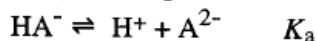
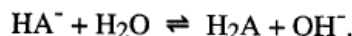


- 11-1. The  $K_a$  reaction, with a much greater equilibrium constant than  $K_b$ , releases  $H^+$ :



Each mole of  $H^+$  reacts with one mole of  $OH^-$  from the  $K_b$  reaction:



The net result is that the  $K_b$  reaction is driven almost as far toward completion as the  $K_a$  reaction.

- 11-4. (a)  $\frac{x^2}{0.100 - x} = K_1 \Rightarrow x = 3.11 \times 10^{-3} = [H^+] = [HA^-] \Rightarrow \text{pH} = 2.51$

$$[H_2A] = 0.100 - x = 0.0969 \text{ M} \quad [A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1.00 \times 10^{-8} \text{ M}$$

- (b)  $[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = 1.00 \times 10^{-6} \Rightarrow \text{pH} = 6.00$

$$[HA^-] \approx 0.100 \text{ M}$$

$$[H_2A] = \frac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-3} \text{ M} \quad [A^{2-}] = \frac{K_2[HA^-]}{[H^+]} = 1.00 \times 10^{-3} \text{ M}$$

- (c)  $\frac{x^2}{0.100 - x} = \frac{K_w}{K_2} \Rightarrow x = [OH^-] = [HA^-] = 3.16 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.50$

$$[A^{2-}] = 0.100 - x = 9.97 \times 10^{-2} \text{ M} \quad [H_2A] = \frac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-10} \text{ M}$$

	pH	$[H_2A]$	$[HA^-]$	$[A^{2-}]$
0.100 M $H_2A$	2.51	$9.69 \times 10^{-2}$	$3.11 \times 10^{-3}$	$1.00 \times 10^{-8}$
0.100 M NaHA	6.00	$1.00 \times 10^{-3}$	$1.00 \times 10^{-1}$	$1.00 \times 10^{-3}$
0.100 M $Na_2A$	10.50	$1.00 \times 10^{-10}$	$3.16 \times 10^{-4}$	$9.97 \times 10^{-2}$

- 11-5. (a)  $H_2M = H^+ + HM^- \quad K_1 = 1.42 \times 10^{-3}$   
 $\begin{array}{ccc} F-x & x & x \end{array}$

$$\frac{x^2}{0.100 - x} = K_1 \Rightarrow x = 1.12 \times 10^{-2} \Rightarrow \text{pH} = -\log x = 1.95$$

$$[H_2M] = 0.100 - x = 0.089 \text{ M}$$

$$[HM^-] = x = 1.12 \times 10^{-2} \text{ M} \quad [M^{2-}] = \frac{[HM^-] K_2}{[H^+]} = 2.01 \times 10^{-6} \text{ M}$$

- (b)  $[H^+] = \sqrt{\frac{K_1 K_2 (0.100) + K_1 K_w}{K_1 + 0.100}} = 5.30 \times 10^{-5} \Rightarrow \text{pH} = 4.28$

$$[HM^-] \approx 0.100 \text{ M} \quad [H_2M] = \frac{[HM^-][H^+]}{K_1} = 3.7 \times 10^{-3} \text{ M}$$

$$[M^{2-}] = \frac{K_2[HM^-]}{[H^+]} = 3.8 \times 10^{-3} \text{ M}$$

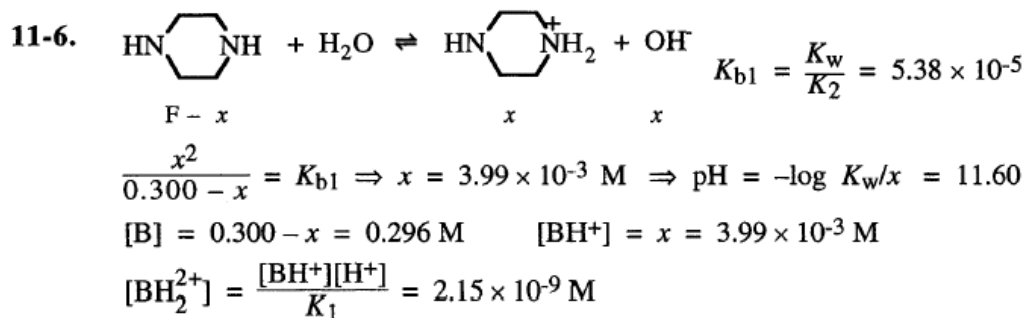
The method of Box 11-2 would give more accurate answers, since  $[HM^-]$  is not that much greater than  $[H_2M]$  or  $[M^{2-}]$  in this case.

- (c)  $M^{2-} + H_2O \rightleftharpoons HM^- + OH^- \quad K_{b1} = K_w/K_{a2} = 4.98 \times 10^{-9}$   
 $\begin{array}{ccc} F-x & x & x \end{array}$

$$\frac{x^2}{0.100 - x} = K_{b1} \Rightarrow x = 2.23 \times 10^{-5} \Rightarrow \text{pH} = -\log \frac{K_w}{x} = 9.35$$

$$[M^{2-}] = 0.100 - x = 0.100 \text{ M} \quad [HM^-] = x = 2.23 \times 10^{-5} \text{ M}$$

$$[H_2M] = \frac{[H^+][HM^-]}{K_1} = 7.04 \times 10^{-12} \text{ M}$$



11-7. For  $\text{H}_2\text{A}$ ,  $K_1 = 5.60 \times 10^{-2}$  and  $K_2 = 5.42 \times 10^{-5}$

First approximation ( $[\text{HA}^-]_1 \approx 0.00100 \text{ M}$ ):

$$[\text{H}^+]_1 = \sqrt{\frac{K_1 K_2 (0.00100) + K_1 K_w}{K_1 + 0.00100}} = 2.31 \times 10^{-4} \text{ M} \Rightarrow \text{pH}_1 = 3.64$$

$$[\text{H}_2\text{A}]_1 = \frac{[\text{H}^+]_1 [\text{HA}^-]_1}{K_1} = 4.13 \times 10^{-6} \text{ M}$$

$$[\text{A}^{2-}]_1 = \frac{K_2 [\text{HA}^-]_1}{[\text{H}^+]} = 2.35 \times 10^{-4} \text{ M}$$

Second approximation:

$$[\text{HA}^-]_2 \approx 0.00100 - [\text{H}_2\text{A}]_1 - [\text{A}^{2-}]_1 = 0.000761 \text{ M}$$

$$[\text{H}^+]_2 = \sqrt{\frac{K_1 K_2 (0.000761) + K_1 K_w}{K_1 + 0.000761}} = 2.02 \times 10^{-4} \text{ M} \Rightarrow \text{pH}_2 = 3.70$$

11-11.  $\text{pH} = \text{p}K_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

$$10.00 = 10.329 + \log \frac{(x \text{ g})/(105.99 \text{ g/mol})}{(5.00 \text{ g})/(84.01 \text{ g/mol})} \Rightarrow x = 2.96 \text{ g}$$

11-12. We begin with  $(25.0 \text{ mL})(0.0233 \text{ M}) = 0.5825 \text{ mmol}$  salicylic acid ( $\text{H}_2\text{A}$ ,  $\text{p}K_1 = 2.97$ ,  $\text{p}K_2 = 13.74$ ). At  $\text{pH} 3.50$ , there will be a mixture of  $\text{H}_2\text{A}$  and  $\text{HA}^-$ .



$$\text{Initial mmol: } \quad 0.5825 \quad x \quad \text{---}$$

$$\text{Final mmol: } \quad 0.5825 - x \quad \text{---} \quad x$$

$$3.50 = 2.97 + \log \frac{x}{0.5825 - x} \Rightarrow x = 0.4498 \text{ mmol}$$

$$(0.4498 \text{ mmol})/(0.202 \text{ M}) = 2.23 \text{ mL NaOH}$$

11-13. Picolinic acid is  $\text{HA}$ , the intermediate form of a diprotic system with  $\text{p}K_1 = 1.01$  and  $\text{p}K_2 = 5.39$ . To achieve  $\text{pH} 5.50$ , we need a mixture of  $\text{HA} + \text{A}^-$ .



$$\text{Initial mmol: } \quad 10.0 \quad x \quad \text{---}$$

$$\text{Final mmol: } \quad 10.0 - x \quad \text{---} \quad x$$

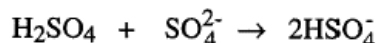
$$5.50 = 5.39 + \log \frac{x}{10.0 - x} \Rightarrow x = 5.63 \text{ mmol} \approx 5.63 \text{ mL NaOH}$$

Procedure: Dissolve 10.0 mmol (1.23 g) picolinic acid in  $\approx 75 \text{ mL H}_2\text{O}$  in a beaker. Add NaOH ( $\approx 5.63 \text{ mL}$ ) until the measured  $\text{pH}$  is 5.50. Transfer to a 100 mL volumetric flask and use small portions of  $\text{H}_2\text{O}$  to rinse the contents of the beaker into the flask. Dilute to 100.0 mL and mix well.

11-14. At pH 2.80, we have a mixture of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$ , since  $\text{p}K_a$  for  $\text{HSO}_4^-$  is 1.99.

$$2.80 = 1.99 + \log \frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \Rightarrow \text{HSO}_4^- = 0.1549 [\text{SO}_4^{2-}]$$

The reaction between  $\text{H}_2\text{SO}_4$  and  $\text{SO}_4^{2-}$  produces 2 moles of  $\text{HSO}_4^-$ :



Initial mmol:  $x$              $y$             —

Final mmol: —             $y - x$              $2x$

The Henderson-Hasselbalch equation told us that  $[\text{HSO}_4^-] = 0.1549 [\text{SO}_4^{2-}] \Rightarrow$

$2x = 0.1549 (y - x)$ . Since the total sulfur is 0.200 M,  $x + y = 0.200$  mol.

Substituting  $x = 0.200 - y$  into the equation  $2x = 0.1549 (y - x)$  gives

$\text{Na}_2\text{SO}_4 = y = 0.1866$  mol = 26.50 g and  $\text{H}_2\text{SO}_4 = x = 0.0134$  mol = 1.32 g.

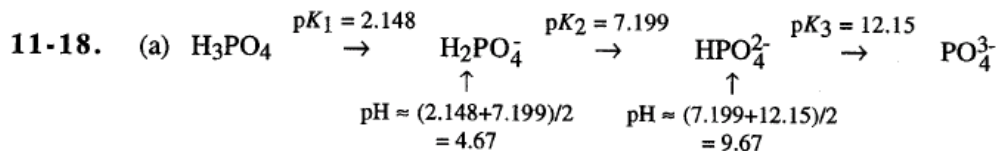
11-15.  $\text{p}K_2$  for phosphoric acid is 7.2, so it has a high buffer capacity at pH 7.45 (from the buffer pair  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ). At pH 8.5 the buffer capacity of phosphate would be low and it would not be very useful.

11-17. (a) For 0.0500 M  $\text{KH}_2\text{PO}_4$ ,  $[\text{H}^+] = \sqrt{\frac{K_1 K_2 (0.0500) + K_1 K_w}{K_1 + 0.0500}} = 1.98 \times 10^{-5}$   
 $\Rightarrow \text{pH} = 4.70$

$$4.70 = 2.148 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} = 2.8 \times 10^{-3}$$

(b) For 0.0500 M  $\text{K}_2\text{HPO}_4$ ,  $[\text{H}^+] = \sqrt{\frac{K_2 K_3 (0.0500) + K_2 K_w}{K_2 + 0.0500}} = 2.40 \times 10^{-10}$   
 $\Rightarrow \text{pH} = 9.62$

$$9.62 = 2.148 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_2\text{PO}_4^-]} = 3.4 \times 10^{-8}$$



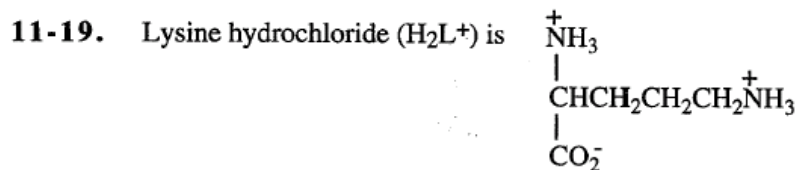
pH 7.45 corresponds to a mixture of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . (You could get the same result by mixing other combinations such as  $\text{H}_3\text{PO}_4$  and  $\text{Na}_3\text{PO}_4$  or  $\text{H}_3\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ .)

(b)  $\text{pH} = \text{p}K_2 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$   
 $7.45 = 7.199 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \Rightarrow \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 1.782$

Combining this last result with  $[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] = 0.0500$  M gives

$[\text{HPO}_4^{2-}] = 0.03203$  M and  $[\text{H}_2\text{PO}_4^-] = 0.01797$  M. Use 4.55 g of  $\text{Na}_2\text{HPO}_4$  and 2.16 g of  $\text{NaH}_2\text{PO}_4$ .

(c) Here is one of several ways: Weigh out 0.0500 mol  $\text{Na}_2\text{HPO}_4$  and dissolve it in 900 mL of water. Add HCl while monitoring the pH with a pH electrode. When the pH is 7.45, stop adding HCl and dilute up to exactly 1 L with  $\text{H}_2\text{O}$ .



$$\text{for which } [\text{H}^+] = \sqrt{\frac{K_1 K_2 (0.0100) + K_1 K_w}{K_1 + 0.0100}} = 1.99 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.70$$

$$[\text{H}_2\text{L}^+] = 0.0100 \text{ M}$$

$$[\text{H}_3\text{L}^{2+}] = \frac{[\text{H}^+][\text{H}_2\text{L}^+]}{K_1} = 2.19 \times 10^{-6} \text{ M}$$

$$[\text{HL}] = \frac{K_2[\text{H}_2\text{L}^+]}{[\text{H}^+]} = 4.17 \times 10^{-6} \text{ M} \quad [\text{L}^-] = \frac{K_3[\text{HL}]}{[\text{H}^+]} = 4.19 \times 10^{-11} \text{ M}$$

11-22. (a) HA (b)  $\text{A}^-$

$$(c) \text{pH} = \text{p}K_a + \frac{[\text{A}^-]}{[\text{HA}]}$$

$$7.00 = 7.00 + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{A}^-]/[\text{HA}] = 1.0$$

$$6.00 = 7.00 + \log \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{A}^-]/[\text{HA}] = 0.10$$

11-23. (a) 4.00 (b) 8.00 (c)  $\text{H}_2\text{A}$  (d)  $\text{HA}^-$  (e)  $\text{A}^{2-}$

$$11-26. \text{ Fraction in form HA} = \alpha_{\text{HA}} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a} = \frac{10^{-5}}{10^{-5} + 10^{-4}} = 0.091$$

$$\text{Fraction in form } \text{A}^- = \alpha_{\text{A}^-} = \frac{K_a}{[\text{H}^+] + K_a} = 0.909.$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{\alpha_{\text{A}^-}}{\alpha_{\text{HA}}} = 10, \text{ which makes sense.}$$