.0219 + x

Assume x is negligible compared to 0.0190 M and 0.0219 M, and substitute into the equilibrium-constant equation to get

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{FO}^-]}{[\text{HFO}]} = \frac{(0.0219 + x)(x)}{(0.0190 - x)} \cong \frac{(0.0219)(x)}{(0.0190)} = 1.7 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = 1.47 \times 10^{-4} \text{ M}$$

Now, calculate the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.47 \times 10^{-4}) = 3.831 = 3.83$$

- 17.14 All the OH^- reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+ .

$$\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol}$$

$$\text{Mol OH}^- = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L} = 0.0015 \text{ mol}$$

The total volume of solution is

$$\text{Total volume} = 0.025 \text{ L} + 0.015 \text{ L} = 0.040 \text{ L}$$

(continued)

Subtract the mol of OH^- from the mol of H_3O^+ , and divide by the total volume to get the concentration of H_3O^+ .

$$\text{Mol H}_3\text{O}^+ \text{ left} = (0.0025 - 0.0015) \text{ mol} = 0.0010 \text{ mol}$$

$$[\text{H}_3\text{O}^+] = \frac{0.0010 \text{ mol}}{0.040 \text{ L}} = 0.0250 \text{ M}$$

Now calculate the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0250) = 1.602 = 1.60$$

- 17.15 At the equivalence point, the solution will contain NaF. The molar amount of F^- is equal to the molar amount of HF and is calculated as follows.

$$(0.10 \text{ mol HF/L}) \times 0.025 \text{ L} = 0.0025 \text{ mol F}^-$$

The volume of 0.15 M NaOH added and the total volume of solution are calculated next.

$$\text{Volume NaOH} = \frac{M_{\text{acid}} V_{\text{acid}}}{M_{\text{base}}} = \frac{(0.10 \text{ M})(25 \text{ mL})}{0.15 \text{ M}} = 16.6 \text{ mL}$$

$$\text{Total volume} = 25 \text{ mL} + 16.6 \text{ mL} = 41.6 \text{ mL} = 0.0416 \text{ L}$$

The concentration of F^- at the equivalence point can now be calculated.

$$[\text{F}^-] = \frac{0.0025 \text{ mol}}{0.0416 \text{ L}} = 0.0600 \text{ M}$$

Next, consider the hydrolysis of F^- . Start by calculating the hydrolysis constant of F^- from the K_a of its conjugate acid, HF.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

Now, assemble the usual table of concentrations, assume x is negligible compared to 0.0600, and calculate $[\text{OH}^-]$.

Conc. (M)	$\text{F}^- + \text{H}_2\text{O}$	$\text{HF} + \text{OH}^-$
Starting	0.0600	0
Change	-x	+x
Equilibrium	0.0600 - x	x

(continued)

Substitute into the equilibrium-constant equation to get

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{(x)^2}{(0.0600 - x)} \cong \frac{(x)^2}{(0.0600)} = 1.47 \times 10^{-11}$$

$$x = [\text{OH}^-] = 9.39 \times 10^{-7} \text{ M}$$

Finally, calculate the pOH and then the pH.

$$\text{pOH} = -\log [\text{OH}^-] = -\log (9.39 \times 10^{-7}) = 6.026$$

$$\text{pH} = 14.00 - 6.026 = 7.974 = 7.97$$

- 17.16 At the equivalence point, the solution will contain NH_4Cl . The molar amount of NH_4^+ is equal to the molar amount of NH_3 and is calculated as follows.

$$(0.20 \text{ mol NH}_3 / \text{L}) \times 0.035 \text{ L} = 0.00700 \text{ mol NH}_4^+$$

The volume of 0.12 M HCl added and the total volume of solution are calculated next.

$$\text{Volume HCl} = \frac{M_{\text{base}} V_{\text{base}}}{M_{\text{acid}}} = \frac{(0.20 \text{ M})(35 \text{ mL})}{0.12 \text{ M}} = 58.3 \text{ mL}$$

$$\text{Total volume} = 35 \text{ mL} + 58.3 \text{ mL} = 93.3 \text{ mL} = 0.0933 \text{ L}$$

The concentration of NH_4^+ at the equivalence point can now be calculated.

$$[\text{NH}_4^+] = \frac{0.00700 \text{ mol}}{0.0933 \text{ L}} = 0.0750 \text{ M}$$

Next, consider the hydrolysis of NH_4^+ . Start by calculating the hydrolysis constant of NH_4^+ from the K_b of its conjugate base, NH_3 .

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

Now, assemble the usual table of concentrations, assume x is negligible compared to 0.0750, and calculate $[\text{H}_3\text{O}^+]$.

Conc. (M)	$\text{NH}_4^+ + \text{H}_2\text{O}$	$\text{NH}_3 + \text{H}_3\text{O}^+$
Starting	0.0750	0
Change	-x	+x
Equilibrium	0.0750 - x	x

(continued)

Substitute into the equilibrium-constant equation to get

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)^2}{(0.0750 - x)} \cong \frac{(x)^2}{(0.0750)} = 5.56 \times 10^{-10}$$

$$x = [\text{H}_3\text{O}^+] = 6.46 \times 10^{-6} \text{ M}$$

Finally, calculate the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.46 \times 10^{-6}) = 5.189 = 5.19$$

■ Answers to Concept Checks

- 17.1 You would probably guess the pH's of the acid solutions depend on their respective K_a 's; the larger the K_a , the greater the acidity or the lower the pH. We can put this on a firm basis by looking at the acid ionization equilibrium. An acid, HA, ionizes in water as follows:



The corresponding equilibrium constant, K_a , equals $[\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$. When you start with the same concentration of HA, the concentration of HA in solution is essentially the same for each acid. Also, $[\text{H}_3\text{O}^+] = [\text{A}^-]$. This means K_a is proportional to $[\text{H}_3\text{O}^+]^2$, or $\text{pH} = -\log [\text{H}_3\text{O}^+]$ is proportional to $-\log K_a$. Therefore, the larger the K_a , the lower the pH. As an example, compare two acids, one with $K_a = 10^{-5}$ and the other with K_a equal to 10^{-4} . The corresponding $-\log K_a$ values are five and four, respectively. The second acid (the one with the greater K_a) would have the lower pH. If you look at Table 17.1, the acid with the largest K_a of those listed in the problem statement is HF. So the ranking from lowest to highest pH is: $\text{HCN} < \text{HC}_2\text{H}_3\text{O}_2 < \text{HNO}_2, \text{HF}$.

- 17.2 By examining the contents of the beaker, you see there are three different species present, the ions BH^+ and OH^- as well as unreacted B molecules. This represents a weak base. The ionization reaction for this base is



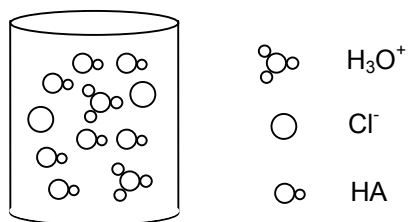
- 17.3 Ammonia, NH_3 , is a weak base; the other compounds are salts. You can decide the acidity or basicity of salt solutions by noting whether the corresponding acid and base are strong or weak. For example, NH_4Br is the salt of a weak base (NH_3) and a strong acid (HBr), so the salt is acidic. Similarly, NaF is basic (it is the salt of a strong base, NaOH , and a weak acid, HF). NaCl is neutral. This means two of the solutions are basic (NH_3 and NaF), one solution is neutral (NaCl), and the other is acidic (NH_4Br). Although a salt might be as basic as NH_3 , this occurs only when the acid from which the salt formed is quite weak (for example, NaCN is quite basic). So, the solution with highest pH is 0.1 M NH_3 (a), and the solution of lowest pH is 0.1 M NH_4Br (b).

17.4 The amount of any substance in a solution is proportional to the volume times molarity. Lets look at each solution:

- The 1.5 mL of 1 M HCl just neutralizes 15 mL of 0.1 M NaOH, giving a solution of NaCl. Thus, the pH of the original solution changes from very basic to neutral ($\text{pH} = 7$) after the addition of HCl.
- The solution of acetic acid changes from weakly acidic to strongly acidic with the addition of HCl.
- Equal amounts of NaOH and $\text{HC}_2\text{H}_3\text{O}_2$ in the original solution exactly neutralize each other to produce the salt, $\text{NaC}_2\text{H}_3\text{O}_2$, which is slightly basic. The addition of the strong acid, HCl, gives an acidic solution.
- The 30 mL of NaOH reacts with 30 mL of $\text{HC}_2\text{H}_3\text{O}_2$ to give the salt, $\text{NaC}_2\text{H}_3\text{O}_2$, leaving an equal amount of the corresponding acid, $\text{HC}_2\text{H}_3\text{O}_2$. The result is a buffer solution. The addition of HCl to the buffer does not change the pH appreciably. (This is true as long as the amount of added acid does not overwhelm the capacity of the buffer. In this case, it does not. The amount of acid and base conjugates in the buffer is twice the amount of added acid.)

Only d does not change appreciably in pH.

- 17.5
- When two formula units of NaOH are added to the beaker on the left, a reaction occurs consuming two HA molecules and forming two A^- ions. This results in a solution with two HA molecules and five A^- ions, which is depicted in beaker Y.
 - Since the original buffer contains three A^- ions, three HCl molecules could be added before the buffer capacity would be exceeded.
 - The beaker would contain seven HA molecules. In addition, the extra HCl molecules would dissociate into H_3O^+ and Cl^- ions. This could be represented by the following



■ Answers to Review Questions

- 17.1 The equation is



The equilibrium-constant expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

- 17.2 HCN is the weakest acid. Its K_a of 4.9×10^{-10} is $< K_a$ of 1.7×10^{-5} of $\text{HC}_2\text{H}_3\text{O}_2$; HClO_4 is a strong acid, of course.

- 17.3 Both methods involve direct measurement of the concentrations of the hydronium ion and the anion of the weak acid and calculation of the concentration of the un-ionized acid. All concentrations are substituted into the K_a expression to obtain a value for K_a . In the first method, the electrical conductivity of a solution of the weak acid is measured. The conductivity is proportional to the concentration of the hydronium ion and anion. In the second method, the pH of a known starting concentration of weak acid is measured. The pH is converted to $[\text{H}_3\text{O}^+]$, which will be equal to the [anion].

- 17.4 The degree of ionization of a weak acid decreases as the concentration of the acid added to the solution increases. Compared to low concentrations, at high concentrations, there is less water for each weak acid molecule to react with as the weak acid ionizes:



- 17.5 You can neglect x if C_a/K is ≥ 100 . In this case, $C_a/K = [(0.0010 \text{ M} \div 6.8 \times 10^{-4}) = 1.47]$, which is significantly less than 100, and x cannot be neglected in the $(0.0010 - x)$ term. This says the degree of ionization is significant.

- 17.6 The ionization of the first H_3O^+ is



The equilibrium-constant expression is

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_3^-]}{[\text{H}_2\text{PHO}_3]}$$

(continued)

The ionization of the second H_3O^+ is



The equilibrium-constant expression is

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{PO}_3^{2-}]}{[\text{HPO}_3^{2-}]}$$

- 17.7 As shown in Example 17.4, the concentration of a -2 anion of a polyprotic acid in a solution of the diprotic acid alone is approximately equal to the value of K_{a2} . For oxalic acid, begin by noting that the $[\text{H}_3\text{O}^+] \cong [\text{HC}_2\text{O}_4^-]$. Then, substitute $[\text{H}_3\text{O}^+]$ for the $[\text{HC}_2\text{O}_4^-]$ term in the equilibrium-constant equation for K_{a2} :

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} \cong \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{H}_3\text{O}^+]} = [\text{C}_2\text{O}_4^{2-}]$$

- 17.8 The balanced chemical equation for the ionization of aniline is



The equilibrium-constant equation, or expression for K_b , is defined without an $[\text{H}_2\text{O}]$ term; this term is included in the value for K_b as discussed in Section 17.3. The expression is

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

- 17.9 First, decide whether any of the three is a strong base or not. Because all the molecules are among the nitrogen-containing weak bases listed in Table 17.2, none is a strong base. Next, recognize the greater the $[\text{OH}^-]$, the stronger the weak base. Because $[\text{OH}^-]$ can be calculated from the square root of the product of K_b and concentration, the larger the K_b , the greater the $[\text{OH}^-]$ and the stronger the weak base. Thus, CH_3NH_2 is the strongest of these three weak bases because its K_b is the largest.
- 17.10 Anilinium chloride is not a weak base nor a weak acid but a salt that contains the anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$, and the Cl^- ion. The chloride ion does not hydrolyze because it could only form HCl , a strong acid. The anilinium ion does hydrolyze as follows:



(continued)

The equilibrium-constant expression for this reaction is

$$K_a = \frac{[\text{C}_6\text{H}_5\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

Obtain the value for K_a by calculating the value of K_w/K_b , where K_b is the ionization constant for aniline, $\text{C}_6\text{H}_5\text{NH}_2$.

- 17.11 The common-ion effect is the shift in an ionic equilibrium caused by the addition of a solute that furnishes an ion that is common to, or takes part in, the equilibrium. If the equilibrium involves the ionization of a weak acid, then the common ion is usually the anion formed by the ionization of the weak acid. If the equilibrium involves the ionization of a weak base, then the common ion is usually the cation formed by the ionization of the weak base. An example is the addition of F^- ion (as NaF) to a solution of the weak acid HF , which ionizes as shown below:



The effect of adding F^- to this equilibrium is that it causes a shift in the equilibrium composition to the left. The additional F^- reacts with H_3O^+ , lowering its concentration and raising the concentration of HF .

- 17.12 The addition of $\text{CH}_3\text{NH}_3\text{Cl}$ to 0.10 M CH_3NH_2 exerts a common-ion effect that causes the equilibrium below to exhibit a shift in composition to the left:



This shift lowers the equilibrium concentration of the OH^- ion, which increases the $[\text{H}_3\text{O}^+]$. An increase in $[\text{H}_3\text{O}^+]$ lowers the pH below 11.8. The shift in composition to the left occurs according to Le Chatelier's principle, which states that a system shifts to counteract any change in composition.

- 17.13 A buffer is most often a solution of a mixture of two substances that is able to resist pH changes when limited amounts of acid or base are added to it. A buffer must contain a weak acid and its conjugate (weak) base. Strong acids and/or bases cannot form effective buffers because a buffer acts by converting H_3O^+ (strong acid) to the un-ionized (weak) buffer acid and by converting OH^- (strong base) to the un-ionized (weak) buffer base. An example of a buffer pair is a mixture of H_2CO_3 and HCO_3^- , the principal buffer in the blood.
- 17.14 The capacity of a buffer is the amount of acid or base with which the buffer can react before exhibiting a significant pH change. (A significant change in blood pH might mean 0.01-0.02 pH units; for other systems a significant change might mean 0.5 pH units.) A high-capacity buffer might be of the type discussed for Figure 17.10: one mol of buffer acid and one mol of buffer base. A low-capacity buffer might involve quite a bit less than these amounts: 0.01-0.05 mol of buffer acid and buffer base.

- 17.15 The pH of a weak base before titration is relatively high, around pH 10 for a 0.1 M solution of a typical weak base. As a strong acid titrant is added, the $[\text{OH}^-]$ decreases, and the pH decreases. At 50 percent neutralization, a buffer of equal amounts of buffer acid and base is formed. The $[\text{OH}^-]$ equals the K_b , or the pOH equals the $\text{p}K_b$. At the equivalence point, the pH is governed by the hydrolysis of the salt of the weak base formed and is usually in the pH 4-6 region. After the equivalence point, the pH decreases to a level just greater than the pH of the strong acid titrant.
- 17.16 If the pH is 8.0, an indicator that changes color in the basic region would be needed. Of the indicators mentioned in the text, phenolphthalein (pH 8.2-10.0) and thymol blue would work. In actual practice, cresol red (pH 7.2-8.8) would be the best choice because the pH should be closer to the middle of the range than to one end.

■ Answers to Conceptual Problems

- 17.17 A solution of the weak acid, HA, will contain hydronium ions (H_3O^+) and anions (A^-) in equal amounts as well as some undissociated acid (HA) molecules. This is represented by the solution in container A, which contains six HA molecules, two H_3O^+ and two A^- ions. The solution in container B contains eight HA molecules and represents an undissociated acid. In container C, all of the HA molecules have dissociated, so this represents a strong acid.
- 17.18 For equal molar solutions,
- The greater the pH of the solution, the less H_3O^+ present in solution. When comparing the three acid solutions of equal concentration, HX produced the least amount of H_3O^+ in solution (highest pH), so it must be the least ionized.
 - When comparing the three acids, HZ was the most ionized in solution (lowest pH) producing the greatest concentration of H_3O^+ . Therefore, HZ must be the strongest acid with the largest K_a .

- 17.19 a. When HF is dissolved in water, the F^- hydrolyzes. The reaction is



- b. When NaF is dissolved in water, F^- hydrolyzes. The reaction is



- c. When $\text{C}_6\text{H}_5\text{NH}_2$ is dissolved in water, the following reaction occurs:



(continued)

d. When $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ is dissolved in water, $\text{C}_6\text{H}_5\text{NH}_3^+$ hydrolyzes. The reaction is



17.20 The KBr solution is made from a neutral salt. Thus, it should have a pH of 7.0. The HBr solution is a strong acid with $\text{pH} < 7.0$. The CH_3NH_2 solution is a weak base with $\text{pH} > 7.0$. The NH_4Cl solution is made from a salt with a weak acid cation, NH_4^+ , with $\text{pH} < 7.0$. Therefore, the ranking from lowest to highest hydroxide concentrations is: $\text{HBr} < \text{NH}_4\text{Cl} < \text{KBr} < \text{CH}_3\text{NH}_2$.

17.21 A solution of rantidine hydrochloride should be acidic. Let Ran represent rantidine. Then RanHCl is the chloride salt, rantidinium chloride. The cation rantidinium, RanH^+ , should hydrolyze according to the following equation



17.22 NH_3 is a weak base; therefore, the solution would have $\text{pH} > 7$. The NH_4Br solution is made from a salt with a weak acid cation, NH_4^+ , with $\text{pH} < 7.0$. The NaF solution is made from a salt with a basic anion, F^- , with a $\text{pH} > 7$. The NaCl solution is made from a neutral salt; therefore, it should have a $\text{pH} = 7$. In order to rank the relative strengths of the F^- and NH_3 , you should estimate K_b for each. Using data from Appendices E and F of your text, K_b for NH_3 is about 10^{-5} and about 10^{-10} for F^- , which indicates NH_3 is a stronger base than F^- . Therefore, the ranking from highest to lowest pH is: $\text{NH}_3 > \text{NaF} > \text{NaCl} > \text{NH}_4\text{Br}$.

17.23 To prepare a buffer solution that has a pH equal to the pK_a of the acid, you need equal amounts of acid and conjugate base in the solution. The easiest way to make the buffer is to mix equal volumes of equal molar solutions of HA and NaA. Thus, mix 100 mL of 0.10 M NaA with the 100 mL of 0.10 M HA to prepare the buffer.

17.24 Of the three titrations, the weak base-strong acid titration is easiest to identify. The attributes to look for are a high pH at the start and a gradual decrease in pH as the titration proceeds. The other two titrations both start with low pH and increase in pH as the titration proceeds. Of the two, the strong acid-strong base titration should show a more rapid increase in pH before the endpoint is reached along with a well-defined, sharp equivalence point at pH 7. The weak acid-strong base titration will show a more gradual change in pH before the equivalence point, which should be less sharply defined and occur at a pH above seven.

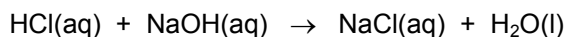
17.25 a. First, since the pH of the solution is less than seven at the beginning of the titration, you can conclude that an acid is being titrated with a base.

b. The pH of the equivalence point is about 8.5. Therefore, the acid being titrated is a weak acid.

(continued)

- c. You need to pick an indicator that changes color in the pH range of about 7 to 10. Therefore, thymol blue or phenolphthalein would work fine for this titration.

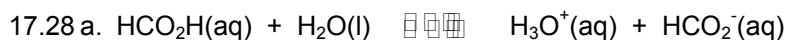
17.26 a. The balanced chemical equation for the titration of aqueous NaOH with HCl is



- b. Beaker A contains four Cl^- ions and four water molecules. There are no OH^- ions present. This represents the equivalence point. Beaker B contains two OH^- and two Cl^- ions and two water molecules. Since some OH^- is still present, this represents the titration at a point before the equivalence point. Beaker C contains six Cl^- and two H_3O^+ ions and four water molecules. This represents the titration at a point after the equivalence point.
- c. The solution in beaker A is at the equivalence point and is neutral. The solution in beaker B contains OH^- ions and is basic. The solution in beaker C contains H_3O^+ ions and is acidic.

■ Solutions to Practice Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.



- 17.29 HAc will be used throughout as an abbreviation for acrylic acid and Ac^- for the acrylate ion. At the start, the H_3O^+ from the self-ionization of water is so small it is approximately zero. Once the acrylic acid solution is prepared, some of the 0.10 M HAc ionizes to H_3O^+ and Ac^- . Then, let x equal the mol/L of HAc that ionize, forming x mol/L of H_3O^+ and x mol/L of Ac^- and leaving $(0.10 - x)$ M HAc in solution. We can summarize the situation in tabular form:

Conc. (M)	HAc + H ₂ O ⇌	H ₃ O ⁺ + Ac ⁻
Starting	0.10	0 0
Change	-x	+x +x
Equilibrium	0.10 - x	x x

The equilibrium-constant equation is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{x^2}{(0.10 - x)}$$

The value of x can be obtained from the pH of the solution:

$$x = [\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2.63) = 2.34 \times 10^{-3} = 0.00234 \text{ M}$$

Note that $(0.10 - x) = (0.10 - 0.00234) = 0.09766$, which is significantly different from 0.10, so x cannot be ignored in the calculation. Thus, we substitute for x in both the numerator and denominator to obtain the value of K_a :

$$K_a = \frac{x^2}{(0.10 - x)} = \frac{(0.00234)^2}{(0.10 - 0.00234)} = 5.606 \times 10^{-5} = 5.6 \times 10^{-5}$$

- 17.30 HN_3 will be used throughout as an abbreviation for hydrazoic acid and N_3^- for the hydrazoate ion. At the start, the H_3O^+ from the self-ionization of water is so small it is approximately zero. Once the hydrazoic acid solution is prepared, some of the 0.20 M HN_3 ionizes to H_3O^+ and N_3^- . Then, let x equal the mol/L of HN_3 that ionizes, forming x mol/L of H_3O^+ and x mol/L of N_3^- and leaving $(0.20 - x)$ M HN_3 in solution. We can summarize the situation in tabular form:

Conc. (M)	$\text{HN}_3 + \text{H}_2\text{O} \rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{N}_3^-$
Starting	0.20	0 0
Change	-x	+x +x
Equilibrium	0.20 - x	x x

(continued)

The equilibrium-constant equation is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{N}_3^-]}{[\text{HN}_3]} = \frac{x^2}{(0.20 - x)}$$

The value of x can be obtained from the pH of the solution:

$$x = [\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.21) = 6.16 \times 10^{-4} = 0.000616 \text{ M}$$

Note that $(0.20 - x) = (0.20 - 0.000616) = 0.1993$, which is not significantly different from 0.20, so x can be ignored in the calculation. Thus, we substitute for x in only the numerator, not the denominator, to obtain the value of K_a :

$$K_a = \frac{x^2}{(0.20 - x)} \cong \frac{(0.000616)^2}{(0.20)} \cong 1.89 \times 10^{-6} = 1.9 \times 10^{-6}$$

- 17.31 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBo as the symbol for boric acid and Bo^- as the symbol for $\text{B}(\text{OH})_4^-$.

Conc. (M)	HBo + H ₂ O	H ₃ O ⁺ + Bo ⁻
Starting	0.021	0 0
Change	-x	+x +x
Equilibrium	0.021 - x	x x

The value of x equals the value of the molarity of the H_3O^+ ion, which can be obtained from the equilibrium-constant expression. Substitute into the equilibrium-constant expression, and solve for x .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Bo}^-]}{[\text{HBo}]} = \frac{(x)^2}{(0.021 - x)} = 5.9 \times 10^{-10}$$

Solve the equation for x , assuming x is much smaller than 0.021.

$$\frac{(x)^2}{(0.021 - x)} \cong \frac{(x)^2}{(0.021)} = 5.9 \times 10^{-10}$$

$$x^2 = 5.9 \times 10^{-10} \times (0.021) = 1.239 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = 3.519 \times 10^{-6} \text{ M}$$

(continued)

Check to make sure the assumption that $(0.021 - x) \cong 0.021$ is valid:

$$0.021 - (3.519 \times 10^{-6}) = 0.02099, \text{ or } \cong 0.021 \text{ to two sig. figs.}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.519 \times 10^{-6}) = 5.453 = 5.45$$

The degree of ionization is

$$\text{degree of ionization} = \frac{3.519 \times 10^{-6}}{(0.021)} = 0.000167 = 0.00017 = 1.7 \times 10^{-4}$$

- 17.32 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HFo as the symbol for formic acid and Fo⁻ as the symbol for CHO₂⁻.

Conc. (M)	HFo + H ₂ O ⇌ H ₃ O ⁺ + Fo ⁻		
Starting	0.10	0	0
Change	-x	+x	+x
Equilibrium	0.10 - x	x	x

The value of x equals the value of the molarity of the H₃O⁺ ion, which can be obtained from the equilibrium-constant expression. Substitute into the equilibrium-constant expression, and solve for x.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFo}]} = \frac{(x)^2}{(0.10 - x)} = 1.7 \times 10^{-4}$$

Solve the equation for x, assuming x is much smaller than 0.10.

$$\frac{(x)^2}{(0.10 - x)} = \frac{(x)^2}{(0.10)} = 1.7 \times 10^{-4}$$

$$x^2 = 1.7 \times 10^{-4} \times (0.10) = 1.7 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 4.123 \times 10^{-3} = 0.0041 \text{ M}$$

Check to make sure the assumption that $(0.10 - x) \cong 0.10$ is valid:

$$0.10 - (0.004123) = 0.0958, \text{ or } \cong 0.10 \text{ to two sig. figs}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (4.123 \times 10^{-3}) = 2.384 = 2.38$$

The degree of ionization is

$$\text{Degree of ionization} = \frac{0.0041}{(0.10)} = 0.0412 = 0.041$$

- 17.33 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HPaba as a symbol for p-aminobenzoic acid (PABA), and use Paba⁻ as the symbol for the -1 anion.

Conc. (M)	HPaba + H ₂ O	H ₃ O ⁺ + Paba ⁻
Starting	0.055	0 0
Change	-x	+x +x
Equilibrium	0.055 - x	x x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.055 - x):

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Paba}^-]}{[\text{HPaba}]} = \frac{(x)^2}{(0.055 - x)} = 2.2 \times 10^{-5}$$

Solve the equation for x, assuming x is smaller than 0.055.

$$x^2 = (2.2 \times 10^{-5}) \times 0.055 = 1.21 \times 10^{-6}$$

$$x = [\text{H}_3\text{O}^+] = [\text{Paba}^-] \cong 1.10 \times 10^{-3} = 0.0011 = 1.1 \times 10^{-3} \text{ M}$$

Check to make sure the assumption that (0.055 - x) \cong 0.055 is valid.

$$0.055 - 0.00110 = 0.0539, \text{ or } 0.054$$

- 17.34 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HBar as a symbol for barbituric acid and Bar⁻ as the symbol for the -1 anion.

Conc. (M)	HBar + H ₂ O	H ₃ O ⁺ + Bar ⁻
Starting	0.15	0 0
Change	-x	+x +x
Equilibrium	0.15 - x	x x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and (0.15 - x):

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Bar}^-]}{[\text{HBar}]} = \frac{(x)^2}{(0.15 - x)} = 9.8 \times 10^{-5}$$

Solve the equation for x, assuming x is negligible compared to 0.15.

$$x^2 \cong (9.8 \times 10^{-5}) \times 0.15 = 1.47 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = [\text{Bar}^-] \cong 3.83 \times 10^{-3} = 0.0038 \text{ M}$$

- 17.35 To solve, first convert the pH to $[\text{H}_3\text{O}^+]$, which also equals $[\text{C}_2\text{H}_3\text{O}_2^-]$, here symbolized as $[\text{Ac}^-]$. Then, assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[\text{HC}_2\text{H}_3\text{O}_2]$, here symbolized as $[\text{HAc}]$.

$$[\text{H}_3\text{O}^+] = \text{antilog}(-2.68) = 2.089 \times 10^{-3} \text{ M}$$

Conc. (M)	HAc + H ₂ O ⇌	H ₃ O ⁺ +	Ac ⁻
Starting	x	0	0
Change	-2.089 × 10 ⁻³	+2.089 × 10 ⁻³	+2.089 × 10 ⁻³
Equilibrium	x - (2.089 × 10 ⁻³)	2.089 × 10 ⁻³	2.089 × 10 ⁻³

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the x - (2.089 × 10⁻³) terms into the expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(2.089 \times 10^{-3})^2}{(x - 2.089 \times 10^{-3})} = 1.7 \times 10^{-5}$$

Solve the equation for x, assuming 0.002089 is much smaller than x.

$$x = [\text{HAc}] \cong \frac{(2.089 \times 10^{-3})^2}{(1.7 \times 10^{-5})} = 0.256 = 0.26 \text{ M}$$

- 17.36 To solve, first convert the pH to $[\text{H}_3\text{O}^+]$, which also equals the $[\text{C}_3\text{H}_5\text{O}_3^-]$, here symbolized as $[\text{Lac}^-]$. Then, assemble the usual table, and substitute into the equilibrium-constant expression to solve for $[\text{HC}_3\text{H}_5\text{O}_3]$, here symbolized as $[\text{HLac}]$.

$$[\text{H}_3\text{O}^+] = \text{antilog}(-2.51) = 3.09 \times 10^{-3} \text{ M}$$

Conc. (M)	HLac + H ₂ O ⇌	H ₃ O ⁺ +	Lac ⁻
Starting	x	0	0
Change	-3.09 × 10 ⁻³	+3.09 × 10 ⁻³	+3.09 × 10 ⁻³
Equilibrium	x - (3.09 × 10 ⁻³)	3.09 × 10 ⁻³	3.09 × 10 ⁻³

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the x - (3.09 × 10⁻³) terms into the expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Lac}^-]}{[\text{HLac}]} = \frac{(3.09 \times 10^{-3})^2}{(x - 3.09 \times 10^{-3})} = 1.4 \times 10^{-4}$$

(continued)

Solve the equation for x . It appears 3.09×10^{-3} is not much smaller than x , so do not ignore x in the denominator.

$$\frac{(3.09 \times 10^{-3})^2}{1.4 \times 10^{-4}} = 0.0682 = (x - 3.09 \times 10^{-3})$$

$$x = [\text{HLac}] = 0.0682 + 0.00309 = 0.0712 = 0.071 \text{ M}$$

- 17.37 To solve, assemble the usual table of starting, change, and equilibrium concentrations of HF and F^- ions.

Conc. (M)	HF + H ₂ O	\rightleftharpoons	H ₃ O ⁺ + F ⁻
Starting	0.040		0 0
Change	-x		+x +x
Equilibrium	0.040 - x		x x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(0.040 - x)$:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)^2}{(0.040 - x)} = 6.8 \times 10^{-4}$$

In this case, x cannot be ignored compared to 0.040 M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 0.040 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x^2 + (6.8 \times 10^{-4})x - (2.72 \times 10^{-5}) = 0$$

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 + 4(2.72 \times 10^{-5})}}{2}$$


$$x = \frac{-6.8 \times 10^{-4} \pm 0.01045}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] = 4.88 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(4.88 \times 10^{-3}) = 2.311 = 2.31$$

- 17.38 To solve, assemble the usual table of starting, change, and equilibrium concentrations of $\text{HC}_2\text{H}_2\text{ClO}_2$, symbolized as HChI , and the $\text{C}_2\text{H}_2\text{ClO}_2^-$ ion, symbolized as ChI^- .

Conc. (M)	$\text{HChI} + \text{H}_2\text{O}$ 	$\text{H}_3\text{O}^+ + \text{ChI}^-$
Starting	0.015	0 0
Change	-x	+x +x
Equilibrium	$0.015 - x$	x x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(0.015 - x)$:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ChI}^-]}{[\text{HChI}]} = \frac{(x)^2}{(0.015 - x)} = 1.3 \times 10^{-3} = 0.0013$$

In this case, x cannot be ignored compared to 0.015 M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 0.015 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x^2 + (0.0013)x - 1.95 \times 10^{-5} = 0$$

$$x = \frac{-0.0013 \pm \sqrt{(0.0013)^2 + 4(1.95 \times 10^{-5})}}{2}$$


$$x = \frac{-0.0013 \pm 0.008926}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] = 3.813 \times 10^{-3} = 0.0038 \text{ M}$$

$$\text{pH} = -\log(3.813 \times 10^{-3}) = 2.418 = 2.42$$

- 17.39 To solve, assemble the usual table of starting, change, and equilibrium concentrations of $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2\text{H}$, symbolized as HDin , and the $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2^-$ ion, symbolized as Din^- .

Conc. (M)	$\text{HDin} + \text{H}_2\text{O}$ 	$\text{H}_3\text{O}^+ + \text{Din}^-$
Starting	2.00	0 0
Change	-x	+x +x
Equilibrium	$2.00 - x$	x x

(continued)

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(2.00 - x)$:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Din}^-]}{[\text{HDin}]} = \frac{(x)^2}{(2.00 - x)} = 7.94 \times 10^{-2} = 0.0794$$

In this case, x cannot be ignored compared to 2.00 M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 2.00 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x^2 + (0.0794)x - 0.1588 = 0$$

$$x = \frac{-0.0794 \pm \sqrt{(0.0794)^2 + 4(0.1588)}}{2}$$

$$x = \frac{-0.0794 \pm 0.8009}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] = 0.3607 = 0.361 \text{ M}$$

- 17.40 To solve, assemble the usual table of starting, change, and equilibrium concentrations of $\text{BrC}_6\text{H}_4\text{CO}_2\text{H}$, symbolized as HpBr , and the $\text{BrC}_6\text{H}_4\text{CO}_2^-$ ion, symbolized as pBr^- .

Conc. (M)	$\text{HpBr} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{pBr}^-$	H_3O^+	pBr^-
Starting	2.00×10^{-4}	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(2.00 \times 10^{-4} - x)$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms x and $(2.00 \times 10^{-4} - x)$:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{pBr}^-]}{[\text{HpBr}]} = \frac{(x)^2}{(2.00 \times 10^{-4} - x)} = 1.00 \times 10^{-4}$$

In this case, x cannot be ignored compared to 2.00×10^{-4} M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 2.00×10^{-4} yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x^2 + (1.00 \times 10^{-4})x - 2.00 \times 10^{-8} = 0$$

(continued)

Plugging into the quadratic formula gives

$$x = \frac{-1.00 \times 10^{-4} \pm \sqrt{(1.00 \times 10^{-4})^2 + 4(2.00 \times 10^{-8})}}{2}$$

$$x = \frac{-1.00 \times 10^{-4} \pm 3.00 \times 10^{-4}}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] = 1.000 \times 10^{-4} = 1.00 \times 10^{-4} \text{ M}$$

- 17.41 a. To solve, note that $K_{a1} = 1.2 \times 10^{-3} > K_{a2} = 3.9 \times 10^{-6}$, and hence the second ionization and K_{a2} can be neglected. Assemble a table of starting, change, and equilibrium concentrations. Let $\text{H}_2\text{Ph} = \text{H}_2\text{C}_8\text{H}_4\text{O}_4$ and $\text{HPh}^- = \text{HC}_8\text{H}_4\text{O}_4^-$.

Conc. (M)	$\text{H}_2\text{Ph} + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+ + \text{HPh}^-$
Starting	0.015		0 0
Change	-x		+x +x
Equilibrium	$0.015 - x$		x x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute x and (0.015 - x):

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HPh}^-]}{[\text{H}_2\text{Ph}]} = \frac{(x)^2}{(0.015 - x)} = 1.2 \times 10^{-3} = 0.0012$$

In this case, x cannot be ignored in the (0.015 M - x) term. (If it is ignored, the calculated $[\text{H}_3\text{O}^+]$ when subtracted from 0.0015 M yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (0.0012)x - 1.80 \times 10^{-5} = 0$$

$$x = \frac{-0.0012 \pm \sqrt{(0.0012)^2 - 4(-1.80 \times 10^{-5})}}{2}$$

$$x = \frac{-0.0012 \pm 0.008569}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] \cong 3.684 \times 10^{-3} = 0.0037 = 3.7 \times 10^{-3} \text{ M}$$

(continued)

b. Because $[\text{HPh}^-] \cong [\text{H}_3\text{O}^+]$, these terms cancel in the K_{a2} expression. This reduces to

$$[\text{Ph}^2] = K_{a2} = 3.9 \times 10^{-6} \text{ M.}$$

17.42 a. To solve, note that $K_{a1} = 4.3 \times 10^{-7} > K_{a2} = 4.8 \times 10^{-11}$, and hence the second ionization and K_{a2} can be neglected. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$		
Starting	5.45×10^{-4}	0	0
Change	-x	+x	+x
Equilibrium	$(5.45 \times 10^{-4} - x)$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute x and $(5.45 \times 10^{-4} - x)$:

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)^2}{(5.45 \times 10^{-4} - x)} = 4.3 \times 10^{-7}$$

In this case, x cannot be ignored compared to 5.45×10^{-4} M. (If it is ignored, the calculated $[\text{H}_3\text{O}^+]$ when subtracted from 5.45×10^{-4} M yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a, b, and c in the quadratic formula.

$$x^2 + (4.3 \times 10^{-7})x - 2.3435 \times 10^{-10} = 0$$

$$x = \frac{-4.3 \times 10^{-7} \pm \sqrt{(4.3 \times 10^{-7})^2 + 4(2.3435 \times 10^{-10})}}{2}$$

$$x = \frac{-4.3 \times 10^{-7} \pm 3.06 \times 10^{-5}}{2}$$

Use the positive root.

$$x = [\text{H}_3\text{O}^+] = 1.51 \times 10^{-5} = 1.5 \times 10^{-5} \text{ M}$$

(continued)

- b. To calculate $[\text{CO}_3^{2-}] = y$, note from the equilibrium concentrations in the table above that $[\text{HCO}_3^-] \cong [\text{H}_3\text{O}^+]$. In exact terms, $[\text{H}_3\text{O}^+] = (1.5 \times 10^{-5} + y)$ from the ionization of HCO_3^- , and $[\text{HCO}_3^-] = (1.5 \times 10^{-5} - y)$ from ionization. Substituting into the K_{a2} expression gives

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(1.5 \times 10^{-5} + y)(y)}{(1.5 \times 10^{-5} - y)} = 4.8 \times 10^{-11}$$

Assuming y is much smaller than 1.5×10^{-5} , note the $(1.5 \times 10^{-5}) + y$ term cancels the $(1.5 \times 10^{-5}) - y$ term, leaving

$$[\text{CO}_3^{2-}] \cong K_{a2} = 4.8 \times 10^{-11} \text{ M}$$

- 17.43 The equation is



The K_b expression is

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

- 17.44 The equation is



The K_b expression is

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

- 17.45 To solve, convert the pH to $[\text{OH}^-]$:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 11.34 = 2.66$$

$$[\text{OH}^-] = \text{antilog}(-2.66) = 2.188 \times 10^{-3} \text{ M}$$

Using the symbol EtN for ethanolamine, assemble a table of starting, change, and equilibrium concentrations.

(continued)

Conc. (M)	EtN + H ₂ O	⇌	HEtN ⁺	+	OH ⁻
Starting	0.15		0		0
Change	-x		+x		+x
Equilibrium	0.15 - (2.188 × 10 ⁻³)		2.188 × 10 ⁻³		2.188 × 10 ⁻³

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for K_b :

$$K_b = \frac{[\text{HEtN}^+][\text{OH}^-]}{[\text{EtN}]} = \frac{(2.188 \times 10^{-3})^2}{(0.15 - 2.188 \times 10^{-3})} = 3.23 \times 10^{-5} = 3.2 \times 10^{-5}$$

17.46 To solve, convert the pH to [OH⁻]:

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 11.63 = 2.37$$

$$[\text{OH}^-] = \text{antilog}(-2.37) = 4.266 \times 10^{-3} \text{ M}$$

Using the symbol TMeN for trimethylamine, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	TMeN + H ₂ O	⇌	HTMeN ⁺	+	OH ⁻
Starting	0.25		0		0
Change	-x		+x		+x
Equilibrium	0.25 - (4.266 × 10 ⁻³)		4.266 × 10 ⁻³		4.266 × 10 ⁻³

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms, and solve for K_b :

$$K_b = \frac{[\text{HTMeN}^+][\text{OH}^-]}{[\text{TMeN}]} = \frac{(4.266 \times 10^{-3})^2}{(0.25 - 4.266 \times 10^{-3})} = 7.40 \times 10^{-5} = 7.4 \times 10^{-5}$$

17.47 To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	CH ₃ NH ₂ + H ₂ O	⇌	CH ₃ NH ₃ ⁺	+	OH ⁻
Starting	0.060		0		0
Change	-x		+x		+x
Equilibrium	0.060 - x		x		x

(continued)

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of K_b :

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(x)^2}{(0.060 - x)} = 4.4 \times 10^{-4}$$

In this case, x cannot be ignored compared to 0.060 M. (If it is ignored, subtracting the calculated $[\text{H}_3\text{O}^+]$ from 0.060 yields a significant change.) The quadratic formula must be used. Reorganize the equilibrium-constant expression into the form $ax^2 + bx + c = 0$, and substitute for a , b , and c in the quadratic formula.

$$x^2 + (4.4 \times 10^{-4})x - 2.64 \times 10^{-5} = 0$$

$$x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 + 4(2.64 \times 10^{-5})}}{2}$$

$$x = \frac{-4.4 \times 10^{-4} \pm 0.01028}{2}$$

Use the positive root.

$$x = [\text{OH}^-] = 4.92 \times 10^{-3} = 0.0049 = 4.9 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(4.92 \times 10^{-3}) = 2.307$$

$$\text{pH} = 14.00 - 2.307 = 11.692 = 11.69$$

17.48 To solve, assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	$\text{HONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONH}_3^+ + \text{OH}^-$		
Starting	0.18	0	0
Change	-x	+x	+x
Equilibrium	$0.18 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and the value of K_b :

$$K_b = \frac{[\text{HONH}_3^+][\text{OH}^-]}{[\text{HONH}_2]} = \frac{(x)^2}{(0.18 - x)} = 1.1 \times 10^{-8}$$

(continued)

Solve the equation for x , assuming x can be ignored compared to 0.18 M.

$$\frac{(x)^2}{(0.18 - x)} \cong \frac{(x)^2}{(0.18)} = 1.1 \times 10^{-8}$$

$$x^2 = 1.1 \times 10^{-8} \times (0.18)$$

$$x = [\text{OH}^-] = 4.44 \times 10^{-5} = 4.4 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log (4.44 \times 10^{-5}) = 4.351$$

$$\text{pH} = 14.00 - 4.351 = 9.648 = 9.65$$

17.49 a. No hydrolysis occurs because the nitrate ion (NO_3^-) is the anion of a strong acid.

b. Hydrolysis occurs. Equation:



Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_a} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

c. Hydrolysis occurs. Equation:



Equilibrium-constant expression:

$$K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+][\text{NH}_2\text{NH}_2]}{[\text{NH}_2\text{NH}_3^+]}$$

d. No hydrolysis occurs because the bromide ion (Br^-) is the anion of a strong acid.

17.50 a. Hydrolysis occurs. Equation:



Equilibrium-constant expression:

$$K_a = \frac{K_w}{K_b} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$$

(continued)

b. No hydrolysis occurs because the iodide ion (I^-) is the anion of a strong acid.

c. Hydrolysis occurs. Equation:



Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_a} = \frac{[\text{HClO}_2][\text{OH}^-]}{[\text{ClO}_2^-]}$$

d. Hydrolysis occurs. Equation:



Equilibrium-constant expression:

$$K_b = \frac{K_w}{K_{a_3}} = \frac{[\text{HPO}_4^{2-}][\text{OH}^-]}{[\text{PO}_4^{3-}]}$$

17.51 Acid ionization is



17.52 Acid ionization is



17.53 a. $\text{Fe}(\text{NO}_3)_3$ is a salt of a weak base, $\text{Fe}(\text{OH})_3$, and a strong acid, HNO_3 , so it would be expected to be acidic. Fe^{3+} is not in Group IA or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.

b. Na_2CO_3 is a salt of a strong base, NaOH , and the anion of a weak acid, HCO_3^- , so it would be expected to be basic.

c. $\text{Ca}(\text{CN})_2$ is a salt of a strong base, $\text{Ca}(\text{OH})_2$, and a weak acid, HCN , so it would be expected to be basic.

d. NH_4ClO_4 is a salt of a weak base, NH_3 , and a strong acid, HClO_4 , so it would be expected to be acidic.

- 17.54 a. Na_2S is a salt of a strong base, NaOH , and the anion of a weak acid, HS^- , so it would be expected to be basic.
- b. $\text{Cu}(\text{NO}_3)_2$ is a salt of a weak base, $\text{Cu}(\text{OH})_2$, and a strong acid, HNO_3 , so it would be expected to be acidic. Cu^{2+} is not in Group IA or IIA, so it would be expected to form a metal hydrate ion that would hydrolyze to form an acidic solution.
- c. KClO_4 is a salt of a strong base, KOH , and a strong acid, HClO_4 , so no reaction would occur to change the neutral pH (7.00) of water.
- d. $\text{C}_3\text{NH}_3\text{Cl}$ is a salt of a weak base, CH_3NH_2 , and a strong acid, HCl , so it would be expected to be acidic.

17.55 a. Both ions hydrolyze:



Calculate the K_a and K_b constants of each to compare them:

$$\text{NH}_4^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

$$\text{C}_2\text{H}_3\text{O}_2^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

Because the K_b for the hydrolysis of $\text{C}_2\text{H}_3\text{O}_2^-$ is slightly larger than the constant, K_a , for the hydrolysis of NH_4^+ , the solution will be slightly basic but close to pH 7.0.

b. Both ions hydrolyze:



Calculate the K_a and K_b constants of each to compare them:

$$\text{C}_6\text{H}_5\text{NH}_3^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^{-5}$$

(continued)

$$\text{C}_2\text{H}_3\text{O}_2^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

Because the constant, K_a , for the hydrolysis of $\text{C}_6\text{H}_5\text{NH}_3^+$ is larger than the hydrolysis constant, K_b , for the hydrolysis of $\text{C}_2\text{H}_3\text{O}_2^-$, the solution will be acidic and significantly less than pH 7.0.

17.56 a. Both ions hydrolyze:



Calculate the K_a and K_b constants of each to compare them:

$$\text{NH}_4^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

$$\text{CNO}^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.86 \times 10^{-11}$$

Because the constant, K_a , for the hydrolysis of NH_4^+ is larger than the hydrolysis constant, K_b , for the hydrolysis of CNO^- , the solution will be acidic and significantly less than pH 7.0.

b. Both ions hydrolyze:



Calculate the K_a and K_b constants of each to compare them:

$$\text{C}_6\text{H}_5\text{NH}_3^+ \text{ as an acid: } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-10}} = 2.38 \times 10^{-5}$$

$$\text{CNO}^- \text{ as a base: } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.86 \times 10^{-11}$$

Because the constant, K_a , for the hydrolysis of $\text{C}_6\text{H}_5\text{NH}_3^+$ is larger than the hydrolysis constant, K_b , for the hydrolysis of CNO^- , the solution will be acidic and significantly less than pH 7.0.

17.57 a. The reaction is



The constant, K_b , is obtained by dividing K_w by the K_a of the conjugate acid, HNO_2 :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-11} = 2.2 \times 10^{-11}$$

b. The reaction is



The constant, K_a , is obtained by dividing K_w by the K_b of the conjugate base, $\text{C}_5\text{H}_5\text{N}$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^{-6} = 7.1 \times 10^{-6}$$

17.58 a. The reaction is



The constant, K_b , is obtained by dividing K_w by the K_a of the conjugate acid, HClO :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.857 \times 10^{-7} = 2.9 \times 10^{-7}$$

b. The reaction is



The constant, K_a , is obtained by dividing K_w by the K_b of the conjugate base, NH_2OH :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7} = 9.1 \times 10^{-7}$$

- 17.59 Assemble the usual table, letting $[\text{Pr}^-]$ equal the equilibrium concentration of the propionate anion (the only ion that hydrolyzes). Then, calculate the K_b of the Pr^- ion from the K_a of its conjugate acid, HPr . Assume x is much smaller than the 0.025 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pOH from the $[\text{OH}^-]$ and pH from the pOH .

Conc. (M)	$\text{Pr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HPr} + \text{OH}^-$		
Starting	0.025	0	0
Change	-x	+x	+x
Equilibrium	$0.025 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}$$

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[\text{HPr}][\text{OH}^-]}{[\text{Pr}^-]} = \frac{(x)^2}{(0.025 - x)} \cong \frac{(x)^2}{(0.025)} = 7.69 \times 10^{-10}$$

$$x = [\text{OH}^-] = [\text{HPr}] \cong 4.38 \times 10^{-6} = 4.4 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (4.38 \times 10^{-6}) = 5.358$$

$$\text{pH} = 14.00 - 5.358 = 8.642 = 8.64$$

- 17.60 Assemble the usual table, letting $[\text{CN}^-]$ equal the equilibrium concentration of the cyanide anion (the only ion that hydrolyzes). Then, calculate the K_b of the CN^- ion from the K_a of its conjugate acid, HCN . Assume x is much smaller than the 0.010 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. (This is a borderline case, but the quadratic equation gives a value of $4.415 \times 10^{-4} \text{ M}$ for x , not much different than the approximation.) Finally, calculate pOH from the $[\text{OH}^-]$ and pH from the pOH .

Conc. (M)	$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$		
Starting	0.010	0	0
Change	-x	+x	+x
Equilibrium	$0.010 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

(continued)

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{(x)^2}{(0.010 - x)} \cong \frac{(x)^2}{(0.010)} = 2.04 \times 10^{-5}$$

$$x = [\text{OH}^-] = [\text{HCN}] \cong 4.52 \times 10^{-4} = 4.5 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (4.52 \times 10^{-4}) = 3.3448$$

$$\text{pH} = 14.00 - 3.3448 = 10.6552 = 10.66$$

The cyanide ion concentration is

$$[\text{CN}^-] = 0.010 - x = 0.010 - 4.52 \times 10^{-4} = 0.009548 = 0.0095 \text{ M}$$

- 17.61 Assemble the usual table, letting $[\text{PyNH}^+]$ equal the equilibrium concentration of the pyridinium cation (the only ion that hydrolyzes). Then, calculate the K_a of the PyNH^+ ion from the K_b of its conjugate base, PyN . Assume x is much smaller than the 0.15 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pH from the $[\text{H}_3\text{O}^+]$.

Conc. (M)	$\text{PyNH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{PyN}$		
Starting	0.15	0	0
Change	-x	+x	+x
Equilibrium	$0.15 - x$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^{-6}$$

Write the equilibrium-constant expression in terms of chemical symbols and then substitute the terms and solve for K_a :

$$K_a = \frac{[\text{PyN}][\text{H}_3\text{O}^+]}{[\text{PyNH}^+]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 7.14 \times 10^{-6}$$

$$x = [\text{H}_3\text{O}^+] = [\text{PyN}] \cong 1.03 \times 10^{-3} = 0.0010 = 1.0 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.03 \times 10^{-3}) = 2.987 = 2.99$$

- 17.62 Assemble the usual table, letting $[\text{MeNH}_3^+]$ equal the equilibrium concentration of the methylammonium cation (the only ion that hydrolyzes). Then, calculate the K_a of the MeNH_3^+ ion from the K_b of its conjugate base, MeNH_2 . Assume x is much smaller than the 0.35 M concentration in the denominator, and solve for x in the numerator of the equilibrium-constant expression. Finally, calculate pH from the $[\text{H}_3\text{O}^+]$.

Conc. (M)	$\text{MeNH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{MeNH}_2$		
Starting	0.35	0	0
Change	-x	+x	+x
Equilibrium	$0.35 - x$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.27 \times 10^{-11}$$

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for K_a :

$$K_a = \frac{[\text{MeNH}_2][\text{H}_3\text{O}^+]}{[\text{MeNH}_3^+]} = \frac{(x)^2}{(0.35 - x)} \cong \frac{(x)^2}{(0.35)} = 2.27 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = [\text{MeNH}_2] \cong 2.82 \times 10^{-6} = 2.8 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.82 \times 10^{-6}) = 5.549 = 5.55$$

- 17.63 To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume x is much smaller than the 0.75 M starting concentration of HF. Then, solve for x in the numerator of each equilibrium-constant expression by using the product of 6.8×10^{-4} and other terms.

a. 0.75 M Hydrofluoric acid, HF:

Conc. (M)	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$		
Starting	0.75	0	0
Change	-x	+x	+x
Equilibrium	$0.75 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)^2}{(0.75 - x)} \cong \frac{(x)^2}{(0.75)} = 6.8 \times 10^{-4}$$

$$x^2 = 6.8 \times 10^{-4} \times (0.75)$$

(continued)

$$x = [\text{H}_3\text{O}^+] = 0.02258 \text{ M}$$

Check to see if the assumption is valid.

$$0.75 - (0.02258) = 0.727 = 0.73$$

This is a borderline case; the quadratic equation gives $[\text{H}_3\text{O}^+] = 0.02224 \text{ M}$, not much different. The degree of ionization is

$$\text{Degree of ionization} = \frac{0.02258}{0.75} = 0.0301 = 0.030$$

b. 0.75 M HF with 0.12 M HCl:

Conc. (M)	HF + H ₂ O	\rightleftharpoons	H ₃ O ⁺ + F ⁻
Starting	0.75		0.12 0
Change	-x		+x +x
Equilibrium	0.75 - x		0.12 + x x

Assuming x is negligible compared to 0.12 and to 0.75, substitute into the equilibrium-constant expression 0.12 for $[\text{H}_3\text{O}^+]$ from 0.12 M HCl and 0.75 from the HF:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.12 + x)(x)}{(0.75 - x)} \cong \frac{(0.12)(x)}{(0.75)} = 6.8 \times 10^{-4}$$

$$x = [\text{F}^-] = \frac{(0.75)(6.8 \times 10^{-4})}{(0.12)} \cong 4.250 \times 10^{-3} \text{ M}$$

Check to see if the assumptions are valid:

$$0.75 - (4.250 \times 10^{-3}) = 0.7457 = 0.75$$

$$0.12 + (4.250 \times 10^{-3}) = 0.1242 = 0.12$$

$$\text{Degree of ionization} = \frac{4.25 \times 10^{-3}}{0.75} = 0.00566 = 0.0057$$

- 17.64 To solve, assemble a table of starting, change, and equilibrium concentrations for each part. For each part, assume x is much smaller than the 0.22 M starting concentration of HCHO_2 . Then, solve for x in each equilibrium-constant expression by using the product of 1.7×10^{-4} and each starting molarity of formic acid.

a. 0.22 M HCHO_2

Conc. (M)	$\text{HCHO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CHO}_2^-$		
Starting	0.22	0	0
Change	-x	+x	+x
Equilibrium	$0.22 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the terms and solve for K_a :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = \frac{(x)^2}{(0.22 - x)} \cong \frac{(x)^2}{(0.22)} = 1.7 \times 10^{-4}$$

$$x^2 = 1.7 \times 10^{-4} \times (0.22 \text{ M})$$

$$x = [\text{H}_3\text{O}^+] \cong 6.11 \times 10^{-3} \text{ M}$$

Check to see if the assumption is valid:

$$0.22 - (6.11 \times 10^{-3}) = 0.213 = 0.21$$

The degree of ionization is

$$\text{Degree of ionization} = (6.11 \times 10^{-3}) \div 0.22 = 0.0277 = 0.028$$

b. 0.22 M HCHO_2 with 0.12 M HCl :

Conc. (M)	$\text{HCHO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CHO}_2^-$		
Starting	0.22	0.12	0
Change	-x	+x	+x
Equilibrium	$0.22 - x$	$0.12 + x$	x

(continued)

Assuming x is negligible compared to 0.12 and to 0.22, substitute into the equilibrium-constant expression 0.12 for $[\text{H}_3\text{O}^+]$ from 0.12 M HCl and 0.22 from the HCHO_2 :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} = \frac{(0.12 + x)(x)}{(0.22 - x)} \cong \frac{(0.12)(x)}{(0.22)} = 1.7 \times 10^{-4}$$

$$x = [\text{CHO}_2^-] = \frac{(0.22)(1.7 \times 10^{-4})}{(0.12)} \cong 3.11 \times 10^{-4} \text{ M}$$

Check to see if the assumptions are valid:

$$0.12 + 3.11 \times 10^{-4} = 0.1203 \approx 0.12$$

$$0.22 - (3.11 \times 10^{-4}) = 0.219 \approx 0.22$$

The degree of ionization is

$$\text{Degree of ionization} = (3.11 \times 10^{-4}) \div 0.22 = 0.00141 \approx 0.0014$$

- 17.65 Assemble the usual table, using a starting NO_2^- of 0.10 M, from 0.10 M KNO_2 , and a starting HNO_2 of 0.15 M. Assume x is negligible compared to 0.10 M and 0.15 M, and solve for the x in the numerator.

Conc. (M)	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$		
Starting	0.15	0	0.10
Change	-x	+x	+x
Equilibrium	0.15 - x	x	0.10 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{(0.10 + x)(x)}{(0.15 - x)} \cong \frac{(0.10)(x)}{(0.15)} = 4.5 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = 6.75 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.75 \times 10^{-4}) = 3.170 \approx 3.17$$

- 17.66 Use a starting OCN^- of 0.20 M and a starting HOCN of 0.10 M. Assume x is negligible compared to 0.20 M and 0.10 M.

Conc. (M)	$\text{HOCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCN}^-$		
Starting	0.10	0	0.20
Change	-x	+x	+x
Equilibrium	0.10 - x	x	0.20 + x

(continued)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCN}^-]}{[\text{HOCN}]} = \frac{(0.20 + x)(x)}{(0.10 - x)} \cong \frac{(0.20)(x)}{(0.10)} = 3.5 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = 1.75 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.75 \times 10^{-4}) = 3.756 = 3.76$$

- 17.67 Assemble the usual table, using a starting CH_3NH_3^+ of 0.15 M, from 0.15 M $\text{CH}_3\text{NH}_3\text{Cl}$, and a starting CH_3NH_2 of 0.10 M. Assume x is negligible compared to 0.15 M and 0.10 M, and solve for the x in the numerator.

Conc. (M)	$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{NH}_3^+$	
Starting	0.10	0 0.15
Change	-x	+x +x
Equilibrium	0.10 - x	x 0.15 + x

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(0.15 + x)(x)}{(0.10 - x)} \cong \frac{(0.15)(x)}{(0.10)} = 4.4 \times 10^{-4}$$

$$x = [\text{OH}^-] = 2.93 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.93 \times 10^{-4}) = 3.532$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.532 = 10.468 = 10.47$$

- 17.68 Assemble the usual table, using a starting $\text{C}_2\text{H}_5\text{NH}_3^+$ of 0.10 M, from 0.10 M $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$, and a starting $\text{C}_2\text{H}_5\text{NH}_2$ of 0.15 M. Assume x is negligible compared to 0.10 M and 0.15 M, and solve for the x in the numerator.

Conc. (M)	$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{C}_2\text{H}_5\text{NH}_3^+$	
Starting	0.15	0 0.10
Change	-x	+x +x
Equilibrium	0.15 - x	x 0.10 + x

$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{(0.10 + x)(x)}{(0.15 - x)} \cong \frac{(0.10)(x)}{(0.15)} = 4.7 \times 10^{-4}$$

$$x = [\text{OH}^-] = 7.05 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (7.05 \times 10^{-4}) = 3.151$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.1518 = 10.848 = 10.85$$

- 17.69 Find the mol/L of HF and the mol/L of F^- , and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume x is negligible compared to the starting concentrations of both HF and F^- . Solve for x in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

$$\text{Total volume} = 0.045 \text{ L} + 0.035 \text{ L} = 0.080 \text{ L}$$

$$(0.10 \text{ mol HF/L}) \times 0.035 \text{ L} = 0.0035 \text{ mol HF } (\div 0.080 \text{ L total volume} = 0.04375 \text{ M})$$

$$(0.15 \text{ mol } F^-/\text{L}) \times 0.045 \text{ L} = 0.00675 \text{ mol } F^- (\div 0.080 \text{ L total volume} = 0.084375 \text{ M})$$

Now, substitute these starting concentrations into the usual table:

Conc. (M)	HF + H ₂ O	\rightleftharpoons	H ₃ O ⁺ + F ⁻
Starting	0.04375		0 0.084375
Change	-x		+x +x
Equilibrium	0.04375 - x		x 0.084375 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.084375 + x)}{(0.04375 - x)} \cong \frac{(x)(0.084375)}{(0.04375)} = 6.8 \times 10^{-4}$$

$$x = [H_3O^+] = 3.52 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [H_3O^+] = -\log (3.52 \times 10^{-4}) = 3.453 = 3.45$$

- 17.70 Find the mol/L of NH_3 and the mol/L of NH_4^+ , and assemble the usual table. Substitute the equilibrium concentrations into the equilibrium-constant expression; then, assume x is negligible compared to the starting concentrations of both NH_3 and NH_4^+ . Solve for x in the numerator of the equilibrium-constant expression, and calculate the pH from this value.

$$\text{Total volume} = 0.115 \text{ L} + 0.145 \text{ L} = 0.260 \text{ L}$$

$$(0.30 \text{ mol } NH_3/\text{L}) \times 0.115 \text{ L} = 0.0345 \text{ mol } NH_3 (\div 0.260 \text{ L total vol} = 0.1327 \text{ M})$$

$$(0.15 \text{ mol } NH_4^+/\text{L}) \times 0.145 \text{ L} = 0.02175 \text{ mol } NH_4^+ (\div 0.260 \text{ L total vol} = 0.08365 \text{ M})$$

(continued)

Now, substitute these starting concentrations into the usual table:

Conc. (M)	$\text{NH}_3 + \text{H}_2\text{O}$	$\text{NH}_4^+ + \text{OH}^-$
Starting	0.1327	0.08365 0
Change	-x	+x +x
Equilibrium	0.1327 - x	0.08365 + x x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.08365 + x)(x)}{(0.1327 - x)} \cong \frac{(0.08365)(x)}{(0.1327)} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = 2.855 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.855 \times 10^{-5}) = 4.544$$

$$\text{pH} = 14.00 - 4.544 = 9.456 = 9.46$$

- 17.71 First, use the 0.10 M NH_3 and 0.10 M NH_4^+ to calculate the $[\text{OH}^-]$ and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume x is negligible compared to 0.10 M, and substitute the approximate concentrations into the equilibrium-constant expression.

Conc. (M)	$\text{NH}_3 + \text{H}_2\text{O}$	$\text{NH}_4^+ + \text{OH}^-$
Starting	0.10	0.10 0
Change	-x	+x +x
Equilibrium	0.10 - x	0.10 + x x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.10 + x)(x)}{(0.10 - x)} \cong \frac{(0.10)(x)}{(0.10)} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.8 \times 10^{-5}) = 4.744$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.744 = 9.256 = 9.26 \text{ (before HCl added)}$$

Now, calculate the pH after the 0.012 L (12 mL) of 0.20 M HCl is added by noting that the H_3O^+ ion reacts with the NH_3 to form additional NH_4^+ . Calculate the stoichiometric amount of HCl; then, subtract the moles of HCl from the moles of NH_3 . Add the resulting moles of NH_4^+ to the 0.0125 starting moles of NH_4^+ in the 0.125 L of buffer.

(continued)

$$(0.20 \text{ mol HCl/L}) \times 0.012 \text{ L} = 0.0024 \text{ mol HCl (reacts with 0.0024 mol NH}_3\text{)}$$

$$\text{Mol NH}_3 \text{ left} = (0.0125 - 0.0024) \text{ mol} = 0.0101 \text{ mol}$$

$$\text{Mol NH}_4^+ \text{ present} = (0.0125 + 0.0024) \text{ mol} = 0.0149 \text{ mol}$$

The concentrations of NH_3 and NH_4^+ are

$$[\text{NH}_3] = \frac{0.0101 \text{ mol NH}_3}{0.137 \text{ L}} = 0.0737 \text{ M}$$

$$[\text{NH}_4^+] = \frac{0.0149 \text{ mol NH}_3}{0.137 \text{ L}} = 0.108 \text{ M}$$

Now, account for the ionization of NH_3 to NH_4^+ and OH^- at equilibrium by assembling the usual table. Assume x is negligible compared to 0.0737 M and 0.108 M, and solve the equilibrium-constant expression for x in the numerator. Calculate the pH from x , the $[\text{OH}^-]$.

Conc. (M)	$\text{NH}_3 + \text{H}_2\text{O}$	\rightleftharpoons	$\text{NH}_4^+ + \text{OH}^-$
Starting	0.0737		0.108 0
Change	-x		+x +x
Equilibrium	$0.0737 - x$		$0.108 + x$ x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.108 + x)(x)}{(0.0737 - x)} \cong \frac{(0.108)(x)}{(0.0737)} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] \cong 1.22 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.22 \times 10^{-5}) = 4.913$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.913 = 9.086 = 9.09 \text{ (after HCl added)}$$

- 17.72 First, use the 0.525 L of 0.50 M HCHO_2 (H₂FO) and 0.475 L of 0.50 M NaCHO_2 (Na^+Fo^-) to calculate the $[\text{H}_3\text{O}^+]$ and pH before HCl is added. Assemble a table of starting, change, and equilibrium concentrations. Assume x is negligible compared to both concentrations; substitute into the K_a expression.

$$0.50 \text{ M HFO} \times 0.525 \text{ L} = 0.263 \text{ mol HFO } (\div 1.00 \text{ L} = 0.263 \text{ M})$$

$$0.50 \text{ M Fo}^- \times 0.475 \text{ L} = 0.238 \text{ mol Fo}^- (\div 1.00 \text{ L} = 0.238 \text{ M})$$

(continued)

Set up the table:

Conc. (M)	HFO + H ₂ O	H ₃ O ⁺ + FO ⁻
Starting	0.263	0 0.238
Change	-x	+x +x
Equilibrium	0.263 - x	x 0.238 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{FO}^-]}{[\text{HFO}]} = \frac{(x)(0.238 + x)}{(0.263 - x)} \cong \frac{(x)(0.238)}{(0.263)} = 1.7 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = 1.88 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.88 \times 10^{-4}) = 3.726 = 3.73 \text{ (before HCl added)}$$

Now, calculate the pH after the 0.0085 L (8.5 mL) of 0.15 M HCl is added by noting that the H₃O⁺ ion reacts with the FO⁻ to form additional HFO. Calculate the stoichiometric amount of HCl; then, subtract the moles of HCl from the moles of FO⁻. Add the resulting moles of HFO to the 0.02227 starting moles of HFO in the 0.085 L of buffer.

$$(0.15 \text{ mol HCl/L}) \times 0.0085 \text{ L} = 0.00128 \text{ mol HCl (reacts with 0.00128 mol FO}^-)$$

$$\text{Mol FO}^- \text{ left} = (0.02023 - 0.00128) \text{ mol} = 0.01895 \text{ mol FO}^-$$

$$\text{Mol HFO present} = (0.02227 + 0.00128) = 0.02355 \text{ mol HFO}$$

The concentrations of HFO and FO⁻ are

$$[\text{HFO}] = \frac{0.02355 \text{ mol HFO}}{0.0935 \text{ L}} = 0.2518 \text{ M}$$

$$[\text{FO}^-] = \frac{0.01895 \text{ mol FO}^-}{0.0935 \text{ L}} = 0.2026 \text{ M}$$

Now, account for the ionization of HFO to H₃O⁺ and FO⁻ at equilibrium by assembling the usual table. Assume x is negligible compared to 0.2518 M and 0.2026 M, and solve the equilibrium-constant expression for x in the numerator. Calculate the pH from x, the [H₃O⁺].

Conc. (M)	HFO + H ₂ O	H ₃ O ⁺ + FO ⁻
Starting	0.2518	0 0.2026
Change	-x	+x +x
Equilibrium	0.2518 - x	x 0.2026 + x

(continued)

Substitute into the equilibrium-constant equation to get

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Fo}^-]}{[\text{HFo}]} = \frac{(x)(0.2026 + x)}{(0.2518 - x)} \cong \frac{(x)(0.2026)}{(0.2518)} = 1.7 \times 10^{-4}$$

$$x = [\text{H}_3\text{O}^+] = 2.11 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.11 \times 10^{-4}) = 3.6757 = 3.68 \text{ (after HCl added)}$$

17.73 Use the Henderson-Hasselbalch equation, where $\text{p}K_a = -\log K_a$.

$$\begin{aligned} \text{pH} &= -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]} \\ &= -\log (1.4 \times 10^{-3}) + \log \frac{(0.10 \text{ M})}{(0.15 \text{ M})} = 2.677 = 2.68 \end{aligned}$$

17.74 Use the Henderson-Hasselbalch equation ($\text{p}K_a = -\log K_a$), and do the calculations in one step.

$$\begin{aligned} \text{pH} &= -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]} \\ &= -\log (1.3 \times 10^{-5}) + \log \frac{(0.20 \text{ M})}{(0.10 \text{ M})} = 5.187 = 5.19 \end{aligned}$$

17.75 Calculate the K_a of the pyridinium ion from the K_b of pyridine, and then use the Henderson-Hasselbalch equation where $\text{p}K_a = -\log K_a$.

$$\begin{aligned} K_a &= \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-9}} = 7.14 \times 10^{-6} \\ \text{pH} &= -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]} \\ &= -\log (7.14 \times 10^{-6}) + \log \frac{(0.15 \text{ M})}{(0.10 \text{ M})} = 5.322 = 5.32 \end{aligned}$$

- 17.76 Calculate the K_a of the methylammonium ion from the K_b of methylamine, and then use the Henderson-Hasselbalch equation where $pK_a = -\log K_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.27 \times 10^{-11}$$

$$pH = -\log K_a + \log \frac{[\text{buff. base}]}{[\text{buff. acid}]}$$

$$= -\log (2.27 \times 10^{-11}) + \log \frac{(0.20 \text{ M})}{(0.15 \text{ M})} = 10.768 = 10.77$$

- 17.77 Symbolize acetic acid as HOAc and sodium acetate as Na^+OAc^- . Use the Henderson-Hasselbalch equation to find the log of $[\text{OAc}^-]/[\text{HOAc}]$. Then, solve for $[\text{OAc}^-]$ and for moles of NaOAc in the 2.0 L of solution.

$$pH = -\log K_a + \log \frac{[\text{OAc}^-]}{[\text{HOAc}]} = 5.00$$

$$5.00 = -\log (1.7 \times 10^{-5}) + \log \frac{[\text{OAc}^-]}{(0.10 \text{ M})}$$

$$5.00 = 4.770 + \log [\text{OAc}^-] - \log (0.10)$$

$$\log [\text{OAc}^-] = 5.00 - 4.770 - 1.00 = -0.770$$

$$[\text{OAc}^-] = 0.1698 \text{ M}$$

$$\text{Mol NaOAc} = 0.1698 \text{ mol/L} \times 2.0 \text{ L} = 0.3396 = 0.34 \text{ mol}$$

- 17.78 Use the Henderson-Hasselbalch equation to find the log of $[\text{F}^-]/[\text{HF}]$. Then, solve for $[\text{HF}]$ and for moles of HF in the 0.5000 L of solution.

$$pH = -\log K_a + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.50$$

$$3.50 = -\log (6.8 \times 10^{-4}) + \log \frac{(0.30 \text{ M})}{[\text{HF}]}$$

(continued)

$$3.50 = 3.167 + \log [0.30] - \log [\text{HF}]$$

$$\log [\text{HF}] = 3.167 - 0.523 - 3.50 = -0.856$$

$$[\text{HF}] = 0.1393 \text{ M}$$

$$\text{Mol HF} = 0.1393 \text{ mol/L} \times 0.5000 \text{ L} = 0.06965 = 0.070 \text{ mol HF}$$

- 17.79 All the OH^- (from the NaOH) reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+ , and subtract the mol of OH^- from the mol of H_3O^+ . Then, divide the remaining H_3O^+ by the total volume of 0.015 L + 0.025 L, or 0.040 L, to find the $[\text{H}_3\text{O}^+]$. Then calculate the pH.

$$\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol HCl/L}) \times 0.025 \text{ L HCl} = 0.0025 \text{ mol H}_3\text{O}^+$$

$$\text{Mol OH}^- = (0.10 \text{ mol NaOH/L}) \times 0.015 \text{ L NaOH} = 0.0015 \text{ mol OH}^-$$

$$\text{Mol H}_3\text{O}^+ \text{ left} = (0.0025 - 0.0015) \text{ mol H}_3\text{O}^+ = 0.0010 \text{ mol H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = 0.0010 \text{ mol H}_3\text{O}^+ \div 0.040 \text{ L total volume} = 0.0250 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0250) = 1.602 = 1.60$$

- 17.80 All the H^+ (from the HCl) reacts with the OH^- from NaOH. Calculate the stoichiometric amounts of OH^- and H_3O^+ , and subtract the mol of H_3O^+ from the mol of OH^- . Then, divide the remaining OH^- by the total volume of 0.040 L + 0.025 L, or 0.065 L, to find the $[\text{OH}^-]$. Then calculate the pOH and pH.

$$\text{Mol OH}^- = (0.10 \text{ mol NaOH/L}) \times 0.040 \text{ L NaOH} = 0.0040 \text{ mol OH}^-$$

$$\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol HCl/L}) \times 0.025 \text{ L HCl} = 0.0025 \text{ mol H}_3\text{O}^+$$

$$\text{Mol OH}^- \text{ left} = (0.0040 - 0.0025) \text{ mol OH}^- = 0.0015 \text{ mol OH}^-$$

$$[\text{OH}^-] = 0.0015 \text{ mol OH}^- \div 0.065 \text{ L total volume} = 0.0230 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.0230) = 1.636$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.636 = 12.363 = 12.37$$

- 17.81 Use HBen to symbolize benzoic acid and Ben⁻ to symbolize the benzoate anion. At the equivalence point, equal molar amounts of HBen and NaOH react to form a solution of NaBen. Start by calculating the moles of HBen. Use this to calculate the volume of NaOH needed to neutralize all of the HBen (and use the moles of HBen as the moles of Ben⁻ formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

$$\text{Mol HBen} = 1.24 \text{ g HBen} \div (122.1 \text{ g HBen/mol HBen}) = 0.01016 \text{ mol HBen}$$

$$\text{Volume NaOH} = 0.01016 \text{ mol NaOH} \div (0.180 \text{ mol NaOH/L}) = 0.05644 \text{ L}$$

$$\text{Total volume} = 0.05644 \text{ L} + 0.050 \text{ L HBen soln} = 0.10644 \text{ L}$$

$$[\text{Ben}^-] = (0.01016 \text{ mol Ben}^- \text{ from HBen}) \div 0.10644 \text{ L} = 0.09545 \text{ M}$$

Because the Ben⁻ hydrolyzes to OH⁻ and HBen, use this to calculate the [OH⁻]. Start by calculating the K_b constant of Ben⁻ from the K_a of its conjugate acid, HBen. Then, assemble the usual table of concentrations, assume x is negligible, and calculate [OH⁻] and pH.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.59 \times 10^{-10}$$

Conc. (M)	Ben ⁻ + H ₂ O	HBen + OH ⁻
Starting	0.09545	0
Change	-x	+x
Equilibrium	0.09545 - x	x

$$K_b = \frac{[\text{HBen}][\text{OH}^-]}{[\text{Ben}^-]} = \frac{(x)^2}{(0.09545 - x)} \cong \frac{(x)^2}{(0.09545)} = 1.59 \times 10^{-10}$$

$$x = [\text{OH}^-] = 3.895 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (3.895 \times 10^{-6}) = 5.4094$$

$$\text{pH} = 14.00 - 5.4094 = 8.5905 = 8.59$$

- 17.82 Use HPr to symbolize propionic acid and Pr^- to symbolize the propionate anion. At the equivalence point, equal molar amounts of HPr and NaOH react to form a solution of NaPr. Start by calculating the moles of HPr. Use this to calculate the volume of NaOH needed to neutralize all of the HPr (and use the moles of HPr as the moles of Pr^- formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

$$\text{Mol HPr} = 0.400 \text{ g HPr} \div (74.08 \text{ g HPr/mol HPr}) = 0.00540 \text{ mol HPr}$$

$$\text{Volume NaOH} = 0.00540 \text{ mol NaOH} \div (0.150 \text{ mol NaOH/L}) = 0.03600 \text{ L}$$

$$\text{Total volume} = 0.03600 \text{ L} + 0.050 \text{ L HPr soln} = 0.08600 \text{ L}$$

$$[\text{Pr}^-] = (0.00540 \text{ mol } \text{Pr}^- \text{ from HPr}) \div 0.08600 \text{ L} = 0.06279 \text{ M}$$

Because the Pr^- hydrolyzes to OH^- and HPr, use this to calculate the $[\text{OH}^-]$. Start by calculating the K_b constant of Pr^- from the K_a of its conjugate acid, HPr. Then, assemble the usual table of concentrations, assume x is negligible, and calculate $[\text{OH}^-]$ and pH.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}$$

Conc. (M)	$\text{Pr}^- + \text{H}_2\text{O}$	\rightleftharpoons	HPr + OH^-
Starting	0.06279		0 0
Change	-x		+x +x
Equilibrium	0.06279 - x		x x

$$K_b = \frac{[\text{HPr}][\text{OH}^-]}{[\text{Pr}^-]} = \frac{(x)^2}{(0.06279 - x)} \cong \frac{(x)^2}{(0.06279)} = 7.69 \times 10^{-10}$$

$$x = [\text{OH}^-] = 6.948 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (6.948 \times 10^{-6}) = 5.158$$

$$\text{pH} = 14.00 - 5.158 = 8.841 = 8.84$$

- 17.83 Use EtN to symbolize ethylamine and EtNH⁺ to symbolize the ethylammonium cation. At the equivalence point, equal molar amounts of EtN and HCl react to form a solution of EtNHCl. Start by calculating the moles of EtN. Use this to calculate the volume of HCl needed to neutralize all of the EtN (and use the moles of EtN as the moles of EtNH⁺ formed at the equivalence point). Add the volume of HCl to the original 0.032 L to find the total volume of solution.

$$(0.087 \text{ mol EtN/L}) \times 0.032 \text{ L} = 0.00278 \text{ mol EtN}$$

$$\text{Volume HCl} = 0.00278 \text{ mol HCl} \div (0.15 \text{ mol HCl/L}) = 0.0185 \text{ L}$$

$$\text{Total volume} = 0.0185 \text{ L} + 0.032 \text{ L EtN soln} = 0.0505 \text{ L}$$

$$[\text{EtNH}^+] = (0.00278 \text{ mol EtNH}^+ \text{ from EtN}) \div 0.0505 \text{ L} = 0.0550 \text{ M}$$

Because the EtNH⁺ hydrolyzes to H₃O⁺ and EtN, use this to calculate the [H₃O⁺]. Start by calculating the K_a constant of EtNH⁺ from the K_b of its conjugate base, EtN. Then, assemble the usual table of concentrations, assume x is negligible, and calculate [H₃O⁺] and pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-4}} = 2.13 \times 10^{-11}$$

Conc. (M)	EtNH ⁺ + H ₂ O	EtN + H ₃ O ⁺
Starting	0.0550	0
Change	-x	+x
Equilibrium	0.0550 - x	x

$$K_a = \frac{[\text{EtN}][\text{H}_3\text{O}^+]}{[\text{EtNH}^+]} = \frac{(x)^2}{(0.0550 - x)} \cong \frac{(x)^2}{(0.0550)} = 2.13 \times 10^{-11}$$

$$x = [\text{H}_3\text{O}^+] = 1.08 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.08 \times 10^{-6}) = 5.9656 = 5.97$$

- 17.84 Use HyN to symbolize hydroxylamine and HyNH^+ to symbolize the hydroxylammonium cation. At the equivalence point, equal molar amounts of HyN and HCl react to form a solution of HyNHCl . Start by calculating the moles of HyN. Use this to calculate the volume of HCl needed to neutralize all of the HyN (and use the moles of HyN as the moles of HyNH^+ formed at the equivalence point). Add volumes.

$$(0.20 \text{ mol HyN/L}) \times 0.022 \text{ L} = 0.00440 \text{ mol HyN}$$

$$\text{Volume HCl} = 0.00440 \text{ mol HCl} \div (0.15 \text{ mol HCl/L}) = 0.0293 \text{ L}$$

$$\text{Total volume} = 0.0293 \text{ L} + 0.022 \text{ L HyN soln} = 0.0513 \text{ L}$$

$$[\text{HyNH}^+] = (0.00440 \text{ mol HyNH}^+ \text{ from HyN}) \div 0.0513 \text{ L} = 0.0858 \text{ M}$$

Use HyNH^+ hydrolysis to calculate the $[\text{H}_3\text{O}^+]$. Calculate the K_a constant of HyNH^+ from the K_b of HyN. Assemble the concentration table; assume x is negligible, and calculate $[\text{H}_3\text{O}^+]$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7}$$

Conc. (M)	$\text{HyNH}^+ + \text{H}_2\text{O}$	$\text{HyN} + \text{H}_3\text{O}^+$
Starting	0.0858	0
Change	-x	+x
Equilibrium	$0.0858 - x$	x

$$K_a = \frac{[\text{HyN}][\text{H}_3\text{O}^+]}{[\text{HyNH}^+]} = \frac{(x)^2}{(0.0858 - x)} \cong \frac{(x)^2}{(0.0858)} = 9.09 \times 10^{-7}$$

$$x = [\text{H}_3\text{O}^+] = 2.79 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.79 \times 10^{-4}) = 3.554 = 3.55$$

- 17.85 Calculate the stoichiometric amounts of NH_3 and HCl, which forms NH_4^+ . Then, divide NH_3 and NH_4^+ by the total volume of $0.500 \text{ L} + 0.200 \text{ L} = 0.700 \text{ L}$ to find the starting concentrations. Calculate the $[\text{OH}^-]$, the pOH, and the pH.

$$\text{Mol NH}_3 = (0.10 \text{ mol NH}_3/\text{L}) \times 0.500 \text{ L} = 0.0500 \text{ mol NH}_3$$

$$\text{Mol HCl} = (0.15 \text{ mol HCl/L}) \times 0.200 \text{ L} = 0.0300 \text{ mol HCl} \quad (0.0300 \text{ mol NH}_4^+)$$

$$\text{Mol NH}_3 \text{ left} = 0.0500 \text{ mol} - 0.0300 \text{ mol HCl} = 0.0200 \text{ mol NH}_3$$

$$0.0200 \text{ mol NH}_3 \div 0.700 \text{ L} = 0.0286 \text{ M NH}_3$$

(continued)

$$0.0300 \text{ mol NH}_4^+ \div 0.700 \text{ L} = 0.0429 \text{ M NH}_4^+$$

Conc. (M)	NH ₃ + H ₂ O	NH ₄ ⁺ + OH ⁻
Starting	0.0286	0.0429 0
Change	-x	+x +x
Equilibrium	0.0286 - x	0.0429 + x x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.0429 + x)(x)}{(0.0286 - x)} \cong \frac{(0.0429)(x)}{(0.0286)} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = 1.20 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.20 \times 10^{-5}) = 4.920$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.920 = 9.079 = 9.08$$

- 17.86 Use the symbols HAc for acetic acid and Ac⁻ for the acetate ion from sodium acetate. Calculate the stoichiometric amounts of HAc and Ac⁻. Then, divide the HAc and Ac⁻ by the total volume of 0.035 L + 0.025 L, or 0.060 L, to find the starting concentrations. Calculate the [H₃O⁺] and pH.

$$\text{Mol HAc} = (0.15 \text{ mol HAc/L}) \times 0.035 \text{ L HAc} = 0.00525 \text{ mol HAc}$$

$$\text{Mol Ac}^- = (0.10 \text{ mol NaAc/L}) \times 0.025 \text{ L NaAc} = 0.00250 \text{ mol Ac}^-$$

$$0.00525 \text{ mol HAc} \div 0.060 \text{ L} = 0.0875 \text{ M HAc}$$

$$0.00250 \text{ mol Ac}^- \div 0.060 \text{ L} = 0.0417 \text{ M Ac}^-$$

Set up a table.

Conc. (M)	HAc + H ₂ O	H ₃ O ⁺ + Ac ⁻
Starting	0.0875	0 0.0417
Change	-x	+x +x
Equilibrium	0.0875 - x	x 0.0417 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} = \frac{(0.0417 + x)(x)}{(0.0875 - x)} \cong \frac{(0.0417)(x)}{(0.0875)} = 1.7 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] \cong 3.57 \times 10^{-5} \text{ M}$$


$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.57 \times 10^{-5}) = 4.447 = 4.45$$

■ Solutions to General Problems

- 17.87 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HSal to symbolize salicylic acid, and use Sal⁻ for the anion. Start by converting pH to [H₃O⁺]:

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-2.43) = 3.72 \times 10^{-3} \text{ M}$$

$$\text{Starting M of HSal} = (2.2 \text{ g} \div 138 \text{ g/mol}) \div 1.00 \text{ L} = 0.0159 \text{ M}$$

Conc. (M)	HSal + H ₂ O		H ₃ O ⁺ + Sal ⁻
Starting	0.0159		0 0
Change	-x		+x +x
Equilibrium	0.0159 - x		x x


The value of x equals the value of the molarity of the H₃O⁺ ion, which is 3.72 × 10⁻³ M. Substitute into the equilibrium-constant expression to find K_a:

$$\begin{aligned} K_a &= \frac{[\text{H}_3\text{O}^+][\text{Sal}^-]}{[\text{HSal}]} = \frac{(x)^2}{(0.0159 - x)} = \frac{(3.72 \times 10^{-3})^2}{(0.0159 - 3.72 \times 10^{-3})} \\ &= 1.13 \times 10^{-3} = 1.1 \times 10^{-3} \end{aligned}$$

- 17.88 To solve, assemble a table of starting, change, and equilibrium concentrations. Use HCyn to symbolize cyanoacetic acid, and use Cyn⁻ for the anion. Start by converting pH to [H₃O⁺]:

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-1.89) = 1.29 \times 10^{-2} \text{ M}$$

$$\text{Starting M of HCyn} = (5.0 \text{ g} \div 85.1 \text{ g/mol}) \div 1.00 \text{ L} = 0.0588 \text{ M}$$

Conc. (M)	HCyn + H ₂ O		H ₃ O ⁺ + Cyn ⁻
Starting	0.0588		0 0
Change	-x		+x +x
Equilibrium	0.0588 - x		x x

The value of x equals the value of the molarity of the H₃O⁺ ion, which is 1.29 × 10⁻² M. Substitute into the equilibrium-constant expression to find K_a:

(continued)


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Cyn}^-]}{[\text{HCyn}]} = \frac{(x)^2}{(0.0588 - x)} = \frac{(1.29 \times 10^{-2})^2}{(0.0588 - 1.29 \times 10^{-2})}$$

$$= 3.62 \times 10^{-3} = 3.6 \times 10^{-3}$$

- 17.89 To solve, assemble a table of starting, change, and equilibrium concentrations. Start by converting pH to $[\text{H}_3\text{O}^+]$:

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-1.73) = 1.86 \times 10^{-2} \text{ M}$$

Starting M of $\text{HSO}_4^- = 0.050 \text{ M}$

Conc. (M)	$\text{HSO}_4^- + \text{H}_2\text{O}$ 	$\text{H}_3\text{O}^+ + \text{SO}_4^{2-}$
Starting	0.050	0 0
Change	-x	+x +x
Equilibrium	$0.050 - x$	x x

The value of x equals the value of the molarity of the H_3O^+ ion, which is $1.86 \times 10^{-2} \text{ M}$. Substitute into the equilibrium-constant expression to find K_a :


$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(x)^2}{(0.050 - x)} = \frac{(1.86 \times 10^{-2})^2}{(0.050 - 1.86 \times 10^{-2})}$$

$$= 1.10 \times 10^{-2} = 1.1 \times 10^{-2}$$

- 17.90 To solve, assemble a table of starting, change, and equilibrium concentrations. Start by converting pH to $[\text{H}_3\text{O}^+]$:

$$[\text{H}_3\text{O}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-4.10) = 7.94 \times 10^{-5} \text{ M}$$

Starting M of $\text{H}_2\text{PO}_4^- = 0.10 \text{ M}$

Conc. (M)	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$ 	$\text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$
Starting	0.10	0 0
Change	-x	+x +x
Equilibrium	$0.10 - x$	x x

(continued)

The value of x equals the value of the molarity of the H_3O^+ ion, which is $7.94 \times 10^{-5} \text{ M}$. Substitute into the equilibrium-constant expression to find K_{a2} :

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(x)^2}{(0.10 - x)} = \frac{(7.94 \times 10^{-5})^2}{(0.10 - 7.94 \times 10^{-5})}$$

$$= 6.304 \times 10^{-8} = 6.3 \times 10^{-8}$$

- 17.91 For the base ionization (hydrolysis) of CN^- to $\text{HCN} + \text{OH}^-$, the base-ionization constant is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5} = 2.0 \times 10^{-5}$$

For the base ionization (hydrolysis) of CO_3^{2-} to $\text{HCO}_3^- + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant (K_{a2}) of HCO_3^- , the conjugate acid of CO_3^{2-} .

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.08 \times 10^{-4} = 2.1 \times 10^{-4}$$

Because the constant of CO_3^{2-} is larger, it is the stronger base.

- 17.92 For the base ionization (hydrolysis) of PO_4^{3-} to $\text{HPO}_4^{2-} + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant (K_{a3}) of HPO_4^{2-} , the conjugate acid of PO_4^{3-} .

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 2.08 \times 10^{-2} = 2.1 \times 10^{-2}$$

For the base ionization (hydrolysis) of SO_4^{2-} to $\text{HSO}_4^- + \text{OH}^-$, the base-ionization constant is calculated from the ionization constant (K_{a2}) of HSO_4^- , the conjugate acid of SO_4^{2-} .

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13} = 9.1 \times 10^{-13}$$

Because the constant of PO_4^{3-} is larger, it is the stronger base.

- 17.93 Assume Al^{3+} is $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Assemble the usual table to calculate the $[\text{H}_3\text{O}^+]$ and pH. Use the usual equilibrium-constant expression.

Conc. (M)	$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$		
Starting	0.15	0	0
Change	-x	+x	+x
Equilibrium	$0.15 - x$	x	x

$$K_a = \frac{[\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}][\text{H}_3\text{O}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 1.4 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 1.449 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.449 \times 10^{-3}) = 2.838 = 2.84$$

- 17.94 Assume Zn^{2+} is $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. Assemble the usual table to calculate the $[\text{H}_3\text{O}^+]$ and pH.

Conc. (M)	$\text{Zn}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Zn}(\text{H}_2\text{O})_5(\text{OH})^+$		
Starting	0.15	0	0
Change	-x	+x	+x
Equilibrium	$0.15 - x$	x	x

Write the equilibrium-constant expression in terms of chemical symbols and substitute.

$$K_a = \frac{[\text{Zn}(\text{H}_2\text{O})_5(\text{OH})^+][\text{H}_3\text{O}^+]}{[\text{Zn}(\text{H}_2\text{O})_6^{2+}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 2.5 \times 10^{-10}$$

$$x = [\text{H}_3\text{O}^+] = 6.12 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.12 \times 10^{-6}) = 5.213 = 5.21$$

- 17.95 Calculate the concentrations of the tartaric acid (H_2Tar) and the hydrogen tartrate ion (HTar^-).

$$(11.0 \text{ g H}_2\text{Tar} \div 150.1 \text{ g/mol}) \div 1.00 \text{ L} = 0.07328 \text{ M H}_2\text{Tar}$$

$$(20.0 \text{ g KHTar}^- \div 188.2 \text{ g/mol}) \div 1.00 \text{ L} = 0.1063 \text{ M [HTar}^-]$$

Conc. (M)	$\text{H}_2\text{Tar} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HTar}^-$		
Starting	0.07328	0	0.1063
Change	-x	+x	+x
Equilibrium	$0.07328 - x$	x	$0.1063 + x$

Ignoring x compared to 0.07328 and 0.1063 and substituting into the K_{a1} expression gives

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HTar}^-]}{[\text{H}_2\text{Tar}]} = \frac{(0.1063 + x)(x)}{(0.07328 - x)} \cong \frac{(0.1063)(x)}{(0.07328)} = 1.0 \times 10^{-3}$$

$$x = [\text{H}_3\text{O}^+] = 6.89 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.89 \times 10^{-4}) = 3.161 = 3.16$$

- 17.96 Calculate the concentrations of the dihydrogen phosphate ion (H_2PO_4^-) and the hydrogen phosphate ion (HPO_4^{2-}).

$$(13.0 \text{ g NaH}_2\text{PO}_4 \div 120.0 \text{ g/mol}) \div 1.00 \text{ L} = 0.1082 \text{ M H}_2\text{PO}_4^-$$

$$(15.0 \text{ g Na}_2\text{HPO}_4 \div 142.0 \text{ g/mol}) \div 1.00 \text{ L} = 0.1056 \text{ M HPO}_4^{2-}$$

Conc. (M)	$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$		
Starting	0.1082	0	0.1056
Change	-x	+x	+x
Equilibrium	$0.1082 - x$	x	$0.1056 + x$

Ignoring x compared to 0.1082 and 0.1056 and substituting into the K_{a1} expression gives

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(0.1056 + x)(x)}{(0.1082 - x)} \cong \frac{(0.1056)(x)}{(0.1082)} = 6.2 \times 10^{-8}$$

$$x = [\text{H}_3\text{O}^+] = 6.35 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.353 \times 10^{-8}) = 7.197 = 7.20$$

- 17.97 Use the Henderson-Hasselbalch equation where $[\text{H}_2\text{CO}_3]$ = the buffer acid, $[\text{HCO}_3^-]$ = the buffer base, and K_{a1} of carbonic acid is the ionization constant.

$$\text{pH} = -\log K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40$$

$$7.40 = -\log (4.3 \times 10^{-7}) + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40 - 6.366 = 1.034$$

$$\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{10.81}{1} = \frac{11}{1}$$

- 17.98 Use the Henderson-Hasselbalch equation where $[\text{C}_{18}\text{H}_{21}\text{NO}_3] = [\text{Cod}]$ = the buffer base, and $[\text{HC}_{18}\text{H}_{21}\text{NO}_3^+] = [\text{HCod}^+]$ = the buffer acid. The ionization constant is calculated as follows:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-9}} = 1.61 \times 10^{-6}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{Cod}]}{[\text{HCod}^+]} = 4.50$$

$$4.50 = -\log (1.61 \times 10^{-6}) + \log \frac{[\text{Cod}]}{[\text{HCod}^+]}$$

$$\log \frac{[\text{Cod}]}{[\text{HCod}^+]} = 4.50 - 5.793 = -1.293$$

$$\log \frac{[\text{HCod}^+]}{[\text{Cod}]} = 1.293$$

$$\frac{[\text{HCod}^+]}{[\text{Cod}]} = \frac{19.6}{1} = \frac{20}{1}$$

- 17.99 All the OH^- (from the NaOH) reacts with the H_3O^+ from HCl. Calculate the stoichiometric amounts of OH^- and H_3O^+ , and subtract the mol of OH^- from the mol of H_3O^+ . Then, divide the remaining H_3O^+ by the total volume of 0.456 L + 0.285 L, or 0.741 L, to find the $[\text{H}_3\text{O}^+]$. Then, calculate the pH.

$$\text{Mol H}_3\text{O}^+ = (0.10 \text{ mol HCl/L}) \times 0.456 \text{ L HCl} = 0.0456 \text{ mol H}_3\text{O}^+$$

$$\text{Mol OH}^- = (0.15 \text{ mol NaOH/L}) \times 0.285 \text{ L NaOH} = 0.0428 \text{ mol OH}^-$$

$$\text{Mol H}_3\text{O}^+ \text{ left} = (0.0456 - 0.0428) \text{ mol H}_3\text{O}^+ = 0.0028 \text{ mol H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = 0.0028 \text{ mol H}_3\text{O}^+ \div 0.741 \text{ L total volume} = 0.0038 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.0038) = 2.42 = 2.4$$

- 17.100 All the H_3O^+ (from the HClO_4) reacts with the OH^- from KOH. Calculate the stoichiometric amounts of OH^- and H_3O^+ , and subtract the mol of H_3O^+ from the mol of OH^- . Then, divide the remaining OH^- by the volume of 0.115 L to find the $[\text{OH}^-]$. Then, calculate the pOH and pH.

$$\text{Mol OH}^- = 2.0 \text{ g KOH} \div (56.1 \text{ g KOH/mol KOH}) = 0.0357 \text{ mol OH}^-$$

$$\text{Mol H}_3\text{O}^+ = (0.19 \text{ mol HClO}_4/\text{L}) \times 0.115 \text{ L HCl} = 0.0219 \text{ mol H}_3\text{O}^+$$

$$\text{Mol OH}^- \text{ left} = (0.0357 - 0.0219) \text{ mol OH}^- = 0.0138 \text{ mol OH}^-$$

$$[\text{OH}^-] = 0.0138 \text{ mol OH}^- \div 0.115 \text{ L volume} = 0.120 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.120) = 0.9208$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 0.9208 = 13.079 = 13.08$$

- 17.101 Use BzN to symbolize benzylamine and BzNH^+ to symbolize the benzylammonium cation. At the equivalence point, equal molar amounts of BzN and HCl react to form a solution of BzNHCl . Start by calculating the moles of BzN. Use this number to calculate the volume of HCl needed to neutralize all the BzN (and use the moles of BzN as the moles of BzNH^+ formed at the equivalence point). Add the volume of HCl to the original 0.025 L to find the total volume of solution.

$$(0.025 \text{ mol BzN/L}) \times 0.065 \text{ L} = 0.00162 \text{ mol BzN}$$

$$\text{Volume HCl} = 0.00162 \text{ mol HCl} \div (0.050 \text{ mol HCl/L}) = 0.0324 \text{ L}$$

$$\text{Total volume} = 0.025 \text{ L} + 0.0324 \text{ L} = 0.0574 \text{ L}$$

$$[\text{BzNH}^+] = (0.00162 \text{ mol BzNH}^+ \text{ from BzN}) \div 0.0574 \text{ L} = 0.0282 \text{ M}$$

(continued)

Because the BzNH^+ hydrolyzes to H_3O^+ and BzN , use this to calculate the $[\text{H}_3\text{O}^+]$. Start by calculating the K_a constant of BzNH^+ from the K_b of its conjugate base, BzN . Then, assemble the usual table of concentrations, assume x is negligible, and calculate $[\text{H}_3\text{O}^+]$ and pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-10}} = 2.13 \times 10^{-5}$$

Conc. (M)	$\text{BzNH}^+ + \text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+ + \text{BzN}$
Starting	0.0282		0 0
Change	-x		+x +x
Equilibrium	0.0282 - x		x x

Substitute into the equilibrium-constant equation.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BzN}]}{[\text{BzNH}^+]} = \frac{(x)^2}{(0.0282 - x)} \cong \frac{(x)^2}{(0.0282)} = 2.13 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 7.7502 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.7502 \times 10^{-4}) = 3.1106 = 3.11$$

- 17.102 At the equivalence point, equal molar amounts of HSO_4^- and NaOH react to form a solution of Na_2SO_4 . Start by calculating the moles of HSO_4^- . Use this number to calculate the volume of NaOH needed to neutralize all the HSO_4^- (and use the moles of HSO_4^- as the moles of SO_4^{2-} formed at the equivalence point). Add the volume of NaOH to the original 0.050 L to find the total volume of solution.

$$\begin{aligned} \text{Mol } \text{HSO}_4^- &= 1.24 \text{ g NaHSO}_4 \div (120.1 \text{ g NaHSO}_4/\text{mol NaHSO}_4) \\ &= 0.01032 \text{ mol } \text{HSO}_4^- \end{aligned}$$

$$\text{Volume NaOH} = 0.01032 \text{ mol NaOH} \div (0.180 \text{ mol NaOH/L}) = 0.05733 \text{ L}$$

$$\text{Total volume} = 0.05733 \text{ L} + 0.0500 \text{ L } \text{HSO}_4^- \text{ soln} = 0.1073 \text{ L}$$

$$[\text{SO}_4^{2-}] = (0.01032 \text{ mol } \text{SO}_4^{2-} \text{ from } \text{HSO}_4^-) \div 0.1073 \text{ L} = 0.0962 \text{ M}$$

Because the SO_4^{2-} hydrolyzes to OH^- and HSO_4^- , use this number to calculate the $[\text{OH}^-]$. Start by calculating the K_a constant of SO_4^{2-} from the K_a of its conjugate acid, HSO_4^- . Assemble the usual table of concentrations, assume x is negligible, and calculate $[\text{OH}^-]$ and pH.

(continued)

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.09 \times 10^{-13}$$

Conc. (M)	$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_4^- + \text{OH}^-$		
Starting	0.0962	0	0
Change	-x	+x	+x
Equilibrium	0.0962 - x	x	x

Substitute into the equilibrium-constant equation.

$$K_b = \frac{[\text{HSO}_4^-][\text{OH}^-]}{[\text{SO}_4^{2-}]} = \frac{(x)^2}{(0.0962 - x)} \cong \frac{(x)^2}{(0.0962)} = 9.09 \times 10^{-13}$$

$$x = [\text{OH}^-] = 2.96 \times 10^{-7} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.96 \times 10^{-7}) = 6.528$$

$$\text{pH} = 14.00 - 6.528 = 7.472 = 7.47$$

17.103a. $[\text{H}_3\text{O}^+] \cong 0.100 \text{ M}$

- b. The 0.100-M H_2SO_4 ionizes to 0.100-M H_3O^+ and 0.100-M HSO_4^- . Assemble the usual table, and substitute into the K_{a2} equilibrium-constant expression for H_2SO_4 . Solve the resulting quadratic equation.

Conc. (M)	$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$		
Starting	0.100	0.100	0
Change	-x	+x	+x
Equilibrium	0.100 - x	0.100 + x	x

$$x^2 + 0.111x - (1.10 \times 10^{-3}) = 0$$

$$x = \frac{-0.111 \pm \sqrt{(0.111)^2 + 4(1.10 \times 10^{-3})}}{2}$$

$$= \frac{-0.111 \pm 0.1293}{2}$$

$$x = 9.154 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.100 + x = 0.100 + 0.009154 = 0.109 = 0.11 \text{ M}$$

17.104a. $[\text{H}_3\text{O}^+] \cong 0.150 \text{ M}$

- b. The 0.150-M H_2SeO_4 ionizes to 0.150-M H_3O^+ and 0.150-M HSeO_4^- . Assemble the usual table, and substitute into the K_{a2} equilibrium-constant expression for H_2SeO_4 . Solve the resulting quadratic equation.

Set up the table.

Conc. (M)	$\text{HSeO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SeO}_4^{2-}$		
Starting	0.150	0.150	0
Change	-x	+x	+x
Equilibrium	$0.150 - x$	$0.150 + x$	x

$$x^2 + 0.162x - (1.80 \times 10^{-3}) = 0$$

$$x = \frac{-0.162 \pm \sqrt{(0.162)^2 + 4(1.8 \times 10^{-3})}}{2}$$

$$= \frac{-0.162 \pm 0.1828}{2}$$

$$x = 1.04 \times 10^{-2}$$

$$[\text{H}_3\text{O}^+] = 0.150 + 0.0104 = 0.1604 = 0.16 \text{ M}$$

- 17.105a. From the pH, calculate the H_3O^+ ion concentration:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.82} = 1.51 \times 10^{-6} \text{ M}$$

Use the table approach, giving the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$		
Starting	0.10	0	0
Change	-x	+x	+x
Equilibrium	$0.10 - x$	x	x

From the hydronium ion concentration, $x = 1.51 \times 10^{-6}$. Substituting into the equilibrium-constant expression gives

$$\begin{aligned} K_a &= \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} = \frac{(x)^2}{(0.10 - x)} \cong \frac{(1.51 \times 10^{-6})^2}{(0.10)} = 2.28 \times 10^{-11} \\ &= 2.3 \times 10^{-11} \end{aligned}$$

(continued)

b. Now, use K_w to calculate the value of K_b :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.28 \times 10^{-11}} = 4.38 \times 10^{-4} = 4.4 \times 10^{-4}$$

c. The equilibrium concentration of CH_3NH_3^+ is approximately $0.450 \text{ mol}/1.00 \text{ L} = 0.450 \text{ M}$. Use $[\text{CH}_3\text{NH}_2] \cong 0.250 \text{ M}$. For K_a , we get

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} \cong \frac{(0.250)[\text{H}_3\text{O}^+]}{(0.450)} = 2.28 \times 10^{-11}$$

Solving for $[\text{H}_3\text{O}^+]$ gives

$$[\text{H}_3\text{O}^+] \cong \frac{(2.28 \times 10^{-11})(0.450)}{(0.250)} = 4.10 \times 10^{-11} \text{ M}$$

Thus, the pH is

$$\text{pH} = -\log(4.10 \times 10^{-11}) = 10.387 = 10.39$$

17.106a. From the pOH, calculate the OH^- ion concentration:

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.31} = 4.90 \times 10^{-6} \text{ M}$$

Use the table approach, giving the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O}$	\rightleftharpoons	$\text{C}_6\text{H}_5\text{COOH} + \text{OH}^-$
Starting	0.15		0
Change	-x		+x
Equilibrium	$0.15 - x$		x

From the hydroxide ion concentration, $x = 4.90 \times 10^{-6}$. Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(4.90 \times 10^{-6})^2}{(0.15)} = 1.60 \times 10^{-10}$$

$$= 1.6 \times 10^{-10}$$

(continued)

b. Now, use K_w to calculate the value of K_a :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.60 \times 10^{-10}} = 6.25 \times 10^{-5} = 6.3 \times 10^{-5}$$

c. The reaction is:



From the pH, calculate the H_3O^+ and $\text{C}_6\text{H}_5\text{COO}^-$ ion concentrations:

$$[\text{C}_6\text{H}_5\text{COO}^-] = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.83} = 1.48 \times 10^{-3} \text{ M}$$

Use the value of K_a to calculate the solubility of $\text{C}_6\text{H}_5\text{COOH} = y$.

$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{(1.48 \times 10^{-3})^2}{y} = 6.25 \times 10^{-5}$$

Solving for y gives the molar solubility

$$y = \frac{(1.48 \times 10^{-3})^2}{(6.25 \times 10^{-5})} = 0.0350 = 0.035 \text{ M}$$

- 17.107 a. True. Weak acids have small K_a values, so most of the solute is present as undissociated molecules.
- b. True. Weak acids have small K_a values, so most of the solute is present as the molecule.
- c. False. The hydroxide concentration equals the hydronium concentration only in neutral solutions.
- d. False. If HA were a strong acid, the pH would be equal to two.
- e. False. The H_3O^+ would be 0.010 if HA were a strong acid.
- f. True. For every HA molecule that dissociates, one H_3O^+ is generated along with one A^- .
- 17.108 a. True. Approximately 1 percent or less of most weak bases react with water.
- b. True. Very little base has reacted with water. For weak bases, most of the base is present as the molecule.

(continued)

- c. False. This is a basic solution, so there will be very little H_3O^+ .
- d. False. If B were a strong base, the $[\text{OH}^-]$ would be equal to 0.10 M.
- e. True. $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$
- f. False. Most B is present as B, so little OH^- is produced upon addition of the base to water.

17.109a. At the equivalence point, moles of acid equal moles of base. Thus,

$$\text{moles acid} = 0.115 \text{ mol/L} \times 0.03383 \text{ L} = 3.890 \times 10^{-3}$$

The molar mass is

$$\text{Molar mass} = \frac{0.288 \text{ g}}{3.890 \times 10^{-3} \text{ mol}} = 74.04 = 74.0 \text{ g/mol}$$

- b. At the 50 percent titration point, $\text{pH} = \text{pK}_a$. Since the pH measurement wasn't made, it is necessary to obtain an $[\text{A}^-]/[\text{HA}]$ ratio. The ratio can be in terms of moles, percent, mL, or M because the units end up canceling out. First, use the pH to obtain the H_3O^+ ion concentration. Express the other concentrations in mL for convenience.

$$[\text{H}_3\text{O}^+] = 10^{-4.92} = 1.20 \times 10^{-5} \text{ M}$$

$$\text{HA}_0 \cong 33.83 \text{ mL}$$

$$[\text{HA}] \cong 33.83 - 17.54 = 16.29 \text{ mL}$$

$$[\text{A}^-] \cong [\text{OH}^-] = 17.54 \text{ mL}$$

$$\begin{aligned} \text{K}_a &= [\text{H}_3\text{O}^+] \times \frac{[\text{A}^-]}{[\text{HA}]} = 1.20 \times 10^{-5} \text{ M} \times \frac{17.54 \text{ mL}}{16.29 \text{ mL}} = 1.29 \times 10^{-5} \\ &= 1.3 \times 10^{-5} \end{aligned}$$

17.110a. At the equivalence point, moles of base equal moles of acid. Thus

$$\text{moles base} = 0.135 \text{ mol/L} \times 0.03924 \text{ L} = 5.297 \times 10^{-3}$$

The molar mass is

$$\text{Molar mass} = \frac{0.239 \text{ g}}{5.297 \times 10^{-3} \text{ mol}} = 45.11 = 45.1 \text{ g/mol}$$

(continued)

- b. At the 50 percent titration point, $pK_b = pOH$. Since the pH measurement wasn't made, it is necessary to obtain a $[HB^+]/[B]$ ratio. The ratio can be in terms of moles, percent, mL, or M because the units end up canceling out. First, use the pH to obtain the OH^- ion concentration. Express the other concentrations in mL for convenience.

$$pOH = 14.00 - 10.73 = 3.27$$

$$[OH^-] = 10^{-3.27} = 5.370 \times 10^{-4}$$

$$B_o \cong 39.24 \text{ mL}$$

$$[B] \cong 39.24 - 18.35 = 20.89 \text{ mL}$$

$$[HB^+] \cong [H_3O^+] = 18.35 \text{ mL}$$

$$K_b = [OH^-] \times \frac{[HB^+][OH^-]}{[B]} = 5.370 \times 10^{-4} \text{ M} \times \frac{18.35 \text{ mL}}{20.89 \text{ mL}} = 4.72 \times 10^{-4}$$

$$= 4.7 \times 10^{-4}$$

- 17.111 a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$NH_3 + H_2O$	$NH_4^+ + OH^-$
Starting	0.10	0 0
Change	-x	+x +x
Equilibrium	$0.10 - x$	x x

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[NH_4^+][OH^-]}{[OH^-]} = \frac{(x)^2}{(0.10 - x)} \cong \frac{(x)^2}{(0.10)} = 1.8 \times 10^{-5}$$

Rearranging and solving for x gives

$$x = [OH^-] = \sqrt{(0.10)(1.8 \times 10^{-5})} = 1.34 \times 10^{-3} \text{ M}$$

$$pOH = -\log(1.34 \times 10^{-3}) = 2.873$$

$$pH = 14 - pOH = 14 - 2.873 = 11.127 = 11.13$$

(continued)

30 percent titration point: Express the concentrations as percents for convenience.

$$[\text{NH}_3] \approx 70\% \text{ and } [\text{NH}_4^+] \approx 30\%$$

Plug into the equilibrium-constant expression.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(30\%)(x)}{(70\%)} = 1.8 \times 10^{-5}$$

Solving for x gives

$$x = [\text{OH}^-] = 1.8 \times 10^{-5} \times \frac{70\%}{30\%} = 4.20 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(4.20 \times 10^{-5}) = 4.377$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.377 = 9.623 = 9.62$$

50 percent titration point:

$$[\text{NH}_4^+] = [\text{NH}_3]$$

$$K_b = [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(1.8 \times 10^{-5}) = 4.744$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.744 = 9.256 = 9.26$$

100 percent titration point:

The NH_4Cl that is produced has undergone a two-fold dilution.

$$[\text{NH}_4^+] = 0.0500 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$		
Starting	0.0500	0	0
Change	-x	+x	+x
Equilibrium	$0.0500 - x$	x	x

(continued)

Now, use K_w to calculate the value of K_a :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

Plug into the equilibrium-constant expression.

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)^2}{(0.0500 - x)} \cong \frac{(x)^2}{(0.0500)} = 5.55 \times 10^{-10}$$

Solving for x gives

$$x = [\text{H}_3\text{O}^+] = \sqrt{0.0500 \times \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 5.27 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log(5.27 \times 10^{-6}) = 5.278 = 5.28$$

- b. The solution is acidic because the NH_4^+ ion reacts with water to produce acid. Ammonium chloride is the salt of a weak base and a strong acid.

- 17.112 a. Initial pH: Use the table approach, and give the starting, change, and equilibrium concentrations. Here, $\text{A}^- = \text{CH}_3\text{CH}_2\text{COO}^-$.

Conc. (M)	$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$	H_3O^+	A^-
Starting	0.15	0	0
Change	-x	+x	+x
Equilibrium	$0.15 - x$	x	x

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)^2}{(0.15 - x)} \cong \frac{(x)^2}{(0.15)} = 1.3 \times 10^{-5}$$

Rearranging and solving for x gives

$$x = [\text{H}_3\text{O}^+] = \sqrt{(0.15)(1.3 \times 10^{-5})} = 1.40 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(1.40 \times 10^{-3}) = 2.853 = 2.85$$

(continued)

50 percent titration point:

$$[\text{H}_3\text{O}^+] = [\text{A}^-] = K_a = 1.3 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log (1.3 \times 10^{-5}) = 4.886 = 4.89$$

60 percent titration point: Express the concentrations as percents for convenience.

$$[\text{HA}] \approx 40\% \text{ and } [\text{A}^-] \approx 60\%$$

Plug into the equilibrium-constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \cong \frac{(60\%)(x)}{(40\%)} = 1.3 \times 10^{-5}$$

Solving for x gives

$$x = [\text{H}_3\text{O}^+] = 1.3 \times 10^{-5} \times \frac{40\%}{60\%} = 8.67 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log (8.67 \times 10^{-6}) = 5.062 = 5.06$$

100 percent titration point:

The salt produced has undergone a two-fold dilution.

$$[\text{A}^-] = 0.0750 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$		
Starting	0.0750	0	0
Change	-x	+x	+x
Equilibrium	$0.0750 - x$	x	x

Now, use K_w to calculate the value of K_b :

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.69 \times 10^{-10}$$

(continued)

Plug into the equilibrium-constant expression.

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x^2}{0.0750 - x} \cong \frac{x^2}{0.0750} = 7.69 \times 10^{-10}$$

Solving for x gives

$$x = [\text{OH}^-] = \sqrt{0.0750 \times 7.69 \times 10^{-10}} = 7.59 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(7.59 \times 10^{-6}) = 5.120$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5.120 = 8.880 = 8.88$$

- b. The solution is basic because the propionate ion reacts with water to produce OH^- . Potassium propionate is the salt of a weak acid and a strong base.

17.113a. Select the conjugate pair that has a pK_a value closest to a pH of 2.88.

$$\text{pK}_a(\text{H}_2\text{C}_2\text{O}_4) = 1.25$$

$$\text{pK}_a(\text{H}_3\text{PO}_4) = 2.16$$

$$\text{pK}_a(\text{HCOOH}) = 3.77$$

Therefore, the best pair is H_3PO_4 and H_2PO_4^- .

- b. Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$2.88 = 2.16 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = 0.72$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{0.72} = 5.24$$

(continued)

Therefore, 5.24 times more conjugate base is needed than acid. Since the starting concentrations of H_3PO_4 (HA) and H_2PO_4^- (A^-) are the same, the volume of A^- needed is 5.24 times the volume of HA needed. For 50 mL of buffer, this is

$$50 \text{ mL} = \text{vol HA} + \text{vol A}^- = \text{vol HA} + 5.24 \text{ vol HA} = 6.24 \text{ vol HA}$$

Therefore, the volume of 0.10 M H_3PO_4 required is

$$\text{vol H}_3\text{PO}_4 = \frac{50 \text{ mL}}{6.24} = 8.01 \text{ mL} = 8 \text{ mL}$$

The volume of 0.10 M H_2PO_4^- required is

$$50 \text{ mL} - 8.01 \text{ mL} = 42.0 \text{ mL} = 42 \text{ mL}$$

17.114a. Select the conjugate pair that has a pK_a value closest to a pH of 6.96.

$$\text{pK}_a (\text{NH}_4^+) = 9.25$$

$$\text{pK}_a (\text{H}_2\text{CO}_3) = 6.37$$

$$\text{pK}_a (\text{H}_2\text{PO}_4^-) = 7.21$$

Therefore, the best pair is H_2PO_4^- and HPO_4^{2-} .

b. Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$6.96 = 7.21 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = -0.25$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{-0.25} = 0.562$$

Therefore, 0.562 times more conjugate base is needed than acid. Since the starting concentrations of H_2PO_4^- (HA) and HPO_4^{2-} (A^-) are the same, the volume of A^- needed is 0.562 times the volume of HA needed. For 100 mL of buffer, this is

$$100 \text{ mL} = \text{vol HA} + \text{vol A}^- = \text{vol HA} + 0.562 \text{ vol HA} = 1.562 \text{ vol HA}$$

(continued)

Therefore, the volume of 0.10 M H_2PO_4^- required is

$$\text{vol } \text{H}_2\text{PO}_4^- = \frac{100 \text{ mL}}{1.562} = 64.02 \text{ mL} = 64 \text{ mL}$$

The volume of 0.10 M HPO_4^{2-} required is

$$100 \text{ mL} - 64.02 \text{ mL} = 35.98 \text{ mL} = 36 \text{ mL}$$

17.115a. At the equivalence point, moles of base equal moles of acid. Therefore,

$$M_{\text{NH}_2\text{OH}} \times 25.0 \text{ mL} = 0.150 \text{ M} \times 35.8 \text{ mL}$$

$$M_{\text{NH}_2\text{OH}} = \frac{0.150 \text{ M} \times 35.8 \text{ mL}}{25.0 \text{ mL}} = 0.2148 = 0.215$$

b. Concentration of NH_3OH^+ at the equivalence point is

$$[\text{NH}_3\text{OH}^+] = \frac{(25.0 \text{ mL})(0.215 \text{ M})}{25.0 \text{ mL} + 35.8 \text{ mL}} = 0.08840 \text{ M}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.09 \times 10^{-7}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{NH}_3\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{OH} + \text{H}_3\text{O}^+$		
Starting	0.08840	0	0
Change	-x	+x	+x
Equilibrium	0.08840 - x	x	x

Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[\text{NH}_2\text{OH}][\text{H}_3\text{O}^+]}{[\text{NH}_3\text{OH}^+]} = \frac{(x)^2}{(0.08840 - x)} \cong \frac{(x)^2}{(0.08840)} = 9.09 \times 10^{-7}$$

Rearranging and solving for x gives

$$x = [\text{H}_3\text{O}^+] = \sqrt{(0.08840)(9.09 \times 10^{-7})} = 2.83 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(2.84 \times 10^{-4}) = 3.547 = 3.55$$

(continued)

- c. You need an indicator to change pH around pH of 3 to 4. Therefore, the appropriate indicator is bromophenol blue. Select an indicator that changes color around the equivalence point.

17.116a. At the equivalence point, moles of base equal moles of acid. The molar mass of NaHCO_3 is 84.01 g/mol. Therefore,

$$\begin{aligned}\text{mol base} &= \text{mol acid} = 0.562 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \\ &= 6.690 \times 10^{-3} \text{ mol}\end{aligned}$$

The molarity of the base is

$$M_{\text{NaOH}} = \frac{6.690 \times 10^{-3} \text{ mol}}{0.04236 \text{ L}} = 0.1579 = 0.158 \text{ M}$$

- b. The concentration of CO_3^{2-} at the equivalence point is

$$[\text{CO}_3^{2-}] = \frac{6.690 \times 10^{-3} \text{ mol}}{0.02500 \text{ L} + 0.04236 \text{ L}} = 0.09932 \text{ M}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.08 \times 10^{-4}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{CO}_3^{2-} + \text{H}_2\text{O}$	$\text{HCO}_3^- + \text{OH}^-$
Starting	0.09932	0 0
Change	-x	+x +x
Equilibrium	0.09932 - x	x x

Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{x^2}{0.09932 - x} \cong \frac{x^2}{0.09932} = 2.08 \times 10^{-4}$$

Rearranging and solving for x gives

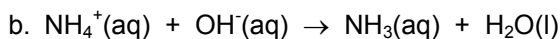
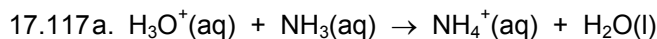
$$x = [\text{OH}^-] = \sqrt{(0.09932)(2.08 \times 10^{-4})} = 4.55 \times 10^{-3} \text{ M}$$

(continued)

$$\text{pOH} = -\log(4.55 \times 10^{-3}) = 2.342$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.342 = 11.658 = 11.66$$

c. Alizarin yellow R. It changes color around the equivalence point.



c. Initial:

$$\text{mol NH}_3 = 1.0 \text{ mol/L} \times 0.100 \text{ L} = 0.100 = 0.10 \text{ mol}$$

$$\text{mol NH}_4^+ = 0.50 \text{ mol/L} \times 0.100 \text{ L} \times \frac{2 \text{ mol NH}_4^+}{1 \text{ mol (NH}_4)_2\text{SO}_4} = 0.100 = 0.10 \text{ mol}$$

After addition of HCl: The HCl is completely consumed by producing 0.0100 mol of NH_4^+ . The amount of NH_3 is decreased by 0.0100 mol.

$$\text{mol HCl added} = 1.00 \text{ mol/L} \times 0.0100 \text{ L} = 0.0100 \text{ mol}$$

$$\text{mol NH}_3 = 0.100 - 0.0100 = 0.090 = 0.090 \text{ mol}$$

$$\text{mol NH}_4^+ = 0.100 + 0.0100 = 0.110 = 0.11 \text{ mol}$$

The reaction is:



Substituting into the equilibrium-constant expression gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.110)[\text{OH}^-]}{(0.090)} = 1.8 \times 10^{-5}$$

Rearranging and solving for $[\text{OH}^-]$ gives

$$[\text{OH}^-] = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.47 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(1.47 \times 10^{-5}) = 4.83$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.83 = 9.17 = 9.2$$

d. This is a buffer system, so the ratio of $\text{NH}_4^+/\text{NH}_3$ has not changed very much.

- 17.118a. Use the table approach, and give the starting, change, and equilibrium concentrations. The initial concentration of formic acid (HCOOH) is 0.150 mol/0.425 L = 0.3529 M.

Conc. (M)	HCOOH + H ₂ O ⇌ H ₃ O ⁺ + HCOO ⁻		
Starting	0.3529	0	0
Change	-x	+x	+x
Equilibrium	0.3529 - x	x	x

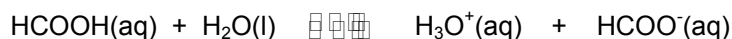
Substituting into the equilibrium-constant expression gives

$$K_a = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} = \frac{(x)^2}{(0.3529 - x)} \cong \frac{(x)^2}{(0.3529)} = 1.7 \times 10^{-4}$$

Rearranging and solving for x gives

$$x = [\text{H}_3\text{O}^+] = [\text{HCOO}^-] = \sqrt{(0.3529)(1.7 \times 10^{-4})} = 7.74 \times 10^{-3} = 7.7 \times 10^{-3} \text{ M}$$

- b. To decrease the HCOO⁻ concentration by a factor of ten, the concentration must be reduced to 7.74×10^{-4} M. The change in equilibrium is



Assume the changes in concentration are small, so [HCOOH] \cong 0.3529 M. Substitute into the rearranged equilibrium-constant equation.

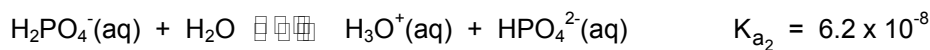
$$[\text{H}_3\text{O}^+] = \frac{[\text{HCOOH}]K_a}{[\text{HCOO}^-]} = \frac{(0.3529)(1.7 \times 10^{-4})}{7.74 \times 10^{-4}} = 0.0775 = 0.078 \text{ M}$$

$$0.0775 \text{ M} \times 425 \text{ mL} = 2.00 \text{ M} \times V$$

$$V = 16.4 = 16 \text{ mL}$$

- c. This is the common ion effect. An increase in the H₃O⁺ concentration shifts the equilibrium so the percent dissociation of HCOOH is decreased.

17.119a. From the pH $[\text{H}_3\text{O}^+] = 10^{-7.44} = 3.63 \times 10^{-8} \text{ M}$. The reaction is



$$K_{a_2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$$

Rearranging gives

$$\frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = \frac{[\text{H}_3\text{O}^+]}{K_{a_2}} = \frac{3.63 \times 10^{-8}}{6.2 \times 10^{-8}} = \frac{0.5855}{1} = 0.59 \text{ to } 1$$

Or, using the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$7.44 = 7.21 + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\log \frac{[\text{base}]}{[\text{acid}]} = 0.23$$

$$\frac{[\text{base}]}{[\text{acid}]} = 10^{0.23} = 1.71$$

You must invert each side. The result is

$$\frac{[\text{acid}]}{[\text{base}]} = \frac{1}{1.71} = \frac{0.5857}{1} = 0.59 \text{ to } 1$$

$$\text{b. } [\text{H}_3\text{O}^+] = K_{a_2} = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

If $\text{HPO}_4^{2-} = 1.00 \text{ mol}$, then when 25 percent of it is converted into H_2PO_4^- , 0.75 mol remain, and H_2PO_4^- becomes $0.586 + 0.25 = 0.836 \text{ mol}$. Therefore,

$$[\text{H}_3\text{O}^+] = 6.2 \times 10^{-8} \times \frac{0.836}{0.75} = 6.91 \times 10^{-8}$$

$$\text{pH} = -\log (6.91 \times 10^{-8}) = 7.161 = 7.16$$

(continued)

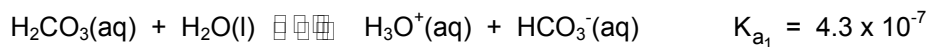
c. Assume $\text{H}_2\text{PO}_4^- = 0.586$ mol. Then, H_2PO_4^- remaining = $0.586 - (0.15 \times 0.586)$
 $= 0.85 \times 0.586 = 0.498$ mol left

The moles of $\text{HPO}_4^{2-} = 1.00 + (0.15 \times 0.586) = 1.088$ mol.

$$[\text{H}_3\text{O}^+] = 6.2 \times 10^{-8} \times \frac{0.498}{1.088} = 2.84 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log(2.84 \times 10^{-8}) = 7.547 = 7.55$$

17.120a. From the pH, $[\text{H}_3\text{O}^+] = 10^{-7.42} = 3.80 \times 10^{-8} \text{ M}$. The reaction is



$$K_{a_1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]}$$

Rearranging gives

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a_1}} = \frac{3.80 \times 10^{-8}}{4.3 \times 10^{-7}} = \frac{0.0884}{1} = 0.088 \text{ to } 1$$

Or, using the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$7.42 = 6.367 + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\log \frac{[\text{base}]}{[\text{acid}]} = 1.053$$

$$\frac{[\text{base}]}{[\text{acid}]} = 10^{1.053} = 11.30$$

You must invert each side. The result is

$$\frac{[\text{acid}]}{[\text{base}]} = \frac{1}{11.30} = \frac{0.0885}{1} = 0.089 \text{ to } 1$$

(continued)

- b. If $\text{HCO}_3^- = 1.00$ mol, then when 15 percent of it is converted into H_2CO_3 , 0.85 mol remain, and H_2CO_3 becomes $0.0884 + 0.15 = 0.238$ mol. Therefore,

$$[\text{H}_3\text{O}^+] = 4.3 \times 10^{-7} \times \frac{0.238}{0.85} = 1.20 \times 10^{-7} \text{ M}$$

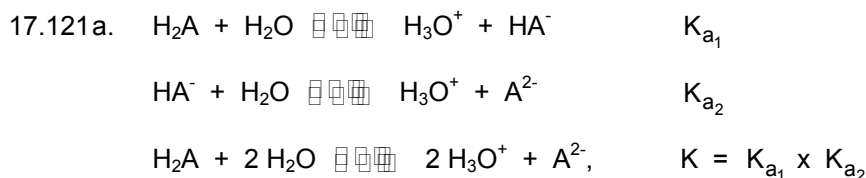
$$\text{pH} = -\log(1.20 \times 10^{-7}) = 6.920 = 6.92$$

- c. Assume $\text{H}_2\text{CO}_3 = 0.0884$ mol. Then, $\text{HCO}_3^- = 0.0884 - 0.25 \times 0.0884$
 $= 0.75 \times 0.0884 = 0.0663$ mol left

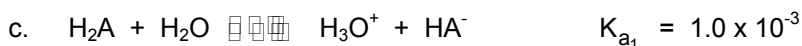
The moles of $\text{HCO}_3^- = 1.000 + 0.25 \times 0.0884 = 1.0221$ mol.

$$[\text{H}_3\text{O}^+] = 4.3 \times 10^{-7} \times \frac{0.0663}{1.0221} = 2.79 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log(2.79 \times 10^{-8}) = 7.547 = 7.55$$



- b. $\text{H}_2\text{A} \gg \text{H}_3\text{O}^+ = \text{HA}^- \gg \text{A}^{2-}$



$$0.0250 - x \quad \quad \quad x \quad \quad x$$

$$K_{a_1} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}]} = \frac{(x)^2}{(0.0250 - x)} = 1.0 \times 10^{-3}$$

Rearranging into a quadratic equation and solving for x gives

$$x^2 + (1.0 \times 10^{-3})x + (-2.50 \times 10^{-5}) = 0$$

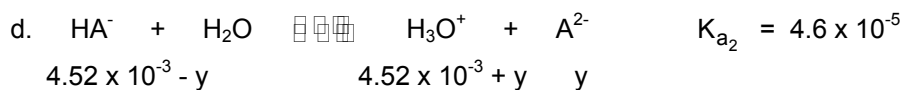
$$x = \frac{-(1.0 \times 10^{-3}) \pm \sqrt{(1.0 \times 10^{-3})^2 - (4)(1)(-2.50 \times 10^{-5})}}{2}$$

$$x = [\text{H}_3\text{O}^+] = [\text{HA}^-] = 4.52 \times 10^{-3} = 4.5 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(4.52 \times 10^{-3}) = 2.344 = 2.34$$

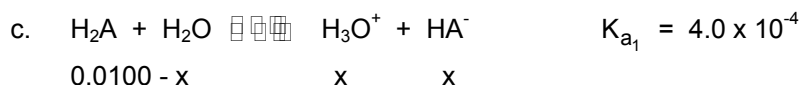
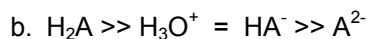
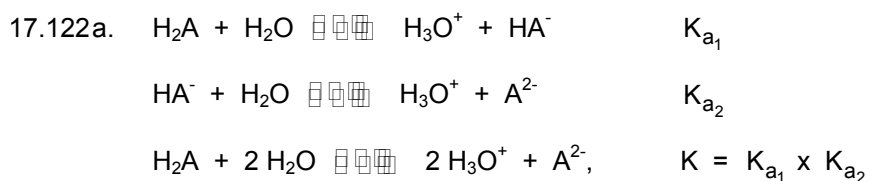
$$[\text{H}_2\text{A}] = 0.0250 - x = 0.0250 - 4.52 \times 10^{-3} = 0.02048 = 0.0205 \text{ M}$$

(continued)



Assume y is small compared to 4.52×10^{-3} M. Substitute into the rearranged equilibrium-constant equation to get

$$[\text{A}^{2-}] = \frac{[\text{HA}^-]K_{a_2}}{[\text{H}_3\text{O}^+]} = \frac{(4.52 \times 10^{-3})(4.6 \times 10^{-5})}{(4.52 \times 10^{-3})} = 4.6 \times 10^{-5} \text{ M}$$



Substitute into the equilibrium-constant equation to get

$$K_{a_1} = \frac{[\text{HA}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{A}]} = \frac{(x)^2}{(0.0100 - x)} = 4.0 \times 10^{-4}$$

Rearranging into a quadratic equation and solving for x gives

$$x^2 + (4.0 \times 10^{-4})x + (-4.00 \times 10^{-6}) = 0$$

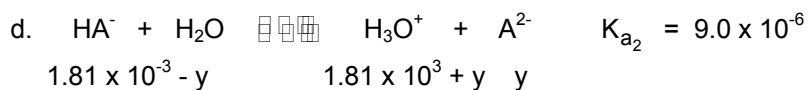
$$x = \frac{-(4.0 \times 10^{-4}) \pm \sqrt{(4.0 \times 10^{-4})^2 - (4)(1)(-4.00 \times 10^{-6})}}{2}$$

$$x = [\text{H}_3\text{O}^+] = [\text{HA}^-] = 1.81 \times 10^{-3} = 1.8 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(1.81 \times 10^{-3}) = 2.742 = 2.74$$

$$[\text{H}_2\text{A}] = 0.0100 - x = 0.0100 - 1.81 \times 10^{-3} = 0.00819 = 0.0082 \text{ M}$$

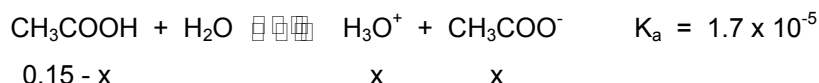
(continued)



Assume y is small compared to 1.81×10^{-3} M. Substitute into the rearranged equilibrium-constant equation to get

$$[\text{A}^{2-}] = \frac{[\text{HA}^-]K_{a_2}}{[\text{H}_3\text{O}^+]} = \frac{(1.81 \times 10^{-3})(9.0 \times 10^{-6})}{(1.81 \times 10^{-3})} = 9.0 \times 10^{-6} \text{ M}$$

- 17.123a. From the pH, $[\text{H}_3\text{O}^+] = 10^{-4.45} = 3.55 \times 10^{-5}$ M. The NaCH_3COO is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Rearranging gives

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{K_a}{[\text{H}_3\text{O}^+]}$$

$$\frac{x}{0.15 - x} = \frac{1.7 \times 10^{-5}}{3.55 \times 10^{-5}}$$

Solving for x gives $x = 0.0486$ mol. Therefore, the molar concentration is

$$[\text{CH}_3\text{COO}^-] = 0.0486 \text{ mol}/0.375 \text{ L} = 0.1296 = 0.13 \text{ M}$$

- b. moles OH^- = moles CH_3COO^-

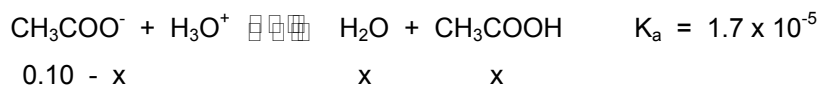
$$0.0486 \text{ mol} = 0.25 \text{ M} \times V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = 0.0486 \text{ mol}/0.25 \text{ M} = 0.194 = 0.19 \text{ L} \quad (1.9 \times 10^2 \text{ mL})$$

- c. The volume of the original acid is $V = 0.375 \text{ L} - 0.194 \text{ L} = 0.181 \text{ L}$. Therefore, the concentration of the original acid is

$$[\text{CH}_3\text{COOH}] = 0.15 \text{ mol}/0.181 \text{ L} = 0.829 = 0.83 \text{ M}$$

17.124a. From the pH, $[\text{H}_3\text{O}^+] = 10^{-4.56} = 2.75 \times 10^{-5} \text{ M}$. The CH_3COOH is generated by the acid-base reaction, resulting in the formation of a buffer solution. The reaction is



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Rearranging gives

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{K_a}{[\text{H}_3\text{O}^+]}$$

$$\frac{0.10 - x}{x} = \frac{1.7 \times 10^{-5}}{2.75 \times 10^{-5}}$$

Solving for x gives $x = 0.0618 \text{ mol}$. Therefore, the molar concentration is

$$[\text{CH}_3\text{COO}^-] = 0.0618 \text{ mol} / 0.650 \text{ L} = 0.0951 = 0.095 \text{ M}$$

b. moles of HCl equal moles of CH_3COOH

$$0.0618 \text{ mol} = 0.15 \text{ M} \times V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = 0.0618 \text{ mol} / 0.15 \text{ M} = 0.412 = 0.41 \text{ L}$$

c. The volume of the original acid is $V = 0.650 \text{ L} - 0.412 \text{ L} = 0.238 \text{ L}$. Therefore, the concentration of the original acid is

$$[\text{CH}_3\text{COOH}] = 0.10 \text{ mol} / 0.238 \text{ L} = 0.420 = 0.42 \text{ M}$$

■ Solutions to Cumulative-Skills Problems

- 17.125 Use the pH to calculate $[\text{H}_3\text{O}^+]$, and then use the K_a of 1.7×10^{-5} and the K_a expression to calculate the molarity of acetic acid (HAc), assuming ionization is negligible. Convert molarity to mass percentage using the formula weight of 60.05 g/mol of HAc.

$$[\text{H}_3\text{O}^+] = \text{antilog}(-2.45) = 3.548 \times 10^{-3} \text{ M}$$

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the (0.003548 M) terms into the expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} \cong \frac{(0.003548)^2}{(x)}$$

Solve the equation for x, assuming 0.003548 is much smaller than x.

$$x = (0.003548)^2 \div (1.7 \times 10^{-5}) \cong [\text{HAc}] \cong 0.7404 \text{ M}$$

$$\begin{aligned} (0.7404 \text{ mol HAc/L}) \times (60.05 \text{ g/mol}) \times (1 \text{ L}/1090 \text{ g})(100\%) \\ = 4.078 = 4.1 \text{ percent HAc} \end{aligned}$$

- 17.126 Use the pH to calculate $[\text{OH}^-]$, and then use the K_b of 1.8×10^{-5} and the K_b expression to calculate the molarity of ammonia (NH_3), assuming ionization is negligible. Convert molarity to mass percentage using the formula weight of 17.03 g/mol of NH_3 .

$$[\text{OH}^-] = \text{antilog}[-(14.00 - 11.87)] = 7.413 \times 10^{-3} \text{ M}$$

Write the equilibrium-constant expression in terms of chemical symbols, and then substitute the x and the (0.007413 M) terms into the expression:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \cong \frac{(0.007413)^2}{(x)} = 1.8 \times 10^{-5}$$

Solve the equation for x, assuming 0.007413 is much smaller than x.

$$x = (0.007413)^2 \div (1.8 \times 10^{-5}) \cong [\text{NH}_3] = 3.053 \text{ M}$$

$$\begin{aligned} (3.053 \text{ mol NH}_3/\text{L}) \times (17.03 \text{ g/mol}) \times (1 \text{ L}/1000 \text{ g}) \times 100\% \\ = 5.199 = 5.2 \text{ percent NH}_3 \end{aligned}$$

- 17.127 Find the $[\text{H}_3\text{O}^+]$ and $[\text{C}_2\text{H}_3\text{O}_2^-]$ by solving for the approximate $[\text{H}_3\text{O}^+]$, noting x is much smaller than the starting 0.92 M of acetic acid. The usual table is used but is not shown; only the final setup for $[\text{H}_3\text{O}^+]$ is shown. Use $K_f = 1.858\text{ }^\circ\text{C/m}$ for the constant for water.

$$[\text{H}_3\text{O}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = (1.7 \times 10^{-5} \times 0.92)^{1/2} = 0.003954 \text{ M}$$

$$\text{Total molarity of acid + ions} = 0.92 + 0.003954 = 0.9239$$

$$\text{Molality} = m = 0.9239 \text{ mol} \div (1.000 \text{ L} \times 0.953 \text{ kg H}_2\text{O/L}) = 0.9695 \text{ m}$$

$$\text{Freezing point} = -\Delta T_f = -K_f c_m = (-1.858\text{ }^\circ\text{C/m}) \times 0.9695 \text{ m} = -1.801 = -1.8\text{ }^\circ\text{C}$$

- 17.128 Find the $[\text{NH}_4^+]$ and $[\text{OH}^-]$ by solving for the approximate $[\text{OH}^-]$, noting x is much smaller than the starting 0.87 M of ammonia. The usual table is used but is not shown; only the final setup for $[\text{OH}^-]$ is shown. Use $K_f = 1.858\text{ }^\circ\text{C/m}$ for the constant for water.

$$[\text{NH}_4^+] = [\text{OH}^-] = (1.8 \times 10^{-5} \times 0.87)^{1/2} = 0.003957 \text{ M}$$

$$\text{Total molarity of base and ions} = 0.87 + 0.003957 = 0.8739 \text{ M}$$

$$\text{kg NH}_3/\text{L} = 0.87 \text{ mol/L} \times 0.017 \text{ kg/mol} = 0.0148 \text{ kg NH}_3/\text{L}$$

$$\text{kg H}_2\text{O/L} = 0.992 \text{ kg soln/L} - 0.0148 \text{ kg NH}_3/\text{L} = 0.977 \text{ kg H}_2\text{O/L}$$

$$\text{Molality} = m = 0.8739 \text{ mol} \div (1.000 \text{ L} \times 0.977 \text{ kg solv/L}) = 0.8944 \text{ m}$$

$$\text{Freezing point} = -\Delta T_f = -K_f c_m = (-1.858\text{ }^\circ\text{C/m}) \times 0.8944 \text{ m} = -1.662 = -1.7\text{ }^\circ\text{C}$$

- 17.129 The $[\text{H}_3\text{O}^+] = -\text{antilog}(-4.35) = 4.46 \times 10^{-5} \text{ M}$. Note that 0.465 L of 0.0941 M NaOH will produce 0.043756 mol of acetate, Ac^- , ion. Rearranging the K_a expression for acetic acid (HAc) and Ac^- and canceling the volume in the mol/L of each, you obtain:

$$\frac{[\text{HAc}]}{[\text{Ac}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{4.46 \times 10^{-5}}{1.7 \times 10^{-5}} = \frac{2.63}{1.00} \cong \frac{x \text{ mol HAc}}{0.043756 \text{ mol Ac}^-}$$

$$x = 0.1149 \text{ mol HAc}$$

$$\text{Total mol HAc added} = 0.1149 + 0.043756 = 0.1587 \text{ mol HAc}$$

$$\text{Mol/L of pure HAc} = 1049 \text{ g HAc/L} \times (1 \text{ mol HAc}/60.05 \text{ g}) = 17.467 \text{ mol/L}$$

$$\text{L of pure HAc needed} = 0.1587 \text{ mol HAc} \times (\text{L}/17.467 \text{ mol}) = 0.00908 \text{ L (9.1 mL)}$$

- 17.130 The $[\text{H}_3\text{O}^+] = -\text{antilog}(-3.50) = 3.16 \times 10^{-4} \text{ M}$. Note that 0.325 L of 0.0857 M NaOH will produce 0.027852 mol of formate, Fo^- , ion. Rearranging the K_a expression for formic acid (HFO) and Fo^- and canceling the volume in the mol/L of each, you obtain:

$$\frac{[\text{HFO}]}{[\text{Fo}^-]} = \frac{[\text{H}^+]}{K_a} = \frac{3.16 \times 10^{-4}}{1.7 \times 10^{-4}} = \frac{1.858}{1.00} \cong \frac{x \text{ mol HFO}}{0.027852 \text{ mol Fo}^-}$$

$$x = 0.05175 \text{ mol HFO}$$

$$\text{Total mol HFO added} = 0.05175 + 0.027852 = 0.079602 \text{ mol HFO}$$

$$\text{Mol/L of pure HFO} = 1220 \text{ g HFO/L} \times (1 \text{ mol HFO}/46.027 \text{ g}) = 26.506 \text{ mol/L}$$

$$\text{L of pure HFO needed} = 0.079602 \text{ mol HAc} \times (\text{L}/26.506 \text{ mol}) = 0.00300 \text{ L (3.0 mL)}$$

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