**0.24** The equation given in the problem is the sum of the chemical equation for the third acid ionization reaction of phosphoric acid

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

and the reverse of the equation for the first acid ionization of carbonic acid ($H_2CO_3$)

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

Hence, the desired equilibrium constant is

$$K = \frac{K_{a_3,H_3PO_4}}{K_{a_1,H_2CO_3}} = \frac{2.2 \times 10^{-13}}{4.3 \times 10^{-7}} = 5.1 \times 10^{-7}$$

$H_2CO_3$ is the stronger acid, and $PO_4^{3-}$ is the stronger base.

**10.28** The molar mass $\mathcal{M}$ of ascorbic acid is 176.126 g $mol^{-1}$. The concentration of ascorbic acid in the 100 mL of water is its chemical amount, $2.839 \times 10^{-3}$ mol (computed by dividing $500 \times 10^{-3}$ g by $\mathcal{M}$) itself divided by the volume of the solution (0.100 L). It is 0.0284 M.

The acid-ionization equilibrium is

$$HC_6H_7O_6(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_7O_6^-(aq)$$

for which the equilibrium expression is

$$\frac{[H_3O^+][C_6H_7O_6^-]}{[HC_6H_7O_6]} = K_a = 8.0 \times 10^{-5}$$

$$\frac{x^2}{0.0284 - x} = 8.0 \times 10^{-5}$$

Solving the equation gives $x = 1.47 \times 10^{-3}$. The pH of the solution is $-\log(1.47 \times 10^{-3}) = 2.83$.

**10.36** Write methylamine as MA. Its initial concentration is (0.070 mol/0.8000 L) = 0.0875 M. It reacts according to a standard base dissociation:

$$MA(aq) + H_2O(l) \rightleftharpoons HMA^+(aq) + OH^-(aq)$$

If $x$ mol $L^{-1}$ of MA dissociates, giving $[HMA^+] = [OH^-] = x$, then the equilibrium expression becomes

$$\frac{x^2}{0.0875 - x} = K_b = 4.4 \times 10^{-4}$$

$$x = 6.0 \times 10^{-3} = [OH^-]$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = 1.7 \times 10^{-12} \text{ M}$$

$$\text{pH} = 11.78$$

**10.44** The reaction of the weak base "bis" in water can be represented:

$$\text{bis}(aq) + H_2O(l) \rightleftharpoons \text{bisH}^+(aq) + OH^-(aq)$$

for which the equilibrium expression is

$$K_b = \frac{[OH^-][\text{bisH}^+]}{[\text{bis}]} = 10^{-8.8}$$

The concentrations of the bis and its conjugate acid are essentially equal under the conditions described in the problem because the amount of the HCl that has been added is just enough to convert half of the bis to $\text{bisH}^+$ and leave half unreacted. It is true that both of these species then react with water, but the changes in amount caused by these interactions are negligible. We therefore have $K_b = [OH^-]$ and $pK_b = pOH$. The pOH is 8.8, and the pH is $14.0 - 8.8 = 5.2$.

**10.48** The $pK_a$ for the first acid ionization of carbonic acid is 6.37. The $pK_a$ for the second acid ionization of phosphoric acid is 7.21. From the standpoint of suitability for pH control, the $H_2PO_4^-/HPO_4^{2-}$ system would be better because the applicable $pK_a$ is closer to the desired pH.

**10.50**

$$[H_3O^+] = 10^{-9.60} = 2.5 \times 10^{-10}$$

$$\frac{[H_3O^-][CN^-]}{[HCN]} = K_a = 6.17 \times 10^{-10}$$

$$\frac{[CN^-]}{[HCN]} = \frac{K_a}{H_3O^+} = 2.46$$

Initially, we have (0.400 L)(0.0800 mol $L^{-1}$ = 0.0320 mol $CN^-$. In the final solution, the ratio of the concentrations equals the ratio of the number of moles. If $x$ = moles HCN, then $0.320 - x$ = mol $CN^-$.

$$\frac{0.0320 - x}{x} = 2.46 \qquad \text{from which} \qquad x = 0.00926 \text{ mol}$$

This is the chemical amount of $H_3O^+$ that must be added, because each mole of $H_3O^+$ gives one of HCN. Then

$$V_{HCl} = \frac{0.00926 \text{ mol}}{0.100 \text{ mol L}^{-1}} = 0.0926 \text{ L} = 92.6 \text{ mL}$$

**10.52** This is the titration of a strong acid with a strong base. Before any base is added, the concentration of $H_3O^+$ in the solution is 0.1439 M, because the HBr is completely ionized, and the pH is 0.842.

It is easy to verify that it requires 31.14 mL of 0.1219 M NaOH to titrate the 26.38 mL of 0.1439 M HBr to the equivalence point. At the equivalence point, the pH is 7.00. When the titration is 1.00 mL short of equivalence 30.14 mL of NaOH has been added. The unreacted $H_3O^+$ comprises 0.122 mmol (the difference between the chemical amount of $H_3O^+$ originally present and the chemical amount of NaOH added), and the volume of the solution is 26.38 mL + 30.14 mL = 56.52 mL. The concentration of the $H_3O^+$ is its chemical amount divided by this volume or $2.16 \times 10^{-3}$ M, and the pH is 2.666.

When 32.14 mL of NaOH has been added, the concentration of $OH^-$ is the chemical amount of unreacted $OH^-$ divided by the volume of the solution. This is 0.122 mmol divided by 58.52 mL or $2.085 \times 10^{-3}$ mol $L^{-1}$. The pOH is 2.681, and the pH is 14.000 − pOH or 11.319.

**10.56** Before any titrating acid is added, we have a 0.175 M solution of aqueous $NH_3$. Ammonia is a base:

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

and we have the equilibrium law

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

If the equilibrium concentration of $NH_4^+$ is $x$, then the equilibrium concentration of $NH_3$ is $0.175 - x$ and that of $OH^-$ is $x$. The other sources of $OH^-$ are negligible. Substitution and solving for $x$ (by iteration) gives $[OH^-] = 1.766 \times 10^{-3}$ M and a pH of 11.25.

**10.58** The total chemical amount of HCl added is 18.393 mmol. The total chemical amount of NaOH added is 7.917 mmol. These numbers, which are the concentrations of the acid and base multiplied by the respective total volumes in mL, are clearly not equal. The tablet supplies the extra base needed to neutralize 18.393 − 7.917 = 10.476 mmol of acid. The reaction is

$$CaCO_3(s) + 2\,H_3O^+(aq) \rightleftharpoons Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$$

Each mole of $CaCO_3$ takes up 2 mol of $H_3O^+$ so there is in the tablet ((10.476/2) = 5.238) mmol of $CaCO_3$. The molar mass $\mathcal{M}$ of $CaCO_3$ is 100.09 g $mol^{-1}$ so the tablet contains 0.5243 g of $CaCO_3$. This is 39.54% of the total.

**10.68** Dissolved carbonates are in the rain drop as either carbonic acid, hydrogen carbonate ion or carbonate ion:

$$3.6 \times 10^{-5} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

where all of the quantities on the right are to be determined. The existence of the acid ionization equilibria of carbonic acid provides additional relationships among these quantities:

$$\frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = K_{a1} = 4.3 \times 10^{-7} \qquad \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = K_{a2} = 4.8 \times 10^{-11}$$

The $[H_3O^+]$ is $1.0 \times 10^{-4}$ M in these equations, so we have three equations in three unknowns. The easiest way to solve this system of equations is to observe that $[CO_3^{2-}]$ is likely to be quite small—almost all of the dissolved carbonate is tied up with hydrogen ion because hydrogen ion is abundant in this acidic solution. Setting $[CO_3^{2-}]$ to zero gives:

$$3.6 \times 10^{-5} \approx [H_2CO_3] + [HCO_3^-]$$

$$\frac{[HCO_3^-](1.0 \times 10^{-4})}{[H_2CO_3]} \approx 4.3 \times 10^{-7}$$

Solving this pair of equations gives $[H_2CO_3] = 3.6 \times 10^{-5}$ M and $[HCO_3^-] = 1.55 \times 10^{-7}$ M. Now, substitution in the $K_{a2}$ expression gives $[CO_3^{2-}] = 7.4 \times 10^{-14}$ M. Almost all of the carbonate is present as carbonic acid, a small amount is present as hydrogen carbonate ion, and a vanishingly tiny fraction is present as $CO_3^{2-}$ ion.