# CHAPTER 10

# ACIDS AND BASES

**10.2** (a) $H_3O^+$   (b) $H_2O$   (c) $C_6H_5NH_3^+$   (d) $HS^-$   (e) $PO_4^{3-}$

(f) $ClO_4^-$

**10.4** (a)

$$\text{conjugate}$$

$$H_2O(l) \quad + \quad CN^-(aq) \quad \rightleftharpoons \quad HCN(l) \quad + \quad OH^-(aq)$$
$$\text{acid}_1 \qquad\qquad \text{base}_2 \qquad\qquad \text{acid}_2 \qquad\quad \text{base}_1$$

$$\text{conjugate}$$

(b)

$$\text{conjugate}$$

$$H_2O(l) \quad + \quad NH_2NH_2(aq) \quad \rightleftharpoons \quad NH_2NH_3^+(aq) \quad + \quad OH^-(aq)$$
$$\text{acid}_1 \qquad\qquad \text{base}_2 \qquad\qquad\qquad \text{acid}_2 \qquad\qquad \text{base}_1$$

$$\text{conjugate}$$

(c)

$$\text{conjugate}$$

$$H_2O(l) \quad + \quad CO_3^{2-}(aq) \quad \rightleftharpoons \quad HCO_3^-(aq) \quad + \quad OH^-(aq)$$
$$\text{acid}_1 \qquad\qquad \text{base}_2 \qquad\qquad\qquad \text{acid}_2 \qquad\qquad \text{base}_1$$

$$\text{conjugate}$$

(d)

$$\text{conjugate}$$

$$H_2O(l) \quad + \quad HPO_4^{2-}(aq) \quad \rightleftharpoons \quad H_2PO_4^-(aq) \quad + \quad OH^-(aq)$$
$$\text{acid}_1 \qquad\qquad \text{base}_2 \qquad\qquad\qquad \text{acid}_2 \qquad\qquad \text{base}_1$$

$$\text{conjugate}$$

(e)

$$\text{conjugate}$$

$$H_2O(l) \quad + \quad NH_2CONH_2(aq) \quad \rightleftharpoons \quad NH_2CONH_3^+(aq) \quad + \quad OH^-(aq)$$
$$\text{acid}_1 \qquad\qquad \text{base}_2 \qquad\qquad\qquad \text{acid}_2 \qquad\qquad \text{base}_1$$

$$\text{conjugate}$$

**10.6** (a)  Brønsted acid: $NH_4^+$

Brønsted base: $HSO_3^-$

(b)  Conjugate base to $NH_4^+$ : $NH_3$

Conjugate acid to $HSO_3^-$ : $H_2SO_3$

**10.8** (a) as an acid: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

Conjugate acid/base pairs:    $H_2PO_4^-(aq)$ / $HPO_4^{2-}(aq)$

$H_3O^+(aq)$ / $H_2O(l)$

as a base: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3PO_4(aq)$

Conjugate acid/base pairs:    $H_3PO_4(aq)$ / $H_2PO_4^-(aq)$

$H_2O(l)$ / $OH^-(aq)$

(c) as an acid: $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq)$

Conjugate acid/base pairs:    $HC_2O_4^-(aq)$ / $C_2O_4^{2-}(aq)$

$H_3O^+(aq)$ / $H_2O(l)$

as a base: $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2C_2O_4(aq)$

Conjugate acid/base pairs:    $H_2C_2O_4(aq)$ / $HC_2O_4^-(aq)$

$H_2O(l)$ / $OH^-(aq)$

**10.10** (a) acidic;   (b) basic;   (c) acidic;   (d) amphoteric

**10.12** (a) $2\ OH^-(aq) + SiO_2(s) \longrightarrow SiO_3^{2-}(aq) + H_2O(l)$

(b)
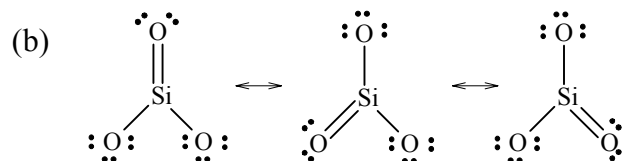


(c) Lewis Acid: $SiO_2(s)$, Lewis Base: $OH^-(aq)$

**10.14** In each case use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$, then

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{[OH^-]}$$

(a) $[H_3O^+] = \dfrac{1.0 \times 10^{-14}}{0.012} = 8.3 \times 10^{-13}$

(b) $[H_3O^+] = \dfrac{1.0 \times 10^{-14}}{6.2 \times 10^{-5}} = 1.6 \times 10^{-10}$

(c) $[H_3O^+] = \dfrac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12}$

**10.16** (a) $[H_3O^+] = [OH^-] = 3.9 \times 10^{-8} \text{ mol} \cdot L^{-1}$

$K_w = [H_3O^+][OH^-] = (3.9 \times 10^{-8})^2 = 1.5 \times 10^{-15}$

$pK_w = -\log K_w = -\log(1.5 \times 10^{-15}) = 14.82$

(b) $pH = -\log(3.9 \times 10^{-8}) = 7.41 = pOH$
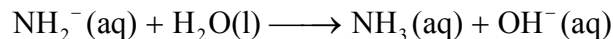
**10.18** $[KNH_2]_0 =$ nominal concentration of $KNH_2$

$$[KNH_2]_0 = \left( \frac{0.5 \text{ g KNH}_2}{0.250 \text{ L}} \right)\left( \frac{1 \text{ mol KNH}_2}{55.13 \text{ g KNH}_2} \right) = 0.036 \text{ mol} \cdot L^{-1}$$

Because $KNH_2$ is a soluble salt, $[KNH_2]_0 = [K^+] = [NH_2^-]_0$ (where

$[NH_2^-]_0$ is the nominal concentration of $NH_2^-$); thus $[K^+]$ and $[NH_2^-] =$

$0.036 \text{ mol} \cdot L^{-1}$.

$NH_2^-$ reacts with water:

$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq)$

Because $NH_2^-$ is a strong base, this reaction goes essentially to

completion; therefore

$[NH_2^-]_0 = [OH^-] = 0.036 \text{ mol} \cdot L^{-1}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.036} = 2.8 \times 10^{-13} \text{ mol} \cdot L^{-1}$$

**10.20** $[H_3O^+] = 10^{-pH} \text{ mol} \cdot L^{-1}$ (antilog pH, $\text{mol} \cdot L^{-1}$)

    (a) $[H_3O^+] = \text{antilog}(-5) = 1 \times 10^{-5} \text{ mol} \cdot L^{-1}$

    (b) $[H_3O^+] = 10^{-2.3} \text{ mol} \cdot L^{-1}$; antilog $(-2.3) = 5 \times 10^{-3} \text{ mol} \cdot L^{-1}$

    (c) $[H_3O^+] = 10^{-7.4} \text{ mol} \cdot L^{-1}$; antilog $(-7.4) = 4 \times 10^{-8} \text{ mol} \cdot L^{-1}$

    (d) $[H_3O^+] = 10^{-10.5} \text{ mol} \cdot L^{-1}$; antilog $(-10.5) = 3 \times 10^{-11} \text{ mol} \cdot L^{-1}$

    Acidity increases as pH decreases. The order is thus:

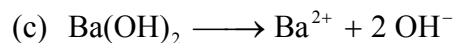    milk of magnesia < blood < urine < lemon juice

**10.22** (a) $pH = -\log(0.0356) = 1.448$
       $pOH = 14.00 - 1.448 = 12.55$

    (b) $pH = -\log(0.0725) = 1.12$
       $pOH = 14.00 - 1.12 = 12.86$

    (c) $Ba(OH)_2 \longrightarrow Ba^{2+} + 2\, OH^-$

       $[OH^-] = 2 \times 3.46 \times 10^{-3} \text{ mol} \cdot L^{-1} = 6.92 \times 10^{-3} \text{ mol} \cdot L^{-1}$
       $pOH = -\log(6.92 \times 10^{-3}) = 2.160$
       $pH = 14.00 - 2.160 = 11.84$

    (d) $\dfrac{10.9 \times 10^{-3} \text{ g}}{56.11 \text{ g} \cdot \text{mol}^{-1}} = 1.94 \times 10^{-4} \text{ mol KOH}$

       $[OH^-] = \dfrac{1.94 \times 10^{-4} \text{ mol}}{0.0100 \text{ L}} = 1.94 \times 10^{-2} \text{ mol} \cdot L^{-1}$

       $pOH = -\log(1.94 \times 10^{-2}) = 1.712$
       $pH = 14.00 - 1.712 = 12.29$

    (e) $[OH^-] = \left(\dfrac{10.0 \text{ mL}}{2500 \text{ mL}}\right) \times (5.00 \text{ mol} \cdot L^{-1}) = 0.0200 \text{ mol} \cdot L^{-1}$
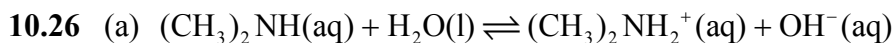
       $pOH = -\log(0.200) = 1.70$
       $pH = 14.00 - 0.699 = 12.30$

    (f) $[H_3O^+] = \left(\dfrac{5.0 \text{ mL}}{25.0 \text{ mL}}\right) \times (3.5 \times 10^{-4} \text{ mol} \cdot L^{-1}) = 7.0 \times 10^{-5} \text{ mol} \cdot L^{-1}$
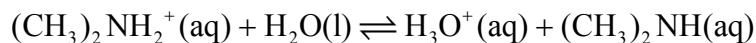
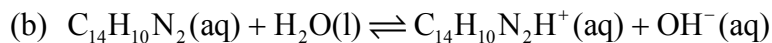       $pH = -\log(7.0 \times 10^{-5}) = 4.15$
       $pOH = 14.00 - 4.15 = 9.85$

**10.24**

| Base | $K_b$ | $pK_b$ |
|------|-------|--------|
| (a) $NH_3$ | $1.8 \times 10^{-5}$ | 4.74 |
| (b) $ND_3$ | $1.1 \times 10^{-5}$ | 4.96 |
| (c) $NH_2NH_2$ | $1.7 \times 10^{-6}$ | 5.77 |
| (d) $NH_2OH$ | $1.1 \times 10^{-8}$ | 7.96 |

(e) $NH_2OH < NH_2NH_2 < ND_3 < NH_3$

**10.26** (a) $(CH_3)_2 NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2 NH_2^+(aq) + OH^-(aq)$

$$K_b = \frac{[(CH_3)_2 NH_2^+][OH^-]}{[(CH_3)_2 NH]}$$

$(CH_3)_2 NH_2^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + (CH_3)_2 NH(aq)$

$$K_a = \frac{[H_3O^+][(CH_3)_2 NH]}{[(CH_3)_2 NH_2^+]}$$

(b) $C_{14}H_{10}N_2(aq) + H_2O(l) \rightleftharpoons C_{14}H_{10}N_2H^+(aq) + OH^-(aq)$

$$K_b = \frac{[C_{14}H_{10}N_2H^+][OH^-]}{[C_{14}H_{10}N_2]}$$

$C_{14}H_{10}N_2H^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_{14}H_{10}N_2(aq)$

$$K_a = \frac{[H_3O^+][C_{14}H_{10}N_2]}{[C_{14}H_{10}N_2H^+]}$$

(c) $C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$
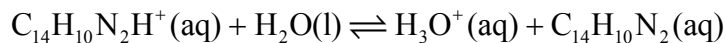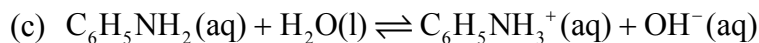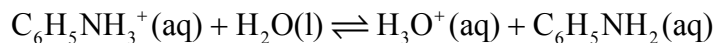
$$K_a = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$$

**10.28** Decreasing $pK_a$ will correspond to increasing acid strength because $pK_a$ $= -\log K_a$. The $pK_a$ values (given in parentheses) determine the following ordering:

$(CH_3)_3 NH^+ (14.00 - 4.19 = 9.71) < N_2H_5^+ (14.00 - 5.77 = 8.23)$

$< HCOOH (3.75) < HF (3.45)$
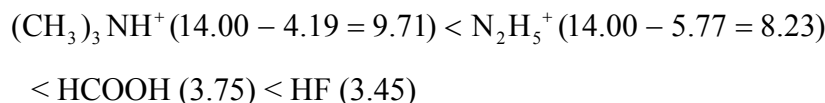
Remember that the $pK_a$ for the conjugate acid of a weak base will be given by

$pK_a + pK_b = 14$.

**10.30** Decreasing $pK_b$ will correspond to increasing base strength because $pK_b$ $= -\log K_b$. The $pK_b$ values (given in parentheses) determine the following ordering:

$N_2H_4 (5.77) < BrO^- (14.00 - 8.69 = 5.31) < CN^- (14.00 - 9.31 = 4.69)$
$< (C_2H_5)_3 N(2.99)$
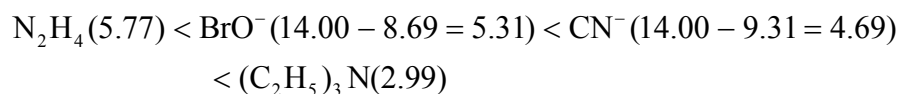
Remember that the $pK_b$ for the conjugate base of a weak acid will be given by

$pK_a + pK_b = 14$.

**10.32** Any base whose conjugate acid lies below water in Table 10.3 will be a strong base, that is, the conjugate acid of the base will be a weaker acid than water, and so water will preferentially protonate the base. Based upon this information, we obtain the following analysis:    (a)  $O^{2-}$ , strong; (b)  $Br^-$ , weak;   (c)  $HSO_4^-$ , weak;   (d)  $HCO_3^-$ , weak;   (e)  $CH_3NH_2$, weak;   (f)  $H^-$ , strong;   (g)  $CH_3^-$ , strong.

**10.34** In oxoacids with the same number of oxygen atoms attached to the central atom, the greater the electronegativity of the central atom, the more the electrons of the O—H bond are withdrawn, making the bond more polar. This allows the hydrogen of the OH group to be more readily donated as a proton to $H_2O$, due to the stronger hydrogen bonds that it forms with the oxygen of water. Therefore, HClO is the stronger acid, with the lower $pK_a$.

**10.36** (a)  $H_3PO_4$ is stronger; it has the more electronegative central atom.

(b)  $HBrO_3$ is stronger; there are more O atoms attached to the central atom in $HBrO_3$, making the H—O bond in $HBrO_3$ more polar than in HBrO.

(c)  We would predict $H_3PO_4$ to be a stronger acid due to more oxygens on the central atom.

(d)  $H_2Te$ is the stronger acid, because the H—Te bond is weaker than the H—Se bond.

(e)  HCl is the stronger acid. Within a period, the acidities of the binary acids are controlled by the bond polarity rather than the bond strength, and HCl has the greater bond polarity, due to the greater electronegativity of Cl relative to S.

(f)  HClO is stronger because Cl has a greater electronegativity than I.

**10.38**  (a)  Methylamine is $CH_3NH_2$, ammonia is $NH_3$. Methylamine can be thought of as being formed from $NH_3$ by replacing one H atom with $CH_3$. Because $CH_3$ is less electron withdrawing than H, $CH_3NH_2$ is a weaker acid and therefore a stronger base.

(b)  Hydroxylamine is $HONH_2$, hydrazine is $H_2N$—$NH_2$. The former can be thought of as being derived from $NH_3$ by replacement of one H atom with OH; the latter by replacement of one H atom with $NH_2$. Because the hydroxyl group is more electron withdrawing than the amino group, $NH_2$, hydroxylamine is the stronger acid and therefore a weaker base.

**10.40**  The solution of 0.10 M $H_2SO_4$ would have the higher pH (would be the weaker acid) because the conjugate base, $HSO_4^-$ is less electronegative than the conjugate base of hydrobromic acid, namely $Br^-$.

**10.42**  The smaller the value of $pK_b$, the stronger the base; hence, aniline is the stronger base.  4-Chloroaniline is the stronger acid due to the presence of the electron-withdrawing Cl atom, making it the weaker base; and again we see that aniline is the stronger base.

**10.44** The higher the $pK_a$ of an acid, the stronger the corresponding conjugate base; therefore, the order is

3-hydroxyaniline < aniline < 2-hydroxyaniline < 4-hydroxyaniline

No simple pattern exists, but the position of the —OH group does affect the basicity.

**10.46** (a) $K_a = 8.4 \times 10^{-4} = \dfrac{[H_3O^+][CH_3CH(OH)CO_2^-]}{[CH_3CH(OH)COOH]} = \dfrac{x^2}{0.12 - x} \approx \dfrac{x^2}{0.12}$

Here we have assumed that $x$ is small enough to neglect it relative to 0.12 $mol \cdot L^{-1}$. This is a borderline case. We will also solve this exercise without making this approximation and compare the results below.

$x = [H_3O^+] = 0.010 \ mol \cdot L^{-1}$
$pH = -\log(0.010) = 2.00$
$pOH = 14.00 - 2.00 = 12.00$

Without the approximation, the quadratic equation that must be solved is

$8.4 \times 10^{-4} = \dfrac{x^2}{0.12 - x}$

or $x^2 + 8.4 \times 10^{-4} x - 1.01 \times 10^{-4} = 0$

$x = \dfrac{-8.4 \times 10^{-4} \pm \sqrt{(8.4 \times 10^{-4})^2 - 4(-1.01 \times 10^{-4})}}{2}$

$x = 0.0096, - 0.018.$

$x = [H_3O^+] = 0.0096$

$pH = -\log(0.0096) = 2.02$

(b) $K_a = 8.4 \times 10^{-4} = \dfrac{x^2}{1.2 \times 10^{-3} - x}$

or $x^2 + 8.4 \times 10^{-4} x - 1.0 \times 10^{-6} = 0$

$x = -1.5 \times 10^{-3}, 1.1 \times 10^{-3}$

The negative root can be eliminated:

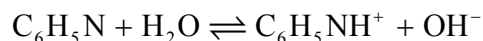$x = [H_3O^+] = 1.1 \times 10^{-3}$
$pH = -\log(1.1 \times 10^{-3}) = 2.96$
$pOH = 14.00 - 2.96 = 11.04$

(c) $8.4 \times 10^{-4} = \dfrac{x^2}{1.2 \times 10^{-5} - x}$

or $x^2 + 8.4 \times 10^{-4} x - 1.0 \times 10^{-8} = 0$

$x = 1.2 \times 10^{-5}, -8.5 \times 10^{-4}$

The negative root can be eliminated.

$[H_3O^+] = 1.2 \times 10^{-5}$

$pH = -\log(1.2 \times 10^{-5})$

$pH = 4.92$

$pOH = 14.00 - 4.92 = 9.08$

**10.48** (a) $K_b(\text{pyridine}) = 1.8 \times 10^{-9}$

$C_6H_5N + H_2O \rightleftharpoons C_6H_5NH^+ + OH^-$

| Concentration $(\text{mol} \cdot L^{-1})$ | $C_6H_5N$ | + | $H_2O$ | $\rightleftharpoons$ | $C_6H_5NH^+$ | + | $OH^-$ |
|---|---|---|---|---|---|---|---|
| initial | 0.075 | | — | | 0 | | 0 |
| change | $-x$ | | — | | $+x$ | | $+x$ |
| final | $0.075 - x$ | | — | | $+x$ | | $+x$ |

$K_b = 1.8 \times 10^{-9} = \dfrac{x^2}{0.075 - x} \approx \dfrac{x^2}{0.075}$

$x = [OH^-] = 1.2 \times 10^{-5} \; \text{mol} \cdot L^{-1}$

$pOH = -\log(1.2 \times 10^{-5}) = 4.92$

$pH = 14.00 - 4.92 = 9.00$

$\text{Percentage ionized} = \dfrac{1.2 \times 10^{-5}}{0.075} \times 100\% = 1.6 \times 10^{-2}\%$

(b) The setup is similar to that in (a).

$K_b = 1.0 \times 10^{-6} = \dfrac{x^2}{0.0112 - x} \approx \dfrac{x^2}{0.0112} \qquad x = [OH^-]$
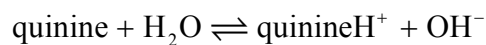
$x = 1.1 \times 10^{-4} \ \text{mol} \cdot \text{L}^{-1}$

$\text{pOH} = -\log(1.1 \times 10^{-4}) = 3.97$

$\text{pH} = 14.00 - 3.97 = 10.03$

$\text{Percentage protonation} = \dfrac{3.2 \times 10^{-4}}{0.0122} \times 100\% = 2.6\%$

(c)  $\text{p}K_b = 14.00 - 8.52 = 5.48$

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

$\text{quinine} + H_2O \rightleftharpoons \text{quinineH}^+ + OH^-$
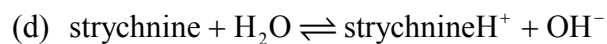
$K_b = 3.3 \times 10^{-6} = \dfrac{x^2}{0.021 - x} \approx \dfrac{x^2}{0.021}$

$x = [OH^-] = 2.6 \times 10^{-4} \ \text{mol} \cdot \text{L}^{-1}$

$\text{pOH} = -\log(2.6 \times 10^{-4}) = 3.58$

$\text{pH} = 14.00 - 3.58 = 10.42$

$\text{Percentage protonation} = \dfrac{2.6 \times 10^{-4}}{0.021} \times 100\% = 1.2\%$

(d)  $\text{strychnine} + H_2O \rightleftharpoons \text{strychnineH}^+ + OH^-$

$x = [OH^-]$

$K_b = \dfrac{K_w}{K_a} = \dfrac{1.00 \times 10^{-14}}{5.49 \times 10^{-9}} = 1.82 \times 10^{-6}$

$K_b = 1.82 \times 10^{-6} = \dfrac{x^2}{0.059 - x} \approx \dfrac{x^2}{0.059}$

$x = [OH^-] = 3.3 \times 10^{-4} \ \text{mol} \cdot \text{L}^{-1}$

$\text{pOH} = -\log(3.3 \times 10^{-4}) = 3.48$

$\text{pH} = 14.00 - 3.48 = 10.52$

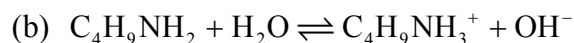$\text{Percentage protonation} = \dfrac{3.3 \times 10^{-4}}{0.059} \times 100\% = 0.56\%$

**10.50** (a)  $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$

$[H_3O^+] = [NO_2^-] = 10^{-2.63} = \text{antilog}\,(-2.63) = 2.3 \times 10^{-3} \text{ mol} \cdot L^{-1}$

$K_a = \dfrac{(2.3 \times 10^{-3})^2}{0.015 - 2.3 \times 10^{-3}} = 4.2 \times 10^{-4}$

$pK_a = -\log(4.3 \times 10^{-4}) = 3.38$

(b)  $C_4H_9NH_2 + H_2O \rightleftharpoons C_4H_9NH_3^+ + OH^-$

$pOH = 14.00 - 12.04 = 1.96$

$[C_4H_9NH_3^+] = [OH^-] = 10^{-1.96} = \text{antilog}\,(-1.96) = 0.011 \text{ mol} \cdot L^{-1}$

$K_b = \dfrac{[C_4H_9NH_3^+][OH^-]}{[C_4H_9NH_2]} = \dfrac{(0.011)^2}{0.10 - 0.011} = 1.4 \times 10^{-3}$

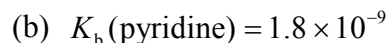$pK_b = -\log(1.4 \times 10^{-3}) = 2.85$


**10.52** (a)  $K_a(HCN) = 4.9 \times 10^{-10}$

$[H_3O^+] = 10^{-pH} = 10^{-5.3} = \text{antilog}\,(-5.3) = 5 \times 10^{-6} \text{ mol} \cdot L^{-1}$

Let $x$ = nominal concentration of HCN, then

| Concentration $(\text{mol} \cdot L^{-1})$ | HCN | + H₂O ⇌ | H₃O⁺ | + CN⁻ |
|---|---|---|---|---|
| nominal | $x$ | — | 0 | 0 |
| equilibrium | $x - 5 \times 10^{-6}$ | — | $5 \times 10^{-6}$ | $5 \times 10^{-6}$ |

$4.9 \times 10^{-10} = \dfrac{(5 \times 10^{-6})^2}{x - 5 \times 10^{-6}}$

Solve for $x$ : $x = 5 \times 10^{-2} \text{ mol} \cdot L^{-1} = 0.05 \text{ mol} \cdot L^{-1}$

(b)  $K_b(\text{pyridine}) = 1.8 \times 10^{-9}$

$pOH = 14.00 - 8.8 = 5.2$

$[OH^-] = 10^{-pOH} = 10^{-5.2} = \text{antilog}\,(-5.2) = 6 \times 10^{-6} \text{ mol} \cdot L^{-1}$

Let $x$ = nominal concentration of $C_5H_5N$, then

| Concentration $(\text{mol} \cdot L^{-1})$ | C₅H₅N + H₂O ⇌ | C₅H₆N⁺ | + OH⁻ |
|---|---|---|---|
| nominal | $x$ | | |
| equilibrium | $x - 6 \times 10^{-6}$ | $6 \times 10^{-6}$ | $6 \times 10^{-6}$ |

$$1.8 \times 10^{-9} = \frac{(6 \times 10^{-6})^2}{x - 6 \times 10^{-6}}$$

Solve for $x$ : $x = 2 \times 10^{-2}$ mol $\cdot$ L$^{-1}$ = 0.02 mol $\cdot$ L$^{-1}$

**10.54** veronal + $H_2O \rightleftharpoons H_3O^+$ + veronalate ion

The equilibrium concentrations are

[veronal] = $0.020 - 0.0014 \times 0.020 = 0.020$ mol $\cdot$ L$^{-1}$

$[H_3O^+]$ = [veronalate ion] = $0.0014 \times 0.020 = 2.8 \times 10^{-5}$ mol $\cdot$ L$^{-1}$

$pH = -\log(2.8 \times 10^{-5}) = 4.55$

$$K_a = \frac{[H_3O^+][\text{veronalate ion}]}{[\text{veronal}]} = \frac{(2.8 \times 10^{-5})^2}{0.020} = 3.9 \times 10^{-8}$$

**10.56** cacodylic acid + $H_2O \rightleftharpoons H_3O^+$ + cacodylate ion
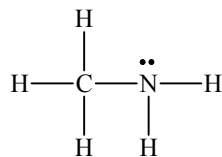
The equilibrium concentrations are

[cacodylic acid] = $0.0110 - (0.0077 \times 0.0110) = 0.0110 - 0.000\ 08 = 0.109$ mol $\cdot$ L$^{-1}$

$[H_3O^+]$ = [cacodylate ion] = $0.0077 \times 0.0110 = 8.5 \times 10^{-5}$ mol $\cdot$ L$^{-1}$
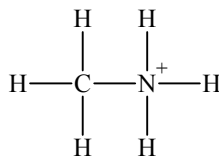
$pH = -\log(8.5 \times 10^{-5}) = 4.07$

$$K_a = \frac{[H_3O^+][\text{cacodylate ion}]}{[\text{cacodylic acid}]} = \frac{(8.5 \times 10^{-5})^2}{0.0109} = 6.6 \times 10^{-7}$$

**10.58** (a)



methylamine                conjugate acid

(b) First determine the concentration of methylamine following dilution.

Moles of methylamine are found by:

$(50 \text{ mL}) \cdot (0.85 \text{ g mL}^{-1}) = 42.5 \text{ g of solution}$

$(42.5 \text{ g}) \cdot (0.35) = 14.9 \text{ g of methylamine}$

$\dfrac{(14.9 \text{ g})}{(31.06 \text{ g } \cdot \text{mol}^{-1})} = 0.479 \text{ mol of methylamine}$

diluted to 1.000 L, the resulting solution is 0.479 M in methylamine

| Concentration $(\text{mol} \cdot \text{L}^{-1})$ | $CH_3NH_2$ | $+ H_2O \rightleftharpoons$ | $CH_3NH_3^+$ | $+ OH^-$ |
|---|---|---|---|---|
| initial | 0.479 | — | 0 | 0 |
| equilibrium | $0.479 - x$ | — | $x$ | $x$ |

$K_b = 3.6 \times 10^{-4} = \dfrac{\left[CH_3NH_3^+\right]\left[OH^-\right]}{\left[CH_3NH_2\right]} = \dfrac{x^2}{0.479 - x}$

solving for x we find:

$x = 1.3 \times 10^{-2} \text{ M} = \left[OH^-\right]$

$pOH = -\log(1.3 \times 10^{-2}) = 1.9$

$pH = 14.0 - 1.9 = 12.1$

**10.60** (a) pH > 7, basic: $H_2O(l) + C_2O_4^{2-}(aq) \rightleftharpoons HC_2O_4^-(aq) + OH^-(aq)$

(b) pH = 7, neutral: $Ca^{2+}$ is not an acid and $NO_3^-$ is not a base

(c) pH < 7, acidic: $CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3NH_2(aq)$

(d) pH > 7, basic: $H_2O(l) + PO_4^{3-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$

(e) pH < 7, acidic: $Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons$

$$H_3O^+(aq) + Fe(H_2O)_5OH^{2+}(aq)$$

(f) pH < 7, acidic: $C_5H_5NH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_5H_5N(aq)$

**10.62** (a) Concentration

| $(\text{mol} \cdot \text{L}^{-1})$ | $CH_3NH_3^+$ | $+ H_2O(l) \rightleftharpoons$ | $CH_3NH_2$ | $+$ | $H_3O^+$ |
|---|---|---|---|---|---|
| initial | 0.25 | — | 0 | | 0 |
| change | $-x$ | — | $+x$ | | $+x$ |
| equilibrium | $0.25 - x$ | — | $x$ | | $x$ |

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(See Table 10.2 for $K_b$ of $CH_3NH_2$, the conjugate base of $CH_3NH_3^+$.)

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{3.6 \times 10^{-4}} = 2.8 \times 10^{-11} = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]}$$

$$2.8 \times 10^{-11} = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25}$$

$x = 2.6 \times 10^{-6} \ mol \cdot L^{-1} = [H_3O^+]$ and $pH = -\log(2.6 \times 10^{-6}) = 5.58$

(b) Concentration

| $(mol \cdot L^{-1})$ | $SO_3^{2-}$ | + | $H_2O(l)$ | $\rightleftharpoons$ | $HSO_3^-$ | + $OH^-$ |
|---|---|---|---|---|---|---|
| initial | 0.13 | | — | | 0 | 0 |
| change | $-x$ | | — | | $+x$ | $+x$ |
| equilibrium | $0.13 - x$ | | — | | $x$ | $x$ |

[See Table 10.9 for $K_a(HSO_3^-) = K_{a2}(H_2SO_3)$.]

$$K_b = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{1.2 \times 10^{-7}} = 8.3 \times 10^{-8} = \frac{[HSO_3^-][OH^-]}{[SO_3^{2-}]} = \frac{x^2}{0.13 - x} \approx \frac{x^2}{0.13}$$

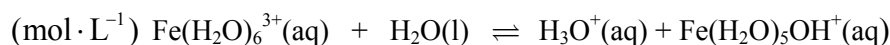$$8.3 \times 10^{-8} = \frac{x^2}{0.13}$$

$x = 1.0 \times 10^{-4} \ mol \cdot L^{-1} = [OH^-]$

$pOH = -\log(1.0 \times 10^{-4}) = 4.00$

$pH = 14.00 - pOH = 10.00$

(c) Concentration

| $(mol \cdot L^{-1})$ | $Fe(H_2O)_6^{3+}(aq)$ | + | $H_2O(l)$ | $\rightleftharpoons$ | $H_3O^+(aq)$ + | $Fe(H_2O)_5OH^+(aq)$ |
|---|---|---|---|---|---|---|
| initial | 0.071 | | — | | 0 | 0 |
| change | $-x$ | | — | | $+x$ | $+x$ |
| equilibrium | $0.071 - x$ | | — | | $x$ | $x$ |

$$K_a = \frac{[H_3O^+][Fe(H_2O)_5OH^+(aq)]}{[Fe(H_2O)_6^{3+}]} = 3.5 \times 10^{-3} = \frac{x^2}{0.071 - x}$$

$x^2 + 3.5 \times 10^{-3} x \qquad 2.5 \times 10^{-4} = 0$

$x = 0.014, \qquad -0.018$

The negative root can be discarded

$[H_3O^+] = 0.014$, $pH = -\log 0.014 = .85$

**10.64** (a) Initial concentration of $C_6H_5NH_3{}^+$ is:

$$\frac{(7.8 \text{ g}) \left( \dfrac{1}{94.133 \text{ g mol}^{-1}} \right)}{0.350 \text{ L}} = 0.24 \text{ M}$$

Given this initial concentration and the Ka for this acid found in Table 10.7, the percent deprotonation is found as follows:

Concentration

| (mol·L$^{-1}$) | $C_6H_5NH_3{}^+$ | + | $H_2O(l)$ | $\rightleftharpoons$ | $C_6H_5NH_2{}^{2+}$ | + | $H_3O^+$ |
|---|---|---|---|---|---|---|---|
| initial | 0.24 | | — | | 0 | | 0 |
| change | $-x$ | | — | | $+x$ | | $+x$ |
| equilibrium | $0.24 - x$ | | — | | $x$ | | $x$ |

$$K_a = 2.3 \times 10^{-5} = \frac{[C_6H_5NH_2^{2+}][H_3O^+]}{[C_6H_5NH_3^+]}$$

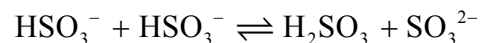$$2.3 \times 10^{-5} = \frac{x^2}{0.24 - x} \approx \frac{x^2}{0.24}$$

$$x = 2.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} = [H_3O^+]$$

$$\text{percent dissociation} = \frac{2.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}}{0.23 \text{ mol} \cdot \text{L}^{-1}} \cdot 100\% = 1.0\%$$

**10.66** (a) $HSO_3{}^-$ can act as both an acid and a base. Both actions need to be considered simultaneously:

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3{}^{2-}$$
$$HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$$

Summing,
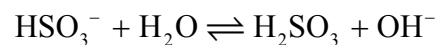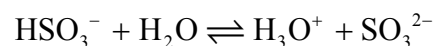
$$HSO_3^- + HSO_3^- \rightleftharpoons H_2SO_3 + SO_3{}^{2-}$$

The simplest approach is to recognize that there are two conjugate acid-base pairs and to use the Henderson-Hasselbalch equation twice, once for each pair.

$$pH = pK_{a1} + \log\left(\frac{[HSO_3^-]}{[H_2SO_3]}\right)$$

$$pH = pK_{a2} + \log\left(\frac{[SO_3^{2-}]}{[HSO_3^-]}\right)$$

Summing,

$$2pH = pK_{a1} + pK_{a2} + \log\left(\frac{[HSO_3^-]}{[H_2SO_3]} \times \frac{[SO_3^{2-}]}{[HSO_3^-]}\right)$$

Because $[H_2SO_3] = [SO_3^{2-}]$, $2pH = pK_{a1} + pK_{a2}$

Therefore, $pH = \frac{1}{2}(pK_{a1} + pK_{a2}) = \frac{1}{2}(1.81 + 6.91) = 4.36$

Note that it is not necessary to know the concentration of $HSO_3^-$, because it cancels out of the equation. At extremely low concentrations of $HSO_3^-$, however, the approximations upon which the use of this equation are based are no longer valid.

(b)  Neither silver ion nor nitrate ion is acidic or basic in aqueous solution. Therefore, the pH is that of neutral water, 7.00.

**10.68**  (a)  $\dfrac{0.250 \text{ mol} \cdot L^{-1} \text{ KCN} \times 0.0350 \text{ L}}{0.1000 \text{ L}} = 0.0875 \text{ mol} \cdot L^{-1} \text{ KCN} = [CN^-]_0$

Concentration

| (mol·L$^{-1}$) | H$_2$O(l) | +CN$^-$(aq) | $\rightleftharpoons$ | HCN(aq) + | OH$^-$(aq) |
|---|---|---|---|---|---|
| initial | — | 0.0875 | | 0 | 0 |
| change | — | $-x$ | | $+x$ | $+x$ |
| equilibrium | — | $0.0875 - x$ | | $x$ | $x$ |

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]}$$

$$2.0 \times 10^{-5} = \frac{x^2}{0.0875 - x} \approx \frac{x^2}{0.0875}$$

$$x = 1.3 \times 10^{-3} \text{ mol} \cdot L^{-1} = [HCN]$$

(b) $\dfrac{1.59 \text{ g NaHCO}_3}{84.01 \text{ g NaHCO}_3/\text{mol NaHCO}_3} \times \dfrac{1}{0.200 \text{ L}}$

$= 9.46 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ NaHCO}_3$

Concentration
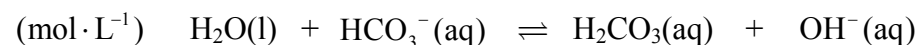
| $(\text{mol} \cdot \text{L}^{-1})$ | $H_2O(l)$ | $+$ | $HCO_3^-(aq)$ | $\rightleftharpoons$ | $H_2CO_3(aq)$ | $+$ | $OH^-(aq)$ |
|---|---|---|---|---|---|---|---|
| initial | — | | $9.46 \times 10^{-2}$ | | $0$ | | $0$ |
| change | — | | $-x$ | | $+x$ | | $+x$ |
| equilibrium | — | | $9.46 \times 10^{-2} - x$ | | $x$ | | $x$ |

$K_{b1} = \dfrac{[H_2CO_3][OH^-]}{[HCO_3^-]} = \dfrac{K_w}{K_{a1}} = \dfrac{1.00 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$

$2.3 \times 10^{-8} = \dfrac{x^2}{9.46 \times 10^{-2} - x} \approx \dfrac{x^2}{9.46 \times 10^{-2}}$, $x = 4.7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

$= [OH^-]$

$pOH = -\log(4.7 \times 10^{-5}) = 4.33$, $pH = 14.00 - 4.33 = 9.67$

**10.70** The reaction of interest is:

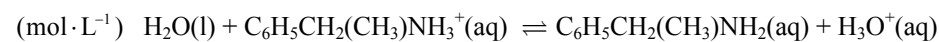$C_6H_5CH_2(CH_3)NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5CH_2(CH_3)NH_2(aq) +$

$H_3O^+(aq)$
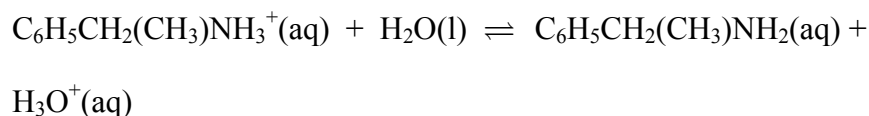
$K_a$ for this reaction is: $K_a = \dfrac{1 \times 10^{-14}}{7.8 \times 10^{-4}} = 1.3 \times 10^{-11}$

The initial concentration of $C_6H_5CH_2(CH_3)NH_3^+(aq)$ is:

$\dfrac{(6.48 \text{ g}) \cdot (216.12 \text{ g mol}^{-1})}{0.200 \text{ L}} = 0.150 \text{ mol L}^{-1}$
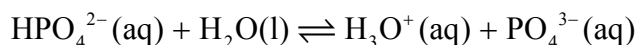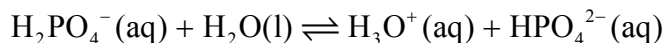
Concentration

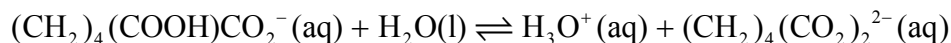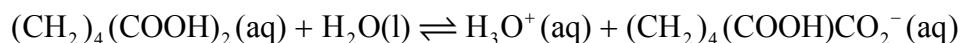| $(\text{mol} \cdot \text{L}^{-1})$ | $H_2O(l) +$ | $C_6H_5CH_2(CH_3)NH_3^+(aq)$ | $\rightleftharpoons$ | $C_6H_5CH_2(CH_3)NH_2(aq) +$ | $H_3O^+(aq)$ |
|---|---|---|---|---|---|
| initial | — | $9.46 \times 10^{-2}$ | | $0$ | $0$ |
| change | — | $-x$ | | $+x$ | $+x$ |
| equilibrium | — | $9.46 \times 10^{-2} - x$ | | $x$ | $x$ |

$$1.3 \times 10^{-11} = \frac{x^2}{0.145 - x} \approx \frac{x^2}{0.145}, \, x = 1.4 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$
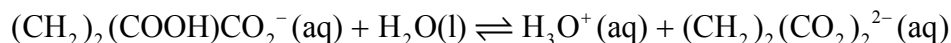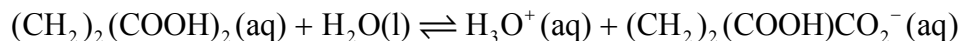
$$= [\text{H}_3\text{O}^+]$$

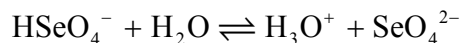$$\text{pH} = -\log(1.4 \times 10^{-6}) = 5.9$$

**10.72** (a) $\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$

$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$

$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$

(b)

$(\text{CH}_2)_4(\text{COOH})_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + (\text{CH}_2)_4(\text{COOH})\text{CO}_2^-(\text{aq})$

$(\text{CH}_2)_4(\text{COOH})\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + (\text{CH}_2)_4(\text{CO}_2)_2^{2-}(\text{aq})$

(c)

$(\text{CH}_2)_2(\text{COOH})_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + (\text{CH}_2)_2(\text{COOH})\text{CO}_2^-(\text{aq})$

$(\text{CH}_2)_2(\text{COOH})\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + (\text{CH}_2)_2(\text{CO}_2)_2^{2-}(\text{aq})$
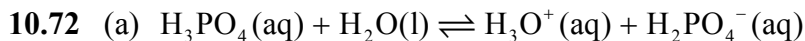
**10.74** The reaction is (after the first, essentially complete ionization)

$$\text{HSeO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SeO}_4^{2-}$$

The initial concentrations of $\text{HSeO}_4^-$ and $\text{H}_3\text{O}^+$ are both 0.010 mol $\cdot$ L$^{-1}$

due to the complete ionization of H$_2$SeO$_4$ in the first step. The second

ionization is incomplete.

Concentration

| (mol $\cdot$ L$^{-1}$) | $\text{HSeO}_4^-$ | + $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+$ | + | $\text{SeO}_4^{2-}$ |
|---|---|---|---|---|---|---|
| initial | 0.010 | — | | 0.010 | | 0 |
| change | $-x$ | — | | $+x$ | | $+x$ |
| equilibrium | $0.010 - x$ | — | | $0.010 + x$ | | $x$ |

$$K_{a2} = 1.2 \times 10^{-2} = \frac{[H_3O^+][SeO_4^{2-}]}{[HSeO_4^-]} = \frac{(0.010 + x)(x)}{0.010 - x}$$
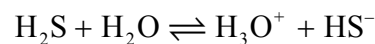
$$x^2 + 0.022x - 1.2 \times 10^{-4} = 0$$

$$x = \frac{-0.022 + \sqrt{(0.022)^2 - (4)(-1.2 \times 10^{-4})}}{2} = 4.5 \times 10^{-3}$$

$$[H_3O^+] = 0.010 + x = (0.010 + 4.5 \times 10^{-3}) \text{ mol} \cdot L^{-1} = 1.5 \times 10^{-2} \text{ mol} \cdot L^{-1}$$

$$pH = -\log(1.5 \times 10^{-2}) = 1.82$$

**10.76** (a) Second ionization is ignored because $K_{a2} \ll K_{a1}$

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$$

$$K_{a1} = 1.3 \times 10^{-7} = \frac{[H_3O^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = [H_3O^+] = 1.1 \times 10^{-4} \text{ mol} \cdot L^{-1}$$

$$pH = -\log(1.1 \times 10^{-4}) = 3.96$$

(b) This is a situation where it may not be justified to ignore the second ionization. $K_{a1} = 6.0 \times 10^{-4}$, $K_{a2} = 1.5 \times 10^{-5}$, and $K_{a2}/K_{a1} = 40$. This is a marginal case; we can work it both ways, first without ignoring the second ionization. Adopt the following notation:
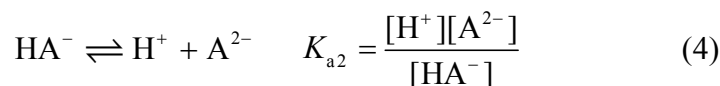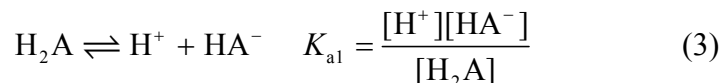
$H^+ = H_3O^+$

$[H^+] = [H_3O^+] =$ equilibrium concentration of $H_3O^+$

$H_2A =$ tartaric acid
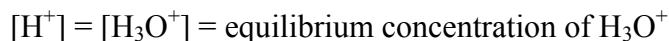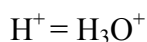
$c_0 =$ solute molarity $= 0.15 \text{ mol} \cdot L^{-1}$

$$c_0 = [H_2A] + [HA^-] + [A^{2-}] \tag{1}$$

$$H = \text{total H present} = [H^+] + 2[H_2A] + [HA^-] = 2c_0 \tag{2}$$

The following equilibria occur:

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \tag{3}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} \tag{4}$$

Examination of Eqs. 1 to 4 shows that there are four unknowns,

$[H^+], [H_2A], [HA^-]$, and $[A^{2-}]$, to be determined. However, these four

simultaneous equations allow for their determination.

The unknowns $[H_2A], [HA^-]$, and $[A^{2-}]$ may all be expressed in terms of

one unknown, $[H^+]$.

According to Eq. 1, $c_0 = [H_2A] + [HA^-] + [A^{2-}]$

From Eq. 3, $[H_2A] = \dfrac{[H^+][HA^-]}{K_{a1}}$

From Eq. 4, $[HA^-] = \dfrac{[H^+][A^{2-}]}{K_{a2}}$

Substituting, $[H_2A] = \dfrac{[H^+]^2[A^{2-}]}{K_{a1}\,K_{a2}}$

Then Eq. 1 becomes $c_0 = [A^{2-}]\left\{1 + \dfrac{[H^+]}{K_{a2}} + \dfrac{[H^+]^2}{K_{a1}K_{a2}}\right\}$ \qquad (5)

Now, subtract $2 \times$ Eq. 1 from Eq. 2 :

$2c_0 = [H^+] + 2[H_2A] + [HA^-]$ \quad Eq. 2

$\dfrac{2c_0 = 2[H_2A] + 2[HA^-] + 2[A^{2-}]}{[H^+] - [HA^-] - 2[A^{2-}] = 0}$ \quad $2 \times$ Eq. 1

$[A^{2-}], [A^{2-}] = \dfrac{[H^+]}{\dfrac{[H^+]}{K_{a2}} + 2}$

Substitute this into Eq. 5 to give

$c_0\left(2 + \dfrac{[H^+]}{K_{a2}}\right) = [H^+] + \dfrac{[H^+]^2}{K_{a2}} + \dfrac{[H^+]^3}{K_{a1}\,K_{a2}}$

Rearranging into standard cubic form gives

$\dfrac{[H^+]^3}{K_{a1}\,K_{a2}} + \dfrac{[H^+]^2}{K_{a2}} + [H^+]\left(1 - \dfrac{c_0}{K_{a2}}\right) - 2c_0 = 0$

Now, put in the numerical values for $c_0$, $K_{a1}$, and $K_{a2}$:

$1.1 \times 10^8 [H^+]^3 + 6.7 \times 10^4 [H^+]^2 - 1.0 \times 10^4 [H^+] - 0.30 = 0$

Solution of this cubic by standard methods gives

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$[H^+] = [H_3O^+] = 9.2 \times 10^{-3} \text{ mol} \cdot L^{-1}$
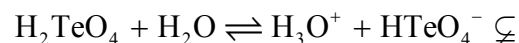
$pH = -\log(9.2 \times 10^{-3}) = 2.04$

It is left as an exercise for the reader to show that, if the second ionization is ignored,

$[H^+] = 9.5 \times 10^{-3} \text{ mol} \cdot L^{-1}$ and $pH = 2.02$

The difference is small but, perhaps, not within experimental error.

(c) The second ionization can be ignored because $K_{a2} \ll K_{a1}$.

$H_2TeO_4 + H_2O \rightleftharpoons H_3O^+ + HTeO_4^- \; \subsetneq$

$K_{a1} = 2.1 \times 10^{-8} = \dfrac{[H_3O^+][HTeO_4^-]}{[H_2TeO_4]} = \dfrac{x^2}{1.1 \times 10^{-3} - x} \approx \dfrac{x^2}{1.1 \times 10^{-3}}$

$x = [H_3O^+] = 4.8 \times 10^{-6} \text{ mol} \cdot L^{-1}$

$pH = -\log(4.8 \times 10^{-6}) = 5.32$

**10.78** (a) The pH is given by $pH = \frac{1}{2}(pK_{a1} + pK_{a2})$. From Table 10.9, we find

$K_{a1} = 4.3 \times 10^{-7} \qquad pK_{a1} = 6.37$
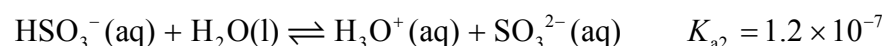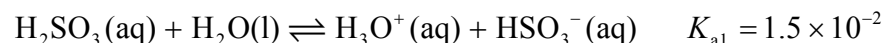
$K_{a2} = 5.6 \times 10^{-11} \qquad pK_{a2} = 10.25$

$pH = \frac{1}{2}(6.37 + 10.25) = 8.31$

(b) The nature of the spectator counter ion does not affect the equilibrium and the pH of a salt solution of a polyprotic acid is independent of the concentration of the salt, therefore $pH = 8.31$.

**10.80** The pH is given by $pH = \frac{1}{2}(pK_{a1} + pK_{a2})$.

$pH = \frac{1}{2}(2.46 + 7.31) = 4.89$

**10.82** The equilibrium reactions of interest are

$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.5 \times 10^{-2}$

$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 1.2 \times 10^{-7}$

Because the second ionization constant is much smaller than the first, we can assume that the first step dominates:

Concentration

| $(mol \cdot L^{-1})$ | $H_2SO_3(aq)$ | + | $H_2O(l)$ | $\rightleftharpoons$ | $H_3O^+(aq)$ | + | $HSO_3^-(aq)$ |
|---|---|---|---|---|---|---|---|
| initial | 0.125 | | — | | 0 | | 0 |
| change | $-x$ | | — | | $+x$ | | $+x$ |
| final | $0.125 - x$ | | — | | $+x$ | | $+x$ |

$$K_{a1} = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]}$$

$$1.5 \times 10^{-2} = \frac{(x)(x)}{0.125 - x} = \frac{x^2}{0.125 - x}$$

Assume that $x \ll 0.125$, then

$$x^2 = (1.5 \times 10^{-2})(0.125)$$

$$x = 0.043$$

Because $x > 5\%$ of 0.0456, the assumption was not valid, and the full expression must be evaluated using the quadratic:

$$x^2 + 1.5 \times 10^{-2}\, x - (1.5 \times 10^{-2})(0.125) = 0$$

Solving with the quadratic equation gives $x = 0.036 \ mol \cdot L^{-1}$.

$$x = [H_3O^+] = [HSO_3^-] = 0.036 \ mol \cdot L^{-1}$$

$$[H_2SO_3] = 0.125 \ mol \cdot L^{-1} - 0.036 \ mol \cdot L^{-1} = 0.089 \ mol \cdot L^{-1}$$

We can then use the other equilibria to determine the remaining concentrations:

$$K_{a2} = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]}$$

$$1.2 \times 10^{-7} = \frac{(0.036)[SO_3^{2-}]}{(0.036)}$$

$$[SO_3^{2-}] = 1.2 \times 10^{-7} \ mol \cdot L^{-1}$$

Because $1.2 \times 10^{-7} \ll 0.036$, the initial assumption that the first dissociation would dominate is valid. To calculate $[OH^-]$, we use the $K_w$ relationship:

$$K_w = [H_3O^+][OH^-]$$
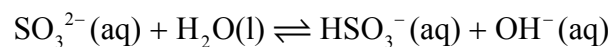
$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{0.036} = 2.8 \times 10^{-13} \ \text{mol} \cdot \text{L}^{-1}$$
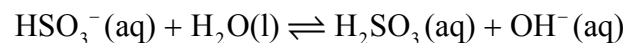
In summary,

$$[H_2SO_3] = 0.089 \ \text{mol} \cdot \text{L}^{-1}, [H_3O^+] = [HSO_3^-] = 0.036 \ \text{mol} \cdot \text{L}^{-1}, [SO_3^{2-}]$$

$$= 1.2 \times 10^{-7} \ \text{mol} \cdot \text{L}^{-1}, [OH^-] = 2.8 \times 10^{-13} \ \text{mol} \cdot \text{L}^{-1}$$

**10.84** The equilibrium reactions of interest are now the base forms of the carbonic acid equilibria, so $K_b$ values should be calculated for the following changes:
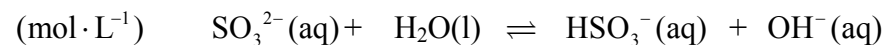
$$SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + OH^-(aq)$$

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{1.2 \times 10^{-7}} = 8.3 \times 10^{-8}$$

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$$

$$K_{b2} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{1.5 \times 10^{-2}} = 6.7 \times 10^{-13}$$

Because the second hydrolysis constant is much smaller than the first, we can assume that the first step dominates:

Concentration

| $(\text{mol} \cdot \text{L}^{-1})$ | $SO_3^{2-}(aq) +$ | $H_2O(l)$ | $\rightleftharpoons$ | $HSO_3^-(aq) \ +$ | $OH^-(aq)$ |
|---|---|---|---|---|---|
| initial | 0.125 | — | | 0 | 0 |
| change | $-x$ | — | | $+x$ | $+x$ |
| final | $0.125 - x$ | — | | $+x$ | $+x$ |

$$K_{b1} = \frac{[HSO_3^-][OH^-]}{[SO_3^{2-}]}$$

$$8.3 \times 10^{-8} = \frac{(x)(x)}{0.125 - x} = \frac{x^2}{0.125 - x}$$

Assume that $x \ll 0.125$, then

$$x^2 = (8.3 \times 10^{-8})(0.125)$$

$$x = 1.0 \times 10^{-4}$$

Because $x < 1\%$ of 0.125, the assumption was valid.

$x = [HSO_3^{-}] = [OH^{-}] = 1.0 \times 10^{-4} \text{ mol} \cdot L^{-1}$

Therefore, $[SO_3^{2-}] = 0.125 \text{ mol} \cdot L^{-1} - 1.0 \times 10^{-4} \text{ mol} \cdot L^{-1} \cong 0.125 \text{ mol} \cdot L^{-1}$

We can then use the other equilibria to determine the remaining concentrations:

$$K_{b2} = \frac{[H_2SO_3][OH^{-}]}{[HCO_3^{-}]}$$

$$6.7 \times 10^{-13} = \frac{[H_2SO_3](1.0 \times 10^{-4})}{(1.0 \times 10^{-4})}$$

$$[H_2SO_3] = 6.7 \times 10^{-13} \text{ mol} \cdot L^{-1}$$

Because $6.7 \times 10^{-13} \ll 1.0 \times 10^{-4}$, the initial assumption that the first hydrolysis would dominate is valid.

To calculate $[H_3O^{+}]$, we use the $K_w$ relationship:

$$K_w = [H_3O^{+}][OH^{-}]$$

$$[H_3O^{+}] = \frac{K_w}{[OH^{-}]} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-14}} = 1.0 \times 10^{-10} \text{ mol} \cdot L^{-1}$$

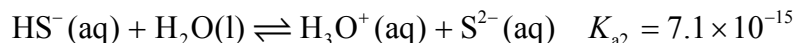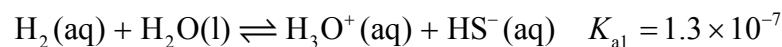In summary, $[H_2SO_3] = 6.7 \times 10^{-13} \text{ mol} \cdot L^{-1}$, $[OH^{-}]$
$= [HSO_3^{-}] = 1.0 \times 10^{-4} \text{ mol} \cdot L^{-1}$, $[SO_3^{2-}]$
$= 0.125 \text{ mol} \cdot L^{-1}$, $[H_3O^{+}] = 1.0 \times 10^{-10} \text{ mol} \cdot L^{-1}$

**10.86** (a) tartaric acid: The two $pK_a$ values are 3.22 and 4.82. Because pH = 5.0 lies above both of these values, the major form present will be the doubly deprotonated ion $A^{2-}$.   (b) hydrosulfuric acid: The two $pK_a$ values are 6.89 and 14.15. Because the pH of the solution lies below both of these values, the dominant form will be the doubly protonated $H_2A$.   (c) phosphoric acid: The three $pK_a$ values are 2.12, 7.21, and 12.68. The pH of the solution lies between the first and second ionization, so the predominant species should be the singly deprotonated ion $H_2PO_4^{-}$.

**10.88** The equilibria present in the solution are:

$$H_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 1.3 \times 10^{-7}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 7.1 \times 10^{-15}$$

The calculation of the desired concentrations follows exactly after the method derived in Eq. 25, substituting $H_2S$ for $H_2CO_3$, $HS^-$ for $HCO_3^-$, and $S^{2-}$ for $CO_3^{2-}$. First, calculate the quantity

$f$ (at pH = 9.35 $[H_3O^+] = 10^{-9.35} = 4.5 \times 10^{-10} \text{ mol} \cdot L^{-1}$):

$$f = [H_3O^+]^2 + [H_3O^+]K_{a1} + K_{a1} K_{a2}$$
$$= (4.5 \times 10^{-10})^2 + (4.5 \times 10^{-10})(1.3 \times 10^{-7}) + (1.3 \times 10^{-7})(7.1 \times 10^{-15})$$
$$= 5.9 \times 10^{-17}$$

The fractions of the species present are then given by

$$\alpha(H_2S) = \frac{[H_3O^+]}{f} = \frac{(4.5 \times 10^{-10})^2}{5.9 \times 10^{-17}} = 3.4 \times 10^{-3}$$

$$\alpha(HS^-) = \frac{[H_3O^+]K_{a1}}{f} = \frac{(4.5 \times 10^{-10})(1.3 \times 10^{-7})}{5.9 \times 10^{-17}} = 0.99$$

$$\alpha(S^{2-}) = \frac{K_{a1}K_{a2}}{f} = \frac{(1.3 \times 10^{-17})(7.1 \times 10^{-15})}{5.9 \times 10^{-17}} = 1.6 \times 10^{-15}$$

Thus, in a solution at pH 9.35, the dominant species will be $HS^-$ with a concentration of $(0.250 \text{ mol} \cdot L^{-1})(0.99) \cong 0.25 \text{ mol} \cdot L^{-1}$. The concentration of $H_2S$ will be

$(3.4 \times 10^{-3})(0.250 \text{ mol} \cdot L^{-1}) = 8.5 \times 10^{-4} \text{ mol} \cdot L^{-1}$, and the concentration of $S^{2-}$ will be $(1.6 \times 10^{-5})(0.250 \text{ mol} \cdot L^{-1}) = 4.0 \times 10^{-6} \text{ mol} \cdot L^{-1}$.

**10.90** For the first ionization of $(COOH)_2$—or $H_2C_2O_4$—we write

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-, \quad K_{a1} = 5.9 \times 10^{-2}$$
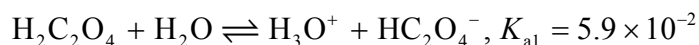
Concentration

| (mol·L⁻¹) | $H_2C_2O_4$ | + | $H_2O$ | ⇌ | $H_3O^+$ | + | $HC_2O_4^-$ |
|---|---|---|---|---|---|---|---|
| initial | 0.10 | | — | | 0 | | 0 |
| change | −x | | — | | +x | | +x |
| equilibrium | 0.10 − x | | — | | x | | x |

$K_{a1} = 5.9 \times 10^{-2}$, $K_{a2} = 6.5 \times 10^{-5}$

Because $K_{a2} << K_{a1}$, the second ionization can safely be ignored in the calculation of $[H_3O^+]$.

$$K_{a1} = 5.9 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

$$x^2 + 0.059x - 0.0059 = 0$$

$$x = \frac{-0.059 + \sqrt{(0.059)^2 + (4)(1)(0.0059)}}{2} = 0.053 \text{ mol} \cdot L^{-1} = [H_3O^+]$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.053} = 1.9 \times 10^{-13} \text{ mol} \cdot L^{-1}$$

$$[H_2C_2O_4] = 0.10 - 0.053 = 0.05 \text{ mol} \cdot L^{-1}$$

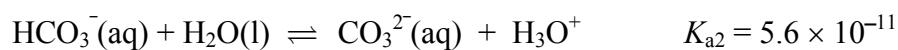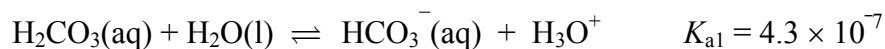| Concentration (mol·L⁻¹) | $HC_2O_4^-$ | +$H_2O$ | ⇌ | $H_3O^+$ | + | $C_2O_4^{2-}$ |
|---|---|---|---|---|---|---|
| initial | 0.053 | | — | 0.053 | | 0 |
| change | −x | | — | +x | | +x |
| equilibrium | 0.053 − x | | — | 0.053 + x | | x |

$$K_{a2} = 6.5 \times 10^{-5} = \frac{(0.053 + x)(x)}{0.053 - x} \approx x \text{ (because } x \text{ is small)}$$

or $x = [C_2O_4^{2-}] = 6.5 \times 10^{-5} \text{ mol} \cdot L^{-1}$, and

$$[HC_2O_4^-] = 0.053 - x = 0.053 - 0.000\ 065 = 0.053 \text{ mol} \cdot L^{-1}$$

**10.92** The equilibria involved are:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+ \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+ \qquad K_{a2} = 5.6 \times 10^{-11}$$

Given these two equilibria, two equations can be written:

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

also, enough information is provided to construct two other equations:

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 4.5 \times 10^{-3}$$

$$[H_3O^+] = 10^{-4.8} = 1.6 \times 10^{-5}$$

Solving this set of simultaneous equations for the three unknown concentrations, one finds:

$$[H_2CO_3] = 4.38 \times 10^{-3}$$

$$[HCO_3^-] = 1.19 \times 10^{-4}$$

$$[CO_3^{2-}] = 4.23 \times 10^{-10}$$

**10.94**  We can use the relationship derived in the text:

$$[H_3O^+]^2 - [HA]_{initial}[H_3O^+] - K_w = 0$$

$$[H_3O^+]^2 - (7.49 \times 10^{-8})[H_3O^+] - (1.00 \times 10^{-14}) = 0$$

Solving using the quadratic equation gives

$$[H_3O^+] = 1.44 \times 10^{-7}; \; pH = 6.842$$

This value is lower than the value calculated, based on the acid concentration alone $(pH = -\log(7.49 \times 10^{-8}) = 7.126)$.

**10.96**  We can use the relationship derived in the text:

$$[H_3O^+]^2 + [B]_{initial}[H_3O^+] - K_w = 0, \text{ in which B is any strong base.}$$

$$[H_3O^+]^2 + (8.23 \times 10^{-7})[H_3O^+] - (1.00 \times 10^{-14}) = 0$$

Solving using the quadratic equation gives
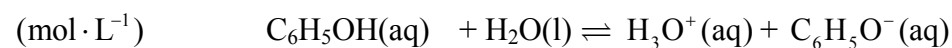
$$[H_3O^+] = 1.20 \times 10^{-8}, \; pH = 7.922$$

This value is slightly higher than the value calculated, based on the base concentration alone

$$(pOH = -\log(8.23 \times 10^{-7}) = 6.084, \; pH = 14.00 - 6.084 = 7.916).$$

**10.98** (a) In the absence of a significant effect due to the autoprotolysis of water, the pH values of the $2.50 \times 10^{-4}$ M and $2.50 \times 10^{-6}$ M $C_6H_5OH$ solutions can be calculated as described earlier.

For $2.50 \times 10^{-4}$ mol $\cdot$ L$^{-1}$ :

Concentration

| (mol $\cdot$ L$^{-1}$) | $C_6H_5OH(aq)$ | $+ H_2O(l) \rightleftharpoons$ | $H_3O^+(aq) +$ | $C_6H_5O^-(aq)$ |
|---|---|---|---|---|
| initial | $2.50 \times 10^{-4}$ | — | 0 | 0 |
| change | $-x$ | — | $+x$ | $+x$ |
| final | $2.50 \times 10^{-4} - x$ | — | $+x$ | $+x$ |

$$K_a = \frac{[H_3O^+][C_6H_5O^-]}{[C_6H_5OH]}$$

$$1.3 \times 10^{-10} = \frac{(x)(x)}{2.50 \times 10^{-4} - x} = \frac{x^2}{2.50 \times 10^{-4} - x}$$
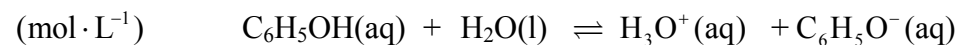
Assume $x \ll 2.50 \times 10^{-4}$

$$x^2 = (1.3 \times 10^{-10})(2.50 \times 10^{-4})$$
$$x = 1.8 \times 10^{-7}$$

Because $x < 1\%$ of $2.50 \times 10^{-4}$, the assumption was valid. Given this value, the pH is then calculated to be $-\log(1.8 \times 10^{-8}) = 6.74$.

For $2.50 \times 10^{-6}$ mol $\cdot$ L$^{-1}$ :

Concentration

| (mol $\cdot$ L$^{-1}$) | $C_6H_5OH(aq)$ | $+ H_2O(l) \rightleftharpoons$ | $H_3O^+(aq) +$ | $C_6H_5O^-(aq)$ |
|---|---|---|---|---|
| initial | $2.50 \times 10^{-6}$ | — | 0 | 0 |
| change | $-x$ | — | $+x$ | $+x$ |
| final | $2.50 \times 10^{-6} - x$ | — | $+x$ | $+x$ |

$$K_a = \frac{[H_3O^+][C_6H_5O^-]}{[C_6H_5OH]}$$

$$1.3 \times 10^{-10} = \frac{(x)(x)}{2.50 \times 10^{-6} - x} = \frac{x^2}{2.50 \times 10^{-6} - x}$$

Assume $x \ll 2.50 \times 10^{-6}$

$$x^2 = (1.3 \times 10^{-10})(2.50 \times 10^{-6})$$
$$x = 1.8 \times 10^{-8}$$

Because $x < 1\%$ of $2.50 \times 10^{-6}$, the assumption is valid and the pH should be 7.74. However, this number does not make sense because an acid was added to the water.

(b)  To calculate the value, taking into account the autoprotolysis of water, we can use Eq. 22:

$$x^3 + K_a x^2 - (K_w + K_a \cdot [HA]_{initial})x - K_w \cdot K_a = 0, \text{ where } x = [H_3O^+].$$

To solve the expression, you substitute the values of $K_w = 1.00 \times 10^{-14}$, the initial concentration of acid, and $K_a = 1.3 \times 10^{-10}$ into this equation and then solve the expression either by trial and error or, preferably, using a graphing calculator. Alternatively, you can use a computer program designed to solve simultaneous equations. Because the unknowns include $[H_3O^+]$, $[OH^-]$, $[HClO]$, and $[ClO^-]$, you will need four equation. As seen in the text, the pertinent equations are

$$K_a = \frac{[H_3O^+][C_6H_5O^-]}{[C_6H_5OH]}$$

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = [OH^-] + [C_6H_5O^-]$$

$$[C_6H_5OH]_{initial} = [C_6H_5OH] + [C_6H_5O^-]$$

Using either method should produce the same result.

The values obtained for $2.50 \times 10^{-4} \text{ mol} \cdot L^{-1}$ are

$$[H_3O^+] = 2.1 \times 10^{-7} \text{ mol} \cdot L^{-1}, pH = 6.68 \text{ (compare to 6.74 obtained in (a))}$$

$$[C_6H_5O^-] = 1.6 \times 10^{-7} \text{ mol} \cdot L^{-1}$$
$$[C_6H_5OH] \cong 2.5 \times 10^{-4} \text{ mol} \cdot L^{-1}$$
$$[OH^-] = 4.8 \times 10^{-8} \text{ mol} \cdot L^{-1}$$

Similarly, for $[C_6H_5OH]_{initial} = 2.50 \times 10^{-6}$:

$$[H_3O^+] = 1.0 \times 10^{-7} \text{ mol} \cdot L^{-1}, pH = 7.00 \text{ (compare to 7.74 obtained in (a))}$$

$[C_6H_5O^-] = 3.2 \times 10^{-9} \ mol \cdot L^{-1}$
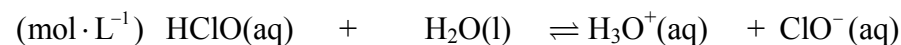
$[C_6H_5OH] \cong 2.5 \times 10^{-6} \ mol \cdot L^{-1}$

$[OH^-] = 9.8 \times 10^{-8} \ mol \cdot L^{-1}$

Note that for the more concentrated solution, the effect of the autoprotolysis of water is very small. Notice also that the less concentrated solution is more acidic, due to the autoprotolysis of water, than would be predicted if this effect were not operating.

**10.100** (a)  In the absence of a significant effect due to the autoprotolysis of water, the pH values of the $1.89 \times 10^{-5}$ M and $9.64 \times 10^{-7}$ M HClO solutions can be calculated as described earlier.

For $1.89 \times 10^{-5} \ mol \cdot L^{-1}$:

Concentration

| $(mol \cdot L^{-1})$ | HClO(aq) | + | H₂O(l) | ⇌ H₃O⁺(aq) | + ClO⁻(aq) |
|---|---|---|---|---|---|
| initial | $1.89 \times 10^{-5}$ | | — | 0 | 0 |
| change | $-x$ | | — | $+x$ | $+x$ |
| final | $1.89 \times 10^{-5} - x$ | | — | $+x$ | $+x$ |

$$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$3.0 \times 10^{-8} = \frac{(x)(x)}{1.89 \times 10^{-5} - x} = \frac{x^2}{1.89 \times 10^{-5} - x}$$

Assume $x \ll 1.89 \times 10^{-5}$

$x^2 = (3.0 \times 10^{-8})(1.89 \times 10^{-5})$

$x = 7.5 \times 10^{-7}$

Because $x < 5\%$ of $1.89 \times 10^{-5}$, the assumption was valid. Given this value, the pH is then calculated to be $-\log(7.5 \times 10^{-7}) = 6.12$.

For $9.64 \times 10^{-7} \ mol \cdot L^{-1}$:

Concentration

| (mol·L$^{-1}$) HClO(aq) + | H$_2$O(l) | ⇌ H$_3$O$^+$(aq) + | ClO$^-$(aq) |
|---|---|---|---|
| initial | $9.64 \times 10^{-7}$ | — | 0 | 0 |
| change | $-x$ | — | $+x$ | $+x$ |
| final | $9.64 \times 10^{-7} - x$ | — | $+x$ | $+x$ |

$$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$3.0 \times 10^{-8} = \frac{(x)(x)}{9.64 \times 10^{-7} - x} = \frac{x^2}{9.64 \times 10^{-7} - x}$$

Assume $x \ll 9.64 \times 10^{-7} - x$

$$x^2 = (3.0 \times 10^{-8})(9.64 \times 10^{-7} - x)$$
$$x = 1.7 \times 10^{-7}$$

$x$ is approximately 10% of $9.64 \times 10^{-7}$; the assumption is not reasonable, and so you must calculate the value explicitly for the following expression, using the quadratic equation.

$$x^2 + 3.0 \times 10^{-8} x - (3.0 \times 10^{-8})(9.64 \times 10^{-7}) = 0$$

Upon solving the quadratic equation, a value of $x = 1.6 \times 10^{-7}$ is obtained, yielding pH = 6.80.

(b) To calculate the value, taking into account the autoprotolysis of water, we can use Eq. 21:

$$x^3 + K_a x^2 - (K_w + K_a \cdot [HA]_{initial})x - K_w \cdot K_a = 0, \text{ where } x = [H_3O^+].$$

To solve the expression, you substitute the values of $K_w = 1.00 \times 10^{-14}$, the initial concentration of acid, and $K_a = 3.0 \times 10^{-8}$ into this equation and then solve the expression either by trial and error or, preferably, using a graphing calculator. Alternatively, you can use a computer program designed to solve simultaneous equations. Because the unknowns include $[H_3O^+]$, $[OH^-]$, $[HClO]$, and $[ClO^-]$, you will need four equations. As seen in the text, the pertinent equations are

$$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = [OH^-] + [ClO^-]$$

$$[HClO]_{initial} = [HClO] + [ClO^-]$$

Using either method should produce the same result.

The values obtained for $1.89 \times 10^{-5}$ mol·L$^{-1}$ are

$[H_3O^+] = 7.4 \times 10^{-7}$ mol·L$^{-1}$, pH = 6.13 (compare to 6.12 obtained in (a))

$[ClO^-] = 7.3 \times 10^{-7}$ mol·L$^{-1}$

$[HClO] \cong 1.8 \times 10^{-5}$ mol·L$^{-1}$

$[OH^-] = 1.3 \times 10^{-8}$ mol·L$^{-1}$

Similarly, for $[HClO]_{initial} = 9.64 \times 10^{-7}$ :

$[H_3O^+] = 1.9 \times 10^{-7}$ mol·L$^{-1}$, pH = 6.72 (compare to 6.80 obtained in (a))

$[ClO^-] = 1.3 \times 10^{-7}$ mol·L$^{-1}$

$[HClO] \cong 8.3 \times 10^{-7}$ mol·L$^{-1}$

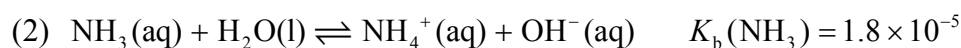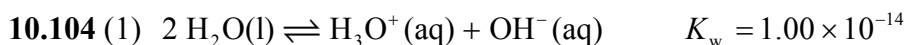$[OH^-] = 5.3 \times 10^{-8}$ mol·L$^{-1}$

Note than for the more concentrated solution, the effect of the autoprotolysis of water is very small. Notice also that the less concentrated solution is more acidic, due to the autoprotolysis of water, than would be predicted if this effect were not operating.

**10.102** Because the process is only 90% efficient, to remove 50.0 kg of SO$_2$ one must supply enough CaCO$_3$ to remove 55.6 kg of SO$_2$ (50.0 kg is 90% of 55.6 kg). The moles of SO$_2$ to be removed is given by:

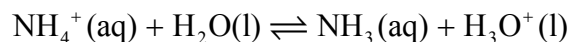$$\frac{55600 \text{ g}}{65.06 \text{ g mol}^{-1}} = 867 \text{ mol SO}_2$$

1 mole of SO$_2$ is consumed by 1 mole of CaCO$_3$. Therefore,

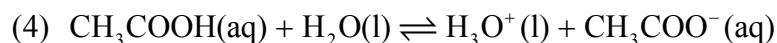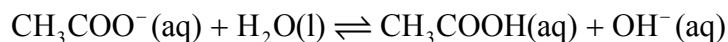$$(867 \text{ mol CaCO}_3)(100.09 \text{ g mol}^{-1}) = 86.8 \text{ kg}$$

**10.104** (1)  $2 H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$        $K_w = 1.00 \times 10^{-14}$

(2)  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$        $K_b(NH_3) = 1.8 \times 10^{-5}$

or

(3)

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(l)$

$$K_a(NH_4^+) = K_w / K_b(NH_3) = 5.56 \times 10^{-10}$$

(4)  $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(l) + CH_3COO^-(aq)$

$$K_a(CH_3COOH) = 1.8 \times 10^{-5}$$

or

(5)

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$$K_b(CH_3COO)^- = K_w / K_a(CH_3COOH)$$
$$= 5.56 \times 10^{-10}$$

(6)

$NH_4^+(aq) + CH_3COO^-(aq) \rightleftharpoons NH_3(aq) + CH_3COOH(aq)$
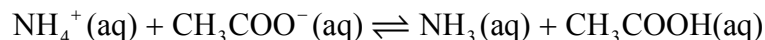
$$K(NH_4CH_3COO) = \frac{[NH_3][CH_3COOH]}{[NH_4^+][CH_3COO^-]}$$

This equation is obtained by adding Equations (3) and (5) and subtracting Equation (1):

$+[NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(l)]$

$\quad K_w / K_b(NH_3)$

$+[CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH(aq)]$
$\quad K_w / K_a(CH_3COOH)$

$-[2 H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)] K_w$
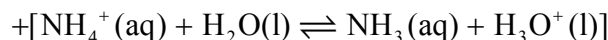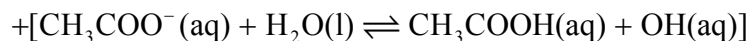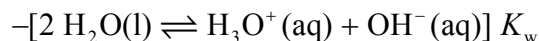
Because we are starting with pure ammonium acetate, we will use the last relationship to calculate the concentrations of

$NH_4^+$, $CH_3COO^-$, $NH_3$, and $CH_3COOH$ in solution.

Concentration

$$(\text{mol}\cdot\text{L}^{-1})\ NH_4^+(aq)\ +\ CH_3COO^-(aq) \rightleftharpoons NH_3(aq)\ +\ CH_3COOH(aq)$$
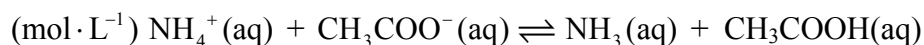
| | | | | |
|---|---|---|---|---|
| initial | 0.100 | 0.100 | 0 | 0 |
| change | $-x$ | $-x$ | $+x$ | $+x$ |
| equilibrium | $0.100 - x$ | $0.100 - x$ | $+x$ | $+x$ |

For the initial calculation, we will assume that the subsequent deprotonation of acetic acid by water or the protonation of ammonia by water will be small compared to the reaction of the ammonium ion with the acetate ion.

$$\frac{[NH_3][CH_3COOH]}{[NH_4^+][CH_3COO^-]} = 3.09 \times 10^{-5}$$

$$\frac{x^2}{(0.100 - x)^2} = 3.09 \times 10^{-5}$$

$$\frac{x}{0.100 - x} = \sqrt{3.09 \times 10^{-5}}$$

$$x = (0.100 - x)\sqrt{3.09 \times 10^{-5}}$$

$$(1 + \sqrt{3.09 \times 10^{-5}})x = (0.100)\sqrt{3.09 \times 10^{-5}}$$

$$x = 5.52 \times 10^{-4}$$

By using this as the value of the concentrations of $NH_3$ and $CH_3COOH$, we can calculate the concentrations of $NH_4^+$, $CH_3COO^-$, $H_3O^+$, and $OH^-$ in solution using the above equilibrium relationship. The values calculated are

$$[NH_4^+] = [CH_3COOH] = 0.099$$

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$$

If we substitute these numbers back into each of the equilibrium constants expressions, we get very good agreement. This justifies the assumption that the subsequent hydrolysis reactions of the $NH_3$ and $CH_3COOH$ were small compared to the main reaction.

Alternatively (had this not been the case), we could have solved the system of equations using a graphing calculator or suitable computer

software package by setting up a system of simultaneous equations. The answer is the same in any case. This problem is simplified by the fact that the tendency for subsequent hydrolysis of $NH_3$ and $CH_3COOH$ have the same magnitude.

**10.106** According to Table 10.3, the amide ion that is formed from the autoionization of ammonia, $2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-$, is a stronger base than $OH^-$. Therefore, carbonic acid (and other weak acids) is expected to be stronger in liquid ammonia than in water. Furthermore, carbonic acid is a stronger acid than $NH_4^+$; therefore, it will donate a proton to $NH_3$ to form $NH_4^+$. It can then be concluded that carbonic acid will be leveled in liquid $NH_3$ and will behave as a strong acid.

**10.108** (a)  The pH is given by $pH = \frac{1}{2}\left(pK_{a1} + pK_{a2}\right)$. The first and second dissociations of $H_3AsO_4$ are the pertinent values for $NaH_2AsO_4$:

$pH = \frac{1}{2}\left(2.25 + 6.77\right) = 4.51$

(b)  For $Na_2HAsO_4$ the second and third acid dissociation constants must be used:

$pH = \frac{1}{2}\left(6.77 + 11.60\right) = 9.19$

**10.110** (a)  $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(b)  acid $= NH_4^+$, base $= NH_2^-$

(c)  $pK_{am} = -\log K_{am} = -\log(1 \times 10^{-33}) = 33.0$

(d)  $pK_{am} = [NH_4^+][NH_2^-] = x^2 \ (x = [NH_4^+] = [NH_2^-])$
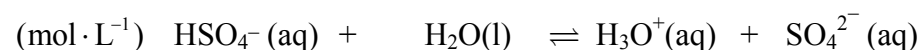
$[NH_4^+] = \sqrt{1 \times 10^{-33}} = 3 \times 10^{-17} \ mol \cdot L^{-1}$

(e)  $pNH_4^+ = pNH_2^- = -\log(3.2 \times 10^{-17}) = 17$

(f)  $pNH_4^+ = pNH_2^- = pK_{am} \approx 33.0$

**10.112** The osmotic pressure of 0.10 $H_2SO_4$ will be slightly higher than that of 0.10 M HCl. When $H_2SO_4$ is added to solution it completely deprotonates into $HSO_4^-$, a small fraction of which deprotonates further to $SO_4^{2-}$. Therefore, each mole of $H_2SO_4$ gives rise to slightly more than 2 moles of dissolved ions. HCl, on the other hand, is a strong monoprotic acid giving exactly two moles of dissolved ions per mole of HCl molecules.

To calculate the moles of dissolved ions in a 0.10 M solution of $H_2SO_4$ one assumes that $H_2SO_4$ is completely deprotonated, and solves the equilibrium problem:

Concentration

| $(mol \cdot L^{-1})$ | $HSO_4^-$ (aq) + | $H_2O$(l) | $\rightleftharpoons$ $H_3O^+$(aq) + | $SO_4^{2-}$ (aq) |
|---|---|---|---|---|
| initial | 0.10 | — | 0.10 | 0 |
| change | $-x$ | — | $+x$ | $+x$ |
| final | $0.10 - x$ | — | $0.10 + x$ | $+x$ |

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$1.2 \times 10^{-2} = \frac{(0.10 + x)(x)}{0.10 - x}$$

Using the quadratic equation one finds that $x = 9.8 \times 10^{-3}$ and, therefore: $[HSO_4^-] = 0.0902$ M, $[H_3O^+] = 0.1098$ M, and $[SO_4^{2-}] = 0.0098$ M giving a total dissolved ion concentration of 0.210 M (compared to a total dissolved ion concentration of 0.20 for the 0.10 M HCl solution). Assuming a temperature of 298 K, the osmotic pressure of the 0.10 M $H_2SO_4$ solution is:

$$\Pi = RTc = \left(0.082057 \text{ L} \cdot atm \cdot K^{-1} \text{ mol}^{-1}\right)\left(298 \text{ K}\right)\left(0.210 \text{ mol} \cdot L^{-1}\right)$$
$$= 5.13 \text{ atm}$$

While that of the HCl solution is:

$$\Pi = RTc = \left(0.082057 \text{ L} \cdot atm \cdot K^{-1} \cdot mol^{-1}\right)\left(298 \text{ K}\right)\left(0.200 \text{ mol} \cdot L^{-1}\right)$$
$$= 4.89 \text{ atm}$$

**10.114** $\Delta H° = +57 \text{ kJ} \cdot \text{mol}^{-1}$ (where 1 mol refers to the reaction as written)

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$2.303 \log \frac{K_1}{K_2} = -\frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$-2.303 \log \frac{K_1}{K_2} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$pK_1 - pK_2 = \frac{\Delta H°}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Let condition 2 be 25°C, where $pK_w = 14$:

$$pK_1 - 14 = \frac{57\,000 \text{ J}}{2.303 \cdot 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\left(\frac{1}{T_1} - \frac{1}{298 \text{ K}}\right)$$

$$pK_1 = 14 + \frac{57\,000 \text{ J}}{2.303 \cdot 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\left(\frac{1}{T_1} - \frac{1}{298 \text{ K}}\right)$$

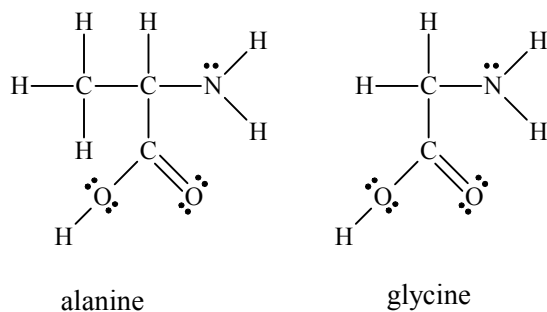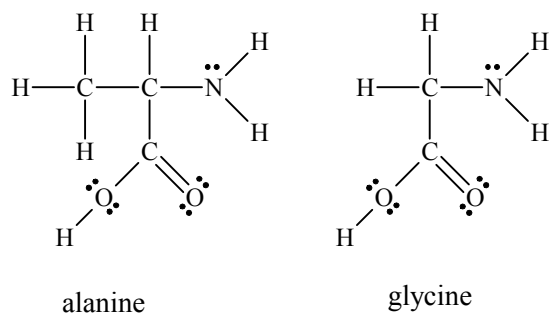We will not define $K_1$ as the $K_w$ value at some unknown temperature T:

$$pK_w = 14 + \frac{57\,000 \text{ J} \cdot \text{mol}^{-1}}{2.303 \cdot 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\left(\frac{1}{T} - \frac{1}{298 \text{ K}}\right)$$

$$pK_w = \frac{3.0 \times 10^3 \text{ K}}{T} + 4.00$$

Substituting the value of T = 373 K gives $pK_w$ = 12.04. If the solution is neutral, the pH = pOH = 6.02.

**10.116** (a)  The structures of alanine, glycine, phenylalanine, and cysteine are



alanine                    glycine

alanine          glycine
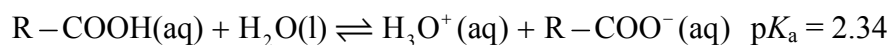
All the amino acids have an amine —$NH_2$ function as well as a carboxylic acid —COOH group.

(b) The $pK_a$ value of the —COOH group of alanine is 2.34 and the $pK_b$ of the —$NH_2$ group is 4.31. Often, we find instead of the $pK_b$ value, the $pK_a$ value of the conjugate acid of the —$NH_2$ group. The relationship $pK_a \cdot pK_b = pK_w$ is used to convert to the $pK_b$ value.

(c) To find the equilibrium constant of the reaction of the acid function, with the base function in the amino acid, we first write the known equilibrium reactions and corresponding $K$ values:
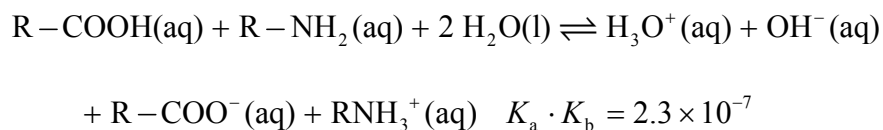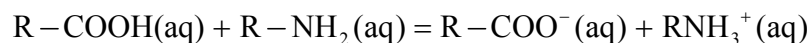
$$R - COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + R - COO^-(aq) \quad pK_a = 2.34$$

$$K_a = 4.6 \times 10^{-3}$$

$$R - NH_2(aq) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq) \quad pK_b = 4.31$$

$$K_b = 4.9 \times 10^{-5}$$

If we sum these reactions, we obtain

$$R - COOH(aq) + R - NH_2(aq) + 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$+ R - COO^-(aq) + RNH_3^+(aq) \quad K_a \cdot K_b = 2.3 \times 10^{-7}$$

The presence of the $H_2O$, $H_3O^+$, and $OH^-$ can be eliminated by subtracting the autoprotolysis reaction of water to give the desired final equation:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w = 1.00 \times 10^{-14}$$

$$R-COOH(aq) + R-NH_2(aq) = R-COO^-(aq) + RNH_3^+(aq)$$

$$K = K_a \cdot K_b \cdot K_w^{-1}$$
$$K = 2.3 \times 10^7$$

(d)  A zwitterion is a compound that contains both a positive ion and a negative ion in the same molecule. Overall, the molecule is neutral, but it is ionic in that it possesses both positive and negative ions within itself. This is a common occurrence for the amino acids in which the acid function reacts to protonate the base site. Given the large value of the equilibrium constant found in (c), it is more appropriate to write an amino acid as $R(NH_3^+)(COO^-)$ then as $R(NH_2)(COOH)$.

**10.118** (a)
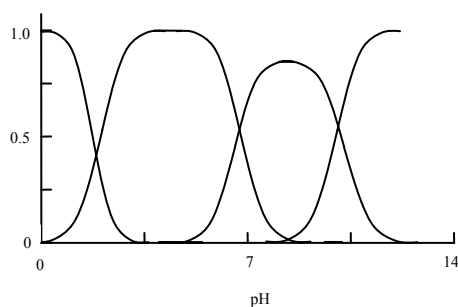


(b)  The major species at pH 7.5 is the doubly deprotonated form.

(c)  pH = 5.97

(d)  at pH values greater than about 11.4

(e)  from approximately pH = 7.0 to 8.4