**S9-1.**  $[H^+] + [^+H_3NCH_2CO_2H] = [OH^-] + [H_2NCH_2CO_2^-]$

**S9-2.**  $[H^+] + 3[Al^{3+}] + 2[AlOH^{2+}] + [Al(OH)_2^+] + [K^+] = [OH^-] + [Al(OH)_4^-]$

**S9-3.**  $[H_2NCH_2CO_2^-] + [^+H_3NCH_2CO_2^-] + [^+H_3NCH_2CO_2H] = 0.05$ M

**S9-4.**  $[Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3(aq)] + [Al(OH)_4^-] = 0.005\ 0$ M

      $[K^+] = 0.45$ M

**S9-5.**  1.  Pertinent reaction:         $(Hg_2)_3[Co(CN)_6]_2\ (s) \rightleftharpoons 3Hg_2^{2+} + 2Co(CN)_6^{3-}$

      2.  Charge balance:             $2[Hg_2^{2+}] = 3[Co(CN)_6^{3-}]$

      3.  Mass balance:                $2[Hg_2^{2+}] = 3[Co(CN)_6^{3-}]$

      4.  Equilibrium constant:    $K_{sp} = 1.9 \times 10^{-37} = [Hg_2^{2+}]^3[Co(CN)_6^{3-}]^2$
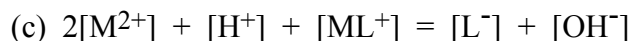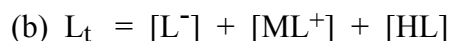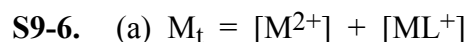
      Solve:  If $[Hg_2^{2+}] = x$, then $[Co(CN)_6^{3-}] = \frac{2}{3}\ x$. Putting these values into the solubility

         product gives $(x)^3\ (\frac{2}{3}x)^2 = K_{sp} \Rightarrow x = [Hg_2^{2+}] = 5.3 \times 10^{-8}$ M

**S9-6.**  (a) $M_t = [M^{2+}] + [ML^+]$

      (b) $L_t = [L^-] + [ML^+] + [HL]$

      (c) $2[M^{2+}] + [H^+] + [ML^+] = [L^-] + [OH^-]$

      (d) $K = 1.0 \times 10^8 = \dfrac{[ML^+]}{[M^{2+}][L^-]}$                          (1)

        $K_a = 1.0 \times 10^{-5} = \dfrac{[H^+][L^-]}{[HL]}$                          (2)

        Equation (2) gives $[L^-] = [HL]$ when $[H^+] = 1.0 \times 10^{-5}$ M .
        Putting $[L^-] = [HL]$ into the $L_t$ equation gives
        $L_t = 0.1$ M $= 2[L^-] + [ML^+] \Rightarrow [L^-] = 0.05 - \frac{1}{2}\ [ML^+]$.

        Substituting this last expression for $[L^-]$ and the expression
        $[M^{2+}] = M_t - [ML^+] = 0.1 - [ML^+]$ into Equation (1) gives

                                          Solve quadratic
                                        equation

        $1.0 \times 10^8 = \dfrac{[ML^+]}{(0.10 - [ML^+])(0.050 - \frac{1}{2}[ML^+])} \Rightarrow [ML^+] \approx 0.10$ M

$$\text{Equation (1) gives } [M^{2+}] = \frac{[ML^+]}{K[L^-]} = \frac{0.10}{(1.0 \times 10^8)(0.050)} = 2.0 \times 10^{-8} \text{ M}$$

**S9-7.** (a) $\dfrac{[HF][OH^-]}{[F^-]} = 1.5 \times 10^{-11} \underset{[OH^-]\,=\,10^{-11}\text{ M}}{\overset{\text{pH 3.00}}{\Rightarrow}} [HF] = 1.5 [F^-]$

Mass balance: $[F^-] + [HF] = 2.5\,[F^-] = 2[Mg^{2+}] \Rightarrow [F^-] = 0.80[Mg^{2+}]$

Substitution into solubility product gives

$$[Mg^{2+}][F^-]^2 = [Mg^{2+}](0.80[Mg^{2+}])^2 = 6.6 \times 10^{-9} \Rightarrow [Mg^{2+}] = 2.1_8 \times 10^{-3} \text{ M}$$

$$[F^-] = 0.80[Mg^{2+}] = 1.7_4 \times 10^{-3} \text{ M}$$

$$[HF] = 1.5\,[F^-] = 2.6_1 \times 10^{-3} \text{ M}$$

(b) $\dfrac{[MgF^+]}{[Mg^{2+}][F^-]} = K = 10^{2.05} = 1.1_2 \times 10^2 \Rightarrow [MgF^+] = (1.1_2 \times 10^2)[Mg^{2+}][F^-]$

$$= (1.1_2 \times 10^2)[2.1_8 \times 10^{-3}][1.7_4 \times 10^{-3}] = 4.2 \times 10^{-4} \text{ M}$$

(c) Mass balance: total F $= 2$(total Mg)

$$[F^-] + [HF] + [MgF^+] = 2[Mg^{2+}] + 2[MgF^+] \qquad [F^-] + [HF] = 2[Mg^{2+}] + [MgF^+]$$

**S9-8.** $\dfrac{[A^-]}{[HA(aq)][OH^-]} = 6.3 \times 10^5.$

Putting in $[HA(aq)] = 0.008\,5$ M and $[OH^-] = 1.0 \times 10^{-4}$ M $\Rightarrow [A^-] = 0.536$ M

$[HA] + [A^-] = 0.54$ M .

**S9-9.** (a) Mass balance: $\qquad [Sr^{2+}] = [SO_4^{2-}] + [HSO_4^-]$ (1)

Charge balance: $\quad 2[Sr^{2+}] + [H^+] = 2[SO_4^{2-}] + [HSO_4^-] + [OH^-]$ (2)

(b) If pH $= 2.50$, $[OH^-] = 3.1_6 \times 10^{-12}$ M

$$\frac{[HSO_4^-][OH^-]}{[SO_4^{2-}]} = 9.8 \times 10^{-13} \Rightarrow [HSO_4^-] = 0.31_0[SO_4^{2-}]$$

Putting this expression for $[HSO_4^-]$ into the mass balance gives

$$[Sr^{2+}] = [SO_4^{2-}] + 0.31_0[SO_4^{2-}] = 1.31_0[SO_4^{2-}]$$

Putting this expression for $[SO_4^{2-}]$ into the solubility product gives

$$[Sr^{2+}][SO_4^{2-}] = [Sr^{2+}]\frac{[Sr^{2+}]}{1.31_0} = K_{sp} \Rightarrow [Sr^{2+}] = 6.5 \times 10^{-4} \text{ M} .$$

**S9-10.** (a) Mass balance:      $[Sr^{2+}] + [SrSO_4] = [SO_4^{2-}] + [HSO_4^-] + [SrSO_4]$

The net mass balance is unchanged from the previous problem because $[SrSO_4]$ cancels on both sides of the equation.

(b) The procedure from the previous problem is still entirely valid because the mass balance and the equilibria are unchanged. The only addition is the ion pair whose concentration is

$$[SrSO_4] = K[Sr^{2+}][SO_4^{2-}] = K[Sr^{2+}]\frac{[Sr^{2+}]}{1.31_0} = 5.2 \times 10^{-5} \text{ M}$$

$$\text{Fraction in ion pair} = \frac{[SrSO_4]}{[SrSO_4] + [Sr^{2+}]} = 0.074$$

**S9-11.** (a) Mass balance:      $[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$

Charge balance:    $2[Ca^{2+}] + [H^+] = 2[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-]$

(b) If pH = 2.30, $[OH^-] = 2.0_0 \times 10^{-12}$ M

$$\frac{[HC_2O_4^-][OH^-]}{[C_2O_4^{2-}]} = K_{b1} \Rightarrow [HC_2O_4^-] = 90._0[C_2O_4^{2-}]$$

$$\frac{[H_2C_2O_4][OH^-]}{[HC_2O_4^-]} = K_{b2} \Rightarrow [H_2C_2O_4] = 0.090[HC_2O_4^-] = 8.1[C_2O_4^{2-}]$$

Substituting into the mass balance gives

$$[Ca^{2+}] = [C_2O_4^{2-}] + 90._0[C_2O_4^{2-}] + 8.1[C_2O_4^{2-}] = 99.1[C_2O_4^{2-}]$$

Substituting into the solubility product gives

$$[Ca^{2+}][C_2O_4^{2-}] = [Ca^{2+}]\frac{[Ca^{2+}]}{99.1} = 1.3 \times 10^{-8} \Rightarrow [Ca^{2+}] = 1.1_4 \times 10^{-3} \text{ M}$$

**S9-12.** (a) Mass balance:      $2[Zn^{2+}] = 3\{[AsO_4^{3-}] + [HAsO_4^{2-}] + [H_2AsO_4^-] + [H_3AsO_4]\}$

Charge balance:    $2[Zn^{2+}] + [H^+] = 3[AsO_4^{3-}] + 2[HAsO_4^{2-}] + [H_2AsO_4^-] + [OH^-]$

(b) pH = 6.00 $\Rightarrow$ $[OH^-] = 1.0 \times 10^{-8}$

$$\frac{[HAsO_4^{2-}][OH^-]}{[AsO_4^{3-}]} = K_{b1} \Rightarrow [HAsO_4^{2-}] = 3.1 \times 10^5[AsO_4^{3-}]$$

$$\frac{[H_2AsO_4^-][OH^-]}{[HAsO_4^{2-}]} = K_{b2} \Rightarrow [H_2AsO_4^-] = 9.1[HAsO_4^{2-}] = 2.82 \times 10^6[AsO_4^{3-}]$$

$$\frac{[H_3AsO_4][OH^-]}{[H_2AsO_4^-]} = K_{b3} \Rightarrow [H_3AsO_4] = 1.7 \times 10^{-4}[H_2AsO_4^-] = 480[AsO_4^{3-}]$$

Putting these expressions into the mass balance gives

$$2[Zn^{2+}] = 3[AsO_4^{3-}](1+ 3.1 \times 10^5 + 2.82 \times 10^6 + 480) = 9.39 \times 10^6[AsO_4^{3-}]$$

$$[AsO_4^{3-}] = 2.13 \times 10^{-7}[Zn^{2+}]$$

Substituting into the solubility product gives $[Zn^{2+}]$:

$$[Zn^{2+}]^3 \{2.13 \times 10^{-7}[Zn^{2+}]\}^2 = K_{sp} \Rightarrow [Zn^{2+}] = 0.001\,8_6 \text{ M}$$

**S9-13.** Concentrations in $ML_2$ solution

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| **1** | K = | pH | [H+] | b | [M2+] | [L-] | [ML+] | [HL] |
| **2** | 1.0E+08 | 0 | 1E+00 | 1.0E+05 | 9.5E-03 | 9.5E-08 | 9.0E-02 | 9.5E-03 |
| **3** | Ka = | 2 | 1E-02 | 1.0E+03 | 1.0E-03 | 9.9E-07 | 9.9E-02 | 9.9E-04 |
| **4** | 1.0E-05 | 5 | 1E-05 | 2.0E+00 | 4.5E-05 | 2.2E-05 | 1.0E-01 | 2.2E-05 |
| **5** | M(total) = | 6 | 1E-06 | 1.1E+00 | 3.3E-05 | 3.0E-05 | 1.0E-01 | 3.0E-06 |
| **6** | 0.1 | 8 | 1E-08 | 1.0E+00 | 3.2E-05 | 3.2E-05 | 1.0E-01 | 3.2E-08 |
| **7** | L(total) = | 10 | 1E-10 | 1.0E+00 | 3.2E-05 | 3.2E-05 | 1.0E-01 | 3.2E-10 |
| **8** | 0.1 | 12 | 1E-12 | 1.0E+00 | 3.2E-05 | 3.2E-05 | 1.0E-01 | 3.2E-12 |
| **9** | | 14 | 1E-14 | 1.0E+00 | 3.2E-05 | 3.2E-05 | 1.0E-01 | 3.2E-14 |
| **10** | C2 = 10^-B2 | | | | | | | |
| **11** | D2 = 1+$A$2*$A$8-$A$2*$A$6+(C2/$A$4) | | | | | | | |
| **12** | E2=(-D2+Sqrt(D2^2+4*$A$2*$A$6*(1+C2/$A$4)))/(2*$A$2) | | | | | | | |
| **13** | F2 = ($A$6/E2-1)/$A$2 | | | | | | | |
| **14** | G2 = $A$2*E2*F2 | | | | | | | |
| **15** | H2 = F2*C2/$A$4 | | | | | | | |

**S10-1.** (a) $pH = -\log [H^+] = -\log (5.0 \times 10^{-4}) = 3.30$

(b) $pH = -\log (K_w/[OH^-]) = -\log (1.0 \times 10^{-14}) / (5.0 \times 10^{-4}) = 10.70$

**S10-2.** $[OH^-] = [H^+] + [(CH_3)_4N^+] = [H^+] + 2.0 \times 10^{-7}$

$[H^+] [OH^-] = K_w = [H^+] ([H^+] + 2.0 \times 10^{-7}) \Rightarrow [H^+] = 4.14 \times 10^{-8} \text{ M}$

$pH = -\log [H^+] = 7.38$

$[OH^-]_{total} = K_w/[H^+] = 2.41 \times 10^{-7} \text{ M} \qquad [OH^-]_{from\ H_2O} = [H^+] = 4.1 \times 10^{-8} \text{ M}$

Fraction of $[OH^-]$ from $H_2O = \dfrac{4.1 \times 10^{-8}\,M}{2.41 \times 10^{-7}\,M} = 0.17$

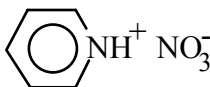**S10-3.** (a) For 0.050 M   HBr, $pH = -\log [H^+]\, \gamma_{H^+} = -\log[(0.050)(0.86)] = 1.37$

(b) For 0.050 M   NaOH, $pH = -\log \mathcal{A}_{H^+} = -\log(\dfrac{K_w}{\mathcal{A}_{OH^-}}) = -\log \dfrac{K_w}{[OH^-]\, \gamma_{OH^-}}$

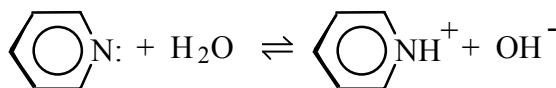$$= -\log \dfrac{1.0 \times 10^{-14}}{(0.050)(0.81)} = 12.61$$

**S10-4.**
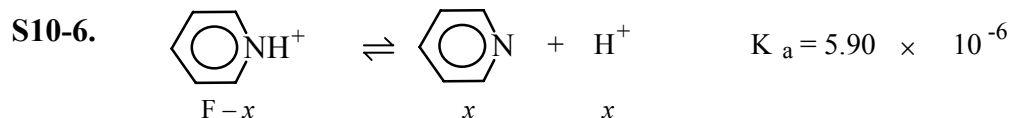


pyridine                          pyridinium nitrate
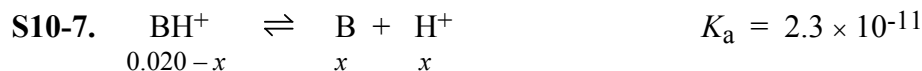


$K_b = K_w/K_a = 1.69 \times 10^{-9}$

$pK_b = 8.77$

**S10-5.** Let $x = [H^+] = [A^-]$ and $0.0100 - x = [HA]$.

$\dfrac{x^2}{0.0100 - x} = 1.00 \times 10^{-4} \Rightarrow x = 9.51 \times 10^{-4} \text{ M} \Rightarrow pH = -\log x = 3.02$

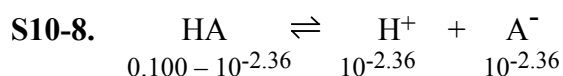$\alpha = \dfrac{x}{F} = \dfrac{9.51 \times 10^{-4}}{0.0100} = 9.51 \times 10^{-2}$

**S10-6.**



$$C_6H_5NH^+ \rightleftharpoons C_6H_5N + H^+ \qquad K_a = 5.90 \times 10^{-6}$$

F – x                              x                x

$$\frac{x^2}{0.085\,0 - x} = K_a \Rightarrow x = 7.05 \times 10^{-4} \Rightarrow pH = 3.15$$

**S10-7.**   $BH^+ \rightleftharpoons B + H^+ \qquad\qquad K_a = 2.3 \times 10^{-11}$

0.020 – x          x      x

$$\frac{x^2}{0.020 - x} = 2.3 \times 10^{-11} \Rightarrow x = 6.78 \times 10^{-7}\ M$$

$pH = -\log x = 6.17 \qquad [B] = x = 6.8 \times 10^{-7}\ M \qquad [BH^+] = 0.020\ M$

**S10-8.**     $HA \rightleftharpoons H^+ + A^-$

0.100 – $10^{-2.36}$    $10^{-2.36}$    $10^{-2.36}$

$$K_a = \frac{(10^{-2.36})(10^{-2.36})}{0.100 - 10^{-2.36}} = 1.99 \times 10^{-4}$$

$pK_a = -\log K_a = 3.70$

**S10-9.** (a)   $HA \rightleftharpoons H^+ + A^- \qquad\qquad K_a = 4.2 \times 10^{-10}$

0.010 0 – x          x      x
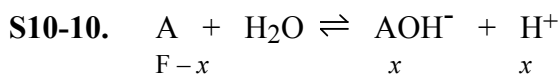
$$\frac{x^2}{0.0100 - x} = 4.2 \times 10^{-10} \Rightarrow x = 2.05 \times 10^{-6}\ M \Rightarrow pH = 5.69$$

$$\alpha = \frac{x}{F} = 2.05 \times 10^{-4}$$

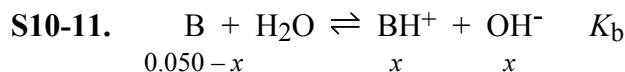(b)  For $F = 10^{-9.00}\ M$ , the pH must be very close to 7.00.

$$K_a = 4.2 \times 10^{-10} = \frac{[H^+][A^-]}{F - [A^-]} = \frac{(10^{-7.00})[A^-]}{F - [A^-]} \Rightarrow [A^-] = 4.18 \times 10^{-12}\ M$$

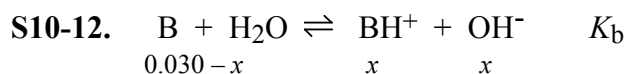$$\alpha = \frac{x}{F} = \frac{4.18 \times 10^{-12}}{10^{-9.00}} = 0.004\,2$$

**S10-10.**   $A + H_2O \rightleftharpoons AOH^- + H^+$

F – x                    x          x

$$\frac{x^2}{F - x} = 10^{-5.4} \Rightarrow x = 2.8 \times 10^{-4}\ M \Rightarrow pH = 3.55$$

**S10-11.**   $B + H_2O \rightleftharpoons BH^+ + OH^-$   $K_b$
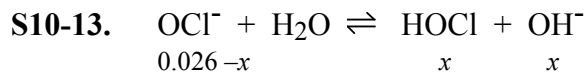   $0.050 - x \qquad\qquad x \qquad x$

$$\frac{x^2}{0.050 - x} = 1.00 \times 10^{-4} \Rightarrow x = 2.19 \times 10^{-3}$$

$pH = -\log(K_w/x) = 11.34 \qquad\qquad \alpha = \frac{x}{F} = 0.044$

**S10-12.**   $B + H_2O \rightleftharpoons BH^+ + OH^-$   $K_b$
   $0.030 - x \qquad\quad x \qquad x$

$$\frac{x^2}{0.030 - x} = 4.7 \times 10^{-10} \Rightarrow x = 3.75 \times 10^{-6}$$

$pH = -\log(K_w/x) = 8.57 \qquad [B] = [(CH_3CH_2)_2NH] = 0.030\ M \qquad [BH^+] = 3.8 \times 10^{-6}\ M$

**S10-13.**   $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$
   $0.026 - x \qquad\qquad x \qquad x$

$K_b = K_w/K_a = K_w/(3.0 \times 10^{-8}) = 3.33 \times 10^{-7}$

$$\frac{x^2}{0.026 - x} = K_b \Rightarrow x = [OH^-] = 9.3 \times 10^{-5}\ M$$

$pH = -\log(K_w/[OH^-]) = 9.97 \quad \alpha = \frac{x}{F} = \frac{9.3 \times 10^{-5}}{0.026} = 0.003\,6$

**S10-14.**   $HCO_2^- + H_2O \rightleftharpoons HCO_2H + OH^-$
   $F - x \qquad\qquad x \qquad x$
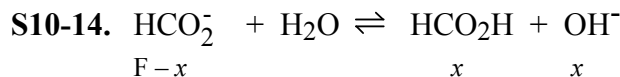
$K_b = K_w/K_a = 5.56 \times 10^{-11}$

For $F = 10^{-1}$ and $10^{-2}\ M$, we solve the equation $x^2/(F - x) = K_b$.

The fraction of association is $\alpha = \frac{x}{F}$ .

This gives $x = 2.36 \times 10^{-6}\ M$ for $F = 10^{-1}\ M$ ($\Rightarrow \alpha = 2.36 \times 10^{-5}$) and

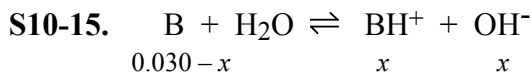$x = 7.46 \times 10^{-7}\ M$ for $F = 10^{-2}$ ($\Rightarrow \alpha = 7.46 \times 10^{-5}$).

For $F = 10^{-12}\ M$, $pH = 7.00$ and $[OH^-] = 10^{-7}\ M$ .

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{[BH^+]\,10^{-7}}{[B]} \Rightarrow [BH^+] = 10^7\,K_b\,[B]$$

Putting this relation between $[BH^+]$ and $[B]$ into the definition of fraction of association gives

$$\alpha = \frac{[BH^+]}{[BH^+] + [B]} = \frac{10^7\,K_b\,[B]}{10^7\,K_b[B] + [B]} = \frac{10^7\,K_b}{10^7\,K_b + 1} = 5.56 \times 10^{-4}$$

| F | $\alpha$ |
|---|---|
| $10^{-1}$ | $2.36 \times 10^{-5}$ |
| $10^{-2}$ | $7.46 \times 10^{-5}$ |
| $10^{-12}$ | $5.56 \times 10^{-4}$ |

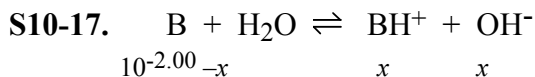**S10-15.**   $\underset{0.030 - x}{B} + H_2O \rightleftharpoons \underset{x}{BH^+} + \underset{x}{OH^-}$

$pH = 10.50 \Rightarrow [OH^-] = 10^{-3.50} = 3.16 \times 10^{-4}$ M

$$K_b = \frac{x^2}{0.030 - x} = \frac{(3.16 \times 10^{-4})^2}{0.030 - 3.16 \times 10^{-4}} = 3.3_6 \times 10^{-6}$$

**S10-16.**  $\alpha = \frac{x}{F} = 0.002\,7$.  Since F = 0.030 M , $x = 8.10 \times 10^{-5}$ M .

$$K_b = \frac{x^2}{F - x} = \frac{(8.10 \times 10^{-5})^2}{0.030 - 8.10 \times 10^{-5}} = 2.2 \times 10^{-7}$$

**S10-17.**   $\underset{10^{-2.00} - x}{B} + H_2O \rightleftharpoons \underset{x}{BH^+} + \underset{x}{OH^-}$

$K_b = K_w/K_a = 2.38 \times 10^{-5}$

$\dfrac{x^2}{10^{-2.00} - x} = K_b \Rightarrow x = 4.76 \times 10^{-4} \Rightarrow pH = -\log (K_w/x) = 10.68$

$\alpha = \dfrac{x}{F} = 0.048$

**S10-18.**  The $pK_a$ values are  (a) 10.774, (b) 9.244, (c) 5.96 and (d) 8.39.  Since $pK_a$ for 3-nitrophenol is closest to 8.5, buffer (d) will have the greatest buffer capacity at pH 8.5.

**S10-19.**  $pH = pK_a + \log \dfrac{[A^-]}{[HA]} = 3.46 + \log \dfrac{(5.13 \text{ g})/(112.126 \text{ g/mol})}{(2.53 \text{ g})/(74.036 \text{ g/mol})} = 3.59$
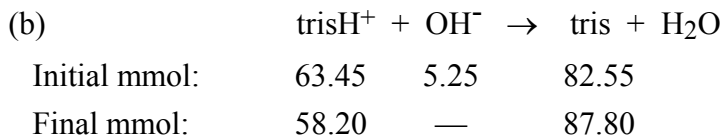
**S10-20.**  $pH = 10.64 + \log \dfrac{[CH_3NH_2]}{[CH_3NH_3^+]}$

| pH | $[CH_3NH_2]/[CH_3NH_3^+]$ |
|---|---|
| 4.00 | $2.3 \times 10^{-7}$ |
| 10.64 | 1.00 |
| 12.00 | 23 |

**S10-21.**  $pK_a = 14.00 - pK_b = 0.17$          $pH = 0.17 + \log \dfrac{[IO_3^-]}{[HIO_3]}$

| pH | $[HIO_3]/[IO_3^-]$ |
|---|---|
| 7.00 | $1.5 \times 10^{-7}$ |
| 1.00 | 0.15 |

**S10-22.** (a) $pH = pK_a + \log \dfrac{[\text{tris}]}{[\text{trisH}^+]} = 8.075 + \log \dfrac{(10.0 \text{ g})/(121.136 \text{ g/mol})}{(10.0 \text{ g})/(157.597 \text{ g/mol})} = 8.19$
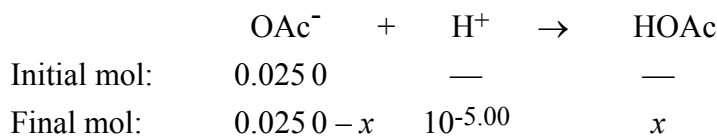
(b)

|  | trisH$^+$ | + | OH$^-$ | $\rightarrow$ | tris | + | H$_2$O |
|---|---|---|---|---|---|---|---|
| Initial mmol: | 63.45 | | 5.25 | | 82.55 | | |
| Final mmol: | 58.20 | | — | | 87.80 | | |

$pH = 8.075 + \log \dfrac{87.80}{58.20} = 8.25$

**S10-23.**

|  | B | + | H$^+$ | $\rightarrow$ | BH$^+$ |
|---|---|---|---|---|---|
| Initial mmol: | 0.699 5 | | $x$ | | — |
| Final mmol: | 0.699 5 $- x$ | | — | | $x$ |
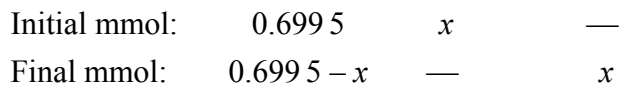
$8.00 = 8.492 + \log \dfrac{0.699\,5 - x}{x} \Rightarrow x = 0.529\,1 \text{ mmol}$

mL required $= (0.529\,1 \text{ mmol})/(0.113 \text{ mmol/mL}) = 4.68 \text{ mL}$

**S10-24.** (a)  250.0 mL of 0.100 M buffer requires 0.025 0 mol NaOAc $\cdot$ 2H$_2$O = 2.95 g

|  | OAc$^-$ | + | H$^+$ | $\rightarrow$ | HOAc |
|---|---|---|---|---|---|
| Initial mol: | 0.025 0 | | — | | — |
| Final mol: | 0.025 0 $- x$ | | $10^{-5.00}$ | | $x$ |

$pH = pK_a + \log \dfrac{[\text{OAc}^-]}{[\text{HOAc}]}$

$5.00 = 4.757 - \log \dfrac{0.025\,0 - x}{x} \Rightarrow x = 9.091 \text{ mmol} = 90.9 \text{ mL HCl}$

(b) 1. Calibrate the pH electrode and meter at 5°C.

2. Dissolve 2.95 g NaOAc $\cdot$ 2H$_2$O in ~100 mL H$_2$O at 5°C.

3. While measuring the pH, add enough HCl to bring the pH to 5.00 at 5°C.

4. Dilute to exactly 250 mL at 5°C.

**S10-25.**  The solution will have a pH near $pK_a$ ( $= 10.566$), so we can neglect $[H^+]$ relative to $[OH^-]$ in Equations 10-20 and 10-21:

$$[HA] \approx F_{HA} + [OH^-] \qquad\qquad [A^-] \approx F_A - [OH^-]$$

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad K_b = 3.68 \times 10^{-4}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(F_{BH^+} + [OH^-])[OH^-]}{F_B - [OH^-]}$$

$$3.68 \times 10^{-4} = \frac{(0.000\ 100 + [OH^-])[OH^-]}{0.000\ 100 - [OH^-]} \quad\Rightarrow [OH^-] = 6.86 \times 10^{-5}\ M$$

$$[B] = 0.000\ 100 - [OH^-] = 3.14 \times 10^{-5}\ M$$

$$[BH^+] = 0.000\ 100 + [OH^-] = 1.69 \times 10^{-4}\ M$$

**S10-26.**  (a)  Assume that the activity coefficients of neutral species are 1.

Equilibria:  $\qquad\qquad B + H_2O \rightleftharpoons BH^+ + OH^- \quad K_b = \dfrac{[BH^+][OH^-]}{[B]}$ (a)

$\qquad\qquad\qquad\qquad H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = [H^+][OH^-]$ (b)

Charge balance: $\quad [H^+] + [BH^+] = [OH^-]$ (c)

Mass balance: $\quad F = [B] + [BH^+]$ (d)

Substitute $[BH^+] = [OH^-] - [H^+]$ from the charge balance,
and $[B] = F - [BH^+] = F - [OH^-] + [H^+]$ from the mass and charge balances
into the $K_b$ equilibrium.

This gives  $K_b = \dfrac{([OH^-] - [H^+])\ [OH^-]}{F - [OH^-] + [H^+]}$ .

Now replace $[H^+]$ by $K_w/[OH^-]$ to get $K_b = \dfrac{([OH^-] - K_w/[OH^-])\ [OH^-]}{F - [OH^-] + K_w/[OH^-]}$ .

This equation can be rearranged to:
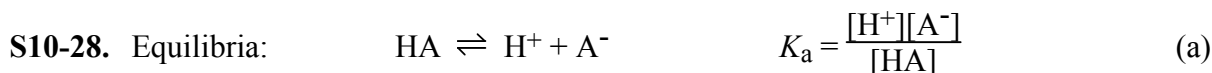
$$K_bF - K_b[OH^-] + K_bK_w/[OH^-] = [OH^-]^2 - K_w.$$

Multiplying both sides by $[OH^-]$ and rearranging gives a cubic polynomial:

$$[OH^-]^3 + K_b[OH^-]^2 - (K_bF + K_w)[OH^-] - K_bK_w = 0$$

(b)  pH of $10^{-3}$ M B ($K_b = 10^{-5}$) is 9.978; pH of $10^{-5}$ M B ($K_b = 10^{-9}$) is 7.150.

|   | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | Solving cubic polynomial for pH of B | | | | |
| 2 | | | | | |
| 3 | Kb = | Guess for pH | [H+] | [OH-] | Value of polynomial |
| 4 | 1.00E-05 | 9 | 1E-09 | 0.00001 | -9.80002E-14 |
| 5 | Kw = | 10 | 1E-10 | 0.0001 | 9.99989E-14 |
| 6 | 1.00E-14 | 9.5 | 3.2E-10 | 3.2E-05 | -2.74605E-13 |
| 7 | F = | 9.9 | 1.3E-10 | 7.9E-05 | -2.30046E-13 |
| 8 | 1.00E-03 | 9.9783 | 1.1E-10 | 9.5E-05 | 2.2675E-17 |
| 9 | | | | | |
| 10 | E4 = D4^3 + $A$4*D4^2 - ($A$4*$A$8+$A$6)*D4 - $A$4*$A$6 | | | | |

**S10-27.** At 5°C, $K_a$ increases with increasing temperature, so the reaction must be endothermic, by Le Châtelier's principle.  At 45°C, $K_a$ decreases with temperature, so the reaction must be exothermic.

**S10-28.** Equilibria:

$$HA \rightleftharpoons H^+ + A^- \qquad\qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad\qquad (a)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad\qquad K_w = [H^+][OH^-] \qquad\qquad (b)$$

Charge balance:  $[H^+] = [A^-] + [OH^-]$ \hfill (c)

Mass balance:  $F = [A^-] + [HA]$ \hfill (d)

Substitute $[A^-] = [H^+] - [OH^-]$ from the charge balance, and $[HA] = F - [A^-] = F - [H^+] + [OH^-]$ from the mass and charge balances into the $K_a$ equilibrium.

This gives  $K_a = \dfrac{[H^+]\,([H^+] - [OH^-])}{F - [H^+] + [OH^-]}$ .

Now replace $[OH^-]$ by $K_w/[H^+]$ to get  $K_a = \dfrac{[H^+]\,([H^+] - K_w/[H^+])}{F - [H^+] + K_w/[H^+]}$ .

This equation can be rearranged to:

$$K_aF - K_a[H^+] + K_aK_w/[H^+] = [H^+]^2 - K_w.$$
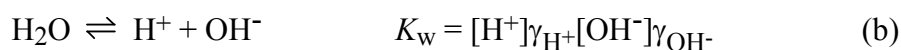
Multiplying both sides by $[H^+]$ and rearranging gives a cubic polynomial:

$$[H^+]^3 + K_a[H^+]^2 - (K_aF + K_w)[H^+] - K_aK_w = 0$$

**S10-29.**

|    | A | B | C | D |
|----|---|---|---|---|
| 1  | Solving cubic polynomial for pH of HA | | | |
| 2  | | | | |
| 3  | Ka = | Guess for pH | [H+] | Value of polynomial |
| 4  | 1.00E-04 | 4 | 0.0001 | 9.99998E-13 |
| 5  | Kw = | 4.1 | 7.9E-05 | 3.37815E-13 |
| 6  | 1.00E-14 | 4.2 | 6.3E-05 | 1.83368E-14 |
| 7  | F = | 4.3 | 5E-05 | −1.24108E-13 |
| 8  | 1.00E-04 | 4.208 | 6.2E-05 | 1.94858E-15 |
| 9  | | | | |
| 10 | D4 = C4^3 + $A$4*C4^2 - ($A$4*$A$8+$A$6)*C4 - $A$4*$A$6 | | | |

**S10-30.**  We will assume that the activity coefficients of neutral species are 1.

Equilibria:  $\quad\quad$ HA $\rightleftharpoons$ H$^+$ + A$^-$ $\quad\quad\quad$ $K_a = \dfrac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]}$ $\quad\quad$ (a)

$\quad\quad\quad\quad\quad\quad$ H$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$ $\quad\quad\quad$ $K_w = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-}$ $\quad\quad$ (b)

Charge balance:  $\quad$ [H$^+$] = [A$^-$] + [OH$^-$] $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (c)

Mass balance:  $\quad$ F = [A$^-$] + [HA] $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (d)

$\quad\quad\quad$ Substitute [A$^-$] = [H$^+$] – [OH$^-$] from the charge balance, and

$\quad\quad\quad$ [HA] = F – [A$^-$] = F – [H$^+$] + [OH$^-$] from the mass and charge balances

$\quad\quad\quad$ into the $K_a$ equilibrium.

$\quad\quad\quad$ This gives $\quad K_a = \dfrac{[H^+]\gamma_{H^+}([H^+] - [OH^-])\gamma_{A^-}}{F - [H^+] + [OH^-]}$ .

$\quad\quad\quad$ Now replace [OH$^-$] by $K_w/[H^+]\gamma_{H^+}\gamma_{OH^-}$ to get

$\quad\quad\quad\quad K_a = \dfrac{[H^+]\gamma_{H^+}([H^+] - K_w/[H^+]\gamma_{H^+}\gamma_{OH^-})\gamma_{A^-}}{F - [H^+] + K_w/[H^+]\gamma_{H^+}\gamma_{OH^-}}$ .

$\quad\quad\quad$ This equation can be rearranged to:

$\quad\quad\quad\quad K_a F - K_a[H^+] + K_a K_w/[H^+]\gamma_{H^+}\gamma_{OH^-} = [H^+]^2\gamma_{H^+} - K_w\gamma_{A^-}/\gamma_{OH^-}.$

$\quad\quad\quad$ Multiplying both sides by [H$^+$] and rearranging gives a cubic polynomial:

$$[H^+]^3\gamma_{H^+} + K_a[H^+]^2 - \left(K_a F + \frac{K_w\gamma_{A^-}}{\gamma_{OH^-}}\right)[H^+] - \frac{K_a K_w}{\gamma_{H^+}\gamma_{OH^-}} = 0$$

**S11-1.**

$$\underset{\displaystyle H_2NCHCO_2^-}{\overset{\displaystyle CH_2OH}{|}} + H_2O \rightleftharpoons \underset{\displaystyle H_3\overset{+}{N}CHCO_2^-}{\overset{\displaystyle CH_2OH}{|}} + OH^- \qquad K_{b1} = K_w/K_{a2} = 1.62 \times 10^{-5}$$

$$\underset{\displaystyle H_3\overset{+}{N}CHCO_2^-}{\overset{\displaystyle +\,CH_2OH}{|}} + H_2O \rightleftharpoons \underset{\displaystyle H_3\overset{+}{N}CHCO_2H}{\overset{\displaystyle CH_2OH}{|}} + OH^- \quad K_{b2} = K_w/K_{a1} = 1.54 \times 10^{-12}$$
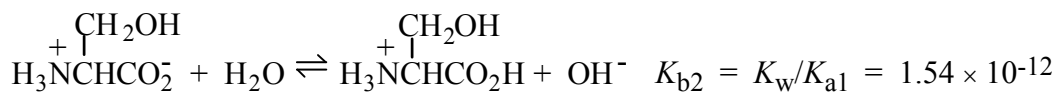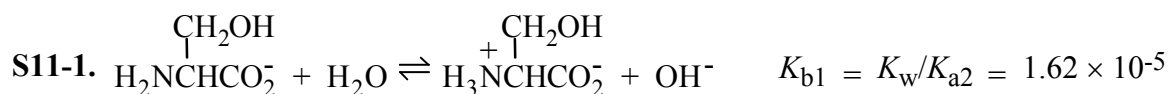
**S11-2.** (a) $\dfrac{x^2}{0.100 - x} = K_1 \Rightarrow x = 9.95 \times 10^{-4}\,M = [H^+] = [HA^-] \Rightarrow pH = 3.00$

$[H_2A] = 0.100 - x = 0.099\,0\,M$ $\qquad\qquad [A^{2-}] = \dfrac{K_2\,[HA^-]}{[H^+]} = 1.00 \times 10^{-9}\,M$

(b) $[H^+] = \sqrt{\dfrac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = 1.00 \times 10^{-7}\,M \Rightarrow pH = 7.00$

$[HA^-] \approx 0.100\,M$

$[H_2A] = \dfrac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-3}\,M$

$[A^{2-}] = \dfrac{K_2[HA^-]}{[H^+]} = 1.00 \times 10^{-3}\,M$

(c) $\dfrac{x^2}{0.100 - x} = \dfrac{K_w}{K_2} \Rightarrow x = [OH^-] = [HA^-] = 9.95 \times 10^{-4}\,M \Rightarrow pH = 11.00$

$[A^{2-}] = 0.100 - x = 0.099\,0\,M$

$[H_2A] = \dfrac{[H^+][HA^-]}{K_1} = 1.00 \times 10^{-9}\,M$

|                 | pH    | $[H_2A]$           | $[HA^-]$           | $[A^{2-}]$         |
|-----------------|-------|--------------------|--------------------|--------------------|
| 0.100 M $H_2A$  | 3.00  | $9.90 \times 10^{-2}$ | $9.95 \times 10^{-4}$ | $1.00 \times 10^{-9}$ |
| 0.100 M NaHA    | 7.00  | $1.00 \times 10^{-3}$ | 0.100              | $1.00 \times 10^{-3}$ |
| 0.100 M $Na_2A$ | 11.00 | $1.00 \times 10^{-9}$ | $9.95 \times 10^{-4}$ | $9.90 \times 10^{-2}$ |

**S11-3.** $N\!\!-\!\!\bigcirc\!\!-\!\!NH^+\,Cl^-$ $(BH^+\,Cl^-)$ $(BH^+\,Cl^-)$ is the intermediate form of a diprotic system, with

$F = 0.150\,M$ , $K_1 = 4.65 \times 10^{-6}$ and $K_2 = 1.86 \times 10^{-10}$.

$[H^+] = \sqrt{\dfrac{K_1 K_2 F + K_1 K_w}{K_1 + F}} = 2.94 \times 10^{-8}\,M \Rightarrow pH = 7.53$

$[BH^+] \approx 0.150\,M$ $\quad [B] = \dfrac{K_2[BH^+]}{[H^+]} = 9.49 \times 10^{-4}\,M$

$$[BH_2^{2+}\ ]\ =\ \frac{[BH^+][H^+]}{K_1}\ =\ 9.48\times10^{-4}\ M$$

**S11-4.**  Charge balance:   $[H^+]+[Na^+]+[BH^+]\ =\ [Cl^-]+[HA^-]+2[A^{2-}]+[OH^-]$

Mass balances:   $[Cl^-]\ =\ F_1$

$[Na^+]\ =\ 2F_2$

$F_2\ =\ [H_2A]\ +\ [HA^-]\ +\ [A^{2-}]$

$F_3\ =\ [B]\ +\ [BH^+]$

Equilibria :   $[H^+]\gamma_{H^+}\,[OH^-]\,\gamma_{OH^-}\ =\ K_w$

$K_1\ =\ [H^+]\gamma_{H^+}\,[HA^-]\,\gamma_{HA^-}\,/\,[H_2A]\,\gamma_{H_2A}$

$K_2\ =\ [H^+]\,\gamma_{H^+}\,[A^{2-}]\,\gamma_{A^{2-}}\,/\,[HA^-]\,\gamma_{HA^-}$

$K_b\ =\ [BH^+]\,\gamma_{BH^+}\,[OH^-]\,\gamma_{OH^-}\,/\,[B]\gamma_B$

**S11-5.**  Tartaric acid:  $H_2A$  $pK_1=3.036$  $pK_2=4.366$

(a)  At pH 3.00, there is a mixture of $H_2A$ and $HA^-$.

$$H_2A\quad+\quad OH^-\quad\rightarrow\quad HA^-$$

Initial mmol:    3.331 6        $x$        —

Final mmol:    3.331 6 $-\ x$      —        $x$
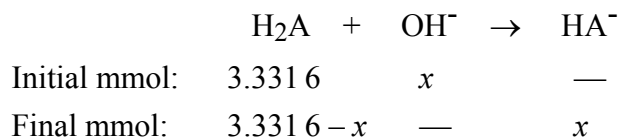
$3.00=3.036+\log\dfrac{x}{3.331\,6-x}$   $\Rightarrow x\ =1.597$ mmol $=\ 3.77$ mL KOH.

(b)  At pH 4.00, there is a mixture of $HA^-$ and $A^{2-}$.  We must add 3.331 6 mmol
(= 7.876 mL) of KOH to convert $H_2A$ into $HA^-$.  Then we need to add more KOH:
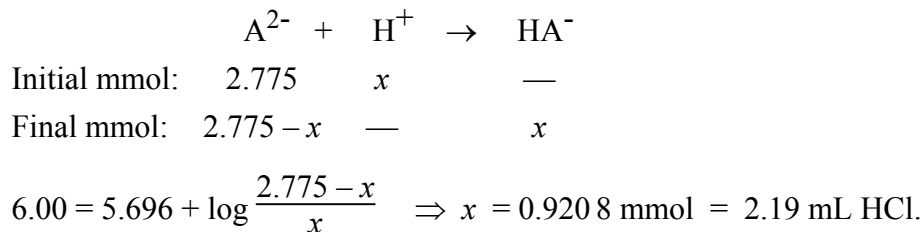
$$HA^-\quad+\quad OH^-\quad\rightarrow\quad A^{2-}\ +\ H_2O$$

Initial mmol:    3.331 6        $x$        —

Final mmol:   3.331 6 $-\ x$      —        $x$
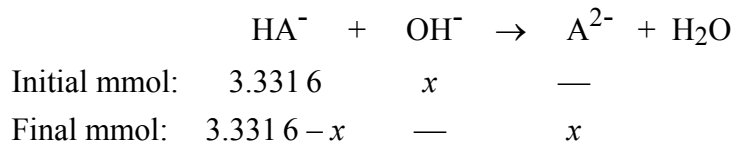
$4.00=4.366+\log\dfrac{x}{3.331\,6-x}$   $\Rightarrow x\ =1.003$ mmol $=\ 2.370$ mL KOH

Total KOH $=\ 7.876+2.370\ =\ 10.25$ mL

**S11-6.**   Malonic acid $= H_2A$   $pK_1 = 2.847$   $pK_2 = 5.696$

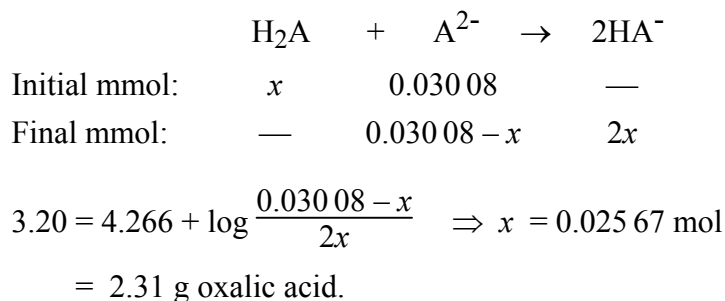(a)  At pH 6.00, there is a mixture of $A^{2-}$ and $HA^-$.

$$A^{2-} \quad + \quad H^+ \quad \rightarrow \quad HA^-$$

| | | | |
|---|---|---|---|
| Initial mmol: | 2.775 | $x$ | — |
| Final mmol: | $2.775 - x$ | — | $x$ |

$6.00 = 5.696 + \log \dfrac{2.775 - x}{x}$   $\Rightarrow x = 0.920\,8$ mmol $= 2.19$ mL HCl.

(b)  At pH 3.20, there is a mixture of $H_2A$ and $HA^-$.  We first add 2.775 mmol ($= 6.591$ mL) of HCl to convert $A^{2-}$ into $HA^-$.  Then we need to add more HCl
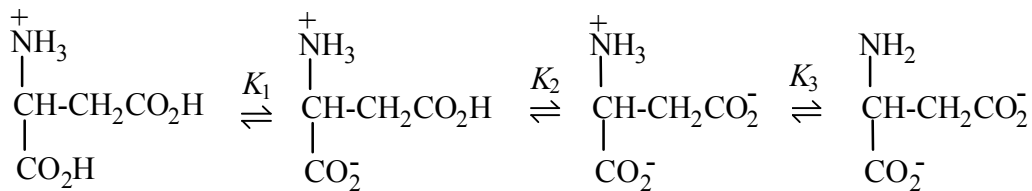
$$HA^- \quad + \quad H^+ \quad \rightarrow \quad H_2A$$

| | | | |
|---|---|---|---|
| Initial mmol: | 2.775 | $x$ | — |
| Final mmol: | $2.775 - x$ | — | $x$ |

$3.20 = 2.847 + \log \dfrac{2.775 - x}{x}$   $\Rightarrow x = 0.852\,7$ mmol $= 2.025$ mL HCl

Total HCl $= 6.591 + 2.025 = 8.62$ mL
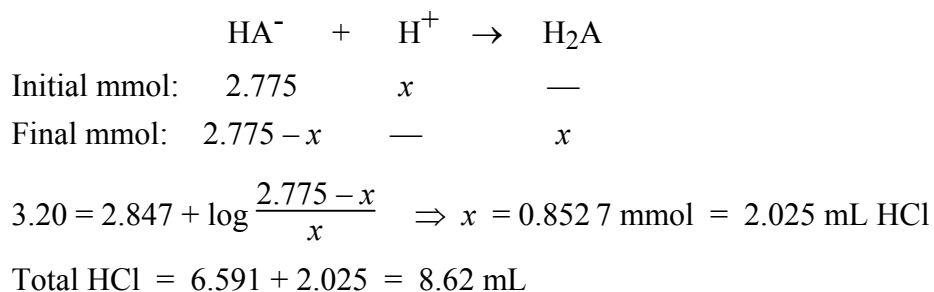
**S11-7.**   Oxalic acid $= H_2A$   $pK_1 = 1.252$   $pK_2 = 4.266$
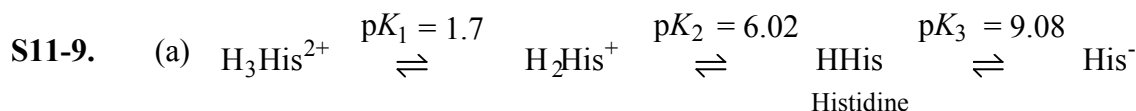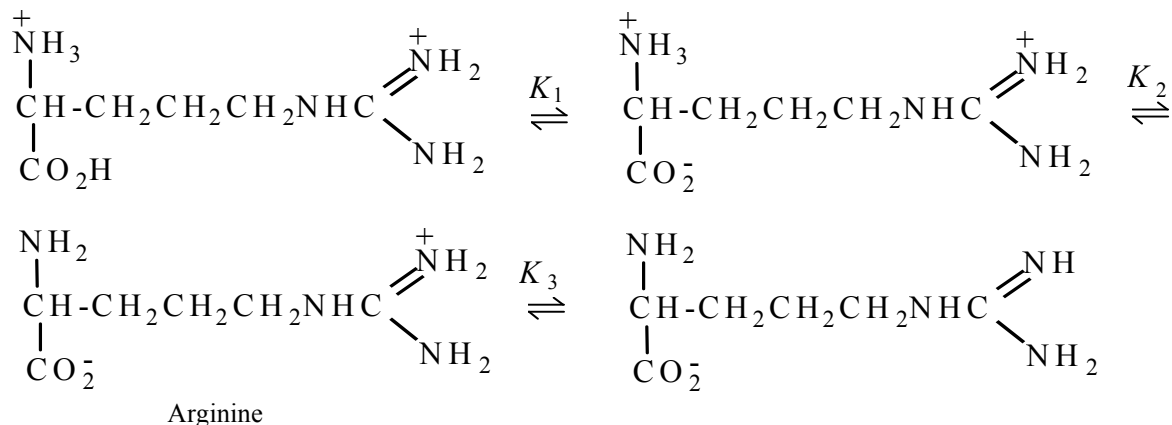
At pH 3.20, there is a mixture of $A^{2-}$ and $HA^-$.  We begin with $5.00$ g $= 0.030\,08$ mol $A^{2-}$.
The reaction of $H_2A$ with $A^{2-}$ creates 2 moles of $HA^-$:

$$H_2A \quad + \quad A^{2-} \quad \rightarrow \quad 2HA^-$$

| | | | |
|---|---|---|---|
| Initial mmol: | $x$ | 0.030 08 | — |
| Final mmol: | — | $0.030\,08 - x$ | $2x$ |

$3.20 = 4.266 + \log \dfrac{0.030\,08 - x}{2x}$   $\Rightarrow x = 0.025\,67$ mol

$= 2.31$ g oxalic acid.

**S11-8.**



Aspartic acid

$$\overset{+}{N}H_3 \\ | \\ CH\text{-}CH_2CH_2CH_2NHC \overset{\displaystyle \overset{+}{N}H_2}{\underset{\displaystyle NH_2}{<}} \\ | \\ CO_2H$$
$\overset{K_1}{\rightleftharpoons}$
$$\overset{+}{N}H_3 \\ | \\ CH\text{-}CH_2CH_2CH_2NHC \overset{\displaystyle \overset{+}{N}H_2}{\underset{\displaystyle NH_2}{<}} \\ | \\ CO_2^-$$
$\overset{K_2}{\rightleftharpoons}$

$$NH_2 \\ | \\ CH\text{-}CH_2CH_2CH_2NHC \overset{\displaystyle \overset{+}{N}H_2}{\underset{\displaystyle NH_2}{<}} \\ | \\ CO_2^-$$
$\overset{K_3}{\rightleftharpoons}$
$$NH_2 \\ | \\ CH\text{-}CH_2CH_2CH_2NHC \overset{\displaystyle NH}{\underset{\displaystyle NH_2}{<}} \\ | \\ CO_2^-$$

Arginine

**S11-9.** (a) $H_3His^{2+}$ $\overset{pK_1 = 1.7}{\rightleftharpoons}$ $H_2His^+$ $\overset{pK_2 = 6.02}{\rightleftharpoons}$ $HHis$ $\overset{pK_3 = 9.08}{\rightleftharpoons}$ $His^-$

Histidine

For 0.050 0 M histidine, $[H^+] = \sqrt{\dfrac{K_2K_3F + K_2K_w}{K_2 + F}}$ $= 2.82 \times 10^{-8}$ M

$\Rightarrow$ pH = 7.55

$7.55 = 6.02 + \log \dfrac{[HHis]}{[H_2His^+]}$ $\Rightarrow \dfrac{[H_2His^+]}{[HHis]} = 0.029\,5$

(b) For 0.050 0 M $H_2His^+Cl^-$, $[H^+] = \sqrt{\dfrac{K_1K_2F + K_1K_w}{K_1 + F}}$ $= 1.17 \times 10^{-4}$ M

$\Rightarrow$ pH = 3.93

$3.93 = 6.02 + \log \dfrac{[HHis]}{[H_2His^+]}$ $\Rightarrow \dfrac{[H_2His^+]}{[HHis]} = 123$

**S11-10.**
$$\overset{+}{N}H_3 \\ | \\ CH\text{-}CH_2CH_2CH_2NHC \overset{\displaystyle \overset{+}{N}H_2}{\underset{\displaystyle NH_2}{<}} \\ | \\ CO_2^-$$
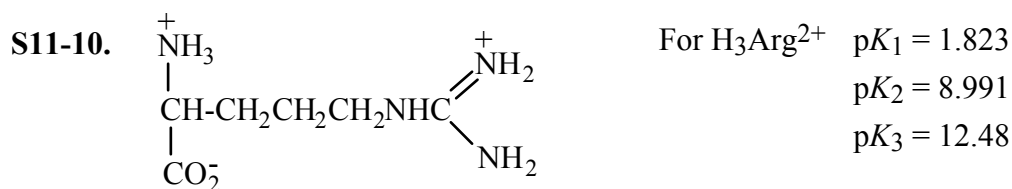
$H_2Arg^+$ found in Arginine · HCl

For $H_3Arg^{2+}$  $pK_1 = 1.823$
$pK_2 = 8.991$
$pK_3 = 12.48$

$[H^+] = \sqrt{\dfrac{K_1K_2(0.012\,0) + K_1K_w}{K_1 + (0.012\,0)}}$ $= 2.61 \times 10^{-6}$ M $\Rightarrow$ pH = 5.58

$\dfrac{[H_2Arg^+][H^+]}{[H_3Arg^{2+}]} = K_1 \Rightarrow [H_3Arg^{2+}] = \dfrac{(0.012\,0)(2.61 \times 10^{-6})}{10^{-1.823}} = 2.08 \times 10^{-6}$ M

$\dfrac{[HArg][H^+]}{[H_2Arg^+]} = K_2 \Rightarrow [HArg] = \dfrac{(10^{-8.991})(0.012\,0)}{2.61 \times 10^{-6}} = 4.69 \times 10^{-6}$ M

$$\frac{[\text{Arg}^-][\text{H}^+]}{[\text{HArg}]} = K_3 \Rightarrow [\text{Arg}^-] = \frac{(10^{-12.48})(4.69 \times 10^{-6})}{2.61 \times 10^{-6}} = 5.95 \times 10^{-13} \text{ M}$$

**S11-11.** (a)  Since $pK = 11.305$, $BH^+$ is predominant at pH 11 and B is predominant at pH 12.

(b)  11.305

(c)  $12.00 = 11.305 + \log \dfrac{[B]}{[BH^+]} \Rightarrow \dfrac{[B]}{[BH^+]} = 5.0$

$2.00 = 11.305 + \log \dfrac{[B]}{[BH^+]} \Rightarrow \dfrac{[B]}{[BH^+]} = 5.0 \times 10^{-10}$

**S11-12.** (a) $HSO_3^-$     (b) $HSO_3^-$     (c) $HSO_3^-$     (d) $SO_3^{2-}$

**S11-13.**  $\overset{pK_1 = 3.128}{H_3Cit} \rightleftharpoons \overset{pK_2 = 4.761}{H_2Cit^-} \rightleftharpoons \overset{pK_3 = 6.396}{HCit^{2-}} \rightleftharpoons Cit^{3-}$

At pH 5.00, $HCit^{2-}$ is dominant.

**S11-14.**  Fraction in form HA $= \alpha_{HA} = \dfrac{[H^+]}{[H^+] + K_a} = \dfrac{10^{-8.00}}{10^{-8.00} + 10^{-7.00}} = 0.090\,9$

Fraction in form $A^- = \alpha_{A^-} = \dfrac{K_a}{[H^+] + K_a} = 0.909\,1.$

$\dfrac{[A^-]}{[HA]} = \dfrac{0.909\,1}{0.090\,9} = 10.0.$

**S11-15.**  Fraction in form $BH_2^{2+} = \alpha_{BH_2^{2+}} = \dfrac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$ ,

where $K_1 = 10^{-6.00}$ and $K_2 = 10^{-12.00} \Rightarrow \alpha_{BH_2^{2+}} = 9.98 \times 10^{-4}$

**S11-16.**  $K_1 = 3.8 \times 10^{-5}$     $K_2 = 3.8 \times 10^{-6}$

|  |  | pH 5.00 | pH 6.00 |
|---|---|---|---|
| $\alpha_{H_2A} = \dfrac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$ | $=$ | 0.16 | 0.005\,4 |
| $\alpha_{HA^-} = \dfrac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2}$ | $=$ | 0.61 | 0.21 |
| $\alpha_{A^{2-}} = \dfrac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2}$ | $=$ | 0.23 | 0.79 |

**S11-17.**  $K_1 = 2.2 \times 10^{-11}$    $K_2 = 1 \times 10^{-12}$

| pH: | 10.00 | 10.66 | 11.00 | 12.00 | 12.50 |
|---|---|---|---|---|---|
| $\alpha_{H_2A}$ | 0.82 | 0.49 | 0.29 | 0.022 | 0.003 4 |
| $\alpha_{HA^-}$ | 0.18 | 0.49 | 0.64 | 0.49 | 0.24 |
| $\alpha_{A^{2-}}$ | 0.001 8 | 0.022 | 0.064 | 0.49 | 0.76 |

**S11-18.**  Isoelectric pH = $\dfrac{pK_1 + pK_2}{2}$ = 7.36

Isoionic pH = $\sqrt{\dfrac{K_1K_2(0.010) + K_1K_w}{K_1 + (0.010)}}$   $\Rightarrow$ $4.38 \times 10^{-8}$ M $\Rightarrow$ pH = 7.36

**S11-19.**  (a)  $K = e^{(\Delta S^\circ/R) - (\Delta H^\circ/RT)}$ $\Rightarrow$ $\dfrac{\Delta S^\circ}{R}$ = -3.23 ($\pm$0.53) and

$\dfrac{\Delta H^\circ}{RT}$ = $\dfrac{1.44\ (\pm 0.15) \times 10^3}{T}$

Using the value $R = 8.314\,5\ \dfrac{J}{mol \cdot K}$   gives:

$\Delta S^\circ$ = [$-3.23\ (\pm 0.53)$][$8.314\,5$] = $-27\ (\pm 4)\ \dfrac{J}{mol \cdot K}$

$\Delta H^\circ$ = [$-1.44\ (\pm 0.15) \times 10^3$][$8.314\,5$] = $-12\ (\pm 1)\ \dfrac{kJ}{mol}$

(b)  $K = \dfrac{[SO_3H^-]}{[HSO_3^-]}$ = $e^{-[3.23\ (\pm 0.53) + 1.44\ (\pm 0.15) \times 10^3\ (1/T)]}$

For $T = 298$ K,  $K = e^{-[3.23\ (\pm 0.53) + (1\,440\ (\pm 150))\ /\ 298]}$

= $e^{-3.23\ (\pm 0.53) + 4.83\ (\pm 0.50)}$

$K$ = $e^{1.60\ (\pm 0.73)}$ = $4.953\ (\pm?)$

For propagation of uncertainty, we consider $K = e^x$ in Table 3-1:

$\dfrac{e_K}{K}$ = $e_x$ $\Rightarrow$ $e_K = Ke_x = (4.953)(\pm 0.73) = \pm 3.6$ $\Rightarrow$ $K = 5.0\ (\pm 3.6)$

**S12-1.** <u>0 mL</u>:     $pH = -\log(0.0500) = 1.30$

<u>1 mL</u>:     $[H^+] = \left(\dfrac{11.5}{12.5}\right)(0.0500\ M)\left(\dfrac{25.0}{26.0}\right) = 0.0442\ M \Rightarrow pH = 1.35$

<u>5 mL</u>:     1.60

<u>10 mL</u>:   2.15

<u>12.4 mL</u>:  3.57

<u>12.5 mL</u>:  Equivalence point $\Rightarrow pH = 7.00$

<u>12.6 mL</u>:  $[OH^-] = \left(\dfrac{0.1}{37.6}\right)(0.100\ M) = 2.66 \times 10^{-4}\ M \Rightarrow pH = 10.42$

<u>13 mL</u>:    11.42

**S12-2.** <u>0 mL</u>:  $HA \rightleftharpoons H^+ + A^-$

$$\dfrac{x^2}{0.0500 - x} = 10^{-4} \Rightarrow x = 2.19 \times 10^{-3}\ M \Rightarrow pH = 2.66$$

<u>1 mL</u>:   $pH = pK_a + \log\dfrac{[A^-]}{[HA]} = 4.00 + \log\dfrac{1}{4} = 3.40$

<u>2.5 mL</u>: $pH = 4.00 + \log\left(\dfrac{2.5}{2.5}\right) = 4.00$

<u>4 mL</u>:   $pH = 4.00 + \log\left(\dfrac{4}{1}\right) = 4.60$

<u>4.9 mL</u>: $pH = 4.00 + \log\left(\dfrac{4.9}{0.1}\right) = 5.69$

<u>5 mL</u>:     $A^- \ + \ H_2O \rightleftharpoons HA + OH^- \qquad\qquad pK_b = 10.00$

$\qquad \left(\dfrac{50}{55}\right)(0.0500)\ -x \qquad\quad x \qquad x$

$$\dfrac{x^2}{0.0455 - x} = 1.00 \times 10^{-10} \Rightarrow x = [OH^-] = 2.13 \times 10^{-6} \Rightarrow pH = 8.33$$

<u>5.1 mL</u>:  $[OH^-] = \left(\dfrac{0.1}{55.1}\right)(0.500\ M) = 9.07 \times 10^{-4}\ M \Rightarrow pH = 10.96$

<u>6 mL</u>:    $[OH^-] = \left(\dfrac{1}{56}\right)(0.500\ M) = 8.93 \times 10^{-3}\ M \Rightarrow pH = 11.95$

**S12-3.** $V_e = 25.0\ mL \qquad\qquad pK_a = 7.15$

<u>0 mL</u>:  $HA \rightleftharpoons A^- + HA$
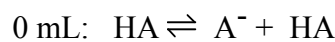
$$\dfrac{x^2}{0.0500 - x} = 7.1 \times 10^{-8} \Rightarrow x = 5.95 \times 10^{-5}\ M \Rightarrow pH = 4.23$$

To find the volume at which $pH = pK_a - 1$, we set up a Henderson-Hasselbalch

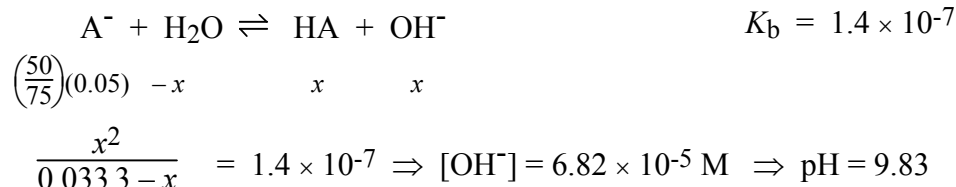equation:  $pK_a - 1 = pK_a + \log\dfrac{[A^-]}{[HA]} \Rightarrow [A^-]/[HA] = 0.1$,

or $[A^-] = 1/11$ and $[HA] = 10/11$ of total.

$$\text{Volume of OH}^- = \frac{V_e}{11} = 2.27 \text{ mL}$$

Similarly, when $\text{pH} = pK_a + 1$, volume of $\text{OH}^- = \frac{10 V_e}{11} = 22.73 \text{ mL}$

When volume of $\text{OH}^- = \frac{1}{2} V_e = 12.5 \text{ mL}$,  $\text{pH} = pK_a$

$\underline{V_e = 25.0 \text{ mL}}$:  HA is converted to $\text{A}^-$:

$$\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \qquad\qquad\qquad K_b = 1.4 \times 10^{-7}$$
$$\left(\frac{50}{75}\right)(0.05) - x \qquad\qquad x \qquad x$$

$$\frac{x^2}{0.033\,3 - x} = 1.4 \times 10^{-7} \Rightarrow [\text{OH}^-] = 6.82 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 9.83$$

$\underline{1.2 V_e = 30.0 \text{ mL}}$:  $[\text{OH}^-] = \left(\frac{5}{80}\right)(0.100 \text{ M}) = 6.25 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.80$

**S12-4.** 

| | HA | + | OH$^-$ | $\rightarrow$ | A$^-$ | + | H$_2$O |
|---|---|---|---|---|---|---|---|
| Initial mmol: | 2.345 0 | | 1.044 2 | | — | | |
| Final mmol: | 1.300 8 | | — | | 1.044 2 | | |

$$3.62 = pK_a + \log \frac{1.044\,2}{1.300\,8} \Rightarrow pK_a = 3.72$$
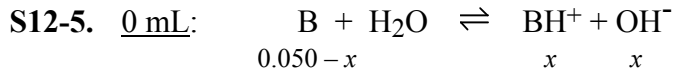
**S12-5.**  $\underline{0 \text{ mL}}$:  $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$
$$\qquad\qquad 0.050 - x \qquad\qquad x \qquad x$$

$$\frac{x^2}{0.050 - x} = 1.00 \times 10^{-4} \Rightarrow x = [\text{OH}^-] = 2.19 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 11.34$$

$\underline{1 \text{ mL}}$:  $\text{pH} = pK_{\text{BH}^+} + \log \dfrac{[\text{B}]}{[\text{BH}^+]} = 10.00 + \log \dfrac{4}{1} = 10.60$

$\underline{2.5 \text{ mL}}$:  $\text{pH} = pK_{\text{BH}^+} = 10.00$

$\underline{4 \text{ mL}}$:  $\text{pH} = 10.00 + \log \dfrac{1}{4} = 9.40$

$\underline{4.9 \text{ mL}}$:  $\text{pH} = 10.00 + \log \dfrac{0.1}{4.9} = 8.31$
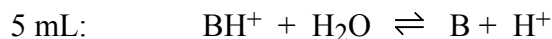
$\underline{5 \text{ mL}}$:  $\text{BH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}^+$
$$\left(\frac{50}{55}\right)(0.050) - x \qquad\qquad x \qquad x$$

$$\frac{x^2}{0.045\,5 - x} = 1.00 \times 10^{-10} \Rightarrow x = [\text{H}^+] = 2.13 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.67$$

$\underline{5.1 \text{ mL}}$:  $[\text{H}^+] = \left(\dfrac{0.1}{55.1}\right)(0.500 \text{ M}) = 9.07 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$

$\underline{6 \text{ mL}}$:  $[\text{H}^+] = \left(\dfrac{1}{56}\right)(0.500 \text{ M}) = 8.93 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.05$

**S12-6.**  Titration reaction:  $CH_3CH_2CO_2^- + H^+ \rightarrow CH_3CH_2CO_2H$

At the equivalence point, moles of HCl $=$ moles of NaA $\Rightarrow V_e = 47.79$ mL.

$\underline{0\text{ mL}}$:      $A^- + H_2O \rightleftharpoons HA + OH^-$

$\qquad\qquad$ $0.040\,0 - x \qquad\quad x \qquad x$

$$\frac{x^2}{0.040\,0-x} = K_b = \frac{K_w}{K_a} \quad \Rightarrow x = 5.47 \times 10^{-6}\text{ M} \qquad pH = -\log\frac{K_w}{x} = 8.74$$

$\underline{1/4\ V_e}$: $pH = pK_a + \log\dfrac{[A^-]}{[HA]} = 4.874 + \log\dfrac{3}{1} = 5.35$

$\underline{1/2\ V_e}$: $pH = pK_a = 4.87$

$\underline{3/4\ V_e}$: $pH = pK_a + \log\dfrac{1}{3} = 4.40$

$\underline{V_e}$:  $HA = H^+ + A^-$

$\qquad\quad$ $F-x \quad x \quad x$

$$F_{HA} = \left(\frac{100.0}{147.79}\right)(0.040\,0) = 0.027\,1\text{ M}$$

$$\frac{x^2}{0.027\,1-x} = K_a \Rightarrow x = 5.96 \times 10^{-4}\text{ M} \quad \Rightarrow pH = 3.22$$

$\underline{1.1\ V_e}$: $[H^+] = \left(\dfrac{V_e/10}{100.0 + 1.1V_e}\right)(0.083\,7) = 2.62 \times 10^{-3}\text{ M} \qquad pH = 2.58$

**S12-7.**  $V_{e1} = 5$ mL $\qquad V_{e2} = 10$ mL

$\underline{0\text{ mL}}$:       $B + H_2O \rightleftharpoons BH^+ + OH^-$

$\qquad\qquad$ $0.050\,0 - x \qquad\qquad x \qquad x$

$$\frac{x^2}{0.050\,0-x} = 10^{-5.00} \Rightarrow x = [OH^-] = 7.02 \times 10^{-4}\text{ M} \quad \Rightarrow pH = 10.85$$

$\underline{1\text{ mL}}$:  $pH = pK_{BH^+} + \log\dfrac{[B]}{[BH^+]} = -\log\dfrac{10^{-14}}{10^{-5}} + \log\dfrac{4}{1} = 9.60$

$\underline{2.5\text{ mL}}$: $pH = pK_{BH^+} = 9.00$

$\underline{4\text{ mL}}$:  $pH = pK_{BH^+} + \log\dfrac{1}{4} = 8.40$

$\underline{4.8\text{ mL}}$: $pH = pK_{BH^+} + \log\dfrac{0.2}{4.8} = 7.62$

$\underline{5\text{ mL}}$:   $[H^+] = \sqrt{\dfrac{K_1K_2F + K_1K_w}{K_1 + F}} = \sqrt{\dfrac{10^{-5}\,10^{-9}\,(0.045\,5) + 10^{-5}\,10^{-14}}{10^{-5} + 0.045\,5}}$

$\qquad\qquad\qquad$ $= 1.00 \times 10^{-7}\text{ M} \Rightarrow pH = 7.00$

$\underline{5.2\text{ mL}}$: $pH = pK_{BH_2^{2+}} + \log\dfrac{[B]}{[BH_2^{2+}]} = 5.00 + \log\dfrac{4.8}{0.2} = 6.38$

$\underline{6\text{ mL}}$:  $pH = pK_{BH_2^{2+}} + \log\dfrac{4}{1} = 5.60$

<u>7.5 mL</u>: $pH = pK_{BH_2^{2+}} = 5.00$

<u>9 mL</u>: $pH = pK_{BH_2^{2+}} + \log \frac{1}{4} = 4.40$

<u>9.8 mL</u>: $pH = pK_{BH_2^{2+}} + \log \frac{0.2}{4.8} = 3.62$

<u>10 mL</u>: $BH_2^{2+} \rightleftharpoons BH^+ + H^+$

$\qquad\qquad$ $0.041\,7 - x \qquad x \qquad x$

$$\frac{x^2}{0.041\,7 - x} = 10^{-5.00} \Rightarrow x = 6.41 \times 10^{-4} \text{ M} \quad \Rightarrow pH = 3.19$$

<u>10.2 mL</u>: $[H^+] = \left(\frac{0.2}{60.2}\right)(0.500 \text{ M}) = 1.66 \times 10^{-3} \text{ M} \Rightarrow pH = 2.78$

<u>11 mL</u>: $[H^+] = \left(\frac{1}{61}\right)(0.500 \text{ M}) = 8.20 \times 10^{-3} \text{ M} \Rightarrow pH = 2.09$

<u>12 mL</u>: $[H^+] = \left(\frac{2}{62}\right)(0.500 \text{ M}) = 1.61 \times 10^{-2} \text{ M} \Rightarrow pH = 1.79$

**S12-8.** $V_{e1} = 5 \text{ mL} \qquad V_{e2} = 10 \text{ mL}$

<u>0 mL</u>: $\qquad H_2A \rightleftharpoons H^+ + HA^-$

$\qquad\qquad$ $0.050\,0 - x \quad x \quad x$

$$\frac{x^2}{0.050\,0 - x} = 10^{-5.00} \Rightarrow x = 7.02 \times 10^{-4} \text{ M} \Rightarrow pH = 3.15$$

<u>1 mL</u>: $pH = pK_1 + \log \frac{[HA^-]}{[H_2A]} = 5.00 + \log \frac{1}{4} = 4.40$

<u>2.5 mL</u>: $pH = pK_1 = 5.00$

<u>4 mL</u>: $pH = pK_1 + \log \frac{4}{1} = 5.60$

<u>4.8 mL</u>: $pH = pK_1 + \log \frac{4.8}{0.2} = 6.38$

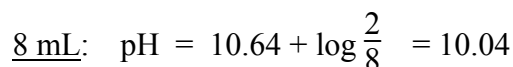<u>5 mL</u>: $[H^+] = \sqrt{\dfrac{K_1 K_2 (0.045\,5) + K_1 K_w}{K_1 + (0.045\,5)}} \Rightarrow pH = 7.00$

<u>5.2 mL</u>: $pH = pK_2 + \log \frac{0.2}{4.8} = 7.62$

<u>6 mL</u>: $pH = pK_2 + \log \frac{1}{4} = 8.40$

<u>7.5 mL</u>: $pH = pK_2 = 9.00$

<u>9 mL</u> $pH = pK_2 + \log \frac{4}{1} = 9.60$

<u>9.8 mL</u>: $pH = pK_2 + \log \frac{4.8}{0.2} = 10.38$

$\underline{10\ mL}$:   $A^- + H_2O \rightleftharpoons HA^- + OH^-$                 $K_{b1} = \dfrac{K_w}{K_2}$   $= 10^{-5.00}$

$\phantom{\underline{10\ mL}}$   $0.041\ 7 - x \qquad\qquad x \qquad x$

$$\dfrac{x^2}{0.041\ 7 - x} \ = K_2 \Rightarrow x = [OH^-] = 6.41 \times 10^{-4}\ M \ \Rightarrow pH = 10.81$$

$\underline{10.2\ mL}$: $[OH^-] = \left(\dfrac{0.2}{60.2}\right)(0.500\ M) = 1.66 \times 10^{-3}\ M \Rightarrow pH = 11.22$

$\underline{11\ mL}$:  $[OH^-] = \left(\dfrac{1}{61}\right)(0.500\ M) = 8.20 \times 10^{-3}\ M \Rightarrow pH = 11.91$

$\underline{12\ mL}$:  $[OH^-] = \left(\dfrac{2}{62}\right)(0.500\ M) = 1.61 \times 10^{-2}\ M \Rightarrow pH = 12.21$

**S12-9.** Titration reaction:  $- NH_2 + H^+ \rightarrow$  $- NH_3^+$   $pK_a = 10.64$

$\phantom{xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx}$ $V_e = 10.0\ mL$

$\underline{0\ mL}$:    $B + H_2O \rightleftharpoons BH^+ + OH^-$     $K_b = \dfrac{K_w}{K_a} = 4.37 \times 10^{-4}$

$\phantom{\underline{0\ mL}}$   $0.100 - x \qquad\qquad x \qquad x$

$$\dfrac{x^2}{0.100 - x} \ = K_b \Rightarrow x = [OH^-] = 6.40 \times 10^{-3}\ M \ \Rightarrow pH = 11.81$$

$\underline{2\ mL}$:  $pH = pK_a + \log\dfrac{[B]}{[BH^+]} \ = 10.64 + \log\dfrac{8}{2} \ = 11.24$

$\underline{4\ mL}$:  $pH = 10.64 + \log\dfrac{6}{4} \ = 10.82$

$\underline{6\ mL}$:  $pH = 10.64 + \log\dfrac{4}{6} \ = 10.46$

$\underline{8\ mL}$:  $pH = 10.64 + \log\dfrac{2}{8} \ = 10.04$

$\underline{10\ mL}$:    $BH^+ \rightleftharpoons B + H^+$    $K_a$

$\phantom{\underline{10\ mL}}$ $\dfrac{25}{35}(0.100) - x \qquad x \qquad x$

$$\dfrac{x^2}{0.071\ 4 - x} \ = 2.3 \times 10^{-11}\ M \ \Rightarrow x = 1.28 \times 10^{-6}\ M \ \Rightarrow pH = 5.89$$

$\underline{12\ mL}$: $[H^+] = \left(\dfrac{2}{37}\right)(0.250\ M) \ = 1.35 \times 10^{-2}\ M \ \Rightarrow pH = 1.87$
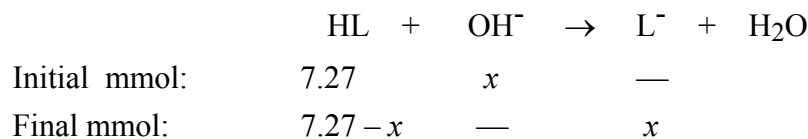
**S12-10.**  (a) 

(b) $V$ mL of tyrosine will require $\dfrac{0.010\ 0}{0.004\ 00}\ V = 2.50\ V$ mL of KOH.  The formal

concentration of product will be $\left(\dfrac{V}{V+2.50\ V}\right)(0.0100) = 0.00286\ M$ .
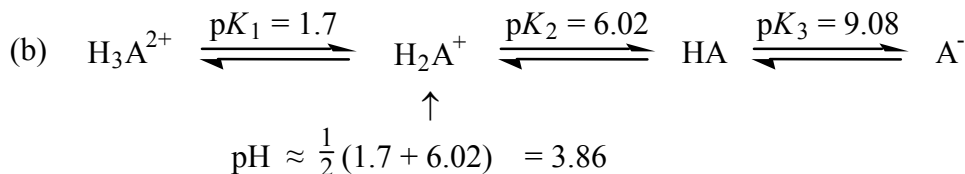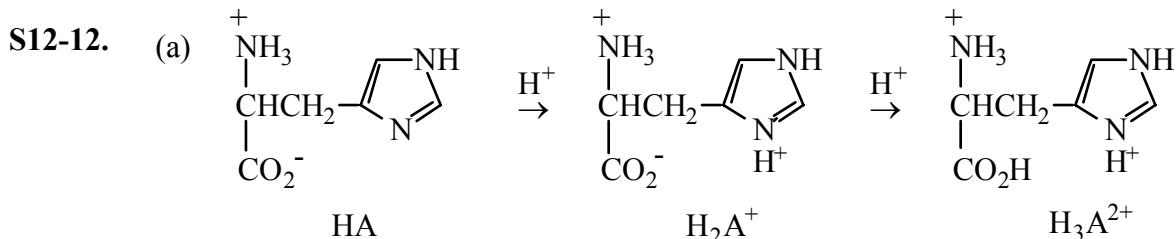
$$[H^+] = \sqrt{\frac{K_2K_3(0.00286) + K_2K_w}{K_2 + 0.00286}} = 1.56 \times 10^{-10}\ M \Rightarrow pH = 9.81$$

**S12-11.**  Leucine is HL.  The reaction is:

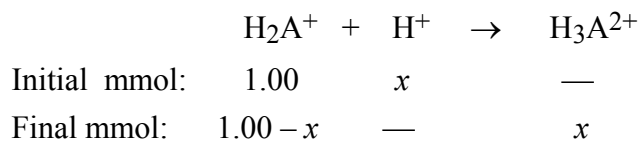$$HL \quad + \quad OH^- \quad \rightarrow \quad L^- \quad + \quad H_2O$$

| | | | |
|---|---|---|---|
| Initial  mmol: | 7.27 | $x$ | — |
| Final mmol: | $7.27 - x$ | — | $x$ |

$pH = 8.00 = pK_2 + \log\dfrac{x}{7.27 - x} \quad \Rightarrow x = 0.128$ mmol

$\dfrac{0.128\ \text{mmol}}{0.0431\ \text{mmol/mL}} = 2.97$ mL of NaOH

**S12-12.**   (a)



$$HA \qquad\qquad\qquad H_2A^+ \qquad\qquad\qquad H_3A^{2+}$$

(b)   $H_3A^{2+} \underset{}{\overset{pK_1 = 1.7}{\rightleftharpoons}} H_2A^+ \underset{}{\overset{pK_2 = 6.02}{\rightleftharpoons}} HA \underset{}{\overset{pK_3 = 9.08}{\rightleftharpoons}} A^-$

$$\uparrow$$

$$pH \approx \tfrac{1}{2}(1.7 + 6.02) = 3.86$$

At pH 3.00, HA has been converted entirely to $H_2A^+$, and some $H_2A^+$ has been converted to $H_3A^{2+}$.

$$H_2A^+ \quad + \quad H^+ \quad \rightarrow \quad H_3A^{2+}$$

| | | | |
|---|---|---|---|
| Initial  mmol: | 1.00 | $x$ | — |
| Final mmol: | $1.00 - x$ | — | $x$ |

$pH = pK_1 + \log\dfrac{[H_2A^+]}{[H_3A^{2+}]}$

$3.00 = 1.70 + \log\dfrac{1 - x}{x} \quad \Rightarrow x = 0.0477$ mmol

We need $1.000 + 0.0477$ mmol HClO$_4$.       Volume $= \dfrac{1.0477\ \text{mmol}}{0.0500\ \text{mmol/mL}} = 21.0$ mL

**S12-13.**  The initial color will be blue.  The color will change near the first equivalence point from blue to green.  After the first equivalence point, the color will turn yellow and will remain yellow.
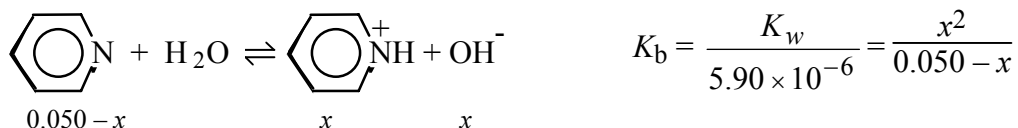
**S12-14.**  (a) red      (b) yellow      (c) yellow      (d) purple

**S12-15.**  There is not an abrupt change in pH at $V_e$.  The color of the indicator would change very gradually.

**S12-16.**

   $pK_a = 5.229$      $K_a = 5.90 \times 10^{-6}$

$\underline{0.99\ V_e}$ :     $pH = pK_a + \log \dfrac{0.99}{0.01} = 7.22$

$\underline{V_e}$ :     This is a 0.050 M  pyridine solution :

     $K_b = \dfrac{K_w}{5.90 \times 10^{-6}} = \dfrac{x^2}{0.050 - x}$

$\Rightarrow x = 9.2 \times 10^{-6}$     $[H^+] = \dfrac{K_w}{x}$   $\Rightarrow pH = 8.96$

$\underline{1.01\ V_e}$ :   This solution contains  $\dfrac{(0.01)(0.10\ \text{M})\ V_e}{(2.01)\ V_e} = 5.0 \times 10^{-4}\ \text{M}\ [OH^-]$   $\Rightarrow pH = 10.70$

Two possibilities are cresol red (orange $\rightarrow$ red) and phenophthalein (colorless $\rightarrow$ red).

**S12-17.**  $[B] + [BH^+] = \dfrac{(6.390 \times 10^{-3}\ \text{g})/(278.16\ \text{g/mol})}{0.1000\ \text{L}} = 2.297 \times 10^{-4}\ \text{M}$

Absorbance $= \varepsilon_B\,[B] + \varepsilon_{BH^+}\,[BH^+]$

$0.350 = (2\,860)[B] + (937)(2.297 \times 10^{-4} - [B])$
$\Rightarrow [B] = 7.007 \times 10^{-5}\ \text{M}$ ,  $[BH^+] = 1.596 \times 10^{-4}\ \text{M}$

$pH = pK_a + \log \dfrac{[B]}{[BH^+]} = (14.00 - 14.79) + \log \dfrac{7.007 \times 10^{-5}}{1.596 \times 10^{-4}} = -1.15$

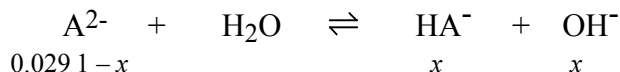**S12-18.**  (a)  First equivalence point :  $pH \approx \frac{1}{2}(pK_1 + pK_2) = 3.46$

Second equivalence point :  We need to estimate the formal concentration of $A^{2-}$ at this point. Volume of NaOH needed to react with 1 g of acid is

$\dfrac{2(1\ \text{g}/132.073\ \text{g/mol})}{0.094\,32\ \text{M}} = 160.6\ \text{mL}.$

$[A^{2-}] \approx \left(\dfrac{100}{260.6}\right)\left(\dfrac{10\ \text{g/L}}{132.073\ \text{g/mol}}\right) = 0.029\,1\ \text{M}\ .$

$$A^{2-} \quad + \quad H_2O \quad \rightleftharpoons \quad HA^- \quad + \quad OH^-$$
$$0.029\,1 - x \qquad\qquad\qquad\qquad x \qquad\quad x$$

$$\frac{x^2}{0.029\ 1 - x} = \frac{K_w}{10^{-4.37}} \Rightarrow x = 2.61 \times 10^{-6}\ M \Rightarrow pH = 8.42$$

(b) 2$^{nd}$.  (There will be little break in the curve near the 1$^{st}$ end point.)

(c) Thymolphthalein  -  first trace of blue.

**S12-19.**  One mole of borax reacts with two moles of $H^+$.

$$[HNO_3](0.021\ 61\ L) = 2\left(\frac{0.261\ 9\ g}{381.367\ g/mol}\right) \Rightarrow [HNO_3] = 0.063\ 56\ M$$

**S12-20.**  Derivation of equation for titration of dibasic B with strong acid (HCl):

Charge balance:  $[H^+] + [BH^+] + 2[BH_2^{2+}] = [OH^-] + [Cl^-]$

$$\phi = \text{fraction of titration} = \frac{C_a V_a}{C_b V_b}$$

Substitutions:  $[Cl^-] = \dfrac{C_a V_a}{V_a + V_b}$

$$[BH^+] = \alpha_{BH^+}\frac{C_b V_b}{V_a + V_b}$$

$$[BH_2^{2+}] = \alpha_{BH_2^{2+}}\frac{C_b V_b}{V_a + V_b}$$

Putting these expressions into the charge balance gives

$$[H^+] + \frac{\alpha_{BH^+} C_b V_b}{V_a + V_b} + \frac{2\alpha_{BH_2^{2+}} C_b V_b}{V_a + V_b} = [OH^-] + \frac{C_a V_a}{V_a + V_b}$$

Now multiply by $V_a + V_b$:

$$[H^+]V_a + [H^+]V_b = \alpha_{BH^+}C_b V_b + 2\alpha_{BH_2^{2+}}\ C_b V_b = [OH^-]V_a + [OH^-]V_b + C_a V_a$$
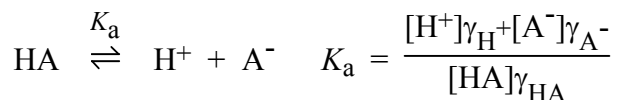
Collect $V_a$ and $V_b$ terms:

$$V_a\left([H^+] - [OH^-] - C_a\right) = V_b\left([OH^-] - [H^+] - \alpha_{BH^+}C_b - 2\alpha_{BH_2^{2+}}\ C_b\right)$$

$$\frac{V_a}{V_b} = \frac{(\alpha_{BH^+} + 2\alpha_{BH_2^{2+}})C_b + [H^+] - [OH^-]}{C_a - [H^+] + [OH^-]}$$

Finally, multiply both sides by $\dfrac{1/C_b}{1/C_a}$

$$\phi = \frac{C_a V_a}{C_b V_b} = \frac{\alpha_{BH^+} + 2\alpha_{BH_2^{2+}} + \dfrac{[H^+] - [OH^-]}{C_b}}{1 - \dfrac{[H^+] - [OH^-]}{C_a}}$$

**S12-21.** Derivation of fractional composition equations with activity coefficients:

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \qquad K_a = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}}$$

Mass balance: $F = [HA] + [A^-] \Rightarrow [A^-] = F - [HA]$

Substitute for $[A^-]$ in the equilibrium expression:

$$K_a = \frac{[H^+]\gamma_{H^+}(F - [HA])\gamma_{A^-}}{[HA]\gamma_{HA}} \Rightarrow [HA] = \frac{[H^+]\gamma_{H^+}\gamma_{A^-}F}{[H^+]\gamma_{H^+}\gamma_{A^-} + K_a\gamma_{HA}}$$

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

To derive an expression for $\alpha_{A^-}$, substitute $[HA] = F - [A^-]$ into the equilibrium expression:

$$K_a = \frac{[H^+]\gamma_{H^+}[A^-]\gamma_{A^-}}{(F - [A^-])\gamma_{HA}} \Rightarrow [A^-] = \frac{K_aF\gamma_{HA}}{[H^+]\gamma_{H^+}\gamma_{A^-} + K_a\gamma_{HA}}$$

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

**S12-22.** $\text{rate} = D_m[T]\,r\tan\theta$

$$= (2.0 \times 10^{-9}\ m^2/s)\left(0.040\ \frac{mol}{L}\ \frac{1\,000\ L}{m^3}\right)(0.20 \times 10^{-6}\ m)(\tan 3.0°) = 8.4 \times 10^{-16}\ \frac{mol}{s}$$

$$= 0.84\ fmol/s$$

In a year, the total volume delivered would be

$$\left(8.4 \times 10^{-16}\ \frac{mol}{s}\right)\left(3\,600\ \frac{s}{h}\right)\left(24\ \frac{d}{day}\right)\left(365\ \frac{day}{year}\right) = 2.6 \times 10^{-8}\ mol.$$

This much titrant is contained in $\dfrac{2.6 \times 10^{-8}\ mol}{0.040\ mol/L} = 6.6 \times 10^{-7}\ L = 0.66\ \mu L.$

The equivalent volumetric flow rate is 0.66 μL per year!