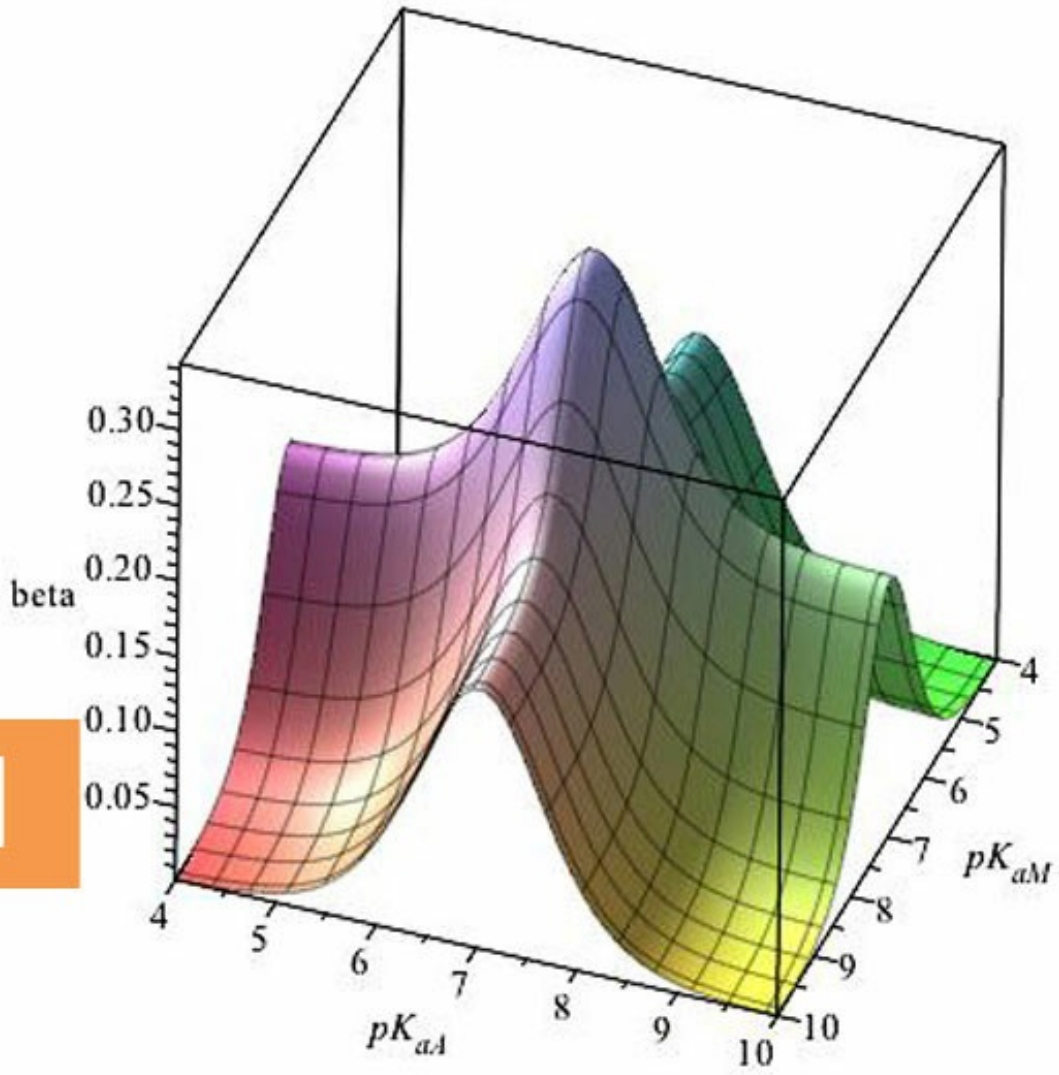
Equilibrium in Analytical Chemistry Using Maple®

An emphasis on Ionic Equilibrium - Part II

Prof. R.V. Whiteley



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8 Polyprotic Acids and Bases

The equilibration of both strong and weak acids and bases has been studied in detail, but the study has been limited to those acids and bases that can provide or accept only one proton. Most acids and bases can exchange several protons. Polyprotic acids are denoted H_nA^m and undergo successive dissociations:

$$\begin{aligned} H_nA^m &\rightleftharpoons H^+ + H_{n-1}A^{m-1} \\ H_{n-1}A^{m-1} &\rightleftharpoons H^+ + H_{n-2}A^{m-2} \\ H_{n-2}A^{m-2} &\rightleftharpoons H^+ + H_{n-3}A^{m-3} \end{aligned}$$

Just as with monoprotic acids, the degree to which each dissociation occurs is expressed as an acid dissociation constant K_{an}.[156]

$$K_{a1} = \frac{[H^+][[H_{n-1}A^{m-1}]}{[H_nA^m]} \qquad \textbf{8-1a}$$

$$K_{a2} = \frac{[H^+][[H_{n-2}A^{m-2}]}{[H_{n-1}A^{m-1}]} \qquad \textbf{8-1b}$$

$$K_{a3} = \frac{[H^+][[H_{n-3}A^{m-3}]}{[H_{n-2}A^{m-2}]} \qquad \textbf{8-1c}$$

It is *always* true that $K_{a1} > K_{a2} > K_{a3} > \ldots > K_{an}$. This should be intuitive because, with each proton loss, the charge on the remaining conjugate base becomes less positive (more negative) and so it would be expected that abstracting a positively charged proton should be increasingly more difficult. Typically each K_a is 10^{-3} to 10^{-6} as large as its previous K_a. So although the number of protons that can be dissociated is limited to n, sometimes n is *effectively* less than the number of protons on H_nA^m. For example NH_4^+ is not a tetraprotic acid: indeed, in water it can dissociate only one of its four protons. The first proton dissociates only slightly, $K°_a = 5.7\ 10^{-10}$, but in aqueous solutions, there is *no* loss of a second proton to produce NH_2^-.[157] So the ammonium ion would more appropriately be written as HNH_3^+ which more correctly depicts it as a monoprotic acid.

Polyprotic bases are not as easily recognized. In Chapter 4 (Part I, page 80) the weak base was introduced as M^n, but such a designation provided no indication as to how many protons can be acquired by this base. In that chapter, it was taken to be 1 and n was taken as zero. But in general terms,

$$\begin{aligned} M^n + H_2O &\rightleftharpoons MH^{n+1} + OH^- \\ MH^{n+1} + H_2O &\rightleftharpoons MH_2^{n+2} + OH^- \\ MH_2^{n+2} + H_2O &\rightleftharpoons MH_3^{n+3} + OH^- \end{aligned}$$

might be possible, and predictably, the number of protons M^n can accept would depend on n. Typically, the charge on the conjugate acid will not exceed +1. (See Problem 4 at the end of this chapter.) So, in order for M^n to acquire two protons and become MH_2^{n+2}, n should be less than or equal to minus one. Likewise M^{1+} would show no affinity for protons; if anything, it would behave as an acid and bind OH^-, as illustrated in Equation **5-8**.

The affinity for a proton by each form of the base is expressed as a K_b:

$$K_{b1} = \frac{[MH^{n+1}][OH^-]}{[M^n]} \qquad \textbf{8-2a}$$

$$K_{b2} = \frac{[MH_2^{n+2}][OH^-]}{[MH^{n+1}]} \qquad \textbf{8-2b}$$

$$K_{b3} = \frac{[MH_3^{n+3}][OH^-]}{[MH_2^{n+2}]} \qquad \textbf{8-2c}$$

Because the charge on the conjugate acid increases with each additional proton, it should be logical that $K_{b1} > K_{b2} > K_{b3} > \ldots > K_{bn}$.

The relationship between K_a and K_b in polyprotic acids and bases is the same as it is for monoprotic acids and bases. Consider the first dissociation of a diprotic acid

$$H_2A \rightleftharpoons H^+ + HA^-$$

and compare it to the behavior of the conjugate base in water

$$HA^- + H_2O \rightleftharpoons H_2A + OH^-.$$

The respective equilibrium constants are:

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

and

$$K_{b2} = \frac{[H_2A][OH^-]}{[HA^-]}$$

By inspection, $K_{a1} \times K_{b2}$ equals $[H^+][OH^-]$, and this is equal to K_w. So,

$$K_{a1} = \frac{K_W}{K_{b2}} \quad \text{and} \quad K_{b2} = \frac{K_W}{K_{a1}}$$

The numerical subscripts might cause confusion, but that relationship is simple too: for an 'n' protic acid, this relationship is between K_{ax} and K_{by} where x + y must equal n + 1. For example, for a tetraprotic acid, the equilibrium constant pairs are K_{a1} and K_{b4}, K_{a2} and K_{b3}, K_{a3} and K_{b2}, and finally, K_{a4} and K_{b1}. So $K_{a1} \times K_{b4} = K_w$ etc.

The relationship between K_{an} and $K°_{an}$ also follows the monoprotic acid model.

$$K°_{an} = \frac{\gamma_{H+}[H^+]\gamma_{Hn-1Am-1}[H_{n-1}A^{m-1}]}{\gamma_{HnAm}[H_nA^m]} \qquad \textbf{8-3a}$$

$$K°_{an} = \frac{\gamma_{H+}\gamma_{Hn-1Am-1}}{\gamma_{HnAm}} K_{an} \qquad \textbf{8-3b}$$

$$K_{an} = \frac{\gamma_{HnAm}}{\gamma_{H+}\gamma_{Hn-1\,Am-1}} K°_{an} \qquad \textbf{8-3c}$$

A practical example is the K_{a3} for the triprotic acid H_3PO_4.

$$K_{a3} = \frac{\gamma_{HPO42-}}{\gamma_{H+}\gamma_{PO43-}} K°_{a3}$$

It should be apparent then, that the ionic strength affects *every* K_{an}, but what might not be so apparent is the degree of that effect as the charge on each specie deviates from zero. Recall from Chapter 2, Equations **2-6** and **2-8**, that an activity coefficient changes with $(10^{-z})^2$. So the activity of a divalent ion is more profoundly affected by an increase in μ than is the activity of a monovalent ion. This will become clear as pH calculations for polyprotic acids are presented.

Although polyprotic acids carry the same K_a to $K°_a$ and K_a to K_b relationships seen with monoprotic acids, there are two issues that make their equilibrium calculations more complicated.

First, the calculation of ionic strength cannot be made by simply adding the concentrations of all of the cations, *or* by adding the concentrations of all of the anions. For a solution of monovalent ions, z equals 1 in **2-5**,

$$\mu = {}^1/_2 \sum M_i \bullet z_i^2 = {}^1/_2 \sum M_i \bullet 1 \qquad \textbf{2-5}$$

and because the sum of the cation charges must equal the sum of the anion charges, the ${}^1/_2$ can be removed when only the cations or only the anions are counted, as we did with Equation **3-13**. When z is not ± 1, the discussion on Part I, page 39 becomes relevant.

Second, that discussion of ionic strength on page 39 pertained only to strong electrolytes and that is of little relevance to polyprotic acids and bases because *none of these* fully dissociate into *all* of their congeners. The correlation between $[H_nA]$ and C_{HnA} for limited dissociation takes the form of Equation **4-9**. But because there will be more than one charged congener of H_nA a somewhat more complicated charge balance expression will emerge.[158]

The most efficient way to develop the charge balance expression for these polyprotic acids (and bases) is to resurrect the concept of α which was first introduced in Equations **4-21** and **4-22**. Consider the acid H_3A. It can (at best) dissociate into three congeners: H_2A^-, HA^{2-} and A^{3-}. That is, along with the parent acid, H_3A, there are four possible forms of this acid in solution. Mass balance will require that:

$$C_{H3A} = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}].$$

Equilibrium expressions can be taken from **8-1a**, **8-1b**, and **8-1c** with n = 3 and m = 0. These will be used to create a set of expressions for the four congeners in terms of the dissociation constants and one of the congeners; *arbitrarily*, $[H_3A]$ is chosen to be that "reference" congener, but any of the four could have been chosen.

```
> restart; H2A:= solve(K[a1] = H*H2A/H3A, H2A); HA:= solve(K[a2] =
  H*HA/H2A, HA); A := solve(K[a3] = H*A/HA, A);
```

$$H2A := \frac{K_{a1}\, H3A}{H}$$

$$HA := \frac{K_{a2} K_{a1}\, H3A}{H^2}$$

$$A := \frac{K_{a3} K_{a2} K_{a1}\, H3A}{H^3}$$

(One could have begun with `H3A:= solve(K[a1]=H*H2A/H3A,H3A);` and had expressions in terms of K_{a1}, K_{a2}, K_{a3}, and $H2A$.) Next, the mass balance requirement is entered followed by the definition of each alpha, analogous to **4-21** and **4-22**. The order in which these are entered is critical so that each assignment can be incorporated into the subsequent assignment. The simplification command is necessary to effect the clearest form of these expressions. Without this `simplify`, the expressions are correct but ambiguous.

```
> C[H3A]:= H3A + H2A + HA + A; alpha['H3A']:= simplify (H3A/
  C['H3A']); alpha['H2A']:= simplify(H2A/C['H3A']); alpha['HA']:=
  simplify(HA/C['H3A']); alpha['A']:= simplify(A/C['H3A']);
```

$$C_{H3A} := H3A + \frac{K_{a1}\, H3A}{H} + \frac{K_{a2} K_{a1}\, H3A}{H^2} + \frac{K_{a3} K_{a2} K_{a1}\, H3A}{H^3}$$

$$\alpha_{H3A} := \frac{H^3}{H^3 + K_{a1} H^2 + K_{a2} K_{a1} H + K_{a3} K_{a2} K_{a1}}$$

$$\alpha_{H2A} := \frac{K_{a1} H^2}{H^3 + K_{a1} H^2 + K_{a2} K_{a1} H + K_{a3} K_{a2} K_{a1}}$$

$$\alpha_{HA} := \frac{K_{a2} K_{a1} H}{H^3 + K_{a1} H^2 + K_{a2} K_{a1} H + K_{a3} K_{a2} K_{a1}}$$

$$\alpha_{A} := \frac{K_{a3} K_{a2} K_{a1}}{H^3 + K_{a1} H^2 + K_{a2} K_{a1} H + K_{a3} K_{a2} K_{a1}}$$

This H_3A example provides just enough structure that one can probably guess the form of *any* alpha for *any* H_nA. Notice that each alpha has the same denominator, as well they should, inasmuch as the denominator represents C_{H3A}. Each denominator contains four (*i.e.* n+1) terms. Each term in the denominator "takes its turn" in the numerator to represent each congener. Predictably, the fully protonated congener (H_3A) is represented by $[H^+]^n$ ($[H^+]$ being represented as H in the output), and the fully deprotonated congener (A^{3-}) is represented by $[H^+]^0 K_{a1} \times K_{a2} \times K_{a3} \ldots \times K_{an}$. So what might α_{H2A3-} be for the *pentaprotic* acid H_5A look like? Is

$$\frac{[H^+]^2 K_{a1} K_{a2} K_{a3}}{[H^+]^5 + [H^+]^4 K_{a1} + [H^+]^3 K_{a1} K_{a2} + [H^+]^2 K_{a1} K_{a2} K_{a3} + [H^+] K_{a1} K_{a2} K_{a3} K_{a4} + K_{a1} K_{a2} K_{a3} K_{a4} K_{a5}}$$

reasonable? The monoprotic example is found in Equations **4-21** and **4-22** which follow this structure: two terms in the denominator for an "n = 1" acid; the protonated form uses $[H^+]^1$ (**4-22**) in the numerator and the deprotonated form uses $[H^+]^0 \times K_a$, *i.e.* K_a in the numerator (**4-21**).

The form of these alphas is consistent with Le Châtelier's Principle just as it was for monoprotic acids. In a solution with a high H^+ concentration, protonation of the acid should be favored, and in a highly alkaline solution where $[H^+] \longrightarrow 0$, the deprotonated forms should prevail. Where a particular K_{an} becomes especially small, the alpha for all congeners that contain that K_{an} in the *numerator* become smaller and smaller. We continue the worksheet to illustrate these points for H_3A.

So that the alphas can be portrayed over a wide range of pH values, H will be replaced with 10^{-pH} (continuing the abuse of "pH"). The values selected for dissociation constants will show the effects of a small and then a large difference between successive K_{an}'s.

```
> H := 10^(-pH): K[a1] := 1e-2: K[a2] := 1e-7: K[a3] := 1e-
  9: alpha['H3A'] := alpha['H3A']; alpha['H2A']: alpha['HA']:
  alpha['A']:
```

Only α_{H3A} is shown.

$$\alpha_{H3A} := \frac{\left(10^{-pH}\right)^3}{\left(10^{-pH}\right)^3 + 0.010\left(10^{-pH}\right)^2 + 1.000\,10^{-9}\,10^{-pH} + 1.000\,10^{-18}}$$

```
> plot([alpha['H3A'], alpha ['H2A'], alpha['HA'], alpha ['A']],
  pH = 0..14, labels = ["-log[H+]", "alpha [HnA]"], axes = boxed,
  color = [red, blue, green, black]);
```

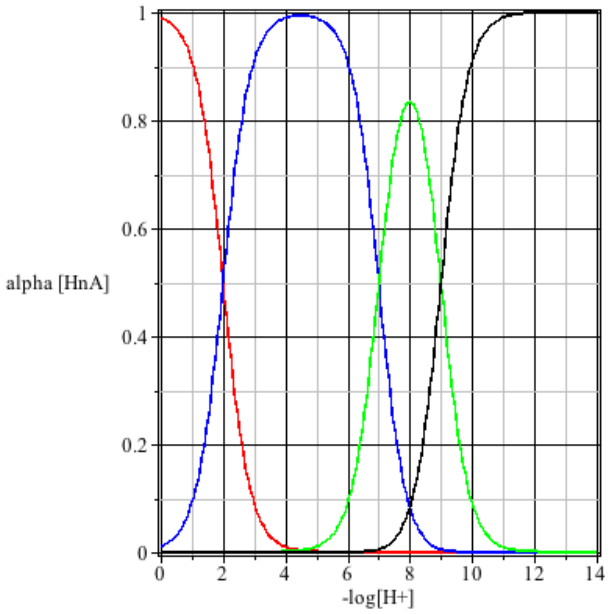

Figure 8-1

H_3A (red) dominates at high $[H^+]$ but where $[H^+]$ is less than about 10^{-11} the acid is entirely deprotonated (black). Had K_{a3} been smaller than 10^{-9}, it would have required a still smaller $[H^+]$ to achieve complete deprotonation (of HA^{-2}). The small difference between K_{a2} and K_{a3} is manifest as coexistence (measurable alphas) of three rather than two congeners. Notice that α_{HA2-} never reaches 0.9. This too is a consequence of the close lying K_{a2} and K_{a3}. In chemical terms, it means that HA^{2-} begins to lose protons before the H_2A^- is completely deprotonated. (*Cf.* problem 6 in chapter 7.) This coexistence of congeners will be shown to create buffer capacity in this pH region, *i.e.* pH ≈ 8.

Before leaving the topic of alphas, the issue of ionic strength effects on these terms will be considered. α is not *directly* a function of C_{HnA}, but μ certainly is, and μ affects γ which affects all K_{an}s which affect α. First, the plot structure for Figure **8-1** will be saved so that it can be plotted along with more rigorously determined results.

```
> Quick_Plot:= plot([alpha['H3A'], alpha['H2A'], alpha['HA'],
  alpha['A']], pH = 0.. 14, labels = ["-log[H+]", "alpha[HnA]"],
  axes = boxed, color = [red, blue, green, black]):
```

Applying Equation **2-5** we begin by calculating the ionic strength based on the given dissociation constants (which imply the existence of four congeners $H_3A\ldots A^3$).

$$\mu = \ ^1/_2\{[H^+] + [H_2A^-](-1^2) + [HA^{2-}](-2^2) + [A^{3-}](-3^2) + [OH^-](-1^2)\}$$

If one expects to *change only* $[H^+]$, this expression for μ is incomplete! Consider this: $[H^+]$ represents the total positive charge. Charge balance would require that if the positive charges decrease, the negative charges must decrease equally, but equilibrium requirements show an increase in α_{HA2-} and α_{A3-} as $[H^+]$ decreases (Figure **8-1**) and mass balance requirements translate those increases into increases in $[HA^{2-}]$ and $[A^{3-}]$. Clearly, the negative charge increases with decreasing $[H^+]$, and that contradicts the charge balance! Mathematically and chemically, this is reconciled by adding a spectator cation, M^{n+}; n equal to 1 is the simplest approach; K^+ or Na^+ would be suitable. This is achieved by adding the strong base MOH.[159] What better way to diminish $[H^+]$ than to add a strong base? This approach is achieved with a simple addition to the ionic strength expression:

$$\mu = \ ^1/_2\{[H^+] + [M^+] + [H_2A^-](-1^2) + [HA^{2-}](-2^2) + [A^{3-}](-3^2) + [OH^-](-1^2)\}$$

In an acid / strong base titration, one could substitute C_{MOH} for $[M^+]$ (see Chapter 7), but charge balance requirements can be used to eliminate $[M^+]$ altogether. Consider

$$[H^+] + [\mathbf{M^+}] = [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + [OH^-]. \qquad \textbf{8-4}$$

So,

$$[\mathbf{M^+}] = [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + [OH^-] - [H^+].$$

Making *this* substitution for $[M^+]$ into the ionic strength expression eliminates $[M^+]$ altogether.

$$\mu = \ ^1/_2\{[H^+] + [H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + [OH^-] - [H^+] + [H_2A^-](-1^2) + [HA^{2-}](-2^2) + [A^{3-}](-3^2) + [OH^-](-1^2)\}$$

$$\mu = \{[H_2A^-] + 3[HA^{2-}] + 6[A^{3-}] + [OH^-]\} \qquad \textbf{8-5}$$

The next step in the process of considering ionic strength effects is to distinguish K_{an} from $K°_{an}$ and K_w from $K°_w$. Figure **8-1** was generated by presuming that each K is equal to its respective K°. We continue the Maple worksheet by making these assignments.[160]

```
> K°[w]:= 1.0e-14: K[w]:= 1.0e-14: K°[a1]:= 1e-2: K°[a2]:= 1e-7:
  K°[a3]:= 1e-9: C['H3A'] := 0.20: pH:= 0:
```

K_w was not assigned in the creation of Figure **8-1** because it was not needed there, but it is needed here. Also, a relatively large C_{H3A} is selected for this illustration so that ionic strength effects will be apparent.

The process of incrementing the pH is done with a "for loop" but not quite as it was done in Chapter 7 (Part I, page 191) which used nested loops. That inner (nested) loop is *not* used to reiterate ionic strength effects; rather, the recalculated K_{an} and K_w at a given pH is fed back to the top of the "for loop" for the next round of calculations. Recall, that in earlier work using nested loops, *every* iteration started with $K°_{an}$ and $K°_w$. So nothing was gained from a previous set of iterations, but here, the system "learns" from its calculation of μ at the previous pH, which differs by only 0.1 pH unit.

```
> for j from 0 to 140 do
> Den:=(10^(-3*pH)) + (K[a1]*10^(-2*pH)) + (K[a1]*K[a2]*10^(-pH))
  + (K[a1]*K[a2]*K[a3]); alpha['H3A']:= (10^(-3*pH))/Den; alpha
  ['H2A']:= (K[a1]*10^(-2*pH))/Den; alpha['HA']:= (K[a1]*K[a2]
  *10^(-pH))/Den; alpha['A']:= (K[a1]*K[a2]*K[a3])/Den;
```

```
> H2A:= alpha['H2A']*C['H3A'] ; HA:= alpha['HA']*C['H3A']; A:=
  alpha['A']*C['H3A']; OH:= K[w]*10^(pH); μ:= H2A + (3*HA) + (6*A)
  + OH;
```

A few explanations are in order before continuing. At the first line, because j is started at 0 rather than the default 1, it is necessary to insert `from` 0.[161] On the second line, each α_{HnA} was derived (and assigned) early in this worksheet, but within this loop, each α_{HnA} will require redefinition as each K_{an} is recalculated in subsequent lines. To do this, a little short cut is used here. Recall that every alpha has the same denominator. So the denominator is defined (as `Den`) and then used in each subsequent assignment. Finally, in the third command line, notice the improved definition of μ which uses Equation **8-5**.

Proceeding with the ionic strength effects, g[1] represents the activity coefficient for all ± 1 ions, *i.e.* H^+, H_2A^- and OH^-, while g[2] is the γ for HA^{2-} and g[3] is for γ_A3-. Notice that all K_{an}'s are not corrected the same way (*cf.* **8-3a**, **8-3b** and **8-3c**). K_{a2} is especially interesting because γ_H+ in the numerator is cancelled out by $\gamma_{H2A}-$ in the denominator.[162]

```
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*sqrt(μ))): g[2]:=
  10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*sqrt(μ))) : g[3]:=
  10^(-0.5*9*((sqrt (μ)/(1 + sqrt(μ))) - 0.15*sqrt (μ))):
> K[a1]:= K°[a1]/g[1]^2: K[a2] := K°[a2]/g[2]: K[a3]:= g[2]*
  K°[a3]/(g[1]*g[3]): K[w]:= K°[w]/g[1]^2:
```

With adjustments made to every equilibrium constant, a second iteration is made. After this second iteration the pH and each alpha is indexed to *j* and assigned. The pH is more appropriately designated as log_H because it is *not* -log{H^+}. Finally, before returning to the top of the "for loop" the pH (which strictly speaking is -log[H^+]) is increased by 0.1 pH unit. The loop is finally closed.

```
> Den:= (10^(-3*pH)) + (K[a1]*10^(-2*pH)) + (K[a1]*K[a2] *10^(-
  pH)) + (K[a1]*K[a2]*K[a3]); alpha['H3A']:= (10^(-3*pH))/
  Den; alpha['H2A']:= (K[a1]*10^(-2*pH))/Den; alpha['HA']:=
  (K[a1]*K[a2]*10^(-pH))/Den; alpha['A']:= (K[a1]*K[a2]*K[a3]) /Den;
> H2A:= alpha['H2A']*C['H3A']; HA:= alpha['HA']*C['H3A']; A :=
  alpha['A']*C['H3A']; OH:= K[w]*10^(pH); μ:= H2A + (3*HA) + (6*A)
  + OH;
> log_H[j]:= pH; alphaH3A[j]:= alpha['H3A']: alphaH2A[j]:= alpha
  ['H2A']: alphaHA[j]:= alpha['HA'] :alphaA[j]:= alpha['A']:
> pH:= pH + 0.1; end:
```

One can call any *log_Hj* or alphaHnAj for reference or to check that the results are reasonable. For example

```
> log_H[10],alphaA[10], alphaHA[10];
```

$$1.000,\ 4.947\ 10^{-15},\ 2.089\ 10^{-7}$$

We continue by packaging the results as sequences of ordered pairs, a log_H_j with its associated α_j.

```
> Alpha_H3A:= [seq([log_H[j], alphaH3A[j]], j= 0..140)]: Alpha_
  H2A:= [seq([log_H[j], alphaH2A[j]], j= 0..140)]: Alpha_
  HA:= [seq([log_H[j], alphaHA[j]], j= 0..140)]: Alpha_A:=
  [seq([log_H[j], alphaA[j]], j= 0..140)]:
```

Each alpha is ready for plotting by `pointplot`, and that is achieved with `plots[pointplot](Alpha_HnA,` ….. *Not* shown below is the step where each set of points is plotted in order to ascertain that, indeed, the plot looks like it was intended to look (as in Part I, page 181). *Then*, one edits the input line by inserting `HnA_plot:=` before each respective plots[pointplot] in order to create a plot structure for each data pair.

```
> H3A_plot:= plots[pointplot](Alpha_H3A, labels = ["-log [H+]",
  "alpha[HnA]"], axes = boxed, color = red): H2A_plot:= plots
  [pointplot](Alpha_H2A, color = blue) ; HA_plot:= plots
  [pointplot](Alpha_HA, color = green): A_plot:= plots[pointplot]
  (Alpha_A, color = black):
```

By using only points (default shape is an open circle), the difference between considering and not considering ionic strength effects becomes clear. For further clarity, the color designation for each α_{HnA} is preserved from Quick_Plot. To achieve the composite plot, `plots[display]` is called with a list {of all plot structures} to be displayed.

```
> plots[display]({Quick_Plot, H3A_plot, H2A_plot, HA_plot, A_
  plot});
```

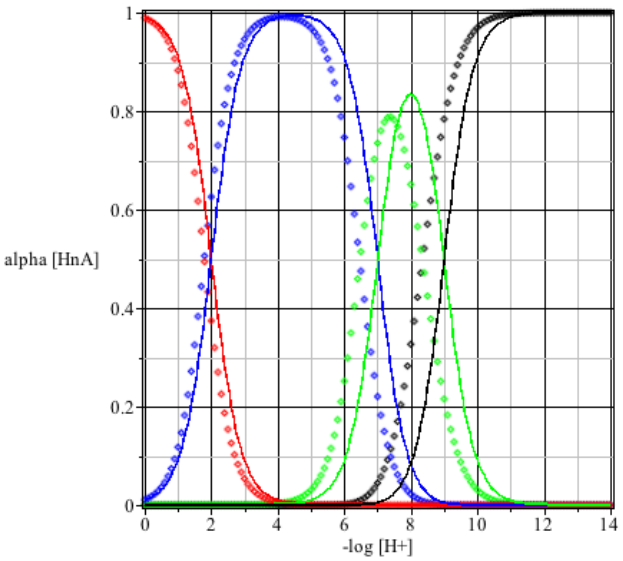

Figure 8-2

The effect of ionic strength is appreciable (at least here, for C_{H3A} = 0.20 **M**) and it is predictable. It should not be surprising that α_{H3A} would be least affected and α_{A3-} would be most affected. At high [H^+] where $\alpha_{H3A} \approx 1$, H_3A is largely associated and so μ is much less than C_{H3A}. On the other hand as [H^+] becomes very small and α_{A3-} becomes significant (approaches 1), H_3A becomes fully dissociated and μ exceeds C_{H3A} ($\approx 6C_{H3A}$ according to Equation **8-5**). So the effects of ionic strength become appreciable. Moreover, consider the numerator of each α_{HnA}: α_{H3A} has no K_{an} in its numerator. So corrections to the dissociation constants have relatively little effect in that alpha. α_{A3-} conversely, has all three constants ($K_{a1}K_{a2}K_{a3}$) in its numerator and corrections to these will measurably alter this alpha. The lesson is that the alpha plots presented in many textbooks are accurate only at low concentrations.

Let's now take a more general look at solutions of a triprotic acid and rather than consider a solution of only C_{H3A}, consider also solutions of C_{MH2A}, C_{M2HA}, and C_{M3A} where M^+ is a spectator ion. For all four solutions charge balance can be written as it was in **8-4**; it just happens that for a solution of C_{H3A}, [M^+] is set equal to zero. The other mass balance requirements are also the same for all four solutions. That is,

$$[H_3A] = \alpha_{H3A}C_{MxH(3-x)A}$$
$$[H_2A^-] = \alpha_{H2A}C_{MxH(3-x)A}$$
$$[HA^{2-}] = \alpha_{HA}C_{MxH(3-x)A}$$
$$[A^{3-}] = \alpha_{A}C_{MxH(3-x)A}.$$

where *x* represents the problem at hand (*x* = 1, 2 or 3). By this point, the reader should be able to write the denominator for any polyprotic acid.[163] Rather than deriving all four alphas, the technique described on page 11 using `Den` is employed. Also, the numerator for each alpha is extracted from the denominator using the `op` command (Part I, page 175). A solution of MH_2A (*i.e.* *x* = 1) would stipulate that

$$[M^+] = C_{MH2A},$$

but an M_2HA (*x* = 2) solution would require

$$[M^+] = 2C_{M2HA},$$

and an M_3A (*x* = 3) solution would require

$$[M^+] = 3C_{M3A}$$

With charge balance requirements settled, a new worksheet is started for the prediction of the pH of each of these solutions over a wide range of concentrations (*i.e.* C = 1.0 10^{-4} to 0.409 **M**).

```
> restart: Den:= H^3 + K[a1]*H^2 + K[a1]*K[a2]*H +
  K[a1]*K[a2]*K[a3]: alpha['H3A']:= op(1, Den)/Den; alpha
  ['H2A']:= op(2, Den)/Den; alpha['HA']:= op(3, Den)/Den; alpha
  ['A']:= op(4, Den)/Den; H3A:= alpha['H3A']*C: H2A:= alpha
  ['H2A']*C: HA:= alpha['HA']*C: A:= alpha['A']*C: OH:= K[w]/H:
  ChBal:= H + M = H2A + 2*HA + 3*A + OH;
```

$$\alpha_{H3A} := \frac{H^3}{H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}}$$

$$ChBal := H + M = \frac{K_{a1} H^2 C}{H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}} + \frac{2 K_{a1} K_{a2} H C}{H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}} + \frac{3 K_{a1} K_{a2} K_{a3} C}{H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}} + \frac{K_w}{H}$$

Only α_{H3A} is shown along with the 5° charge balance expression which will be simplified but *not* reduced to its 4° approximation.

```
> ChBal:= simplify(ChBal*Den*H): ChBal:= lhs(ChBal)- rhs (ChBal):
  ChBal:= collect(ChBal, H):
```

$$ChBal := H^5 + (K_{a1} + M) H^4 + (-K_w - K_{a1} C + K_{a1} K_{a2} + K_{a1} M) H^3 + (K_{a1} K_{a2} K_{a3} + K_{a1} K_{a2} M - K_w K_{a1} - 2 K_{a1} K_{a2} C) H^2 + (K_{a1} K_{a2} K_{a3} M - K_w K_{a1} K_{a2} - 3 K_{a1} K_{a2} K_{a3} C) H - K_w K_{a1} K_{a2} K_{a3}$$

From this general expression for a triprotic acid, we derive a unique charge balance expression for each solution C_{H3A} through C_{M3A} using the `subs` command; these become `ChBal0` (where $x = 0$ *i.e.* for the H_3A solution) through `ChBal3` which pertains to an M_3A solution. Only *ChBal0* and *ChBal3* are shown.

```
> ChBal0 := subs(M=0, ChBal); ChBal1 := algsubs(M = C, ChBal):
  ChBal2 := algsubs(M= 2*C,ChBal): ChBal3 := algsubs(M =
  3*C,ChBal);
```

$$ChBal0 := H^5 + K_{a1} H^4 + \left(-K_w - K_{a1} C + K_{a1} K_{a2}\right) H^3 + \left(K_{a1} K_{a2} K_{a3} - K_w K_{a1} - 2 K_{a1} K_{a2} C\right) H^2 + \left(-K_w K_{a1} K_{a2} - 3 K_{a1} K_{a2} K_{a3} C\right) H - K_w K_{a1} K_{a2} K_{a3}$$

$$ChBal3 := H^4 \left(K_{a1} + 3 C\right) + H^3 \left(-K_w + 2 K_{a1} C + K_{a1} K_{a2}\right) + H^2 \left(K_{a1} K_{a2} K_{a3} + K_{a1} K_{a2} C - K_w K_{a1}\right) - K_w K_{a1} K_{a2} H + H^5 - K_w K_{a1} K_{a2} K_{a3}$$

With all four alphas assigned, the next step is to implement the mass balance requirements *e.g.* `H3A:= alpha['H3A']*C`, *etc*. Then, after assigning an expression for every charged congener in solution, the charge balance requirement is expressed. The final inputs in this group are in preparation for calculating μ within a nested "for loop." As shown previously, within that loop $[H_2A^-]$, $[HA^{2-}]$, $[A^{3-}]$ and $[OH^-]$ are required for μ, and each of these requires $[H^+]$ which is found by solving the charge balance expression for H. A loop (i = 1 to 3) will be used to settle on an ionic strength; H will be assigned to the current `H[i]` for the computation, and then it will be unassigned (`H := 'H'`) so that it can be computed in the next solve command.

Next, the constants can be assigned, and each K is given the same value as its respective K°. This is a one way of presuming that, at each *first* iteration ($i = 1$), $\mu \approx$ zero.

```
> K°[w]:= 1.0e-14: K°[a1]:= 1e-2: K°[a2]:= 1e-7: K°[a3]:= 1e-9:
  K[w]:= K°[w]: K[a1]:= K°[a1]: K[a2]:= K°[a2]: K[a3]:= K°[a3]: C:=
  1.0e-4:
```

The concentration of the solute, C, can be set at any value of interest, but here it is set at what might be considered the lowest value of interest (10^{-4} **M**). In addition to finding the pH for each solution at one C, a loop will be used to increase C to some maximum value of interest (≈ 0.5 **M**). This will be done by doubling C at the end of each trip through the outer (j) loop. At the end of this loop, j, will equal 13 and C will be 2^{12} larger than its initial 10^{-4} **M**. This has two beneficial effects. First it allows one to increase C over several orders of magnitude with only a dozen or so cycles, and second, on a logarithmic plot of C, the points will be equally spaced. So for the effects of $C_{MxH(3-x)A}$ on the pH of a solution over a wide range of concentrations is clear.

Ideally, all four solution types would be addressed using only one loop with its nested loop for μ correction, but inasmuch as C affects μ for a solution of H_3A very differently from how it affects an M_3A solution, each solution type will be handled separately. An inner loop (i) is be used to correct every K° to K using three iterations as presented in Chapter 7. It will be necessary to set "Round calculations to" to ≥ 20 digits.

We begin (arbitrarily) with the H_3A solution. Hi[i] is computed from the solve command and the suitable root was discovered with a preliminary "scout line" followed by a numeric reformatting[165] of the output.

```
> Test:= solve(ChBal0,{H});
```

Test:= {H = 9.91 10^{-5}}, {H = -3.30 10^{-11}} {H = -1.53 10^{-9} }, {H = -1.98 10^{-7} }, {H = -1.01 10^{-2} }

This shows that it is the first root that makes sense. A few points about the inner loop for ionic strength corrections are in order here: `i to 3` has been shown to be adequate for addressing ionic strength effects;[166] the expression for μ does not contain a term for [M^+], but it will for the other three solutions; [H^+] is *temporarily* set equal to Hi[i]. This is so that it can be used in the expression for μ which contains not only [H^+] but also [OH^-] and the three charged congeners of H_3A, and those also contain [H^+]. [H^+] is then unassigned before this inner loop is closed so that it can be solved for again in the next trip through this loop. The activities are calculated with the Davies Equation (**2-8**) because the ion diameters (a) are not known. And because the Davies Equation is used $\gamma_{H}+ = \gamma_{OH}- = \gamma_{H2A1-}$ and this makes the corrections to K° look simple but unfamiliar.

```
> for j to 13 do
> for i to 3 do
```

```
> Rts0:= solve(ChBal0,{H}); Hi[i]:= subs(Rts0[1],H): H:= Hi[i]:
> μ:= 0.5*(H + H2A + 4*HA + 9*A + OH):
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[2]:=10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[3]:=10^(-0.5*9*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
> K[a1]:= K°[a1]/g[1]^2: K[a2] := K°[a2]/g[2]: K[a3]:= g[2]*
  K°[a3]/(g[1]*g[3]): K[w]:= K°[w]/g[1]^2: H:='H':
> end:
> log_C[j]:= log[10](C); pH0[j]:= -log[10](g[1]*Hi[3]); C:= 2*C:
  end:
```

The ordered pairs of the log of C and pH are packaged into `pH_H3A` for point plotting. Then the plot structure is assigned to `H3A_Plot` for composite plotting with the three other solutions that will be investigated.

```
> pH_H3A:= [seq([log_C[j], pH0[j]], j = 1..13)]:
> H3A_Plot:= plots[pointplot](pH_H3A, labels= ["log_C", "pH"],
  axes= boxed, symbol= solidcircle, symbolsize= 20, color= red):
```

Two plot options are added here: the default open circle symbols are replaced with solid circles, and the default symbol size = 10 is enhanced to 20. One might examine this plot with:

```
> plots[display](H3A_Plot);
```

And finally, before addressing the next solution, MH2A, C and the four equilibrium constants must be reset to initial values.

```
> C:= 1.0e-4: K[w]:= K°[w]: K[a1]:= K°[a1]: K[a2]:= K°[a2]: K[a3]:=
  K°[a3]:
```

MH_2A is studied just as H_3A was studied, except for two differences. First, Hi[i] is found by solving a different charge balance expression, namely ChBal1, and μ must now contain $[M^+]$, which for MH_2A, is equal to C. It is presumed that again, it is the first root that produces the viable $[H^+]$; if that were not the case, an error would be received at the `pH1[j]` command which would attempt to find the logarithm of a negative number. Notice that, for clarity, `Rts0` has become `Rts1` and `pH0` has become `pH1`, the 1 representing x from $C_{MxH(3-x)A}$.

```
> for j to 13 do
> for i to 3 do
```

```
> Rts1:= solve(ChBal1,{H}); Hi[i]:= subs(Rts1[1],H): H:= Hi[i]:
> μ:= 0.5*(C + H + H2A + 4*HA + 9*A + OH):
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[2]:=10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[3]:=10^(-0.5*9*((sqrt(μ) /(1 + sqrt(μ))) - 0.15*μ))
> K[a1]:= K°[a1]/g[1]^2: K[a2]:= K°[a2]/g[2]: K[a3]:= g[2]* K°[a3]/
  (g[1]*g[3]): K[w]:= K°[w]/g[1]^2: H:='H': end:
> log_C[j]:= log[10](C); pH1[j]:= -log[10](g[1] *Hi[3]); C:= 2*C:
  end:
> pH_H2A:= [seq([log_C[j], pH1[j]], j = 1..13)]:
> H2A_Plot:= plots[pointplot] (pH_H2A, symbol= solidcircle,
  symbolsize= 20, color= "DarkBlue"):
```

Again, the ordered pairs of the log of C and pH are packaged, this time into `pH_H2A`, and the plot structure is assigned, this time to `H2A_Plot`, but inasmuch as `H3A_Plot` already contains the labels and axes, these can be omitted here. One might inspect the first two plots with

```
> plots[display]({H3A_Plot, H2A_Plot});
```

Before addressing the next solution, C and the four equilibrium constants are again reset to initial values.

```
> C:= 1.0e-4: K[w]:= K°[w]: K[a1]:= K°[a1]: K[a2]:= K°[a2]: K[a3]:=
  K°[a3]:
```

For the next two solutions, simply cutting and pasting the command lines from the previous computations is appropriate. Only a few, critical changes are required. For the M_2HA solution `Rts2:= solve(ChBal2, {H}), μ:= 0.5*(2 *C + H + H2A + 4*HA + 9*A + OH), pH_HA:= [seq([logC[j],pH2[j]], …,` and for its `HA_Plot` it would be wise to change the color of the symbol. (The composite plot (below) has `color = "ForestGreen"`.) For the M_3A solution `Rts3` is used with `ChBal3`, and μ has `3*C` for $[M^+]$, and `A_Plot` does not specify a color which means that the default color = black is rendered.

```
> plots[display]({H3A_Plot, H2A_Plot,HA_Plot, A_Plot});
```

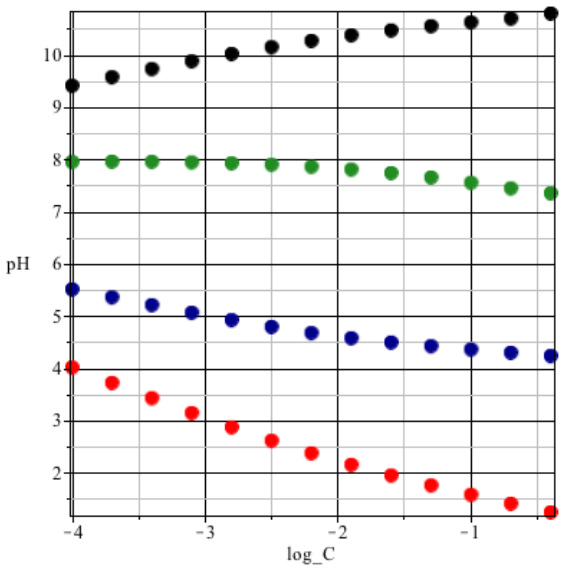

Figure 8-3

We see here the *true* pH (-log{H^+}) of a wide range of concentrations of four solutions made from the triprotic acid and each of the three salts of that acid. The behavior of each solution might have been predicted. H_3A is an acid, and so it should be expected that as C_{H3A} increases, the pH should decrease (just as Equation **4-25** predicts). Likewise $\mathbf{M_3A}$ is a base,

$$A^{3-} + H_2O \rightleftharpoons HA^{2-} + OH^-$$

and one should expect that increasing C_{M3A} would increase the pH. The behavior of MH_2A would imply that it has weakly acidic properties. The small effect C_{MH2A} has on the pH is due to the amphoteric property of H_2A^-

$$H_2A^- \rightleftharpoons H^+ + HA^{2-}$$

and,

$$H_2A^- + H_2O \rightleftharpoons H_3A + OH^-$$

Adding more and more H_2A^- does not materially change the dual nature of this ion which attempts to lower (first equation) and raise (second equation) the pH, simultaneously. Evidently, its acidic property outweighs its alkaline property. The same argument is made for the behavior of M_2HA solution because there

$$HA^{2-} \rightleftharpoons H^+ + A^{3-}$$

and,

$$HA^{2-} + H_2O \rightleftharpoons H_2A^- + OH^-.$$

The amphoteric property is same the reason that MHA, the salt of a weak acid / weak base also has so little effect on pH, as described in Part I, page 109. Recall that Equation **5-15** implies that $[H^+]$ is independent of C_{MHA}.

$$[H^+] = \sqrt{K_{aA}K_{aM}} \qquad \textbf{5-15}$$

How can this be applied to the salts of polyprotic acids (or bases)? Figure **8-3** indicates little dependence of $[H^+]$ on C for MH_2A and no dependence of $[H^+]$ for M_2HA over a wide range of these concentrations. Indeed, for either solution

$$[H^+] \approx \sqrt{K_{an}K_{a(n+1)}}, \qquad \textbf{8-6}$$

where the pair of dissociation constants K_{an} and $K_{a(n+1)}$ pertain to the two most relevant stages of dissociation of H_nA. If we *presume* that a solution of MH_2A is largely driven by

$$H^+ + H_2A^- \rightleftharpoons H_3A$$

This would entail the first and second dissociations of H_3A and so one might expect K_{a1} and K_{a2} to be factors for the MH_2A solutions. Where the ionic strength is negligible (at $C = 10^{-4}$, and $\gamma_{H^+} \approx 1$), the pH is about 5.5 ($[H^+] \approx 10^{-5.5}$). Given that K_{a1} is $1.0\ 10^{-2}$, and K_{a2} is $1.0\ 10^{-7}$, then, applying Equation **8-6**:

$$\sqrt{K_{a1}K_{a2}} = 10^{-4.5}$$

Figure **8-3** indicates pH ≈ 5.5 at $\mu \approx 0$; a fairly crude estimate. **8-6** can be used to better effect on the M_2HA solution. Its pH is quite constant at 8. So $[H^+] \approx 10^{-8}$. Note that with $K_{a3} = 10^{-9}$,

$$\sqrt{K_{a2}K_{a3}} = 10^{-8},$$

an excellent approximation of this solution's pH! Why so much better? A look at Figure **8-2** (solid lines) shows that A^{3-} measurably encroaches on H_2A^{1-} thus pulling the pH above its predicted value for a solution of H_2A^{1-}; the HA^{2-} prediction is quite good because its solutions are nearly equally populated with H_2A^{1-} and A^{3-}, offsetting each other's effect on the pH. Equation **8-6** works very well for diprotic acids where the problem seen with MH_2A cannot occur. (Setting K_{a3} to zero or even to an absurdly small value greater than zero will prove this point.)

When Figure **8-2** is considered along with Figure **8-3**, one can infer that MH_2A and M_2HA behave as buffers, just as MHA was shown to resist pH change (Part I, page 143 *et seq.*): Figure **8-2** shows that several congeners of H_nA^{3-n} coexist in the same pH range where Figure **8-3** shows MH_2A and M_2HA solutions reside. That is to say, in either of these solutions, two or more congeners will coexist at measurable levels and that will stabilize the pH against acid or base additions. This resistance to pH is best illustrated with a pH plot for the titration of H_3A with a strong base, MOH.

For the H_3A titration it should be apparent that

$$H_3A + OH^- \longrightarrow H_2A^- + H_2O$$

will be achieved when the moles of MOH are equal to the moles of H_3A in the titrand, and *if* $C°_{H3A}$ is set equal to $C°_{MOH}$, this will occur when V_{MOH} equals $V°_{H3A}$. Likewise

$$H_2A^- + OH^- \longrightarrow HA^{2-} + H_2O$$

is achieved when V_{MOH} reaches $2\times V°_{H3A}$, and the third proton,

$$H_2A^- + OH^- \longrightarrow HA^{2-} + H_2O,$$

will be removed when V_{MOH} reaches $3\times V°_{H3A}$. So V_{MOH} should extend at least to $3\times V°_{H3A}$ to illustrate the three equivalence points. Recall from Chapter 7 that is instructive to extend the plot well beyond (≥ 10%) the final equivalence point. A new worksheet will be started for this pH plot, but most of the input will be familiar.

```
> restart: Den:= H^3 + K[a1]*H^2 + K[a1]*K[a2]*H +
  K[a1]*K[a2]*K[a3]: alpha['H2A']:= op(2,Den)/Den: alpha['HA']:=
  op (3,Den)/Den: alpha['A']:= op(4,Den)/Den: H2A:= alpha
  ['H2A']*C[H3A]: HA:= alpha['HA']*C[H3A]: A:= alpha['A']*C[H3A]:
  OH:= K[w]/H: M:= C[MOH]: ChBal:= H + M = H2A + 2*HA + 3*A + OH;
```

The output here is nearly identical to the first output of the previous worksheet (page 20) except that M is represented as C_{MOH} and the general concentration for any congener of H_3A is represented here with C_{H3A}. And as in that worksheet the 5° expression for charge balance will be rendered in its $ax^5 + bx^4 + cx^3\ldots$ form.

```
> ChBal:= simplify(ChBal*Den*H): ChBal:= lhs(ChBal) - rhs(ChBal):
  ChBal:= collect(ChBal,H);
```

Then, Equations **7-8a** and **7-8b** will be used to expression these concentrations as volumes of titrant and titrand, respectively.

```
> C[MOH] :=V[MOH]*C°[MOH]/(V[MOH] + V°[H3A]): C[H3A]:= V°[H3A]
  *C°[H3A]/(V[MOH] +V°[H3A]): ChBal;
```

$$H^5 + \left(K_{a1} + \frac{V_{MOH}\,C°_{MOH}}{V_{MOH} + V°_{H3A}}\right) H^4 + \left(-K_w - \frac{K_{a1}\,V°_{H3A}\,C°_{H3A}}{V_{MOH} + V°_{H3A}} + K_{a1}\,K_{a2} + \frac{K_{a1}\,V_{MOH}\,C°_{MOH}}{V_{MOH} + V°_{H3A}}\right) H^3 + \left(K_{a1}\,K_{a2}\,K_{a3} + \frac{K_{a1}\,K_{a2}\,V_{MOH}\,C°_{MOH}}{V_{MOH} + V°_{H3A}} - K_w\,K_{a1} - \frac{2\,K_{a1}\,K_{a2}\,V°_{H3A}\,C°_{H3A}}{V_{MOH} + V°_{H3A}}\right) H^2 + \left(\frac{K_{a1}\,K_{a2}\,K_{a3}\,V_{MOH}\,C°_{MOH}}{V_{MOH} + V°_{H3A}} - K_w\,K_{a1}\,K_{a2} - \frac{3\,K_{a1}\,K_{a2}\,K_{a3}\,V°_{H3A}\,C°_{H3A}}{V_{MOH} + V°_{H3A}}\right) H - K_w\,K_{a1}\,K_{a2}\,K_{a3}$$

This gives the necessary polynomial, expressed in terms of the appropriate equilibrium constants, the C° for the titrand and titrant and the V° of the titrand. Each of these can be set and then [H⁺] can be computed for a given volume of titrant. As introduced in Chapter 7, a "for loop" will handle the sequential calculations. And also, as in Chapter 7, a nested loop will handle the change in ionic strength as titrant is added. We will perform the calculations with and without ionic strength corrections. This will require two charge balance expressions, one using K°'s, the other using K's.

```
> ChBalC:= algsubs(K[w]=K°[w], ChBal): ChBalC:= algsubs(K[a1] =
  K°[a1], ChBalC): ChBalC:= algsubs(K[a2] = K°[a2], ChBalC): ChBalC:=
  algsubs(K[a3] = K°[a3], ChBalC);
```
[167]

This output is not shown because it is simply a reproduction of the previous *ChBal* expression but with $K°_W$ replacing K_w *etc*, although the $ax^5 + bx^4 + cx^3 \ldots$ form is inexplicably lost.

Now all constants will be assigned, and so that ionic strength effects can be demonstrated $C°_{H3A}$ and $C°_{MOH}$ will be set at relatively high values, 0.20 **M**. $V°_{H3A}$ is arbitrarily set to 15.00 mL. So a titration to 50 mL will yield a distinct excess for the third equivalence point (45.00 mL). The call for `solve(ChBalC,{H};` shows that the expression must contain only [H⁺] because otherwise it could not be solved for a numerical value of [H⁺], and it shows that it is the first root that is appropriate.

```
> K°[w]:= 1.0e-14: K°[a1]:= 1e-2: K°[a2]:= 1e-7: K°[a3]:= 1e-9:
  C°[MOH]:= 0.20: C°[H3A]:= 0.20: V°[H3A]:= 15.00 : V[MOH]:= 0.00:
  Test:= solve(ChBalC,{H});
```

$$Test := \{H = 0.040\}, \{H = -1.667\ 10^{-14}\}, \{H = -1.511\ 10^{-9}\}, \{H = -1.985\ 10^{-7}\}, \{H = -0.050\}$$

The loop will entail 501 cycles (j = 1 to 501) to provide V_{MOH} = 0.0 to 50.0 mL in 0.1 mL increments. The nested loop will provide two iterations of μ and the four equilibrium constants. The `ChBalC` calculations are run in the outer loop where ionic strength corrections are not considered, but they require estimates of these equilibrium constants, and this is done by taking all activity coefficients to be exactly 1.[168]

```
> g[1]:= 1.0: g[2]:= 1.0: g[3]:= 1.0:
> for j to 501 do
> for i to 3 do
> K[a1]:= K°[a1]/g[1]^2: K[a2]:= K°[a2]/g[2]: K[a3]:= g[2]*K°[a3]/
  (g[1]*g[3]): K[w]:= K°[w]/g[1]^2:
> H_act:= solve(ChBal,{H}); Ha[i]:= subs(H_act[1],H): H:=Ha[i]:
> μ:= 0.5*(C[MOH] + H + H2A + 4*HA + 9*A + OH):
```

```
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[2]:=10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
  g[3]:=10^(-0.5*9*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
> H:='H': end:
> H_conc:= solve(ChBalC,{H}); Hc:= subs(H_conc[1],H): pH_conc[j]:=
  -log[10](Hc);
> pH_act[j]:= -log[10](g[1]*Ha[3];); V[j]:= V[MOH]; V[MOH]:= V[MOH]
  + 0.10;
> end:
```

These computations require 1505 calculations for the 501 `pH_act` points and 501 calculations for the `pH_conc` points and can require over a minute on slower (≤ 1 GHz) processors. One can inspect points. For example:

```
> V[51], pH_conc[51], pH_act[51];
```

5.000, 1.867, 1.828

We continue by preparing to plot both sets of data. The circle point display will be replaced with `style = line` because this produces a clearer depiction of the results. The same color code for activity *vs.* concentration used for Figure **7-6** is used here.

```
> pH_CONC:= [seq([V[j], pH_conc[j]],j= 1..501)]: pH_ACT:=
  [seq([V[j], pH_act[j]], j= 1..501)]:
> ConcPlot:= plots[pointplot](pH_CONC, style = line, axes = boxed,
  labels = ["Vol of MOH","pH"], color = "DarkRed"): ActPlot:=
  plots[pointplot](pH_ACT, style = line, color = "DarkBlue"):
> plots[display]({ConcPlot, ActPlot});
```

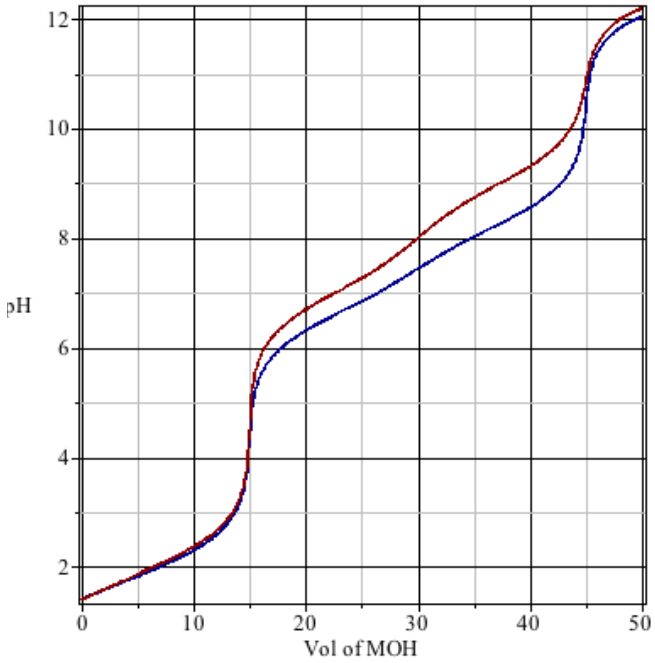

Figure 8-4

This figure shows precisely the same result found for the titration of a monoprotic acid (Figure **7-6**): at the onset, where the acid is largely associated and so μ is not significant, the two plots are indistinguishable; late in the titration where HA^{2-} and A^{3-} become significant, the two plots diverge. They converge again after the third equivalence point (45 mL) because there, K_{3a} is the only important parameter, and the effect of γ on the activity of H^+ and on K_{a3} largely cancel out.

Figure **8-4** also shows that the first equivalence point is easily resolved with its significant $^{\Delta pH}/_{\Delta V}$, that the second equivalence point is barely apparent and that the third equivalence point is marginally useful. The second equivalence point is a victim of the buffer capacity. This could have been predicted from Figure **8-2** which shows no $\alpha > 0.9$ at pH ≈ 8. It was illustrated in Part I, page 184 that $\alpha = 0.991$ was not sufficient to achieve a sharp endpoint.

Indeed, in lieu of a titration plot, a simple calculation of the appropriate α's is quick way to assess the viability of endpoints. Had calculation of the titration plot been skipped in the current worksheet, it might look something like:

```
> H:='H':[169] V[MOH]:= 15.0; H_conc:= solve(ChBalC,{H}): H:= subs(H_
  conc[1],H);[170]
```

$$1.50\ 10^{1}$$
$$3.05\ 10^{-5}$$

```
> Den:= H^3 + K°[a1]*H^2 + K°[a1]*K°[a2]*H + K°[a1]*K°[a2]*K°[a3]:
  alpha[H3A]:= H^3/Den; alpha['H2A']:= K°[a1]*H^2/Den;
```

$$2.99\ 10^{-3}$$
$$3.01\ 10^{-5}$$

This shows (with output formatting in scientific notation) that at the first equivalence point, 0.3% of the triprotic acid retains all three protons and that 99.4% of H_3A now exists as H_2A^-; by inference another 0.3% is in either the HA^{2-} or A^{3-} form. Ideally, the first equivalence point would put 99.9% of H_3A in the H_2A^- form, but this result is quite good. Consider now the second equivalence point, noting the need to reassign all of the parameters.

```
> H:='H':V[MOH]:= 30.0; H_conc:= solve(ChBalC,{H}): H:=
  subs(H_conc[1],H); Den:= H^3 + K°[a1]*H^2 + K°[a1]*K°[a2]*H
  + K°[a1]*K°[a2]*K°[a3]: alpha ['H2A']:= K°[a1]*H^2/
  Den; alpha['HA']:= K°[a1]*K°[a2]*H/Den; alpha['A']:=
  K°[a1]*K°[a2]*K°[a3]/Den;
```

$$3.00\ 10^{1}$$
$$1.00\ 10^{-8}$$
$$8.33\ 10^{-2}$$
$$8.33\ 10^{-1}$$
$$8.33\ 10^{-2}$$

A good, second equivalence point would have $\alpha_{HA2-} > 0.999$, but here it is only 0.833, not only incomplete, but providing good buffer capacity! The third equivalence point (not calculated here) shows $\alpha_{HA2-} = 0.014$ and $\alpha_{A3-} > 0.986$ which is a marginal equivalence point, incomplete and with appreciable buffer capacity. Clearly, one would be advised to titrate to the first equivalence point. And with a $[H^+]_{FirstEqPt} = 3.01\ 10^{-5}$ the ideal indicator[171] would have

```
> H:='H': V[MOH]:= 15.0; H_conc:= solve(ChBalC,{H}): H:= subs(H_
  conc[1], H); pK[Ideal]:= -log[10](solve(0.90909 = K[In]/(H +
  K[In])));
```

$$pK_{Ideal} := 3.521.$$

Appendix V shows that Methyl Orange and Bromophenol Blue bracket this pK_{In}. The first is a bit too strong and would give a premature endpoint; the other too weak giving a late endpoint, but either would likely be acceptable. Better than the rule of thumb (Endnote 124), Appendix V indicates that Bromophenol Blue takes on its In^- form at pH 4.6 which is very close to the $pH_{EqPt} = 4.52$.

If K_{a2} had been at least three orders of magnitude larger than K_{a3}, A^{3-} would not have begun to form until virtually all of the H_2A^- had been deprotonated (by MOH). Indeed, if the reader wishes, this worksheet can be modified to consider a hypothetical H_3A with the same *range* of dissociation constants, but which are *equally* spaced. (Shown below). This plot does not address ionic strength effects because it was created without the nested `i` loop. The new, simpler loop is shown following the new values for equilibrium constants (which, here, are not tied to K° values).

```
> K[w]:= 1.0e-14: K[a1]:= 1e-2: K[a2]:= 10^(-5.5): K[a3]:= 1e-9:
  C°[MOH]:= 0.20: C°[H3A]:= 0.20: V°[H3A]:= 15.00: V[MOH]:= 0.00:
  Test:= solve(ChBal,{H});
```

$$Test := \{H = 4.00 \times 10^{-2}\}, \{H = -1.67 \times 10^{-14}\}, \{H = -1.50 \times 10^{-9}\},$$
$$\{H = -6.32 \times 10^{-6}\}, \{H = -5.00 \times 10^{-2}\},$$

```
> for j to 501 do
> Rt:= solve(ChBal,{H}); H[j]:= subs(Rt[1],H):
> V[j]:= V[MOH]: pH[j]:= -log[10](H[j]): V[MOH]:= V[MOH] + 0.10:
> end:
> pH_fig85:= [seq([V[j], pH[j]], j= 1..501)]: V[151],pH[151];
```

$$15.00 , 3.77$$

We see that the pH at the first equivalence point is unchanged, and this is appropriate because it is largely influenced by only K_{a1}.

```
> plots[pointplot](pH_fig85, style=line, axes = boxed, labels= ["Vol
of MOH","pH"], color= "DarkGreen");
```

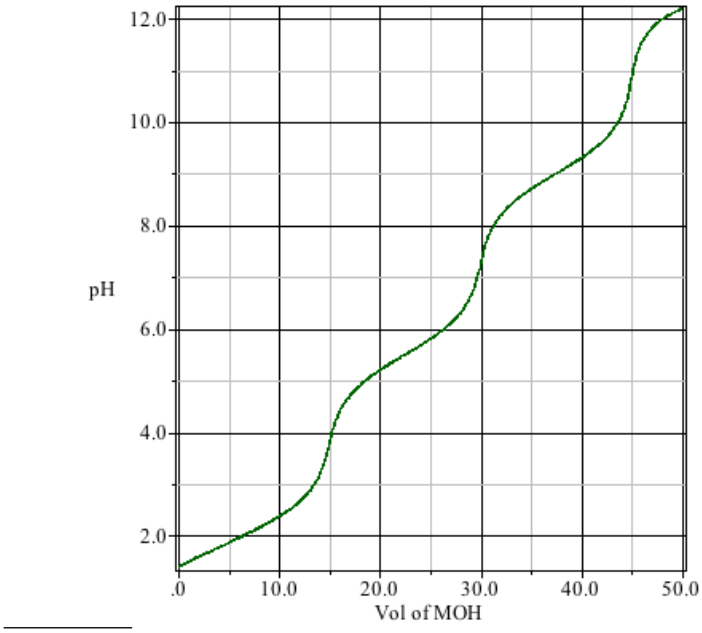

Figure 8-5

But while this change in dissociation constants has improved the second equivalence point, it has noticeably compromised the first equivalence point. Generally, when $K_{an} \geq 10^4 \times K_{a(n+1)} \geq 10^4 \times K_{a(n+2)}$ *etc.*, the endpoints are sharp. This is because the respective α's approach 1.0. This should be logical: when it becomes 10,000 times as difficult to remove a proton from H_nA as it is from $H_{n-1}A^{1-}$, it should be obvious that the base will thoroughly deprotonate H_nA before trying to abstract protons from $H_{n-1}A^{1-}$. So $\alpha_{Hn\text{-}1A^{-}} \longrightarrow 1$ means minimal buffer capacity and that allows a large $^{\Delta pH}/_{\Delta V}$. If one were to recreate this plot with $K_{a1} = 1.0\ 10^{-2}$, $K_{a2} = 1.0\ 10^{-6}$ and $K_{a3} = 1.0\ 10^{-10}$ the first two equivalence points would be sharp, but the third equivalence point would suffer, because achieving $\alpha_{HA^{2-}} \leq 0.001$, that is ≥ 99.9% deprotonation of HA^{2-} would require a pH of about 13. We show this with:

```
> restart; Expr:= alpha[HA]= K[a1]*K[a2]*H/(H^3 + K[a1]*H^2 +
  K[a1]*K[a2]*H + K[a1]*K[a2]*K[a3]);
```

$$Expr := \alpha_{HA} = \frac{K_{a1} K_{a2} H}{H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}}$$

```
> K[a1]:= 1E-2:K[a2]:= 1E-6: K[a3]:= 01E-10: alpha[HA]:= 0.001;
  pH[Reqd]:= -log[10](fsolve(Expr,H));
```

$$pH_{Reqd} := 13.000$$

The titrant is $C°_{MOH} = 0.20$ **M**. This gives $[H^+] \approx 5\ 10^{-14}$ and so the pH of pure titrant is ≈ 13.3 (Equation **3-24**). That is, even pure titrant can barely achieve a pH high enough to deprotonate HA^{2-}, to this degree and this is because K_{a3} is too small for *this* titrant. (This problem was discussed in Problem 3 of Chapter 7 for the very weak monoprotic acid HA.) The remedy for titrating acids with an extraordinarily small K_a is to use a non-aqueous medium (Problem 5, Chapter 7).

This concludes the analysis of polyprotic acids. Their properties as weak acid and buffers can be found in polyprotic bases using exactly the same mass balance and charge balance principles. Indeed, treating a diprotic base, M^- which has two conjugate acids, MH and MH_2^+ is no different than analyzing the diprotic acid H_2A which has two conjugate bases, HA^- and A^{2-}. The analysis of a diprotic base has been deferred to the example problems below. The example problems begin with a problem that ties the salt of a weak acid / weak base discussion in Chapter 6 to the polyprotic acid discussion in this chapter.

Example Problems

1. Neglecting ionic strength effects, calculate the pH of a 0.050 **M** $(NH_4)_3PO_4$ solution.

2. Ethylenediaminetetraacetic acid, EDTA, is a tetraprotic acid.[172] At $\mu = 0.1$, $pK_{a1} = 1.99$, $pK_{a2} = 2.67$, $pK_{a3} = 6.16$, and $pK_{a4} = 10.26$. Presume that μ can be maintained at 0.1 as $[H^+]$ is changed from 10^{-13} to 10^{-1} and show how each alpha changes over that range. (In Chapter 9 this acid will be shown to be very important, so important that it has its own "symbol," H_4Y.)

3. H_2SO_3 has a $pK°_{a1}$ = 1.89 and $pK°_{a2}$ = 7.21. At what pH does α_{HSO3^-} equal $\alpha_{SO3^{2-}}$ if C_{H2SO3} is 0.40 **M**? (It would be wise to presume that at this pH, only HSO_3^{1-} and SO_3^{2-} exist in solution. This can be verified when the pH is found.)

4. Hydrazine, N_2H_4, is a diprotic base. Using the data in Appendix IV, calculate the pH of a 1.00 **M** solution of hydrazine using the Davies Equation to compensate for ionic strength effects.

5. Consider the acidimetric analysis of $NaHC_2O_4$. Because $HC_2O_4^-$ is amphoteric, it can be titrated with a strong acid (to $H_2C_2O_4$) or with a strong base (to $C_2O_4^{2-}$). Create titration plots for the titration of 25.00 mL 0.025 **M** $NaHC_2O_4$ with either 0.030 **M** HCl or 0.030 **M** NaOH. Ignore ionic strength effects.

Solutions to Example Problems

1. We begin by stating mass balance requirements for NH_4^+ and the three charged congeners of H_3PO_4. C will represent the analytical concentration of the $(NH_4)_3PO_4$. Notice that each mole of this salt contains three moles of NH_4^+ (plus its NH_3 congener).

```
> restart; NH4:= 3*alpha["NH4"]173*C; H2PO4:= alpha
  ["H2PO4"]*C;HPO4:= alpha["HPO4"]*C; PO4:= alpha["PO4"]*C;
```

$$NH4 := 3\,a_{\text{"NH4"}}C$$
$$H2PO4 := alpha_{\text{"H2PO4"}}\,C$$

etc.

Next each alpha is expressed. There are two kinds of alpha, the one for $NH_3 \rightleftharpoons NH_4^+$ and the three for the dissociation of H_3PO_4. So they are developed differently. For the $H_nPO_4^{n-3}$ alphas, we will use the "Den shortcut" from page 15.

```
> alpha["NH4"] := H/(H + K[a]); Den := H^3 + K[a1]*H^2 +
  K[a1]*K[a2]*H + K[a1]* K[a2]*K[a3]: alpha["H2PO4"] := op(2,
  Den)/Den; alpha["HPO4"] := op(3, Den)/ Den; alpha["PO4"]
  := op(4, Den)/Den;
```

$$\alpha_{\text{"NH4"}} := \frac{H}{H + K_a}$$
$$\alpha_{\text{"H2PO4"}} := \frac{K_{a1}H^2}{H^3 + K_{a1}H^2 + K_{a1}K_{a2}H + K_{a1}K_{a2}K_{a3}}$$

etc.

Before writing a charge balance expression, we will use Equation **3-24** to replace $[OH^-]$.

```
> OH:= K[w]/H: ChBal:= simplify(H + NH4 = H2PO4 + 2*HPO4 +
  3*PO4 + OH);
```

$$ChBal := \frac{H\left(H + K_a + 3\,C\right)}{H + K_a} = \left(K_{a1} H^3 C + 2\,K_{a1} K_{a2} H^2 C + 3\,K_{a1} K_{a2} K_{a3} C H + K_w H^3 + K_w K_{a1} H^2 + K_w K_{a1} K_{a2} H + K_w K_{a1} K_{a2} K_{a3}\right) \Big/ \left(\left(H^3 + K_{a1} H^2 + K_{a1} K_{a2} H + K_{a1} K_{a2} K_{a3}\right) H\right)$$

The `simplify` command is necessary to render an intelligible expression of *ChBal*. This leaves only the task of assigning C and values to every K and then solving *ChBal* for *H*. The equilibrium constants are taken from Appendix IV.

```
> K[a] := 10^(-9.24): K[a1]:= 10^(-2.23): K[a2]:= 10^(7.21):
  K[a3]:= 10^(-12.32):K[w] := 1.01E-14: C:= 0.05:
> Rts:=solve(ChBal,{H});
```

$$Rts := \left\{H = 1.1519\ 10^{-9}\right\}, \left\{H = -0.0529 + 309.0295\ I\right\}, \left\{H = -6.4030\ 10^{-14}\right\}, \left\{H = -7.5432\ 10^{-13}\right\}, \left\{H = -0.0500\right\}, \left\{H = -0.0529 - 309.0295\ I\right\}$$

Only the first root has real meaning, and so:

```
> pH:= -log[10](subs (Rts[1],H));
```

$$pH := 8.939$$

pH 8.94 would be reported. This is considerably more acidic than a K_3PO_4 solution of this concentration, because K^+ unlike NH_4^+ has no acidic nature.

2. We begin developing the expressions for α, and again, we use the "Den shortcut." Only one alpha is shown; notice how it follows the structure described on page 11.

```
> restart; Den:= H^4 + K[a1]*H^3 + K[a1]*K[a2]*H^2
  + K[a1]*K[a2]* K[a3]*H + K[a1]*K[a2]*K[a3]*K[a4]:
  alpha[H4Y]:= op(1,Den)/Den; alpha[H3Y]:= op(2,Den)/Den:
  alpha[H2Y]:= op(3,Den)/Den: alpha[HY]:= op(4,Den)/Den:
  alpha[Y]:= op(5,Den)/Den:
```

$$\alpha_{H4Y} := H^4 \Big/ \left(H^4 + K_{a1} H^3 + K_{a1} K_{a2} H^2 + K_{a1} K_{a2} K_{a3} H + K_{a1} K_{a2} K_{a3} K_{a4} \right)$$

Setting the ionic strength here (μ = 0.10) will allow H to be expressed in terms of pH with an appropriate adjustment for ionic strength. Given that,

$\{H^+\} = \gamma_{H^+}[H^+] = 10^{-pH}$,

we will, therefore, use

$[H^+] = (10^{-pH})/\ \gamma_{H^+}$.

```
> μ:= 0.1: g[H]:= 10^(-0.511* sqrt (μ)/(1+0.329*9* sqrt(μ))):
```

$$g_H := 0.8252$$

This substitution is done with the algebraic substitution command for each α. Notice that γ_{H^+} is embedded in the replacement for H. Again only one alpha is shown.

```
> alpha[H4Y]:= algsubs(H = (10^(-pH))/g[H], alpha[H4Y]);
  alpha[H3Y]:= algsubs (H = (10^(-pH))/g[H], alpha[H3Y]):
  alpha[H2Y]:= algsubs (H = (10^(-pH))/g[H], alpha[H2Y]);
  alpha[HY]:= algsubs(H = (10^(-pH))/g[H], alpha[HY]):
  alpha[Y]:= algsubs(H = (10^(-pH))/g[H], alpha[Y]):
```

$$\alpha_{H4Y} := (2.1568\,(10^{-pH})^{4}) / (K_{a1}K_{a2}K_{a3}K_{a4} + 2.1568\,(10^{-pH})^{4} + 1.4686\,K_{a1}K_{a2}\,(10^{-pH})^{2} + 1.7797\,K_{a1}\,(10^{-pH})^{3} + 1.2119 K_{a1}K_{a2}K_{a3}\,10^{-pH})$$

This operation does not lead to a simple expression of each α. For example, in α_{H4Y}, above, $(10^{-pH})^4$ is more clearly expressed as 10^{-4*pH} or even more simply as $10000*10^{-pH}$. This can be achieved by `> alpha[H4Y] := simplify(alpha[H4]);`, but that simplification is not necessary and moreover, the resulting "simplified" expression is not simple looking.

Assigning values to each dissociation constant is next. Notice that none is corrected for ionic strength effects. This is because these are K_as not $K°_a$s. Their output is unnecessary. One might add `alpha [H4Y];` to the end of this input group to demonstrate that pH is the only remaining variable in the expression. Then, the five αs are plotted.

```
> K[a1]:= 10^(-1.99): K[a2]:= 10^(-2.67): K[a3]:= 10^(-6.16):
  K[a4]:= 10^(-10.26):
```

```
> plot([alpha[H4Y],alpha[H3Y],alpha[H2Y],alpha[HY],alpha[Y]
  ],pH =0..14,labels = ["pH","alpha[HnY]"], axes = boxed,
  color = [red,blue,green,black,"DarkCyan"]);
```

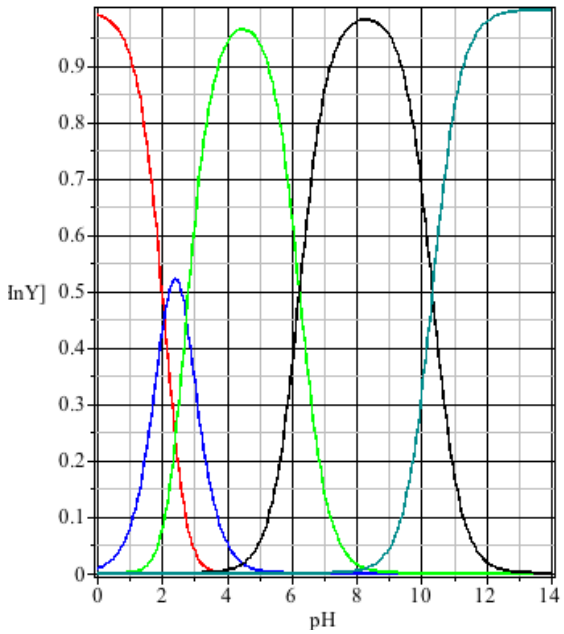

Figure 8-6

Chapter 9 will show that α_{Y4-} ("Dark Cyan") is a very important value, but, it is difficult to extract that value from Figure **8-6** when pH < 8. So the figure is modified. Rather than displaying α, one can display $\log_{10}\alpha$. This is especially useful in looking at each α as it approaches zero.[174] One might enter log[10](alpha[H3Y]) as an argument in the plot command, or much more simply access the plot menu: **`Plot`** > **`Axes`** > **`Properties`** > to reach the dialog box that allows this transformation.

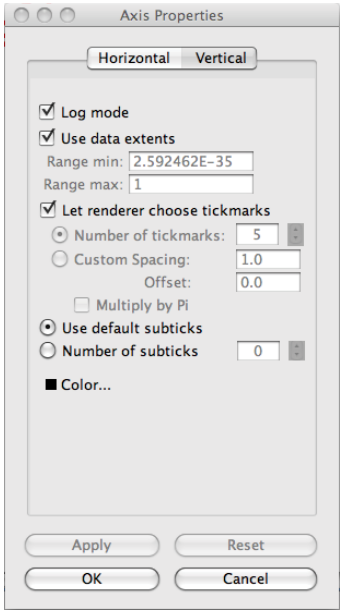

Figure 8-7

This produces the more useful the log-log plot:

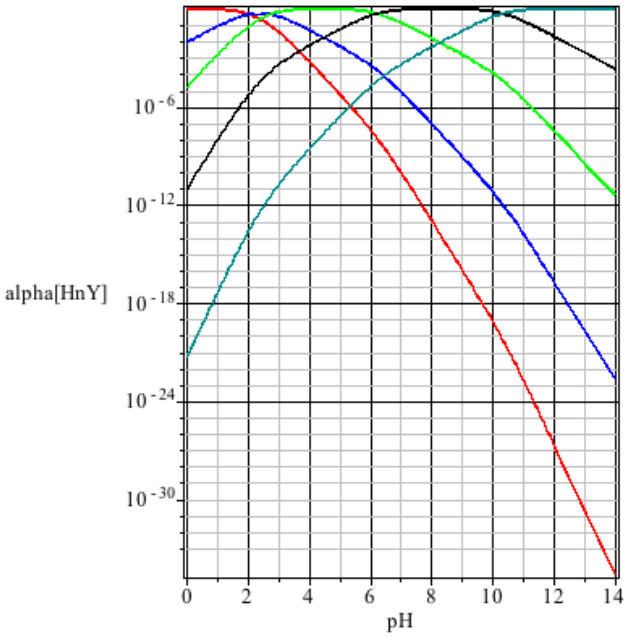

Figure 8-8

One minor point on this transformation. Had this plot been achieved with `> plot (log[10] ([alpha[H4Y]),` ...the scale would have been logarithmic, *i.e.* 0, -1, -2, -3…instead of 10^{-30}, 10^{-24}, 10^{-18}….

3. It might appear that a few reiterations are going to be necessary in order to correct each K° to its respective K, but a little thought can save a lot of computation. Notice that K_{a1} and K_{a2} are quite far apart. This means that the solution, at a given pH will contain *no more than* two (of the three) H_2SO_3 congeners.[175] If HSO_3^- and SO_3^{2-} are the only congeners in solution *and* their αs are equal, then their αs are each equal to 0.5 (or very, very close to that). So

$$[HSO_3^-] \approx 0.5 \times C_{H2SO3}$$

and,

$$[SO_3^{2-}] \approx 0.5 \times C_{H2SO3}.$$

Using the logic that led from Equation **8-4** to **8-5**, $[H^+]$ and $[M^+]$ can be eliminated from the ionic strength expression because

$$[H^+] + [M^+] = [HSO_3^-] + 2[SO_3^{2-}] + [OH^-].$$

So replacing $[H^+] + [M^+]$ in the expression for μ gives:

$$\mu = {}^1/_2\{2[HSO_3^-] + 6[SO_3^{2-}] + 2[OH^-]\}.$$

Guessing that the pH will lie somewhere between 4 and 11 means that $[OH^-]$ (and $[H^+]$) will be negligible.[176] Taking $[OH^-] \approx 0$ and using the substitutions for $[HSO_3^-]$ and $[SO_3^{2-}]$ produces:

$$\mu = {}^1/_2\{C_{H2SO3} + 3C_{H2SO3}\} = 2C_{H2SO3}.$$

This will be verified after the solution pH has been determined, but we can begin the problem with this excellent estimation of μ.

```
> restart; C[H2SO3]:= 0.4: μ := 2*C[H2SO3]:
```

Given the high ionic strength, the Davies Equation will be used to compute activity coefficients. The nomenclature used to generate Figure **8-2** is used here as well. To some, it might be evident that K_{a1} and K_w are not needed for this problem because when α_{HSO3^-} and α_{SO32-} are written out and set equal to each other one finds only that $[H^+]K_{a1} = K_{a1}K_{a2}$ remains. That is $[H^+] = K_{a2}$! All three constants, however, will be needed to verify the ionic strength calculations given above.

```
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)): g[2]:=
  10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)): K°[a1]:=
  10^(-1.89): K°[a2]:= 10^(-7.21):[177] K[a1]:= K°[a1]/g[1]^2:
  K[a2]:= K°[a2]/g[2]:
```

$$K_{a1} := .0290$$
$$K_{a2} := 3.121\ 10^{-7}$$

With excellent estimations of the equilibrium constants in place, the two relevant alphas can be expressed in terms of H only.

```
> Den:= H^2 + K[a1]*H + K[a1]*K[a2]: alpha[HSO3]:=
  op(2,Den)/Den; alpha[SO3]:= op(3,Den)/Den;
```

$$\alpha_{HSO3} := \frac{0.029\ H}{H^2 + 0.029\ H + 9.045\ 10^{-9}}$$
$$\alpha_{SO3} := \frac{9.045\ 10^{-9}}{H^2 + 0.029\ H + 9.045\ 10^{-9}}$$

We need only find the value of H at which these alphas are equal.

```
> H:= solve(alpha[HSO3] = alpha[SO3], H);
```

$$H := 3.121\ 10^{-7}$$

Of course $\alpha_{HSO3^-} = \alpha_{SO32^-}$ does not require that each is equal to 0.50. How close to 0.50 are they? We need to know because our calculation of μ presumed that each equals 0.50. Now that H has been assigned to the value above, the alphas will be fixed. So they need only be called, but with a considerable increase in decimal places.

```
> 'alpha[HSO3]' = alpha[HSO3]; 'alpha[SO3]' = alpha[SO3];
```

$$\alpha_{\text{'HSO3'}} = 0.4999973$$
$$\alpha_{\text{'SO3'}} = 0.4999973$$

Clearly our guess that these will dominate the solution was correct. So μ, and γ_{H^+}, are correct. Finally, then

```
> pH:= -log[10](g[1]*H);
```

$$pH := 6.818$$

And one would report **pH = 6.82** to be consistent with the pK_as.

4. Because N_2H_4 is a base, the reactions under consideration are:

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

and

$$N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$$

These equilibria are described with a K_{b1} and K_{b2}, respectively, but it is K_{a1} and K_{a2} that will be needed, and provided in Appendix IV. Had only $pK°_{b1}$ and $pK°_{b2}$ been provided, the K_a's could have been extracted from:

$$K°_{a1} = \frac{K°_W}{K°_{b2}} \quad \text{and} \quad K°_{a2} = \frac{K°_W}{K°_{b1}}$$

But we have $pK°_{a1}$ and $pK°_{a2}$ and so $K°_{a1} = 10^{-pK°a1}$ and $K°_{a2} = 10^{-pK°a2}$. These are corrected to K_{a1} and K_{a2} using Equations **8-3a** and **8-3b**.

When the Davies equation is used for activity coefficient calculations, γ_{H+} and γ_{N2H5+} will be equal and cancel out of the K_{a1} expression. A first iteration will be made taking $\mu \approx 0$ because $K°_{a2}$ is quite small, implying very little $N_2H_5^+$ formation, and K_{b2} is so small, that there will be virtually no $N_2H_6^{2+}$ in solution. This will be verified later.

```
> restart; K°[w]:= 10^(-13.997): K°[a1]:= 10^(-0.27):
  K°[a2]:= 10^(-7.94): C[N2H4]:= 1.00:
```

$$K°_w := 1.007\ 10^{-14}$$
$$K°_{a1} := 0.537$$
$$K°_{a2} := 1.148\ 10^{-8}$$

These outputs are shown here so that when μ is found and each K is calculated from its respective K°, the modest changes can be seen.

Next, the αs are derived and from them a charge balance expression. Notice that only the αs for *charged* congeners are expressed, and that `N2H6` and `N2H5` require protection because these terms will be used as variables in the next command set. Only α_{N2H6} is shown because either α should be predictable.

```
> Den:= H^2 + K[a1]*H + K[a1]* K[a2]: alpha["N2H6"]:=
  op(1, Den)/Den; alpha["N2H5"]:= op (2,Den)/Den; N2H6:=
  alpha["N2H6"]*C[N2H4]; N2H5 := alpha["N2H5"]*C[N2H4]; OH:=
  K[w]/H: ChBal:= H + N2H5 + 2*N2H6= OH;
```

$$\alpha_{N2H6} := \frac{H^2}{H^2 + K_{a1} H + K_{a1} K_{a2}}$$

$$ChBal := H + \frac{1.000\ K_{a1} H}{H^2 + K_{a1} H + K_{a1} K_{a2}} + \frac{2.000\ H^2}{H^2 + K_{a1} H + K_{a1} K_{a2}} = \frac{K_w}{H}$$

Now we effectively presume that μ is approximately zero by making each γ equal to 1. The exercise of calculating μ and from that the γ's and from those the K's should be familiar. Rather than using the tedious procedure of Chapter 4, we will do the reiterations with a loop as first described in Part I, page 191.

```
> g[1]:= 1: g[2]:= 1: K[w]:= K°[w]/g[1]^2 :K[a1]:=
  K°[a1]/g[2]: K[a2]:= K°[a2]/g[2]^2:
> test:= solve(ChBal,{H});
```

The output is not shown here, but it demonstrates that only the first of the four roots has $[H^+] > 0$. We can now write the "three cycle" loop. The unassignment of H is placed at the beginning of the loop so that there will be a value for $[H^+]$ when the loop terminates at `i = 3`. The loop is terminated with a semicolon so that all three iterations will display. The output will be tabulated below for comparison to the $\mu = 1$ input (above).

```
> for i to 3 do
> H:='H': Rts:= solve(ChBal, {H}): H:= subs(Rts[1],H):
  μ:= 0.5*(H + N2H5 + 4*N2H6 + OH):
> g[1]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)): g[2]:=
  10^(-0.5*4*((sqrt(μ)/(1 + sqrt(μ))) - 0.15*μ)):
> K[w]:= K°[w]/g[1]^2 :K[a1]:= K°[a1]/g[2]: K[a2]:= K°[a2]/g[2]^2: end;
```

	á = Z = N	á = Z = O	á = Z = P
$[H^+]$	$1.076\ 10^{-11}$	1.27510^{-11}	$1.265\ 10^{-11}$
$\gamma_{1\pm}$	0.977	0.968	0.981
$\gamma_{2\pm}$	0.873	0.878	0.878
K_w	$1.078\ 10^{-14}$	$1.074\ 10^{-14}$	$1.075\ 10^{-14}$
K_{a1}	0.615	0.611	0.611
K_{a2}	$1.507\ 10^{-8}$	$1.488\ 10^{-8}$	$1.489\ 10^{-8}$

Clearly `i = 3` is sufficient. So, for the pH:

```
> pH:= -log[10](g[1]*H);
```

$$pH := 10.912$$

5. Both titrations begin at the same point, with a 0.025 **M** $NaHC_2O_4$ solution, but in one titration, HCl is added and in the other NaOH is added. The charge balance expressions will be different only in that the HCl titration will contain a $[Cl^-]$ term; the NaOH titration will not. Nevertheless, one charge balance expression can be used by addressing the $[Cl^-]$ as a function of V_{HCl} and setting V_{HCl} equal to zero throughout the NaOH titration. We begin using what should be familiar expressions for each component of the charge balance equation. This will produce a charge balance expression in terms of the concentrations and volumes of the titrand (NaHOx), and *both* titrants. Notice that unlike Problems 1 and 4, *single* quotation marks around `HOx` and `Ox` are sufficient to protect these expressions. This, protection, recall, is because these terms are subsequently evaluated.

```
> restart; Den:= H^2 + H*K[a1] + K[a1]*K[a2]: alpha['HOx']:=
  op(2,Den)/Den: alpha['Ox']:= op(3,Den)/Den: OH:= K[w]/H:
  C[HCl]:= V[HCl]*C°[HCl]/(V[HCl] + V°[NaHOx]): Cl:= C[HCl]:
  C[NaOH]:= V[NaOH]*C°[NaOH]/(V[NaOH] + V°[NaHOx]):C[NaHOx]:=
  V°[NaHOx]*C°[NaHOx]/(V[HCl] + V[NaOH] + V°[NaHOx]): Na:=
  C[NaOH] + C[NaHOx]: HOx:= alpha['HOx']*C[NaHOx]: Ox:=
  alpha['Ox']*C[NaHOx]: ChBal:= H + Na = HOx + 2*Ox + Cl +
  OH;
```

$$ChBal := H + \frac{V_{NaOH} C^{\circ}_{NaOH}}{V_{NaOH} + V^{\circ}_{NaHOx}} + \frac{V^{\circ}_{NaHOx} C^{\circ}_{NaHOx}}{V_{HCl} + V_{NaOH} + V^{\circ}_{NaHOx}}$$
$$= \frac{H K_{a1} V^{\circ}_{NaHOx} C^{\circ}_{NaHOx}}{\left(H^2 + H K_{a1} + K_{a1} K_{a2}\right)\left(V_{HCl} + V_{NaOH} + V^{\circ}_{NaHOx}\right)}$$
$$+ \frac{2 K_{a1} K_{a2} V^{\circ}_{NaHOx} C^{\circ}_{NaHOx}}{\left(H^2 + H K_{a1} + K_{a1} K_{a2}\right)\left(V_{HCl} + V_{NaOH} + V^{\circ}_{NaHOx}\right)}$$
$$+ \frac{V_{HCl} C^{\circ}_{HCl}}{V_{HCl} + V^{\circ}_{NaHOx}} + \frac{K_w}{H}$$

```
> C°[NaHOx]:= 0.025: C°[NaOH] := 0.030: C°[HCl]:= 0.030:
V°[NaHOx]:= 25: K[w]:= 1.007e-14: K[a1]:= 10^(-1.271):
K[a2]:= 10^(-4.272): ChBal;
```

`ChBal` is called (although not shown here) to verify that only H, V_{NaOH} and V_{HCl} remain to be solved for or assigned. Two expressions, one for each titration, will be created from *ChBal*.

```
> HCl_Titr:= subs(V[NaOH]= 0, ChBal); NaOH_Titr:= subs(V[HCl]
  = 0,ChBal):
```

$$HCl\_Titr := H + \frac{0.625}{V_{HCl} + 25} = \frac{0.033\,H}{\left(H^2 + 0.054\,H + 0.000\right)\left(V_{HCl} + 25\right)} + \frac{0.000}{\left(H^2 + 0.054\,H + 0.000\right)\left(V_{HCl} + 25\right)} + \frac{0.030\,V_{HCl}}{V_{HCl} + 25} + \frac{1.007\,10^{-14}}{H}$$

It should be possible to create both plots within the same loop because in each case the titrant will be incremented by 0.2 mL and each plot has its own charge balance expression. First, to find the suitable root for each using $V_{Titrant} = 0$.

```
> V[HCl]:= 0: V[NaOH]:= 0: test[HCl]:= solve(HCl_Titr, {H});
  test[NaOH]:= solve(NaOH_Titr,{H});
```

$$test_{HCl} := \{H = 0.0009\}, \left\{H = -4.0280\,10^{-13}\right\}, \{H = -0.0010\}, \{H = -0.0785\}$$

$$test_{NaOH} := \{H = 0.0009\}, \left\{H = -4.0280\,10^{-13}\right\}, \{H = -0.0010\}, \{H = -0.0785\}$$

Both outputs show the same $[H^+]$, as expected, and they both have their first root as the only $[H^+] > 0$ root. So the loop can now be written; we will start the loop at `i = 0` only so that V[0] will equal 0.0 mL. Notice the intrepid use of subscripts with subscripts as in `pH[HCl][i]:=`, and the combination of commands like `-log[10](subs`…

```
> for i from 0 to 115 do
> H_HCl:= solve(HCl_Titr,{H}): H_NaOH:= solve(NaOH_Titr, {H}):
```

```
> pH[HCl][i]:= -log[10](subs(H_HCl[1],H)): pH[NaOH][i]:=
  -log[10] (subs(H_NaOH[1],H)): V[i]:= V[HCl]:
> V[HCl]:= V[HCl] + 0.2: V[NaOH]:= V[NaOH] + 0.2:
> end:
> HCl_points := [seq([V[i], pH[HCl][i]], i = 0..115)]: NaOH_
  points := [seq([V[i], pH[NaOH][i]], i = 0..115)]:
> Acid := plots[pointplot] (HCl_points, color = red, style
  = line, thickness = 2, axes = boxed, labels = ["mL of
  Titrant","pH"]): Base := plots[pointplot](NaOH_points,color
  = blue, style = line, thickness = 2):
> plots[display]({Acid, Base});
```

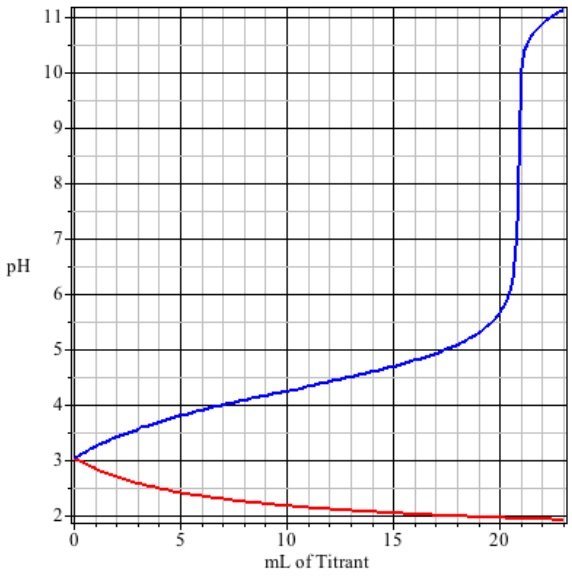

Figure 8-9

The success of an acid / base titration depends entirely on the existence of a large change in pH at the equivalence point. That break is clear in the titration with NaOH but absent in the titration with HCl. Why?

As with the HA^{2-} neutralization (page 36) this is not a buffer issue: it has to do with K_a, K_{a1} here. Let us compare the two equivalence points. Recall that each occurs at 20.8_{333} mL (Equation **7-9**).

```
> V[HCl]:= 20.8333; V[NaOH]:= V[HCl]; H_HCl:= solve
  (HCl_Titr,{H}): H_NaOH:= solve(NaOH_Titr, {H}): H:=
  subs(H_HCl[1],H); 'HCl_alpha['HOx']'= alpha['HOx'];
  'HCl_alpha['Ox']'= alpha['Ox']; H:= subs(H_NaOH[1],H)
  ;'NaOH_alpha['HOx']' = alpha['HOx']; 'NaOH_alpha['Ox']'=
  alpha['Ox'];
```

	HCl Eq. Pt.	NaOH Eq. Pt.
$[H^+]$	0.0113	$6.3138\ 10^{-9}$
α_{HOx^-}	0.8224	0.0001
$\alpha_{Ox^{2-}}$	0.0039	0.9999

For the acid titration, the HCl has failed to protonate a substantial portion of the HOx^- (more than 99%). Again this is not really a buffer capacity issue: it more relates to the fact that H_2Ox with $pK_{a1} = 1.271$ is a pretty strong acid, and so protonating ≥ 99.9% of HOx^{1-} is no easy task, especially for a 0.030 **M** solution of HCl. Compare this to the NaOH titration where less than 0.1% of the HOx^- remains. When OH^- is added to this solution, H_2O is the best source of H^+ and so the pH rises rapidly.

The pH for this equivalence point is calculated so that a suitable indicator might be chosen.

```
> pH[NaOH_EqPt]:= -log[10](H);
```

$$pH_{\text{NaOH\_EqPt}} := 8.1997$$

The "rule of thumb" and Appendix V would suggest Bromothymol Blue at the point of "completely blue," but note that the appendix more precisely describes "completely blue" as pH = 7.6 which is quite early. Appendix V also suggests Phenol Red which it characterizes as "completely red" at pH 8.4. Theoretically late, but given the large $^{\Delta pH}/_{\Delta V}$ shown in Figure **8-9**, the titration error is likely to be insignificant.

9 Complexometric Chemical Equilibrium

The previous four chapters have been dedicated exclusively to acid / base equilibrium, and from that material one should be able to calculate the pH of many kinds of solutions. But, in addition to proton exchange reactions, there are three other types of chemical processes that are important in analytical applications. The first of these pertains to the formation of complex ions and molecules. For example:

$$Fe^{3+} + 6\ CN^{-} \rightleftharpoons Fe(CN)_6^{3-}$$

This is the subject of this chapter. The final reactions of interest involve the formation of insoluble products and oxidation-reduction reactions.

The formation of a metal complex like $Fe(CN)_6^{3-}$ is driven by the ability of most metals (nearly all except those in Group 1A) to accept electron pairs, and the availability of electron pairs from some molecules and anions. The molecules or anions that bind to the metal atom or ion are called ligands. The more available the electron pair, the more effective the is ligand at binding. Because a positive charge on the ligand would render the electron pair unavailable, cations never behave as ligands.

Consider the successive formation of a metal complex between a metal M^{p+} and a ligand L^{q-}.

$$\begin{aligned} M^{p+} + L^{q-} &\rightleftharpoons ML^{p-q} \\ ML^{p-q} + L^{q-} &\rightleftharpoons ML_2^{p-2q} \\ ML_2^{p-2q} + L^{q-} &\rightleftharpoons ML_3^{p-3q} \\ ML_3^{p-3q} + L^{q-} &\rightleftharpoons ML_4^{p-4q} \end{aligned}$$

These formations can continue, but rarely beyond ML_6^{p-6q}. The extent to which each complex is formed is expressed as a formation constant, $K_{f,n}$ where n represents the number of ligands in the complex. The first two formation constants would be expressed:

$$K_{f1} = \frac{[ML^{p-q}]}{[M^{p+}][L^{q-}]}$$

and

$$K_{f2} = \frac{[ML_2^{p-2q}]}{[ML^{p-q}][L^{q-}]}$$

These formation constants can be traced to their thermodynamic equivalents, $K°_{f1}$ and $K°_{f2}$ exactly as K_a is traced to $K°_a$ (*cf.* Equations **2-15** through **2-18**). That is, by expressing the reactants and products in terms of activity rather than molarity, or by applying an activity coefficient to each molarity. This exercise will *not* be addressed in this chapter for two reasons: First, many formation constants are provided at $\mu = 0.1$, a reasonable ionic strength for most analytical calculations.[178] Second, the difference between $K_{f,n}$ and $K°_{f,n}$ rarely produces a meaningful difference in the computations that are routinely carried out.

Like $K_{a,n}$, $K_{f,n}$ is frequently expressed logarithmically; that is as *minus* $\log_{10}K_{f,n}$ which becomes $pK_{f,n}$. But unlike K_{a1}, K_{a2}, ..K_{an}, successive values for K_{f1}, K_{f2}, ..K_{fn} are frequently combined to simplify calculations. For example, suppose that the concentration of ML_4^{p-4q} is to be calculated. What information is necessary? From the expression for K_{f4},

$$K_{f4} = \frac{[ML_4^{p-4q}]}{[ML_3^{p-3q}][L^{q-}]}$$

it is evident that K_{f4}, $[ML_3^{p-3q}]$, and $[L^{q-}]$ are required. By the same analysis, it can be shown that finding $[ML_3^{p-3q}]$ will require K_{f3}, and $[ML_2^{p-2q}]$, and then finding $[ML_2^{p-2q}]$, likewise will require both K_{f2} and $[ML^{p-2}]$. The point is that when using $K_{f,n}$, finding the concentration of the n^{th} complex, requires finding the concentration of *every* preceding complex.

Now consider the expressions for K_{f1} and K_{f2} above and notice that the numerator in K_{f1} is contained in the denominator of K_{f2}. It is shown that:

$$K_{f1} \times K_{f2} = \frac{[\cancel{ML^{p-q}}]}{[M^{p+}][L^{q-}]} \times \frac{[ML_2^{p-2q}]}{[\cancel{ML^{p-q}}][L^{q-}]} = \frac{[ML_2^{p-2q}]}{[M^{p+}][L^{q-}]^2}$$

A little work will show that the numerator of each formation constant is contained in the denominator of its subsequent formation constant. Multiplying a series of these constants produces a simplified expression. So multiplying K_{f1} through $K_{f,n}$ would produce:

$$\prod_{Kf1}^{Kfn} = \frac{[ML_n^{p-nq}]}{[M^{p+}][L^{q-}]^n} \qquad \textbf{9.1}$$

From this relationship, the concentration of the n^{th} complex can be determined from the concentration of the free ligand and free[179] metal, without consideration of any other concentrations. This quantity, the cumulative formation constant, is sufficiently important that it is often reported in lieu of individual $K_{f,n}$ values.[180] Indeed,

$$\prod_{Kf1}^{Kfn} = \beta_n \qquad \textbf{9.1}$$

The similarity to β used for buffer index (Equations **6-12** and **6-13**) is unfortunate. This expression, like each $K_{f,n}$, is sometimes expressed as $-\log_{10}\beta_n$; that is, as $p\beta_n$.

$p\beta_6$ for the hexacyanoferrate(III) is -31 meaning that β_6 is equal to 10^{31}. Given this along with $[CN^-]$ and $[Fe^{3+}]$, it is a simple matter to calculate $[Fe(CN)_6^{3-}]$.

$$\beta_6 = \frac{[Fe(CN)_6^{3-}]}{[Fe^{3+}][CN^{1-}]^6} = 10^{31}$$

The magnitude of β_6 is telling: the concentrations of free Fe^{3+} and CN^- must be remarkably small, because the numerator is limited by solubility to no more than about 10 **M**.[181] If $[Fe^{3+}]$ and $[CN^-]$ come only from the $Fe(CN_6)^{3-}$ complex, then $[CN^-]$ must equal $6[Fe^{3+}]$. For simplicity, if $[Fe(CN)_6^{3-}]$ is taken as 10 **M**, a very generous maximum, then

```
> restart; CN:= 6*Fe: Exp:= beta[6] = FeCN[6]/(Fe*CN^6);
```

$$Exp := \beta_6 = \frac{1}{46656}\,\frac{FeCN_6}{Fe^7}$$

And with $\beta_6 = 10^{31}$, $[Fe(CN)_6^{3-}] = 10$ and a formatting change, the free Fe^{3+} concentration must be.

```
> beta[6]:= 10^31: FeCN[6]:= 10: Fe:= fsolve(Exp,Fe);
```

1.11×10^{-5}

From the earlier stipulation, then, $[CN^-]$ equals $6 \times 1.11\ 10^{-5} = 6.66\ 10^{-5}$ **M**. This calculation is simple but of limited use. Of greater interest would be the determination of $[Fe(CN)_6^{3-}]$ given *analytical* concentrations for Fe^{3+} and CN^-. This would be from $C_{Fe^{3+}}$ and C_{CN^-}. From the definition of analytical concentration (see Part I, page 38 *et seq.*)

$$C_{Fe}^{3+} = [Fe^{3+}] + [FeCN^{2+}] + [Fe(CN)_2^{+}] + [Fe(CN)_3^{0}] + [Fe(CN)_4^{1-}] + [Fe(CN)_5^{2-}] + [Fe(CN)_6^{3-}],$$

and

$$C_{CN^-} = [CN^-] + [FeCN^{2+}] + 2[Fe(CN)_2^{+}] + 3[Fe(CN)_3^{0}] + 4[Fe(CN)_4^{1-}] + 5[Fe(CN)_5^{2-}] + 6[Fe(CN)_6^{3-}].^{182}$$

Strictly speaking, neither of these equations fully accounts for all of the iron(III) or cyanide in solution. These omissions will be addressed on page 60 *et seq.*, but for now, the additional forms of iron and cyanide will be ignored.

The calculation will be pursued in general terms by using the M^{p+} / L^{q-} complex described above. For brevity, the complex will be limited to *n* equals three, but extending *n* to six or beyond is simple enough. We begin by applying the familiar concept of α. Maple will be used to carry out these operations and while using Maple here will provided added practice, it will restrict the way expressions can be written. For example, $[M^{p+}]$ and $[ML_2^{p-2q}]$ are expressed as `M` and `ML[2]`, respectively. ML is expressed as `ML[1]` (*i.e.* ML_1) because *M L* which represents M*L looks too much like *ML*.

Using the definition of C_{Mp+} which equals $[M^{p+}] + [ML^{p-q}]$…and the definition of α_Mp+ we can directly get the expanded form of α_{Mp+}.

```
> restart; C['M']:= M + ML[1] + ML[2] + ML[3]: alpha['M']:=
  M/C['M'];
```

$$\alpha_M := \frac{M}{M + ML_1 + ML_2 + ML_3}$$

Then, using the definition of β *inside* the `solve` command:

```
> ML[1]:= solve(beta[1]= ML[1] /(M*L), ML[1]); ML[2]:=
  solve(beta[2]= ML[2]/(M* L^2), ML[2]); ML[3]:= solve (beta[3]=
  ML[3]/(M*L^3), ML[3]); alpha['M'];
```

$$ML_1 := \beta_1 M L$$
$$ML_2 := \beta_2 M L^2$$
$$ML_3 := \beta_3 M L^3$$

$$\frac{M}{M + \beta_1 M L + \beta_2 M L^2 + \beta_3 M L^3}$$

Notice the similarity of α_M to α_{HnA} (page 11). Every form of M^{p+}, like every form of H_nA, is contained in the denominator and each α is expressed by copying the appropriate operand from the denominator into the numerator. Recognizing this, one could have used the shortcut introduced on page 15 wherein the denominator was defined (as `Den`) and then each numerator was selected as `op(n, Den)`. But all the definitions are already in place in this worksheet to illustrate our point regarding the form of any of the alphas. All four alphas will be needed. So they are defined, although only α_{ML2} is *shown*. Notice that M is embedded in the expression, but it is easily removed.

```
> alpha['ML[1]']:= ML[1]/C ['M']: alpha['ML[2]']:= ML[2]/C['M'];
  alpha['ML[3]']:= ML[3]/C['M']:
```

$$\alpha_{ML_2} := \frac{\beta_2 M L^2}{M + \beta_1 M L + \beta_2 M L^2 + \beta_3 M L^3}$$

```
> alpha['ML[1]']:= simplify (alpha['ML[1]']): alpha ['ML[2]']:=
  simplify(alpha ['ML[2]']); alpha['ML[3]']:= simplify(alpha
  ['ML[3]']):
```

$$\alpha_{ML_2} := \frac{\beta_2 L^2}{1 + \beta_1 L + \beta_2 L^2 + \beta_3 L^3}$$

With any alpha so readily available, it would appear that *any* $[ML_n^{p-nq}]$ could be calculated (from $\alpha_{MLn} \times C_M$). But the problem with these expressions is that they contain $[L^{q-}]$ (as L) which is *not* C_{Lq}-. Indeed, it is necessary to express $[L^{q-}]$ as a function of C_{Lq}- to make these expressions useful. Could this simply be $[L^{q-}] = \alpha_{Lq}\text{-} \times C_L$? No! Look at α_{Lq-} below noting the coefficients for ML_2 *etc.* used in C_L.

```
> alpha['L']:= L/C['L']: C['L']:= ML[1] + 2*ML[2] + 3*ML[3]:
  alpha['L']:= simplify(alpha['L']);
```

$$\alpha_L := \frac{1}{M\left(\beta_1 + 2\,\beta_2 L + 3\,\beta_3 L^2\right)}$$

This alpha contains two predictable properties: it will decrease as the $[M^{p+}]$ concentration increases, which ties up a larger fraction of free L^{q-}, and it will decrease as any β increases, thereby more thoroughly binding L^{q-}. It also contains a problematic property: it depends upon $[L^{q-}]$ itself! If one were to try to find, say, $[ML^{p-q}]$ using $\beta_1 \times [M] \times [L]$, the "L" cannot be removed by replacing it with $\alpha_L q\text{-} \times C_L$ because α_L also contains L.

The problem is solvable by introducing a useful concept. The amount of *free* L^{q-} and the amount of *complexed* L^{q-} depend on n, the number of ligands that can be bound to M, and on the magnitude of every β. C_L is the sum of the concentration of bound L^{q-} *and* the concentration of unbound L^{q-}. The concentration of bound L^{q-} can be found, most simply, from the average number of ligands per M^{p+} times the analytical concentration of M^{p+}. That is $n_{ave} \times C_M$. If n_1 is the number of L's bound in ML_1 and n_2 is the number of L's bound in ML_2 *etc.*, then the concentration of L^{q-} bound in each complex is $n_1 \times [ML_1]$ plus $n_2 \times [ML_2]$ plus $n_3 \times [ML_3]$ *etc.* Dividing the sum of these concentrations by the total concentration will produce the average number of ligands, n_{ave}. (The `0*M` term is included below for completeness.)

```
> n[ave]:= (0*M + 1*ML[1] + 2*ML [2] + 3*ML[3])/C['M'];
```

$$n_{ave} := \frac{\beta_1 ML + 2\,\beta_2 ML^2 + 3\,\beta_3 ML^3}{M + \beta_1 ML + \beta_2 ML^2 + \beta_3 ML^3}$$

```
> n[ave]:= simplify(n[ave]);
```

$$n_{ave} := \frac{L\left(\beta_1 + 2\,\beta_2\,L + 3\,\beta_3\,L^2\right)}{1 + \beta_1\,L + \beta_2\,L^2 + \beta_3\,L^3}$$

Predictably, n_{ave} increases as $[L^{q-}]$ increases, and it increase three times as fast for β_3 as it does for β_1 because there are three times as many ligands on ML_3^{p-3q} as there are on ML^{p-q}.

Now the requirement that the total ligand concentration must equal the concentration of bound ligands *plus* the concentration of free ligands can be applied. A change in nomenclature will be used here: C_{Metal} will be used in place of C_M and C_{Ligand} will be used in place of C_L, because C_M and C_L have already been assigned. Recognizing that C_{Metal} exactly equals C_M and C_{Ligand} exactly equals C_L the mass balance requirement for C_{Ligand} is imposed.

```
> Eqn:= C[Ligand]= n[ave]*C[Metal] + L;
```

$$Eqn := C_{Ligand} = \frac{L\left(\beta_1 + 2\,\beta_2\,L + 3\,\beta_3\,L^2\right) C_{Metal}}{1 + \beta_1\,L + \beta_2\,L^2 + \beta_3\,L^3} + L$$

One could, at this point, `solve Eqn` for `L`, but the output is daunting, even for this example which limits *n* to three. Moreover, there is no real advantage to having an explicit expression for $[L^{q-}]$. Inasmuch as *Eqn* is an expression with $[L^{q-}]$ as the only variable, once C_{Ligand}, C_{Metal}, and every β have been defined, it can be solved numerically for $[L^{q-}]$ and that value can be used to find any desired $[ML_n^{p-nq}]$ or, more usefully, any α_{MLn}. Consider the following analytical concentrations and betas.[183]

```
> C[Ligand]:= 0.10: C[Metal]:= 0.025: beta[1]:= 10^(9.4): beta[2]:=
  10^(16.2): beta[3]:= 10^(20.4): Eqn;
```

$$0.100 = \frac{0.025\,L\left(2.512\,10^9 + 3.170\,10^{16}\,L + 7.536\,10^{20}\,L^2\right)}{1 + 2.512\,10^9\,L + 1.585\,10^{16}\,L^2 + 2.512\,10^{20}\,L^3} + L$$

The output is shown only to demonstrate that all of the parameters have been assigned. $[L^{q-}]$ is the solution to this equation. It is called Lig in order to preempt a recursion error.

```
> Lig:= fsolve(Eqn, L);
```

$$Lig := 0.025$$

Notice that only one fourth of C_{Ligand} (= 0.100) is unbound. That means that three fourths is bound, and that requires a substantial fraction of ML_3^{p-3q} because C_{Metal} (= 0.025) is much less than C_{Ligand}; if ML_2^{p-2q} were substantial, there would not be enough L^{-q} to go around! We can show this.

```
> L:= Lig: 'alpha[M]'=184 alpha ['M']; 'alpha[ML[1]]'=
  alpha['ML[1]']; 'alpha [ML[2]]'= alpha['ML[2]']; 'alpha[ML[3]]'=
  alpha ['ML[3]'];
```

$$\alpha_M = 2.5224\ 10^{-16}$$

$$\alpha_{ML_1} = 1.5880\ 10^{-8}$$

$$\alpha_{ML_2} = 0.0025$$

$$\alpha_{ML_3} = 0.9975$$

As predicted, α_{ML3} dominates, but this might have been apparent from the magnitude of β_3 which is four orders of magnitude larger than β_2. Of course, it is α_{ML3} that "suffers" most as C_{Ligand} approaches zero. The reader is invited to experiment with different concentrations of the metal and ligand. To do this, it is necessary to unassign `L`, or more simply to return to the first input line with its requisite `restart` command.

This problem can be made more general by considering the mixture of two solutions, one of $C°_{Mp+}$ and the other of $C°_{Lq-}$. If the volumes are $V°_{Mp+}$ and $V°_{Lq-}$, respectively, then, analogous to in Equations **7-2a** and **7-2b**:

$$C_{Ligand} = \frac{V_{Ligand} \times C°_{Ligand}}{V_{Ligand} + V°_{Metal}}$$

and,

$$C_{Metal} = \frac{V°_{Metal} \times C°_{Metal}}{V°_{Ligand} + V°_{Metal}}$$

A final point pertains to the nature of L^{q-}. The most effective ligands are also good proton acceptors, that is good bases.[185] This implies a competition between M^{p+} and H^+ for L^{q-}.

$$\begin{array}{lcll} HL^{1-q} & \rightleftharpoons & H^+ + L^{q-} & K_{a1} \\ M^{p+} + L^{q-} & \rightleftharpoons & ML^{p-q} & K_{f1} \end{array}$$

The simplest approach to addressing this competition is to prescribe the pH, or here, $-\log_{10}[H^+]$, and from that pH calculate α_{Lq-}, not as a ligand, but as the anion of a weak acid. That is, from $[H^+]$, K_{a1}, K_{a2} *etc.* as described on page 11. Because the pH is fixed, the α_{Lq-} is then effectively a constant, and if it is multiplied by a formation constant like $K_{f,n}$ or β_n, a *conditional* formation constant, $K'_{f,n}$ or β'_n is created.

The nature of α_{Lq-} is that it approaches 1 as $[H^+]$ approaches zero (*e.g.* Figure **8-1** black line). Clearly then, $K'_{f,n}$ and β'_n approach their respective maxima, $K_{f,n}$ and β_n, as $[H^+]$ approaches zero, or as $-\log_{10}[H^+]$ increases. Increasing the pH of a metal-ligand solution to enhance formation of a metal complex, however, can become counterproductive: As $[H^+]$ approaches zero, $[OH^-]$ becomes substantial (Equation **3-24**), and $[OH^-]$ is, itself, a formidable ligand (Appendix VIa). As the concentration of hydroxide increases, competition between OH^- and L^{q-} for M^{p+} becomes significant if $\beta_{m,OH}$ is appreciable.

$$\begin{array}{rcll} M^{p+} + mOH^- & \rightleftharpoons & MOH^{p-m} & \beta_{m,OH} \\ M^{p+} + nL^{q-} & \rightleftharpoons & ML^{p-nq} & \beta_{n,L} \end{array}$$

This is because α_{mp+} will decrease as $[OH^-]$ increases.

$$\alpha_{mp+} = \frac{1}{1+[OH^-]\beta_1+[OH^-]^2\beta_2 + \ldots + [OH^-]^n\beta_n}$$

(A lower case *m* is used here to distinguish this alpha from α_{Mp+} which pertains to formation of complexes with L^{q-}.) Using Equation **3-24** to replace $[OH^-]$ and then rearranging gives:

$$\alpha_{mp+} = \frac{[H^+]^n}{[H^+]^n + K_w\beta_1[H^+]^{n-1} K_w^{\,2}\beta_2[H^+]^{n-2} + \ldots + K_w^{\,n}\beta_n}$$

By fixing the $[H^+]$ (or $-\log[H^+]$ or pH) at a given value, α_{mp+} becomes a constant that can be multiplied by any of the ML_n^{p-nq} formation constants to give yet another conditional formation constant.

So there are two effects of pH on the formation of M^{p+} /L^{q-} complexes, one that can diminish $[L^{-q}]$ and the other that can diminish $[M^{p+}]$. The α_{Lq-} factor must be considered for all ligands except the anions of strong acids, and the α_{mp+} must be considered for any metal ion that appreciably binds with hydroxide ion, even at what one might consider to be a neutral pH. Often, both factors are considered together, and the results, $\alpha_{Lq-}\times\alpha_{mp+}\times K_{f,n}$ and $\alpha_{Lq-}\times\alpha_{mp+}\times\beta_n$ then become doubly conditional, or conditional-conditional formation constants, $K''_{f,n}$ and β''_n, respectively.[186] These are characterized by having a maximum value, always less than $K_{f,n}$ and β_n at some pH that is usually between 5 and 12. This property will be illustrated below with an important kind of ligand, the chelating agent.

A chelate is a ligand that can provide several electron pairs to a single, central metal (ion). In analytical chemistry, the most important chelating agents, often called chelons, are those that can provide all of the electron pairs, and so the complex is one to one in M^{p+} to L^{q-}. For these special ligands, Lc^{q-} will be used in place of L^{q-} so that only a 1:1 complex will be anticipated.[187] If Lc^{q-} can provide four electron pairs, it is certain that it is the anion of *at least* a triprotic acid. The presence of protons in solution, therefore, impairs its ability to bind with M^{p+} because HLc^{1-q} through H_3Lc^{3-q} can form. Consider the formation of the MLc^{p-q} complex where Lc^{q-} is the anion of a *tetra*protic acid, and that M^{p+} is capable of forming complexes, $M(OH)_n^{p-n}$, with n equal to one through four.

```
> restart; Den[Lc]:= H^4 + K[a1]*H^3 + K[a1]*K[a2]*H^2 + K[a1]*
  K[a2]*K[a3]*H + K[a1]*K[a2]*K[a3]*K[a4]: alpha[Lc]:= op(5,
  Den[Lc])/Den[Lc]; Den[M]:= 1 + beta[1]*OH + beta[2]*OH^2 +
  beta[3]*OH^3 + beta[4]*OH^4: alpha[m]:= 1/Den[M];
```

$$\alpha_{Lc} := \left(K_{a1}K_{a2}K_{a3}K_{a4}\right) \Big/ \left(H^4 + K_{a1}H^3 + K_{a1}K_{a2}H^2 + K_{a1}K_{a2}K_{a3}H + K_{a1}K_{a2}K_{a3}K_{a4}\right)$$

$$\alpha_m := \frac{1}{1 + \beta_1 OH + \beta_2 OH^2 + \beta_3 OH^3 + \beta_4 OH^4}$$

To illustrate the derivation of the expression for α_{mp+} (page 61):

```
> alpha[m]:= algsubs(OH= K[w] /H, alpha[m]);
```

$$\alpha_m := \frac{H^4}{\beta_4 K_w^4 + H\beta_3 K_w^3 + H^4 + H^3 \beta_1 K_w + H^2 \beta_2 K_w^2}$$

From the definition of a doubly conditional formation constant, K''_f is expressed as Kpp_f.

```
> Kpp[f]:= alpha[Lc]*alpha[m]*K[f]:
```

One more modification is recommended before displaying Kpp_f: $[H^+]$ will be varied over several orders of magnitude; so it is more convenient to express $[H^+]$ as 10^{-pH}.

```
> Kpp[f]:= algsubs(H= 10^(-pH), Kpp[f]);
```

$$Kpp_f := \left(K_{a1} K_{a2} K_{a3} K_{a4} K_f \left(10^{-pH}\right)^4\right) \Big/ \left(\left(K_{a1} K_{a2} K_{a3} K_{a4} + \left(10^{-pH}\right)^4 + K_{a1} K_{a2} \left(10^{-pH}\right)^2 + K_{a1} \left(10^{-pH}\right)^3 + K_{a1} K_{a2} K_{a3} 10^{-pH}\right) \left(\beta_4 K_w^4 + \left(10^{-pH}\right)^4 + \beta_2 K_w^2 \left(10^{-pH}\right)^2 + \beta_1 K_w \left(10^{-pH}\right)^3 + \beta_3 K_w^3 10^{-pH}\right)\right)$$

The existence of a maximum K''_f can be illustrated with the Zn^{2+} / EDTA complex. The $K_{a,n}$ values for EDTA, β_n values for $Zn(OH)_n^{2-n}$ and K_w are assigned from Appendix IV and VIa).

```
> K[a1]:= 10^(-1.99): K[a2]:= 10^(-2.67): K[a3]:= 10^(-6.16): K[a4]:= 10^(-10.26): beta[1]:= 10^4.40:
  beta[2] := 10^11.3: beta[3]:= 10^13.14: beta[4]:= 10^14.66: K[f]:= 10^16.50: K[w]:= 1.007e-14;
  'Kpp[f]'= Kpp[f];
```

$$Kpp_f = \left(3.1623\ 10^{16}\ \alpha_{Lc} \left(10^{-pH}\right)^4\right) \Big/ \left(4.7002\ 10^{-42} + \left(10^{-pH}\right)^4 + 2.0233\ 10^{-17} \left(10^{-pH}\right)^2 + 2.5295\ 10^{-10} \left(10^{-pH}\right)^3 + 1.4096\ 10^{-29}\ 10^{-pH}\right)$$

The output for `Kpp[f]` is requested in order to verify that all parameters have been assigned.

```
> plot(Kpp[f], pH= 0..14, labels= ["pH","K[f]"], color = "Purple",
  gridlines = true, axes = box,);
```

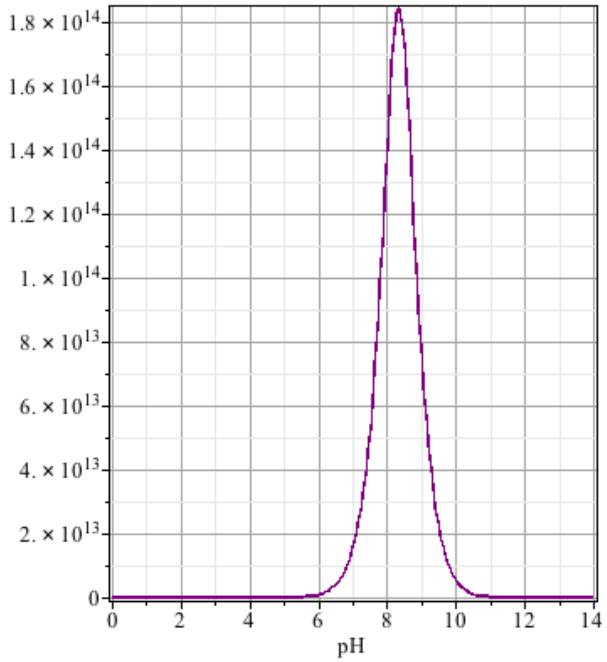

Figure 9-1

This plot shows that the doubly conditional formation constant is very large over a narrow pH range. (Notice that while "pH" was used in the worksheet, the axis is more correctly labeled "-log[H+]".) The plot shows that Zn^{2+} and EDTA bind most strongly when $-\log_{10}[H^+]$ is about 8.3, although even there, K''_f is much less than K_f. Recalling that the maximum K''_f is found where $^{dK''}_{f/dpH}$ is equal to zero, the optimum pH can be calculated.

```
> Max:= diff(Kpp[f],pH): pH[optimum]:= fsolve(Max = 0,pH,0..14);
```

$$pH_{optimum} := 8.344$$

Figure **9-1** does not clearly indicate the pH above or below which K''_f is too small for appreciable complex formation. The appropriate pH range can be made evident by plotting the log of Kpp_f. For further clarity, the log of α_{mp+} and α_{mq-} will also be provided.

```
> logofK[pp[f]]:= log[10] (Kpp[f]): alpha[Lc]:= algsubs(H = 10^(-
  pH), alpha[Lc]); alpha[m]:= algsubs(H = 10^(-pH), alpha[m]):
  logofalpha[Lc]:= log[10](alpha[Lc]): logofalpha[Lc]:= log[10]
  (alpha[Lc]): logofalpha[m]:= log[10](alpha[m]):
```

```
> plot([logofK[pp[f]], logofalpha[Lc], logofalpha[m]], pH= 0..14,
  labels= ["pH", "log of (K[f] or alpha)"], color= ["Purple",
  "DarkCyan" , "DarkGreen"], gridlines[188] = true, axes = box);
```

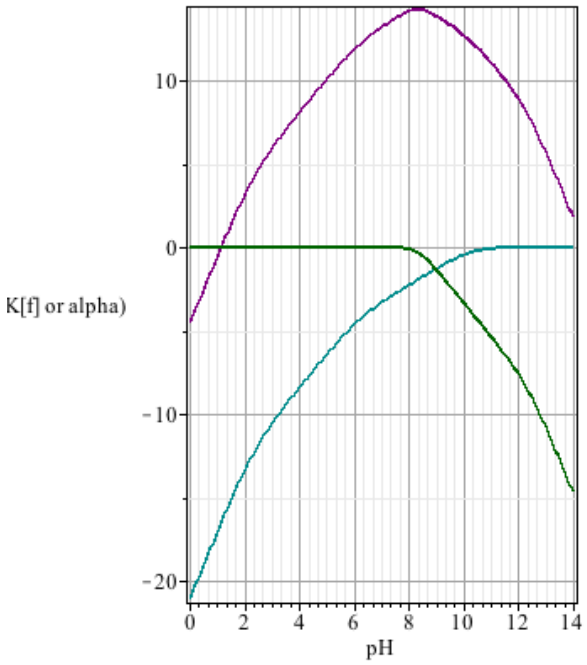

Figure 9-2

The appearance of this figure required some manipulation of the vertical axis through **plot > axes > properties…**

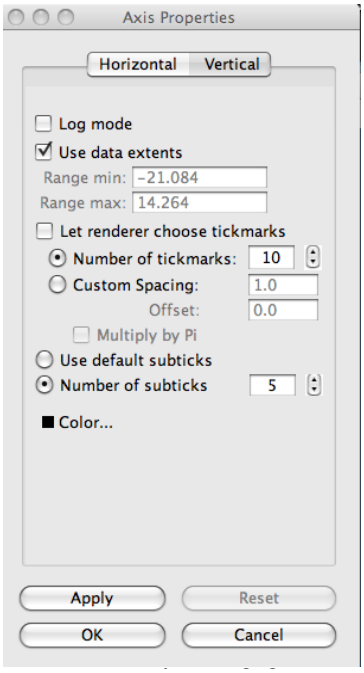

Figure 9-3

The dark cyan line here corresponds to the dark cyan line in Figures **8-6** and **8-8** which also pertain to the protonation of EDTA. The intent of Figure **9-2** is to show that as EDTA is deprotonated at high pH, thereby becoming more available to the Zn^{2+}, the Zn^{2+} (green line) is becoming less available to the EDTA as it binds more and more to the hydroxide ions. The purple line, K''_f is the product[189] of these expressions.

An important question to ask from Figure **9-2** is, what pH range is acceptable for assuring complete binding between Zn^{2+} and EDTA? Recall that "complete" is defined as at least 99.9% (Part I, page 9). So, what is the minimum value for K'_f that will assure ≥ 99.9% for

$$Zn^{2+} + Y^{4-} \rightleftharpoons ZnY^{2-}?$$[190]

To answer this question, the meaning of K''_f should be clarified because it is often misinterpreted. It should be clear that

$$K_f = \frac{[ZnY^{2-}]}{[Zn^{2+}][Y^{4-}]}$$

Also,

$$[Zn^{2+}] = \alpha_{Zn2+} \times (C_{Zn2+} - [ZnY^{2-}])$$

and

$$[Y^{4-}] = \alpha_{Y4-} \times (C_{Y4-} - [ZnY^{2-}]).$$

This might lead one to make the following substitution:

$$K_f = \frac{[ZnY^{2-}]}{\alpha_{Zn2+} X C_{Zn2+} X \alpha_{Y4-} X C_{Y4-}}$$

which would be wrong. Look closely (in the worksheet) at the derivations of α_{Zn2+} (α_m) and α_{Y4-} (α_{Lc}). Neither includes a term for $[ZnY^{2-}]$ (MLc). So neither *completely* considered C_{Zn2+} (C_M) or C_{Y4-} (C_{Lc}); each left out one term, a term that, before the solutions are mixed, cannot exist, but after they mix should be significant! It is not appropriate to multiply an "incomplete" α by a total concentration. When the solutions are mixed, the expressions for $[Zn^{2+}]$ and $[Y^{4-}]$ given above must be modified to compensate for the previously-impossible $[ZnY^{2-}]$.

$$[Zn^{2+}] = \alpha_{Zn2+} \times (C_{Zn2+} - [ZnY^{2-}])$$

and

$$[Y^{4-}] = \alpha_{Y4-} \times (C_{Y4-} - [ZnY^{2-}]).$$

And, now

$$K_f = \frac{[ZnY^{2-}]}{\alpha_{Zn^{2+}} \text{ X } (C_{Zn^{2+}} - [ZnY^{2-}]) \text{ X } \alpha_{Y4-} \text{ X } (C_{Y4-} - [ZnY^{2-}])}$$

Rearranging this gives the appropriate expression for K''_f. That is,

$$K_f'' = \alpha_{Zn^{2+}} \text{ X } \alpha_{Y4-} \text{ X } K_f = \frac{[ZnY^{2-}]}{(C_{Zn^{2+}} - [ZnY^{2-}]) \text{ X } (C_{Y4-} - [ZnY^{2-}])}$$

To answer the question, what K''_f is necessary to assure ≥ 99.9% ZnY^{2-} formation at the equivalence point, first, C_{Zn2+} and C_{Y4-} are made equal because this *is*, by definition, the equivalence point. They are defined as C_{EqPt}, and second $[ZnY^{2-}]$ becomes $0.999C_{EqPt}$ because that represents a 99.9% completion. So,

$$K_f'' \geq \frac{0.999C_{EqPt}}{0.001C_{EqPt} \text{X} 0.001C_{EqPt}} \qquad \textbf{9-3}$$

This shows that to achieve this degree of complexation, a K''_f of at least $10^6/C_{EqPt}$ is required. This is to say that, as the concentration of the titration mixture decreases, a larger and larger formation constant is required to achieve "complete" complex ion formation.[191]

Borrowing from Equation **7-10**:

$$C_{EqPt} = \frac{C°_M \text{ X } C°_{EDTA}}{C°_M + C°_{EDTA}}$$

If one were to attempt a titration of 10^{-3} **M** Zn^{2+} with 10^{-3} **M** EDTA, C_{EqPt} would equal 5×10^{-4} and so K''_f would have to be at least 2×10^9. From Figure **9-2** it is evident that this K''_f can be achieved at a pH greater than 5 but less than 12.

The consequence of operating well outside of the range, say where K''_f is less than 1 ($\log_{10}K''_f < 0$), implies that ZnY^{2-} complex is largely dissociated. This dependence of K''_f on pH can be exploited. Consider the titration of a solution that contains two metals (as ions) and both metals form a complex with a given chelating agent, but with measurably different affinities (different K_fs), or that the two metals have substantially different affinities for OH^- (different β_ns). It might, then, be possible to adjust the pH of the titrand so that, at the equivalence point, one complex "completely" forms while the other is effectively, "completely" dissociated. Completely dissociated, would imply that no more than 0.1% of M^{p+} is associated with Lc^{q-} and likewise no more than 0.1% of Lc^{q-} is associated with M^{p+}. Consequently, at least 99.9% of M^{p+} and Lc^{q-} are free to associate with OH^- and H^+, respectively. Applying these restrictions to $[M^{p+}]$, $[Lc^{q-}]$ and $[MLc^{p-q}]$ gives the largest allowable K''_f that will assure "no" binding between metal and chelate:

$$K_f'' \leq \frac{0.001C_{EqPt}}{0.999C_{EqPt}X0.999C_{EqPt}} \qquad \textbf{9-5}$$

This requires that K''_f must be no greater than $0.001 \div C_{EqPt}$.

For the ZnY^{2-} complex, complete dissociation would be difficult to achieve, even if C_{EqPt} were as small as 10^{-4} **M**. This would require a $K''_f \leq 10$, or $\log_{10}K''_f \leq 1$. Notice, from Figure **9-2**, that this is difficult to achieve, but it is difficult only because the K_f for ZnY^{2-} is so large ($10^{16.50} = 3.2\ 10^{16}$). Problem 2 at the end of this chapter will provide a clearer example of this point.

So far, it has been presumed that K''_f can be adjusted only by protonating Lc^{q-}, or by hydroxylating M^{p+}. There are, however, more effective ways of masking M^{p+} than with OH^-. The most effective way is to add to the solution a second ligand which binds some but not all of the different metal ions in the titrand. Consider for example the titration with EDTA of a solution containing approximately equal concentrations of Ni^{2+} and Pb^{2+}. Both have approximately the same affinity for Y^{4-} and for OH^-. So adjusting the pH will not provide a sufficiently different α_{Ni2+} from α_{Pb2+}. Of course α_{Y2-} would change with changing pH (cyan line, Figure **9-2**) regardless of whether Ni^{2+} or Pb^{2+} is being titrated. However, Pb^{2+} has no appreciable affinity for CN^- while Ni^{2+} has a β_4 of $10^{31.3}$.[192] Providing a C_{CN}- of at least $4\times C_{Ni2+}$ will diminish K''_f for NiY^{2-} to the point that Ni^{2+} is "entirely" unavailable for binding to Y^{4-}.

To demonstrate the effect of cyanide on K''_f for Ni^{2+} and Pb^{2+}, the following worksheet is created. The approach follows that which was used earlier in this chapter. Notice the simple, but important difference in the form of α_{Ni2+} with and without cyanide in solution, and that for some of these full quotations marks are necessary to protect the notation. The `simplify` command is included in the `alpha[…` assignments so that $[Ni^{2+}]$ or $[Pb^{2+}]$ will be factored out of the alpha expressions, directly. For clarity and economy of space, not all of the requested output is provided here; rather, only a few, instructive outputs are provided.

```
> restart; Ni(CN)[4]:= beta['NiCN[4]']*Ni*CN^4; Ni(OH)[1]:=
  beta["Ni(OH)1"]*Ni*OH; Ni(OH)[2]:= beta["Ni(OH)2"]*Ni*OH^2:
  Ni(OH)[3]:= beta["Ni(OH)3"]*Ni*OH^3: Pb(OH)[1]:= beta
  ["Pb(OH)1"]*Pb*OH: Pb(OH)[2]:= beta["Pb(OH)2"]*Pb*OH^2: Pb(OH)
  [3]:= beta["Pb(OH)3"]*Pb*OH^3: alpha['Ni']:= simplify(Ni/ (Ni +
  Ni(CN)[4] + Ni(OH)[1] + Ni(OH)[2] + Ni(OH)[3])); alpha ["Ni no
  CN"]:= simplify(Ni/(Ni + Ni(OH)[1] + Ni(OH)[2] + Ni(OH)[3]));
  alpha['Pb']:= simplify(Pb/(Pb + Pb(OH)[1] + Pb(OH)[2] + Pb(OH)
  [3]));[193]
```

$$\alpha_{\text{"Ni no CN"}} := \frac{1}{1 + \beta_{\text{"Ni(OH)1"}}\, OH + \beta_{\text{"Ni(OH)2"}}\, OH^2 + \beta_{\text{"Ni(OH)3"}}\, OH^3}$$

$$\alpha_{Pb} := \frac{1}{1 + \beta_{\text{"Pb(OH)1"}}\, OH + \beta_{\text{"Pb(OH)2"}}\, OH^2 + \beta_{\text{"Pb(OH)3"}}\, OH^3}$$

In the previous worksheet, OH was replaced with K_w/H and then H was replaced with 10^{-pH}. Here, these steps are combined, and 14 will be used instead of using pK_w. That is, in purely general terms, OH would be $10^{(pH-pKw)}$, but here OH will be replaced with $10^{(pH-14)}$.

```
> alpha['Ni']:= algsubs(OH = 10^(pH-14), alpha['Ni']); alpha["Ni no
  CN"]:= algsubs(OH = 10^(pH-14), alpha["Ni no CN"]); alpha['Pb']:=
  algsubs(OH = 10^(pH -14), alpha['Pb']);
```

$$\alpha_{Ni} := 1 \Big/ \left(1 + \beta_{"Ni(OH)3"} \left(10^{pH-14}\right)^3 + \beta_{"Ni(OH)1"}\, 10^{pH-14} + \beta_{"Ni(OH)2"} \left(10^{pH-14}\right)^2 + \beta_{NiCN_4}\, CN^4\right)$$

The next step is to address the effects of $[H^+]$ on $H^+ + CN^- \rightleftharpoons HCN$ and on $H^+ + Y^{4-} \rightleftharpoons HY^{3-}$ *etc*. The form of α_{CN^-} follows that of Equation **4-21** and α_{Y4-} follows the approach used above but both use 10^{-pH} in place of $[H^+]$.

```
> alpha['CN']:= K[a]/(10^(-pH) + K[a]); alpha['Y4']:= K[a1]
  *K[a2]*K[a3]*K[a4]/(10^(-4*pH) + K[a1]*10^(-3*pH) + K[a1]*K
  [a2]*10^(-2*pH) + K[a1]*K[a2]*K[a3]*10^(-pH) + K[a1]*K[a2]*
  K[a3]*K[a4]);
```

Finally, $[CN^-]$ is calculated for use in α_{Ni2+}, and normally this might follow the discussion on page 56 *et seq*. regarding the calculation of $[L^{q-}]$. But here the problem is simplified in two ways: first, there is effectively only one complex between Ni^{2+} and CN^-, namely $Ni(CN)_4^{2-}$; second, the complex is so stable ($\beta_{Ni(CN)4} = 2.0\ 10^{31}$), that essentially all of the Ni^{2+} will be bound to CN^- *as along as there is enough CN*$^-$. Yes: this is an exercise in circular logic in that we presume that all of the Ni^{2+} is bound to CN^- and *then* we carry out a calculation for α_{Ni2+}, which, by our presumption should be zero. This, however, is an approximation, not a contradiction. The average number of cyanides per Ni^{2+} would be

$$n_{ave} = \frac{4\beta_4[CN^-]^4}{1 + \beta_4[CN^-]^4}$$

The 1 in the numerator is a remnant of $[Ni^{2+}]$ which can been taken as insignificant. Certainly, $1 + \beta_4[CN]^4 \approx \beta_4[CN]^4$ for any measurable concentration of cyanide. That is to say, 1 is insignificant here. For this reason, n_{ave} is taken to be exactly 4. So the concentration of CN^- bound to Ni^{2+} is simply four times the analytical concentration of Ni^{2+}. The total CN^- is the analytical concentration of, say, potassium cyanide, which is the source of CN^- for the titration. Finally, then, the concentration of unbound CN^- is the difference between C_{KCN} and $4\times C_{Ni2+}$. This is multiplied by α_{CN^-} to adjust for the fact that some of this "free" cyanide will be protonated. This is achieved as follows, showing only the α_{Ni} which addresses the three hydroxy forms of Ni^{2+} along with the tetracyano and the free forms.

```
> CN:= alpha['CN']*(C[KCN] - 4*C ['Ni']); 'alpha['Ni']'=
  alpha['Ni'];
```

$$\alpha_{'Ni'} = 1 \Big/ \left(1 + \beta_{"Ni(OH)3"} \left(10^{pH-14}\right)^3 + \beta_{"Ni(OH)1"}\, 10^{pH-14} + \beta_{"Ni(OH)2"} \left(10^{pH-14}\right)^2 + \frac{\beta_{NiCN_4} K_a^4 \left(C_{KCN} - 4\, C_{Ni}\right)^4}{\left(10^{-pH} + K_a\right)^4} \right)$$

α_{Ni2+} shown in order to illustrate its dependence on C_{KCN} and C_{Ni2+}.[194]

Finally, all of the parameters can be assigned. The C_{Ni2+} and C_{Pb2+} are given values that are equal as prescribed in the premise of the problem and C_{KCN} is made greater than $4\times C_{Ni2+}$ as required for the "$n_{ave} = 4$" presumption.

```
> beta[NiCN[4]]:= 10^31.3; beta["Ni(OH)1"]:= 10^4.97;
  beta["Ni(OH)2"]:= 10^8.55; beta["Ni(OH)3"]:= 10^11.33;
  beta["Pb(OH)1"]:= 10^7.82; beta["Pb(OH)2"]:= 10^10.85;
  beta["Pb(OH)3"]:= 10^14.58; K[a]:= 6.2e-10; C['Pb']:= 0.01;
  C['Ni']:= 0.01; C[KCN]:= 0.05; K[a1]:= 10^(-1.99); K[a2]:=
  10^(-2.67); K[a3]:= 10^(-6.16); K[a4]:= 10^(-10.26); K[Ni,f]:=
  10^18.62; K[Pb,f]:= 10^18.04;
```

The values for K''_f will vary over several orders of magnitude when the pH is increased from 0 to 14. So it is prudent to express these constants logarithmically. Expressing these in simple terms:

```
> L['NiCN']:= log[10](alpha['Ni']*alpha['Y4']*K[Ni,f]): L['Ni']:=
log[10](alpha["Ni no CN"]*alpha['Y4']*K[Ni,f]): L['Pb']:= log[10](al
pha['Pb']*alpha['Y4']*K[Pb,f]):
> plot([L['Ni'], L['NiCN'],L ['Pb']],pH= 0..14,labels=
["-log[H+]","log(Kf'')"], color = [magenta, navy, "DarkOrange"],
axes = box);
```

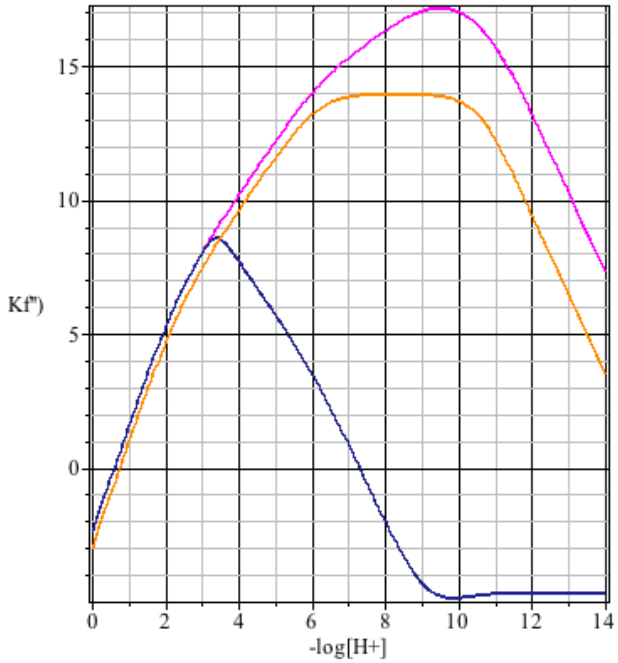

Figure 9-4

In order to complex Ni^{2+} "completely" without at all complexing the Pb^{2+}, a pH must be found where $K''_{Pb,f}$ (dark orange) is less than $0.001/C_{Pb2+}$ while $K''_{Ni,f}$ (magenta) is greater than $10^6/C_{Ni2+}$. So if either C is taken to be, say 0.01 **M**, then we ask, is $K''_{Pb,f}$ ever less than 0.1 ($\log_{10} K''_{Pb,f}$ = *minus* 1) where, at the same pH, $K''_{Ni,f}$ is greater than 10^8? Never. Notice that the three K''_fs are nearly identical when -log[H^+] is less than 4; this means that the titrations are indistinguishable there; it means that CN^- has no effect on Ni^{2+} until pH > 3. And without cyanide in solution, the conditional formation constants for Ni^{2+} and Pb^{2+} (dark orange and magenta) never diverge enough to make a selective titration possible, at *any* $C_{Ni2+} = C_{Pb2+}$. The presence of an appreciable CN^- concentration at pH >8, however, so diminishes $K''_{Ni,f}$ (navy) that Ni^{2+} is invisible to EDTA. Indeed, at pH 8 one would expect nearly optimal binding between Pb^{2+} and Y^{4-} and insignificant binding between Ni^{2+} and Y^{4-}.

Control of K''_f is critical to regulating the composition of a solution at the equivalence point. But what is the makeup of a solution before and after this equivalence point? The composition of a solution throughout the addition of a chelating agent to a metal ion solution (or visa versa) is described with a titration plot, exactly as it was demonstrated in Chapter 7. *Minus* $\log_{10}M^{p+}$ is followed rather than pH, and K''_f is used in place of K_{an}. Because ionic strength effects are disregarded in these titrations, K''_f, unlike K_{an}, is taken to be constant throughout the titration. But inasmuch as K''_f varies as solution conditions vary, it is imperative that the solution be buffered, and if a masking agent (like CN^-) is used, the concentration of that agent must be stabilized to simplify the calculations and to assure consistent masking. To that end, it is wise to buffer both the titrand and titrant, and to add the masking agent, in the same concentration, to both the titrand and titrant.

As an example of this, a simple complexometric (chelomteric) titration will be monitored for the titration of 0.010 **M** Cu^{2+} with 0.015 **M** nitrilotriacetic acid (NTA). NTA is triprotic acid that forms a 1:1[195] complex with Cu^{2+} and because it is a weak acid, its α_{NTA3-} is affected by pH. Cu^{2+} forms four, hydroxy complexes. So α_{Cu2+} is also affected by pH. It is necessary, therefore, to begin the analysis by selecting a pH that will provide a $K''_f \geq 10^6/C_{EqPt}$. For this part of the exercise, only the input and final output are provided. Then, the process of creating a titration plot is addressed with greater detail.

```
> restart; alpha[NTA3]:= K[a1]*K[a2]*K[a3]/(10^(-3*pH) +
  K[a1]*10^(-2*pH) + K[a1]*K[a2]*10^(-pH) + K[a1]*K[a2]*K[a3]);
  alpha['Cu']:= 1/(1 + beta[1]*OH + beta[2]*OH^2 + beta[3]*OH^3
  + beta[4]*OH^4); alpha['Cu']:= algsubs(OH = 10^(pH-14),
  alpha['Cu']);
```

All constants are then assigned.

```
> K[a1]:= 10^(-1.65): K[a2]:= 10^(-2.94): K[a3]:= 10^(-10.33);
  beta[1]:= 10^7.00: beta [2]:= 10^13.68: beta[3]:= 10^17.00:
  beta[4]:= 10^18.5:
```

and then a new metric is defined to find the optimum condition. When $\alpha_{NTA} \times \alpha_{Cu2+}$ reaches a maximum, $K''_{f,CuNTA}$ reaches a maximum.

```
> condition:= alpha['Cu']*alpha[NTA3];
```

$$condition := (1.202\ 10^{-15}) \Big/ ((1 + 3.162\ 10^{18}\ (10^{pH} - 14)^4 + 4.786\ 10^{13}\ (10^{pH} - 14)^2 + 1.000\ 10^{17}\ (10^{pH} - 14)^3 + 1.000\ 10^{7}\ 10^{pH} - 14)\ (10^{-3\,pH} - 0.022\ 10^{-2\,pH} + 0.000\ 10^{-pH} + 1.202\ 10^{-15}))$$

We find that maximum (or minimum) at $^{dCondition}/_{dpH} = 0$. So,

```
> optimum:= diff(condition,pH); pH['optimum']:= fsolve(optimum = 0,
pH, 0..14);
```

$$pH_{optimum} := 7.159$$

This value can be assigned to the pH which will then be used to calculate each alpha, `condition`, and K''_f. The output formatting for the alphas is altered for future use (page 77).

```
> pH:= pH['optimum']; 'alpha ['Cu']'= alpha['Cu']; 'alpha [NTA3]'=
  alpha [NTA3]; 'condition'= condition; K[f]:= 10^ 13.10;
  Kpp[f]:=condition* K[f];
```

$$pH := 7.159$$
$$a_{'Cu'} = 2.906\ 10^{-1}$$
$$a_{NTA3} = 6.746\ 10^{-4}$$
$$condition = 0.000196$$
$$K_f := 1.259\ 10^{13}$$
$$Kpp_f := 2.468\ 10^{9}$$

K''_f is calculated in order to ascertain that the CuNTA complex will be sufficiently stable that ≥99.9% of the Cu^{2+} will be complexed at the equivalence point. Applying Equation **9-4** with $C°_{Cu2+} = 0.010$ **M** and $C°_{NTA} = 0.015$ **M** gives $C_{EqPt} = 0.0060$ **M**. The criterion from Equation **9-3** would require $K''_f \geq 10^6/0.0060 = 1.7\ 10^8$. At pH 7.16, $Kpp_f = 2.468\ 10^9$, is more than good enough!

The expression that provides $[Cu^{2+}]$ as a function of V_{NTA} is derived from mass balance and equilibrium requirements, but does not need charge balance considerations. After beginning the titration, there are three kinds of copper in solution: free Cu^{2+}, copper bound to NTA, and copper bound to at least one hydroxide. So C_{Cu2+} must be the sum of the concentrations of these three forms of copper. The free copper and copper bound to NTA concentrations are simply $[Cu^{2+}]$ and [CuNTA], represented as `Cu2` and `CuNTA`, respectively. *Before*, the solutions are mixed,

$$[Cu^{2+}] = \alpha_{Cu2+} \times C_{Cu2+},$$

and from the definition of α_{Cu2+}, it follows that the remaining forms of copper would be:

$$\Sigma[Cu(OH)_n^{2-n}] = (1 - \alpha_{Cu2+}) \times C_{Cu2+}.$$

Recalling the discussion on page 67, *after* the solutions are mixed, *i.e.* during the titration, a new form of copper appears, and α_{Cu2+} can no longer be applied to C_{Cu2+}; the concentration of that new form must be subtracted from C_{Cu2+}. This gives:

$$\Sigma[Cu(OH)_n^{2-n}] = (1 - \alpha_{Cu}^{2+}) \times (C_{Cu}^{2+} - [CuNTA])$$

On the Maple worksheet, this is carried out *after* a restart command so that the form of the following expressions is evident. Otherwise, the values assigned to α_{Cu2+}, K_f *etc.* would be incorporated in the derivation, and the structure of the mass balance expression would not be clear. Alternatively, of course, each parameter could have been unassigned.

```
> restart; MassBal:= C['Cu'] = Cu2+CuNTA + (1 - alpha['Cu'])*
  (C['Cu'] - CuNTA);
```

$$MassBal := C_{Cu} = Cu2 + CuNTA + (1 - \alpha_{Cu})\,(C_{Cu} - CuNTA)$$

[CuNTA] can be extracted from the equilibrium expression for K_f (not K''_f).

$$K_f = \frac{[CuNTA^-]}{[Cu^{2+}][NTA^{3-}]}$$

[NTA^{3-}] can be expressed as $\alpha_{NTA3} \times (C_{NTA} - [CuNTA])$.[196]

```
> CuNTA:= solve(K[f]= CuNTA/(Cu2*alpha[NTA3]*(C[NTA] - CuNTA)),
  CuNTA);
```

$$CuNTA := \frac{K_f Cu2\, \alpha_{NTA3}\, C_{NTA}}{K_f Cu2\, \alpha_{NTA3} + 1}$$

This will be substituted into the mass balance expression.

```
> MassBal;
```

$$C_{Cu} = Cu2 + \frac{K_f Cu2\, \alpha_{NTA3}\, C_{NTA}}{K_f Cu2\, \alpha_{NTA3} + 1} + \left(1 - \alpha_{Cu}\right)\left(C_{Cu} - \frac{K_f Cu2\, \alpha_{NTA3}\, C_{NTA}}{K_f Cu2\, \alpha_{NTA3} + 1}\right)$$

Solving this expression for [Cu^{2+}] will produce two roots. So the solutions will be listed by using braces around Cu2.

```
> Copper:= solve(MassBal, {Cu2});
```

$$Copper := \left\{Cu2 = \frac{1}{2}\frac{1}{K_f \alpha_{NTA3}}\left(-\alpha_{Cu} K_f \alpha_{NTA3} C_{NTA} - 1 + \alpha_{Cu} C_{Cu} K_f \alpha_{NTA3} + \left(\alpha_{Cu}^2 K_f^2 \alpha_{NTA3}^2 C_{NTA}^2 + 2\,\alpha_{Cu} K_f \alpha_{NTA3} C_{NTA} - 2\,\alpha_{Cu}^2 K_f^2 \alpha_{NTA3}^2 C_{NTA} C_{Cu} + 1 + 2\,\alpha_{Cu} C_{Cu} K_f \alpha_{NTA3} + \alpha_{Cu}^2 C_{Cu}^2 K_f^2 \alpha_{NTA3}^2\right)^{1/2}\right)\right\}, \left\{Cu2 =\right.$$

$$-\frac{1}{2}\frac{1}{K_f\alpha_{NTA3}}\left(\alpha_{Cu}K_f\alpha_{NTA3}C_{NTA}+1\right.$$
$$-\alpha_{Cu}C_{Cu}K_f\alpha_{NTA3}$$
$$+\left(\alpha_{Cu}^2K_f^2\alpha_{NTA3}^2C_{NTA}^2+2\alpha_{Cu}K_f\alpha_{NTA3}C_{NTA}\right.$$
$$-2\alpha_{Cu}^2K_f^2\alpha_{NTA3}^2C_{NTA}C_{Cu}+1+2\alpha_{Cu}C_{Cu}K_f\alpha_{NTA3}+$$
$$\left.\left.\alpha_{Cu}^2C_{Cu}^2K_f^2\alpha_{NTA3}^2\right)^{1/2}\right)\Big\}$$

The first root given is the logical (physically possible, *i.e.* $Cu^{2+} \geq 0$) solution because of its (not-at-all evident) "*+sqrt*" term. It is selected.

```
> Cu[titration]:= subs(Copper [1], Cu2);
```

$Cu_{titration}$ represents [Cu^{2+}] as a function of the two alphas, K_f C_{NTA} and C_{Cu2+}. The expression contains K_f, rather than K''_f, but closer examination shows that each K_f is multiplied by α_{Cu2+} and α_{NTA3-}, which *is* K''_f. The way this is written above allows one to ignore the previous calculation for K''_f and use any legitimate α_{Cu2+} and any α_{NTA3-}, but because the pH of the solution is the same for Cu^{2+} as it is for the NTA, these alphas are linked to each other. A given value for α_{Cu2+} implies a specific pH, and that pH mandates a specific α_{NTA3-}. The values for α_{Cu2+} and α_{NTA3-} (page 74) are cut from the previous worksheet and pasted into the next line. Not only are these appropriately paired, their product (at *condition*) is the maximum possible product. And so, effectively, K''_f is used here, and it is the maximum K''_f. All other parameters are assigned and finally, C_{Cu2+} and C_{NTA} are expressed in terms of their respective C° and V° or V. Cu[titration]; is called (and shown to three decimal places) to ascertain that V_{NTA} is the only remaining parameter.

```
> alpha['Cu']:= 2.9061E-1; alpha[NTA3]:= 6.746E-4; K[f]:= 10^13.10;
  V°['Cu']:= 25.0; C°['Cu']:= 0.010; C°[NTA]:= 0.015; C['Cu']:=
  V°['Cu']*C°['Cu']/(V°['Cu'] + V[NTA]); C[NTA]:= V[NTA]*C°[NTA]/
  (V°['Cu'] + V[NTA]);'Cu[titration]' = Cu [titration];
```

$$Cu_{titration} = -\frac{0.002\ V_{NTA}}{25.000 + V_{NTA}} - 5.887\ 10^{-11} + \frac{0.036}{25.000 + V_{NTA}}$$
$$+ 5.887\ 10^{-11} \left(\frac{1.371\ 10^{15}\ V_{NTA}^2}{\left(25.000 + V_{NTA}\right)^2} + \frac{7.404\ 10^{7}\ V_{NTA}}{25.000 + V_{NTA}} \right.$$
$$- \frac{4.569\ 10^{16}\ V_{NTA}}{\left(25.000 + V_{NTA}\right)^2} + 1 + \frac{1.234\ 10^{9}}{25.000 + V_{NTA}}$$
$$\left. + \frac{3.807\ 10^{17}}{\left(25.000 + V_{NTA}\right)^2} \right)^{1/2}$$

Because $[Cu^{2+}]$ will decrease by orders of magnitude as NTA is added (and as $CuNTA^{1-}$ is formed), it will be plotted logarithmically, just as one would plot $[H^+]$ in an acid / base titration. Given that $V°_{Cu2+}$ = 25.0 mL, $C°_{Cu2+}$ = 0.010 **M** and $C°_{NTA}$ = 0.015 **M**, $V_{NTA,EqPt}$ can be shown[197] to be 16.7 mL. So varying V_{NTA} from 0 to 20 mL should provide a full titration plot.

```
> pCu := -log[10](Cu[titration]): plot(pCu, V[NTA] = 0..20, labels
  = ["mL of NTA","-log[Cu2+]"], axes = boxed);
```

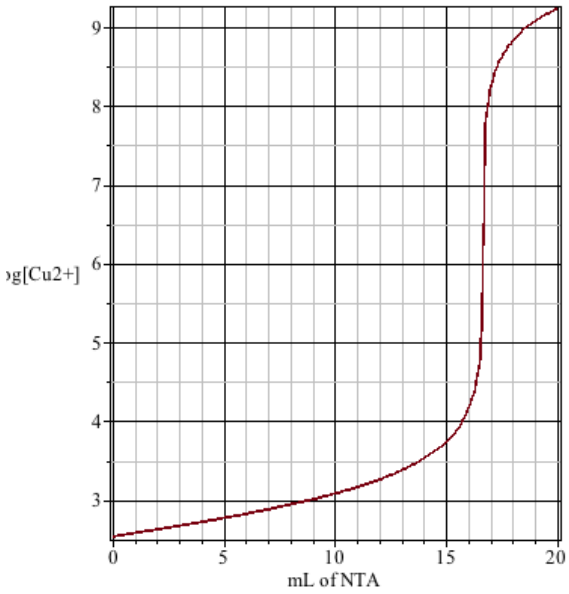

Figure 9-5

Like the acid / base titration, the equivalence point is characterized by a dramatic change in the concentration of the titrand. Both pH and chelometric titrations can be monitored potentiometrically; that is by monitoring the potential at an indicating electrode as titrant is added. The electrode voltage will change linearly with the $\log\{H^+\}$ or with $\log\{M^{p+}\}$. For the Cu^{2+} / NTA titration described here, there would remain the matter of converting the $[Cu^{2+}]$ to its activity, $\{Cu^{2+}\}$, and that would require γ_{Cu2+} which would, in turn, require a calculation of μ at each incremental change in V_{NTA}.[198] This exercise is unimportant because $-\log_{10}\{Cu^{2+}\}$, like $-\log_{10}[Cu^{2+}]$ will change dramatically at the equivalence point as long as K''_f is at least $10^6/C_{EqPt}$. So either measure, concentration or activity, will reveal V_{EqPt}.

Also, like the acid / base titration, the equivalence point can be identified by using an indicator. Instead of using the $HIn \rightleftharpoons H^+ + In^-$ equilibration (Part I, page 169), a metallochrome indicator is used. These exploit the $MIn^{p-r} \rightleftharpoons M^{p+} + In^{r-}$ equilibration. Such indicators are, themselves, weak acids and consequently their behavior toward M^{p+} is affected by the pH of the solution in which they are used. That is, α_{Inr-} must be taken into consideration. α_{Inr-} takes the form that would be found for any polyprotic acid as described in Chapter 8 (page 11).

The complexometric titration using a metallochrome indicator entails competition between the chelating ligand, Lc^{q-} and In^{r-} for the metal ion M^{p+}. Of course, as discussed earlier and again here, H^+ competes with M^{p+} for Lc^{q-} and In^{r-}. At the equivalence point, it is expected that 99.9% of Lc^{q-} has bound to M^{p+}. Recalling the behavior of acid / base indicators, it is expected that the concentration of one form of the indicator (MIn^{p-r} or In^{r-}) would be ten times the concentration of the other form so that one of the two colors clearly dominates. Usually, the titrand contains the M^{p+} and the titrant provides the Lc^{q-}.[199] In this case, the titrand contains M^{p+} along with MIn^{p-r}. As Lc^{q-} is added, it first binds to the more labile, free M^{p+}, but as the supply of free M^{p+} is depleted, then

$$Lc^{q-} + MIn^{p-r} \rightleftharpoons In^{r-} + MLc^{p-q}.$$

The endpoint would coincide with point at which $[In^{r-}]$ reaches $10\times[MIn^{p-r}]$. Given that,

$$K_{f,In} = \frac{[MIn^{p-r}]}{[M^{p+}][In^{r-}]}$$

what, then, is the necessary relationship between K_f and $K_{f,In}$ to achieve this distribution of $[M^{p+}]$, $[MLc^{p-q}]$, $[MIn^{p-r}]$, and $[In^{r-}]$? There is a simple approach to this question that follows from

$$K_f = \frac{[ML^{p-q}]}{[M^{p+}][L^{q-}]}$$

Solving this for $[M^{p+}]$ gives:

$$[M^{p+}] = \frac{[ML^{p-q}]}{K_f X\ L^{q-}]}$$

and substituting this back into the expression for $K_{f,In}$ produces

$$K_{f,In} = \frac{[MIn^{p-r}]\ X\ K_f\ X\ [Lc^{q-}]}{[In^{r-}]\ X\ [MLc^{p-q}]}$$

which provides the relationship between $K_{f,In}$ and K_f. At the equivalence point, recall the expectation that $[MLc^{p-r}]$ is 1000 times larger than $[Lc^{r-}]$ (hence 99.9% association) and that $[In^{r-}]$ is 10 times larger than $[MIn^{p-r}]$ (hence the dominance of its color). Making these substitutions gives:

$$K_{f,In} = {}^{K_f}/_{10,000}.$$

This is a generally accepted rule of thumb,[200] but it cannot be complete in that it ignores α_{Lcq-} and α_{Inr-} which change *differently* with pH, and it ignores any dependence on $C_{Indicator}$ and $C_{Chelate}$, which are sure to influence the distribution of $[M^{p+}]$, $[MLc^{p-q}]$, $[MIn^{p-r}]$, and $[In^{r-}]$.[201] Reilley and Schmid[202] have addressed the problem of indicator choice and concentration but at a level beyond what is appropriate here.

A very different approach to indicator selection is presented here: rather than calculating an ideal $K_{f,In}$, and using that $K_{f,In}$ to choose an indicator, an indicator is chosen and its suitability is checked. This is a practical approach because there is a considerable literature on metallochrome indicators and the metal ions for which they are applicable (*e.g.* Appendix VIb). Moreover, this approach can provide insight into the way that the indicator behaves. That is, it can reveal which form or forms (H_nIn^{n-r}) of the indicator participate in the color change at the endpoint. This indicator evaluation process will be demonstrated by returning to the Cu^{2+} / NTA titration and evaluating 4-(2-pyridylazo)resorcinol (known also as PAR) as an indicator for detecting the equivalence point.

A triprotic acid like PAR is expected to have four congeners, H_nPAR,[203] with n equals 0 to 3, but in the presence of a copper ion to which it can complex, there is a fifth form, CuPAR. The expression for any one of its five alphas is a simple modification of the process described on page 11: but the denominator requires one more term, namely [CuPAR]. The [CuPAR] component can be expressed in terms of $K_{f,In}$, $[Cu^{2+}]$ and $[PAR^{3-}]$ by modifying the expression for $K_{f,In}$ above. That is,

$$\alpha_{CuPAR} = \frac{[CuPAR]}{[H_3PAR] + \ldots + [PAR] + [CuPAR]} = \frac{K_{f,In}[Cu][PAR]}{[H_3PAR] + \ldots + [PAR] + K_{f,In}[Cu][PAR]}$$

Then using substitutions like $[H_3PAR] = [H^+]^3[PAR]/K_{a1}K_{a2}K_{a3}$ and $[HPAR] = [H^+][PAR]/K_{a3}$ produces expressions for alpha in terms of $[H^+]$, $[Cu^{2+}]$ and the four equilibrium constants; [PAR] cancels out giving,

$$\alpha_{CuPAR} = \frac{K_{f,In}[Cu]K_{a1}K_{a2}K_{a3}}{[[H^+]^3 + \ldots + K_{a1}K_{a2}K_{a3} + K_{f,In}[Cu][K_{a1}K_{a2}K_{a3}}$$

which can be adjusted to give any of the five alphas simply by replacing the term in the numerator with the appropriate term from the denominator (again, as on page 11). Notice that when $[Cu^{2+}]$ equals zero the $K_{f,In}\times[Cu^{2+}]\times K_{a1}\times K_{a2}\times K_{a3}$ term will equal zero. Not only does this make α_{CuPAR}- equal zero, but it simplifies all other alphas to their "Chapter 8 form."

Continuing from the >plot command on page 79, the expressions for three (of the four) forms of PAR are derived. These are H_2PAR^{1-}, $HPAR^{2-}$, PAR^{3-} and of course $CuPAR^{-}$. All five might have been articulated, but given the pH of this titration, H_3PAR not likely to be a factor. (See page 84.)

```
> Den:= 10^(-3*pH) + K[a1]*10^(-2*pH) + K[a1]*K[a2]*10^(-pH) + K
  [a1]*K[a2]*K[a3] + K[f,In]*Cu2*K[a1]*K[a2]*K[a3]: alpha [H2PAR]:=
  op(2,Den)/Den; alpha[HPAR2]:= op(3,Den)/Den; alpha[PAR3]:=
  op(4,Den)/Den; alpha[CuPAR]:= op(5,Den)/Den;
```

$$\alpha_{CuPAR} := \left(K_{f,\,In}\, Cu2\, K_{a1} K_{a2} K_{a3}\right) \Big/ \left(10^{-3\,pH} + K_{a1}\, 10^{-2\,pH} + K_{a1} K_{a2}\, 10^{-pH} + K_{a1} K_{a2} K_{a3} + K_{f,\,In}\, Cu2\, K_{a1} K_{a2} K_{a3}\right)$$

Only a_{CuPAR} is shown. Its similarity to the expression in the previous paragraph is made apparent by using *Cu2* in place of $Cu_{titration}$. Recall that $Cu_{titration}$ is the expression for $[Cu^{2+}]$ that is written in terms of $C°_{NTA}$, V_{NTA}, $C°_{Cu}$ and $V°_{Cu}$. *Cu2* will be replaced with $Cu_{titration}$ presently, but first, all of the parameters will be assigned their values from Appendix VIb and then each alpha will be checked to see that it is a function of only *Cu2*. It might seem strange that we are assigning a value to the pH here, *after* we have created a titration plot that strongly depends on pH, but recall, we had effectively assigned the pH by assigning alpha['Cu'] and alpha[NTA3] which were determined from the same pH that is assigned here. The values are not shown, but should be inspected for errors.

```
> K[a1]:= 10^(-2.30); K[a2]:= 10^(-6.95); K[a3]:= 10^(-12.4);
  K[f,In]:= 10^10.3; pH := 7.1594;
```

We might now inspect the new alphas for their *exclusive* dependence on $[Cu^{2+}]$:

```
> 'alpha[H2PAR]'= alpha [H2PAR]; 'alpha[HPAR2]'=alpha[HPAR2];
  'alpha[PAR3]'= alpha [PAR3]; 'alpha[CuPAR]'= alpha[CuPAR];
```

$$\alpha_{H2PAR} = \frac{2.405\ 10^{-17}}{6.301\ 10^{-17} + 4.467\ 10^{-12}\ Cu2}$$

$$\alpha_{HPAR2} = \frac{3.896\ 10^{-17}}{6.301\ 10^{-17} + 4.467\ 10^{-12}\ Cu2}$$

$$\alpha_{PAR3} = \frac{2.239\ 10^{-22}}{6.301\ 10^{-17} + 4.467\ 10^{-12}\ Cu2}$$

$$\alpha_{CuPAR} = \frac{4.467\ 10^{-12}\ Cu2}{6.301\ 10^{-17} + 4.467\ 10^{-12}\ Cu2}$$

And now, *Cu2* can be replaced with the expression that will provide V_{NTA} dependence. The resulting expressions are too long to display and too complicated inspect reliably.

```
> alpha[H2PAR]:= algsubs(Cu2 = Cu[titration], alpha[H2PAR]):
  alpha[HPAR2]:= algsubs(Cu2 = Cu[titration], alpha[HPAR2]):
  alpha[PAR3]:= algsubs(Cu2 = Cu[titration], alpha[PAR3]):
  alpha[CuPAR]:= algsubs(Cu2 = Cu[titration], alpha[CuPAR]):
```

Logarithmic conversions are made, which also are too complex for a useful display.

```
> p_alpha[H2PAR]:= -log[10](alpha[H2PAR]): p_alpha[HPAR2]:= -log[10]
  (alpha[HPAR2]): p_alpha[PAR3]:= -log[10](alpha[PAR3]): p_
  alpha[CuPAR]:= -log[10](alpha[CuPAR]):
```

Along with the plot of these four alphas, the originally plotted pCu (again in red) is included so that comparison to the equivalence point is clear. It shows that a rapid change in $p\alpha_{CuPAR}$ coincides with the 16.67 mL equivalence point where $[Cu^{2+}]$ is shown to change rapidly.

The plot also shows that after the equivalence point, it is the $HPAR^{2-}$ that dominates the solution, and so it is likely that the color transition one sees is due to a $CuPAR^{-} \longrightarrow HPAR^{2-}$ transition.[204] It also shows that that H_2PAR^{-} is the next most abundant congener, and therefore, it probably makes a considerable contribution to the color of the titrand, *after* the equivalence point.

```
> plot([pCu, p_alpha[H2PAR], p_alpha[HPAR2], p_alpha [PAR3], p_
  alpha[CuPAR]], V[NTA] = 0..20, color = [red, black, blue, green,
  "Purple"], labels = ["mL of NTA","-log "],axes = boxed);
```

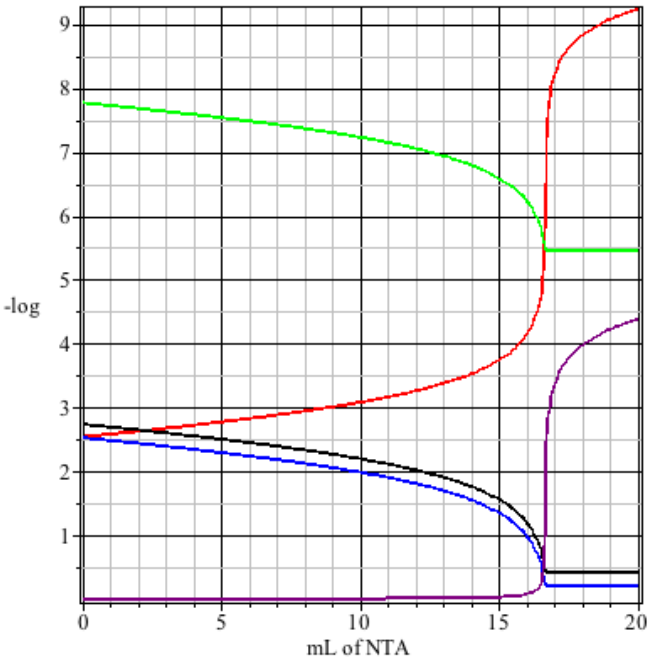

Figure 9-6

Let's take a closer look at the congeners of the indicator, at the equivalence point and 0.1% before and 0.1% after the equivalence point. At the equivalence point:

```
> V[NTA]:= V°['Cu']*C°['Cu']/C°[NTA]; alpha[HPAR2[EqPt]]:=
  alpha[HPAR2]; alpha[PAR3[EqPt]]:= alpha[PAR3]; alpha
  [CuPAR[EqPt]]:= alpha[CuPAR];
```

before the equivalence point:

```
> V[NTA]:= 0.999*V[NTA]; alpha[HPAR2[Early]]:= alpha [HPAR2];
  alpha[PAR3[Early]] := alpha[PAR3]; alpha[CuPAR[Early]]:=
  alpha[CuPAR];
```

and after the equivalence point:

```
> V[NTA]:= 1.001*V°['Cu']*C°['Cu']/C°[NTA]; alpha[HPAR2[Late]]:=
  alpha[HPAR2]; alpha[PAR3[Late]]:= alpha[PAR3];
  alpha[CuPAR[Late]]:= alpha[CuPAR];
```

	0.1% Early	At the Eq. Pt.	0.1% Late
V_{NTA}	16.65	16.67	16.68
$\alpha_{H2PAR1-}$	0.3374	0.3699	0.3788
α_{HPAR2-}	0.5464	0.5990	0.6134
α_{PAR3-}	$3.14\ 10^{-6}$	$3.44\ 10^{-6}$	$3.53\ 10^{-6}$
$\alpha_{CuPAR1-}$	0.1162	0.0311	0.0078

Under these conditions there is only a trace of PAR^{3-}. This is due to the relatively low pH of the titrand; we would have done as well to ignore this congener as we were to ignore H_3PAR.

The key to finding a suitable indicator is finding a substantial $^{\Delta p\alpha}/_{\Delta V}$ at the equivalence point, not as an absolute $\Delta p\alpha$ but as a *relative* change. In absolute terms $p\alpha_{H2PAR1-}$ and $p\alpha_{HPAR2-}$ change the most, but the color of a solution that has, for example, 34% of the indicator in the H_2PAR^{1-} form before and 38% after the equivalence point is not likely to be remarkable, But a change from 12% $CuPAR^{-1}$ to 0.8% is likely to be appreciable.

Recall that on page 75 we found the optimum pH for the titration of Cu^{2+} with NTA^{3-} and that this optimum pH produced a $K''_f = 2.5\ 10^9$, and that we require only $K''_f \geq 1.7\ 10^8$ to achieve a good equivalence point. This means that we could adjust the pH and diminish the K''_f as we attempt to alter $\alpha_{CuPAR1-}$. Suppose that we move to a higher pH where more PAR^{3-} is likely but because of $Cu(OH)_n^{2-n}$, there is less Cu^{2+} to bind. It can be shown that at pH 8.5, for example:[205]

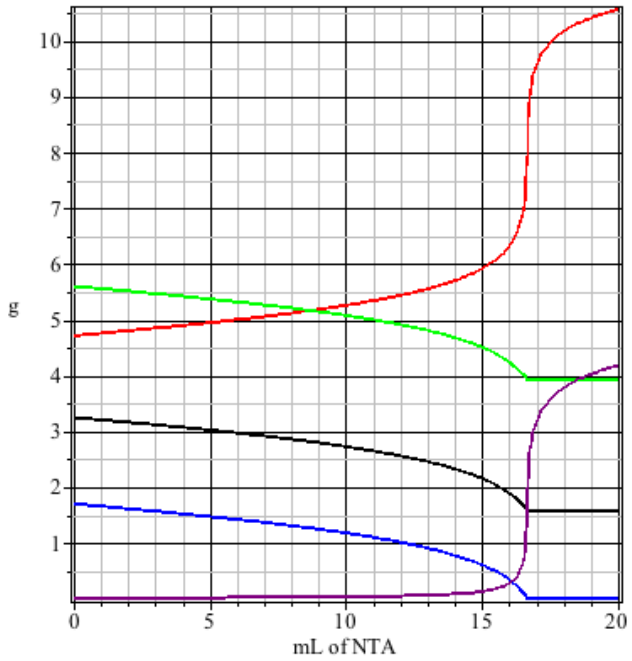

Figure 9-7

Is this an improvement over what is shown in Figure **9-6**? Clearly ΔpCu^{2+} at the equivalence point has been diminished; that was expected because at the higher pH, there is less free Cu^{2+} throughout the titration, and as predicted, there is less H_2PAR^- and more $HPAR^{2-}$ at this higher pH. The color of the solution is dominated by $CuPAR^{1-}$ *well* before the equivalence point and $HPAR^{2-}$ *well* after the equivalence point.

	0.1% Early	At the Eq. Pt.	0.1% Late
V_{NTA}	16.65	16.67	16.68
$\alpha_{H2PAR1-}$	0.0264	0.0269	0.0271
α_{HPAR2-}	0.9365	0.9539	0.9629
α_{PAR3-}	$1.18\ 10^{-4}$	$1.20\ 10^{-4}$	$1.21\ 10^{-4}$
$\alpha_{CuPAR1-}$	0.0370	0.0191	0.0098

The important observation is the magnitude of $^{\Delta p\alpha}/_{\Delta V}$ for $CuPAR^{1-}$ which has clearly been diminished at this pH. Not only has the relative change been mitigated, the absolute value of this alpha has been diminished. So the contribution by $CuPAR^{1-}$ to the solution's color will be considerably smaller and so its color change will be more difficult to perceive. Lowering the pH to 6.5 gives:

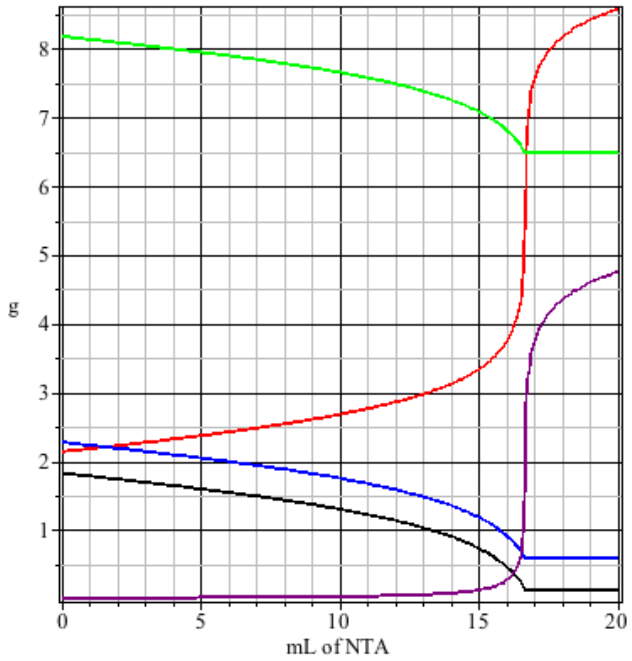

Figure 9-8

This plot shows that the solution color is again dominated by $CuPAR^{-1}$ up to the equivalence point, that $\alpha_{CuPAR1-}$ drops even more precipitously at this lower pH, and that it is H_2PAR^- that replaces $CuPAR^{-1}$ at the equivalence point. This implies a different color change than what is seen at pH 7.16. (**Fig. 9-6**)

$C_{Indicator}$ has not been considered, but it is important for three reasons. First, if $C_{Indicator}$ is too large it can cause a titration error,[202] and second, if it is too large it can become difficult to achieve a large α_{MInp-r} because there is simply not enough M^{p+} in solution to "metallize" enough In^{r-}.[206] Third, if $C_{Indicator}$ is too small, there might be insufficient coloration of the titrand to perceive the endpoint. The third concern is minor because all metallochrome indicators of note are intensely colored and that allows one to use minute concentrations, on the order of 10^{-5} **M**. Only enough indicator should be added to make the titrand color just perceptible. The consequence of too little indicator is obvious, not enough color; the effect too much indicator is often not apparent, but can cause a serious error.

Also omitted from discussion is the issue of kinetics. Every reaction considered came with the presumption of rapid equilibration, but all reactions are not fast. Indeed, some metal ions react so slowly with some chelons that a titration is impractical, and some metals dissociate from indicator complexes so slowly that an endpoint for the titration is not seen. Either of these problems can be circumvented by means of a back titration. In a back titration, a known amount of chelating agent is added, in *excess*, to a metal ion solution. After the M^{p+} / Lc^{q-} or M^{p+} / In^{n-} reaction has reached completion, the excess Lc^{q-} is determined by titration with a *different* metal ion. A back titration problem is included in the Example Problems in this chapter.

What is presented in this chapter should enable the reader to address a wide range of problems in complexometric equilibrium. But for brevity, some other issues have been omitted. For example, some chelating agents form two complexes with metal ions: they form a protonated complex, $HMLc^{1+p-q}$, as well as a non protonated complex MLc^{p-q}. This serves to enhance the effectiveness of this chelon, especially at a pH where protonation can impair the formation of MLc^{p-q}.

Example Problems

1. Consider the formation of the four $CdCl_n^{2-n}$ complexes where n = 1 to 4. Given that $\log_{10}\beta_1$ through $\log_{10}\beta_4$ are 2.05, 2.60, 2.40, and 2.90, respectively. Calculate:
   a) K_{f3} for the trichloro complex.
   b) the α_{Cd2+} through $\alpha_{CdCl42-}$ for a solution that is 0.0050 **M** in total Cd^{2+} (*i.e.* C_{Cd2+}) and 0.0100 **M** in total Cl^- (*i.e.* C_{Cl}-).
   c) the α_{Cd2+} through $\alpha_{CdCl42-}$ for a solution that is 0.0050 **M** in Cd^{2+} (*i.e.* C_{Cd2+}) and 0.0500 **M** in Cl^- (*i.e.* C_{Cl}-).
   d) the minimum C_{Cl}- necessary to assure that α_{CdCl42}- is at least 0.90 (with C_{Cd2+} = 0.0050 **M**).

5. Consider the problem of titrating a 0.0010 **M** solution of Fe^{3+} which is 0.010 **M** in Mn^{2+} using 0.0025 **M** DCYTA[207]. Find a pH at which the Fe^{3+} can be titrated without interference from the Mn^{2+}.

6. Suppose that you have a metal ion, M^{3+} which forms two complexes with a chelate, Ch^{2-}; they are MCh^{+}, and MCh_2^{-}. Suppose that $K_{f1} = 114$ and $K_{f2} = 10200$ and that pK_{a1} and pK_{a2} for H_2Ch are 2.88 and 5.88, respectively, and that $p\beta_1$, $p\beta_2$ and $p\beta_3$ for $M(OH)_n^{3-n}$ are -5.51, -8.83 and -11.77, respectively. Calculate the alphas for the metal and the chelate when C_M = 0.0500 **M** and C_{Ch} = 0.100 **M**.

7. Although sulfate is not a metal ion, it can be determined by an EDTA titration! Ba^{2+} forms an insoluble precipitate with SO_4^{2-}:

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4(s)$$

To assure total precipitation of all of the SO_4^{2-}, an excess of Ba^{2+} is added to a solution containing SO_4^{2-}. The solid is filtered off and washed free of the excess Ba^{2+} and then dissolved in a *measured* excess of EDTA solution. This will dissolve the precipitate.

$$BaSO_4(s) + Y^{4-} \longrightarrow BaY^{2-} + SO_4^{2-}$$

The amount of EDTA in *excess* is determined by a back titration. Specifically, it is titrated with a Mg^{2+} solution of known concentration.[208] Eriochrome Black T (EBT) is the indicator of choice.

EBT is *effectively* a diprotic[209] metallochrome indicator; its deprotonated congener binds with metals to form a pink MIn^{n-3} complex. But for EBT, In^{3-} is orange.[210] So a change in the $[MIn^{n-3}]$: $[In^{3-}]$ ratio is very difficult to detect (orange $\longrightarrow$ pink!). However, HIn^{2-} is blue, and so the $[MIn^{n-3}]$: $[HIn^{2-}]$ ratio can be exploited, but to do this requires titration conditions that yield an appreciable α_{HIn2-} either before or after the equivalence point, depending on whether the titrant is M^{p+} or Lc^{q-}. Here, the titrant is M^{p+} (Mg^{2+}). The $MgEBT^{1-}$ will not exist before the equivalence point, only after the equivalence point. On the other hand $HEBT^{2-}$ will dominate before the equivalence point.

Suppose that 0.15 mmoles (35 mg) of $BaSO_4$ has been isolated. It is dissolved in 10.00 mL of 0.100 **M** EDTA at pH 8.8 and after the $BaSO_4$ has dissolved, the solution is back titrated with 0.110 **M** Mg^{2+}, also maintained at pH 8.8.

Note that Mg^{2+} forms one hydroxy complex $MgOH^{+}$ and an insoluble salt $Mg(OH)_2$. Given the presence of EDTA, the formation of this precipitate can be ignored. (See Chapter 10.)

a) Create a titration curve for this back titration.
b) Provide an analysis for completeness of the Mg^{2+} / Y^{4-} reaction at the equivalence point.
c) Finally, assess the effectiveness of EBT for providing an endpoint that coincides with the equivalence point.

Solutions to Example Problems

1. a. Recalling from page 55 the relationship between β_n and $K_{f,n}$,

$$\beta_2 = K_{f1} \times K_{f2}$$

and

$$\beta_3 = K_{f1} \times K_{f2} \times K_{f3}.$$

So,

$$\beta_3 \div \beta_2 = K_{f3}.$$

Which is:

$$10^{2.05} \div 10^{2.60} = 10^{-0.55} = \mathbf{0.282}.$$

1. b. The expressions for the five αs are created using the principles and techniques developed in Chapter 8.

```
> restart; Den:= Cd + beta[1]*Cd*Cl+beta[2]*Cd*Cl^2 +
  beta[3] *Cd*Cl^3 + beta[4]*Cd*Cl^4; alpha[0]:= op(1,Den)/
  Den; alpha[1]:= op(2,Den)/Den; alpha[2]:= op(3,Den)/Den;
  alpha[3]:= op(4,Den)/Den; alpha[4]:= op(5,Den)/Den;
```

$$\alpha_3 := \frac{\beta_3\, Cd\, Cl^3}{Cd + \beta_1\, Cd\, Cl + \beta_2\, Cd\, Cl^2 + \beta_3\, Cd\, Cl^3 + \beta_4\, Cd\, Cl^4}$$

$$\alpha_4 := \frac{\beta_4\, Cd\, Cl^4}{Cd + \beta_1\, Cd\, Cl + \beta_2\, Cd\, Cl^2 + \beta_3\, Cd\, Cl^3 + \beta_4\, Cd\, Cl^4}$$

`alpha[n]:=simplify(alpha[n]):` would remove *Cd* from the respective expression. This is necessary only in part **d** of this problem, and that is where it will be done.

From page 59, the total Cl^- concentration will equal the bound Cl^- + free Cl^-. Bound chloride will equal the average number of chlorides on each Cd^{2+} times the total cadmium ion concentration, $n_{ave} \times C_{Cd}$. n_{ave} is a function of the four betas and the concentration of free chlorides. This might appear to be an opportunity to replicate the derivation of n_{ave} on page 59, but alternatively one might anticipate the form on n_{ave} by extending the tri-substituted complex to this tetra-substituted complex. In this case:

```
> n[ave]:= Cl*(beta[1]+2*beta [2]*Cl+3*beta[3]*Cl^2+4*bet
  a[4]*Cl^3)/(1+beta[1]*Cl+beta[2]*Cl^2+beta[3]*Cl^3+beta
  [4]*Cl^4);
```

$$n_{ave} := \frac{Cl\,(\beta_1 + 2\,\beta_2\, Cl + 3\,\beta_3\, Cl^2 + 4\,\beta_4\, Cl^3)}{1 + \beta_1\, Cl + \beta_2\, Cl^2 + \beta_3\, Cl^3 + \beta_4\, Cl^4}$$

For those choosing to replicate the derivation on page 59:

```
> n[ave]:= (beta[1]*Cd*Cl+2*beta[2]*Cd*Cl^2 +
  3*beta[3]*Cd*Cl^3 + 4*beta[4]*Cd*Cl^4)/(Cd + beta[1]*Cd*Cl
  + beta[2]*Cd*Cl^2 +beta[3]*Cd*Cl^3 + beta[4]*Cd*Cl^4);
```

$$n_{ave} := \frac{\beta_1\, Cd\, Cl + 2\,\beta_2\, Cd\, Cl^2 + 3\,\beta_3\, Cd\, Cl^3 + 4\,\beta_4\, Cd\, Cl^4}{Cd + \beta_1\, Cd\, Cl + \beta_2\, Cd\, Cl^2 + \beta_3\, Cd\, Cl^3 + \beta_4\, Cd\, Cl^4}$$

`simplify(n[ave])` then produces the output we got (above) directly. Using mass balance requirements, the total chloride concentration is expressed.

```
> Cl[bound]:= n[ave]*C['Cd']: MassBal:= Cl[Total]=Cl[bound] +
Cl;
```

$$MassBal := Cl_{Total} = \frac{Cl\left(\beta_1 + 2\,\beta_2\,Cl + 3\,\beta_3\,Cl^2 + 4\,\beta_4\,Cl^3\right) C_{Cd}}{1 + \beta_1\,Cl + \beta_2\,Cl^2 + \beta_3\,Cl^3 + \beta_4\,Cl^4} + Cl$$

With this, the form of the expression should be clear, particularly that the concentration of *free* chloride depends on the *total* Cd concentration, the *total* Cl^- concentration, and the four formation constants. Solving this expression for Cl will allow the calculation of the five αs. First, all constants must be assigned. Then `fsolve` is used to find Cl, and to preclude physically impossible solutions (*e.g.* $[Cl^-] < 0$), a range of zero to $C_{Chloride}$ is imposed. (It would be just as easy to represent the range as 0..0.01; see part **c**.) The free chloride is called Cl_b (`_b` for part **b**).

```
> beta[1]:= 10^2.05: beta[2]:= 10^2.60: beta[3]:= 10^ 2.40:
  beta[4]:= 10^2.90: Cl[Total]:= 0.010; C['Cd']:= 0.0050;
  Cl_b:=fsolve(MassBal, Cl, 0..Cl[Total]);
```

$$C_{Total} := 0.0100$$
$$C_{Cd} := 0.0050$$
$$Cl\_b := 0.0076$$

```
> Cl:= Cl_b; 'alpha[0]'= alpha [0];'alpha[1]'= alpha[1];
  'alpha[2]'= alpha[2]; 'alpha[3]'= alpha[3]; 'alpha[4]'=
  alpha[4];
```

$$Cl := 0.0076$$
$$\alpha_0 = 0.5330$$
$$\alpha_1 = 0.4547$$
$$\alpha_2 = 0.0123$$
$$\alpha_3 = 0.0001\ (5.88\ 10^{-5})$$
$$\alpha_4 = 0.0000\ (1.41\ 10^{-6})$$

A quick check will show that the sum of these alphas equals 1.00000.

1. c. Unassigning Cl and assigning a new value to $C_{Chloride}$ is all that is necessary for part **c**.

```
> Cl:= 'Cl': Cl[Total]:= 0.050; Cl[bound]:= n[ave]*C['Cd'];
  MassBal:= Cl[Total] = Cl[bound] + Cl:^211 Cl_c:= fsolve
  (MassBal, Cl, 0..C[Total]);
```

$$C_{Chloride} := 0.0500$$
$$Cl\_c := 0.0451$$

And again, calling the free chloride and five alphas:

$$Cl := 0.0451$$
$$\alpha_0 = 0.1450$$
$$\alpha_1 = 0.7338$$
$$\alpha_2 = 0.1174$$
$$\alpha_3 = 0.0033\ (3.34\ 10^{-3})$$
$$\alpha_4 = 0.0005\ (4.76\ 10^{-4})$$

Predictably, with a larger total chloride concentration, the α_{Cd2+} (α_0) has decreased and the remaining αs have increased.

1. d. Again it is necessary to unassign Cl. Also, $\alpha_{CdCl42+}$ will have to be purged of its Cd term. This will happen when `alpha[4]` is simplified.

```
> Cl:= 'Cl': alpha[4]:= simplify(alpha[4]);
```

$$\alpha_4 = \left(7.943\ 10^{24}\ Cl^4\right) \Big/ \left(1.000\ 10^{22} + 1.122\ 10^{24}\ Cl + 3.981\ 10^{24}\ Cl^2 + 2.512\ 10^{24}\ Cl^3 + 7.943\ 10^{24}\ Cl^4\right)$$

Appropriately, this is a function of [Cl^-] only, besides, of course all of the embedded βs. Setting $\alpha_{CdCl42+}$ at the target 0.90 and solving the expression for [Cl^-] will give the *free* chloride concentration. From the expression for $\alpha_{CdCl42+}$ (because of the Cl^4 term) it is evident that there will be four roots. So the solutions will be listed using {Cl}. Alternatively, one could have used `fsolve` with a range beginning at 0.

```
> Free_Cl := solve(0.90 = alpha[4], {Cl});
```

$$Free\_Cl := \{Cl = 4.040\}, \{Cl = -0.009\}, \{Cl = -0.376\}, \{Cl = -0.809\}$$

The first root is the only viable solution. So,

```
> Cl:= subs(Free_Cl[1], Cl);
```

To achieve this concentration of *free* chloride, there must be enough *total* chloride to coordinate the $CdCl^{1+}$, $CdCl_2^0$, $CdCl_3^{1-}$ and $CdCl_4^{2-}$ complexes. Each concentration is its respective α multiplied by C_{Cd} (= 0.050 **M**) Then, the amount necessary for each congener is *n* times each $\alpha \times C_{Cd}$. (This is where the dependence of $C_{Cl,total}$ on C_{Cd2+} comes from.) $C_{Cl,total}$, then, would be the sum of these products *plus* the concentration of free chloride:

```
> Cl[total]:= Cl + (alpha[1] + 2*alpha [2] + 3*alpha[3] +
  4*alpha[4])*C['Cd'];
```

$$C_{Cl,total} := 4.060$$

This is a relatively high concentration, especially given that C_{Cd2+} = 0.0050 **M**, a C_{Cl} that is not easily achieved. At 20°C, the solubility limit of KCl is 4.6 **M** and for NaCl it is 6.1 **M**. Given these limits, it is likely that $\alpha_{CdCl42-}$ cannot get much larger, and 0.99 is impossible. The reader is invited to verify this. (Revisit 1b with C_{Cl}- = 6.1 **M**).

2. Equations **9-3** and **9-5**, respectively, are used to determine the required K''_f for Fe^{3+} to be "completely" titrated, and K''_f for Mn^{2+} to be "ignored." For the Fe^{3+} titration, C_{EqPt} can be calculated from **9-4**

$$C°_{Fe3+} \times C°_{DCYTA} \div (C°_{Fe3+} + C°_{DCYTA}) = 7.14_3\ 10^{-4}\ \mathbf{M}.$$

So the *minimum* practical K''_f would be $10^6 \div 7.14_3\ 10^{-4}$ **M** = $1.4\ 10^9$.

If we (arbitrarily) take $V°_{Fe3+}$ to be 25.00 mL, the DCYTA/Fe^{3+} equivalence point would be at

$$V°_{Fe}2+ \times C°_{Fe2+} \div C°_{DCYTA} = 10.00\ \text{mL}$$

So C_{Mn2+} (contained in the 25.00 mL of Fe^{3+} solution at the Fe^{3+} equivalence point) would be:

$$(25.00\text{mL}\times 0.010\ \mathbf{M})\div(25.00 + 10.00)\text{mL} = 7.14_3\ 10^{-3}\ \mathbf{M}$$

the *maximum* allowable K''_f would be

$$10^{-3} \div 7.14_3\ 10^{-3}\ \mathbf{M} = 0.140.$$

These differ by ten orders of magnitude. From Appendix VIa, the DCYTA formation constants for Fe^{3+} and Mn^{2+} are $10^{29.3}$ and $10^{16.8}$, respectively. This provides a difference of more than twelve orders of magnitude; it's an important start but does not necessarily assure success. If, with rising pH, α_{Fe3+} decreases a lot faster than α_{Mn2+} decreases, the K''_fs could converge in the pH region where α_{D4-} is large enough to make $K''_{f,Fe}$ acceptable. Using the four, acid dissociation constants and the metal-hydroxy formation constants for Fe^{3+} and Mn^{2+}, the doubly conditional formation constants will be compared.

```
> restart; alpha[D4]:= K[a1]*K[a2]*K[a3]*K[a4]/(10^(-
  4*pH) + K[a1]*10^(-3*pH) + K[a1]*K[a2]*10^(-2*pH) +
  K[a1]*K[a2]*K[a3] *10^(-pH) + K[a1]*K[a2]*K[a3]*K[a4]);
  alpha [Mn2]:= 1/(1 + beta[1,Mn]*OH + beta[3,Mn]*OH^3):
  alpha [Mn2]:= algsubs(OH= 10^(pH-14), alpha[Mn2]);
  alpha[Fe3]:= 1/(1 + beta[1,Fe]*OH + beta [2,Fe]*OH^2 +
  beta[1,Fe]*OH + beta[3,Fe]* OH^3): alpha[Fe3]:= algsubs(OH=
  10^(pH-14),alpha[Fe3]);
```

$$\alpha_{D4} := \left(K_{a1} K_{a2} K_{a3} K_{a4}\right) \Big/ \left(10^{-4\,pH} + K_{a1}\, 10^{-3\,pH} + K_{a1} K_{a2}\, 10^{-2\,pH} + K_{a1} K_{a2} K_{a3}\, 10^{-pH} + K_{a1} K_{a2} K_{a3} K_{a4}\right)$$

$$\alpha_{Mn2} := \frac{1}{\beta_{1,\,Mn}\, 10^{pH-14} + \beta_{3,\,Mn}\left(10^{pH-14}\right)^3 + 1}$$

$$\alpha_{Fe3} := 1 \Big/ \left(1 + \beta_{3,\,Fe}\left(10^{pH-14}\right)^3 + \beta_{2,\,Fe}\left(10^{pH-14}\right)^2 + 2\,\beta_{1,\,Fe}\, 10^{pH-14}\right)$$

```
> Kpp[f,MnD]:= alpha[D4]*alpha[Mn2]*K[f,MnD]; Kpp[f,FeD]:=
  alpha[D4]*alpha[Fe3]*K[f,FeD];
```

These outputs should be predictable. So they are not shown. The constants are now assigned. They too are not shown but the reader should inspect the output for typographical errors. Notice that there is no value given for $\beta_{2,Mn}$. This implies that $Mn(OH)_2^0$ is not a significant form of Mn^{2+} in solution. (See Chapter 10.)

```
> K[a1]:= 10^(-2.43); K[a2]:= 10^(-3.54); K[a3]:= 10^(-6.10);
  K[a4]:= 10^(-11.70); beta[1,Mn]:= 10^3.90; beta[3,Mn]:=
  10^ 8.3; beta[1,Fe]:= 10^11.87; beta[2,Fe]:= 10^21.17;
  beta[3,Fe]:= 10^29.67; K[f,MnD]:= 10^16.8; K[f,FeD]:=
  10^29.3;
```

With constants assigned, a logarithmic plot can be created. Notice that the $\log_{10}$ function is embedded in the plot command.

```
> plot([log[10](Kpp[f, MnD]), log[10](Kpp[f,FeD])], pH
  = 0..14, labels = ["-log[H+]","log of Kpp"], color =
  ["DarkGreen", orange], axes = box);
```

Figure **9-9** shows that the two, doubly conditional formation constants remain more than ten orders of magnitude apart over a wide pH range (0 to about 4.5). It remains to be seen if $K''_{f,FeD}$ is sufficiently large when $K''_{f,Mn}$ is ≤ 0.14, or if $K''_{f,Mn}$ is sufficiently small when $K''_{f,FeD} \geq 1.4\ 10^9$. The first of these two options is pursued.

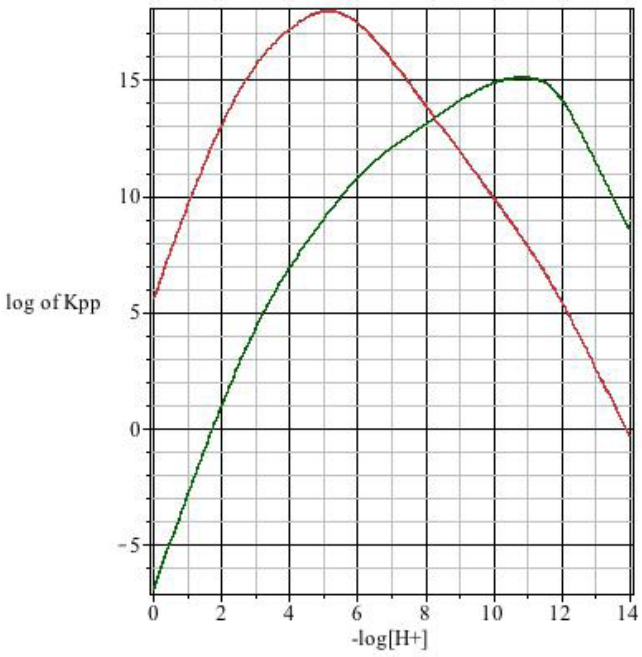

Figure 9-9

```
> pH:= fsolve(Kpp[f,MnD] = 0.140, pH, -1..14);
```

$$pH := 1.542$$

At pH 1.54, $K''_{f,MnD}$ will be sufficiently small to render it "invisible" at the equivalence point. What, then, is $K''_{f,FeD}$ at this pH?

```
> Kpp[f,FeD];
```

$$2.918\ 10^{11}$$

This is clearly an acceptable pH. From Figure **9-9** it appears that a slightly lower pH will reduce $K''_{f,MnD}$ to an even safer value without making $K''_{f,FeD}$ too small.

```
> pH:=1; Kpp[f,MnD]; Kpp[f,FeD];
```

$$pH := 1$$
$$Kpp_{f,MnD} = 0.001$$
$$Kpp_{f,FeD} = 2.845\ 10^{9}$$

This would be quite good: $K''_{f,MnD}$ is less than 1% of its maximum allowed value and $K''_{f,FeD}$ is more than twice its minimum allowed value. These assignments will be maintained for the titration plot calculation. That calculation will follow exactly the process used for the Cu^{2+} / NTA titration. Again, many outputs, although called (with ;) are not shown. They are called because the user should verify the form of each expression at each step.

```
> MassBal:= C[Fe3] = Fe + FeDCYTA + (1 - alpha[Fe3])*(C[Fe3]
  - FeDCYTA);
> EqExp:= K[f,FeD] = FeDCYTA/(Fe*alpha[D4]*(C[DCYTA] -
FeDCYTA));
> FeDCYTA:= solve(EqExp, FeDCYTA);
> MassBal;
> Iron:= solve(MassBal,{Fe});
```

The output must be inspected to decide which of the two roots is suitable for the titration expression. It will be the one with the +sqrt term, not the one with the -sqrt term.

```
> Fe[titration]:= subs(Iron[1],Fe);
```

$$Fe_{titration} := 0.435\, C_{Fe3} - 1.531\, 10^{-10} - 0.435\, C_{DCYTA} + 2.506\, 10^{-49} \left(3.019\, 10^{96}\, C_{Fe3}^2 + 2.123\, 10^{87}\, C_{Fe3} - 6.039\, 10^{96}\, C_{Fe3}\, C_{DCYTA} + 3.731\, 10^{77} + 2.123\, 10^{87}\, C_{DCYTA} + 3.019\, 10^{96}\, C_{DCYTA}^2\right)^{1/2}$$

This confirms that the values for $[Fe^{3+}]$ throughout the titration depend only on the analytical concentrations, C_{Fe3+} and C_{DCYTA}. Next, these concentrations are expressed as C°'s and $V°_{Fe3+}$ and V_{DCYTA}. ($V°_{Fe3+}$ is arbitrarily taken as 25.00 mL.)

```
> C[DCYTA]:= C°[DCYTA]*V[DCYTA]/(V°[Fe3] + V[DCYTA]);
  C[Fe3]:= C°[Fe3]*V°[Fe3]/(V°[Fe3] + V[DCYTA]); C°[Fe3]:=
  0.0010: C°[DCYTA]:= 0.00250: V°[Fe3]:=25.00; Fe[titration];
```

From **7-3** the 25.00 mL implies an equivalence point volume of DCYTA of 10.00 mL. To assure a good look at the post equivalence point, `0..15` is inserted in the `plot` command. Notice also that the conversion of $[Fe^{3+}]$ to *minus* $\log_{10}[Fe^{3+}]$ has been made within the plot command rather than making that conversion in a separate input line.

```
> plot(-log[10](Fe[titration]), V[DCYTA]= 0..15, labels =
  ["mL of DCYTA","-log [Fe3+]"], axes = boxed);
```

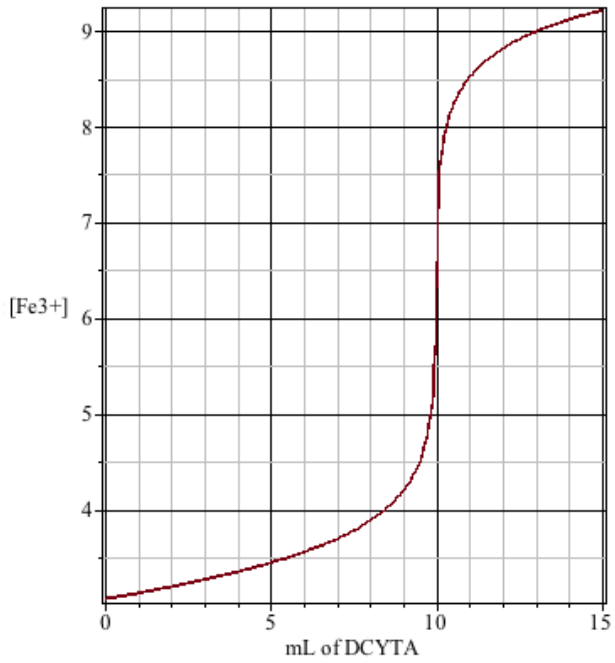

Figure 9-10

This figure indicates that $[Fe^{3+}]$ will change by several orders of magnitude within 0.1 mL of the equivalence point. Even within 0.1% (*i.e.* 0.01 mL) the change is appreciable.

```
> V[DCYTA]:= 0.999*C°[Fe3]*V°[Fe3]/C°[DCYTA]: Fe[before]:=
  Fe[titration]; V[DCYTA]:= C°[Fe3]*V°[Fe3]/C°[DCYTA]:
  Fe[EqPt]:= Fe[titration]; V[DCYTA]:= 1.001*C°[Fe3]*V°[Fe3]/
  C°[DCYTA]: Fe[after]:= Fe[titration];
```

$$Fe_{before} := 8.468\ 10^{-7}$$
$$Fe_{EqPt} := 4.362\ 10^{-7}$$
$$Fe_{after} := 2.248\ 10^{-7}$$

We see a 74% decrease in free Fe^{3+} over this 0.02 mL range of titrand, not spectacular but significant; a change of this magnitude should be easy to recognize. Appendix VIb offers only HQS and QIN as candidate indicators. Both offer the necessary advantage that they bind much more strongly to Fe^{3+} than to Mn^{2+}, a requirement because $C_{Fe3+} = 0.1C_{Mn2+}$.

3. Two mass balance expressions are necessary, one that delineates all forms of M^{3+} in solution and the other for Ch^{2-}. The scripting used below is not perfectly clear, but `'OH'` and even `"OH"` are not successful at protecting OH in the worksheet when OH is used as a variable. A predictable error in the Ch^{2-} mass balance is the omission of the coefficient 2 for the MCh_2 congener.

```
> restart; MassBal[M3]:= C['M']= M + MCh1 + MCh2 + MHy1 +
MHy2 + MHy3; MassBal[Ch2]:= C['Ch']= Ch + HCh + H2Ch + MCh1
+2*MCh2;
```

$$MassBal_{M3} := C_M = M + MCh1 + MCh2 + MHy1 + MHy2 + MHy3$$

$$MassBal_{Ch2} := C_{Ch} = Ch + HCh + H2Ch + MCh1 + 2\,MCh2$$

Each entity is then expressed in terms of equilibrium constants (K_a's, K_f's or β's), H, OH, M and Ch.

```
> MCh1:= M*K[f1]*Ch;MCh2:= M*K[f1]*K[f2]*Ch^2; MHy1:= M*beta
  [1]*OH; MHy2:= M*beta[2]*OH^2; MHy3:= M*beta[3]*OH^3;
  H2Ch:= Ch*H^2/(K[a1]*K[a2]); HCh:= Ch*H/K[a2];
  'MassBal[M3]'= MassBal[M3]; 'MassBal[Ch2]'= MassBal[Ch2];
```

$$MassBal_{M3} = \left(C_M = M + M\,K_{f1}\,Ch + M\,K_{f1}\,K_{f2}\,Ch^2 + M\,\beta_1\,OH + M\,\beta_2\,OH^2 + M\,\beta_3\,OH^3\right)$$

$$MassBal_{Ch2} = \left(C_{Ch} = Ch + \frac{Ch\,H}{K_{a2}} + \frac{Ch\,H^2}{K_{a1}\,K_{a2}} + M\,K_{f1}\,Ch + 2\,M\,K_{f1}\,K_{f2}\,Ch^2\right)$$

The two expressions contain only two unknowns, M and Ch, because all of the equilibrium constants along with C_M and C_{Ch} are known. A lot of unintelligible algebra can be saved by assigning all of these constants and concentrations here, before proceeding.

```
> K[f1]:= 114: K[f2]:= 10200: K[a1]:= 10^(-2.88): K[a2]:=
  10^(-5.88): beta[1]:= 10^(5.51): beta[2]:= 10^(8.83):
  beta[3]:= 10^(11.77): OH:= 1E-10: H:= 1E-4: C['M']:=
  0.050; C['Ch']:= 0.10; MassBal[M3]; MassBal[Ch2];
```

$$0.050 = 1.000\,M + 114\,M\,Ch + 1162800\,M\,Ch^2$$
$$0.100 = 82.612\,Ch + 114\,Ch + 2325600\,M\,Ch^2$$

Here it is perfectly obvious that only $[M^{3+}]$ and $[Ch^{2-}]$ remain. There are several strategies for finding these, for example solve $MassBal_{M3}$ for M (in terms of Ch) and substitute that expression into $MassBal_{Ch2}$ or vice versa. We will introduce a third strategy: we will allow Maple to solve the equations simultaneously. For this we can use the `solve` or `fsolve` command; because each expression is a quadratic in one of the terms, there are four solutions, and only one can have physical reality. The `fsolve` command will produce only that solution. (The numeric formatting should be altered to reveal Ch at a more useful precision.)

```
> fsolve({MassBal[M3], MassBal[Ch2]},{M,Ch});
```

$$\{Ch = 0.00736,\ M = 0.029175\}$$

After assigning these values to Ch and M, all of the alphas can be computed. In so doing we discover a strange calculation: the need to compute α_{MCh} and α_{MCh2} twice! This is because either complex can represent a fraction of C_M or a fraction of C_{Ch}.

```
> Ch:= 0.000736; M:= 0.029175; alpha['H2Ch']:= H2Ch/C['Ch']; alpha['HCh']:= HCh/C['Ch']; alpha['Ch']:= Ch/C['Ch']; alpha['MCh1']:= MCh1/C['Ch']; alpha['MCh2']:= MCh2/C['Ch']; alpha ['M']:= M/C['M']; alpha['MOH']:= MHy1/C['M']; alpha['M(OH)[2]']:= MHy2/C['M']; alpha['M(OH)[3]']:= MHy3/C['M']; alpha['MCh']:= MCh1/C['M']; alpha['MCh2']:= MCh2/C['M'];
```

$$a_{H2Ch} := 0.042352$$
$$a_{HCh} := 0.558313$$
$$a_{Ch} := 0.007360$$
$$a_{MCh1} := 0.024479$$
$$a_{MCh2} := 0.183769$$
$$a_{M} := 0.58500$$
$$a_{MOH} := 0.000019$$
$$a_{M(OH)2} := 3.944944\ 10^{-12}$$
$$a_{M(OH)3} := 3.435903\ 10^{-19}$$
$$a_{MCh} := 0.048958$$
$$a_{MCh2} := 0.367537$$

We might check the validity of these by verifying that all of the alphas associated with C_{Ch} add to one, and that the alphas associated with C_M do the same.

```
> alpha['H2Ch'] + alpha ['HCh'] + alpha['Ch'] + alpha['MCh1'] + alpha ['MCh2']; alpha['M'] + alpha ['MOH'] + alpha['M(OH)[2]'] + alpha['M(OH)[3]'] + alpha['MCh'] + alpha['MCh2'];
```

$$1.000042$$
$$1.000014$$

Not *exactly* one, but recall that M and Ch were not assigned their *exact* values. When two more decimal places are used for these assignments, the sums of the alphas are within 10^{-6} of exactly one.

Other tests can be done on this system. For example, if $C_M = 0$, what happens to the alphas associated with C_{Ch}? (The alphas associated with C_M are undefined with $C_M = 0$.) $[Ch^{2-}]$ becomes $1.21\ 10^{-3}$ and α_{MCh1} and α_{MCh2} predictably become zero. Setting C_{Ch} to zero produces predictable effects as well. There, $[M^{3+}]$ becomes 0.0499984, implying that the $M(OH)_n^{3-n}$ complexes are essentially nonexistent, which is not surprising at pH 4.

4. a. As the $BaSO_4$ dissolves, the 0.15 mmole of Ba^{2+} will bind to 0.15 mmole of the EDTA ($\log_{10}K_f = 7.8$), so effectively that this titration is like titrating 10.00 mL of 0.085 **M** EDTA with 0.11 **M** Mg^{2+}. The $[Ba^{2+}]$ can be ignored because it will exist in solution almost entirely as BaY^{2-}.

   The following work closely replicates the Cu^{2+} / NTA titration curve worksheet developed on page 74 *et seq.* It begins with a Mg mass balance that addresses the three forms of Mg: Mg^{2+}, $MgOH^+$ and MgY^{2-}. The hydroxy forms be collected is $\alpha_{MgOH} \times (C_{Mg} - MgY)$, and that is $(1 - \alpha_{Mg2+}) \times (C_{Mg} - MgY)$.

```
> restart; MassBal:= C['Mg'] = Mg2 + MgY + (1 -
  alpha['Mg'])*(C['Mg'] - MgY);
```

$$MassBal := C_{Mg} = Mg2 + MgY + (1 - \alpha_{Mg})\,(C_{Mg} - MgY)$$

```
> EquilExp:= K[f]= MgY/(alpha['Mg']*(C['Mg'] - MgY)*alpha
  [Y4]*(C[EDTA] - MgY));
```

$$EquilExp := K_f = \frac{MgY}{\alpha_{Mg}\left(C_{Mg} - MgY\right)\alpha_{Y4}\left(C_{EDTA} - MgY\right)}$$

After the equilibrium expression is solved for [MgY^{2-}] and called `FreeMg`, the solution (the second root) can be put back into the mass balance expression.

```
> FreeMg:= solve(EquilExp,{MgY}): MgY:= subs(FreeMg[2],MgY);
```

Output remains much too complicated to show here. We can clean this up by *first* defining the alphas to assure their correctness, and then assigning values to all the equilibrium constants and the pH. These alphas will look familiar, and with numeric assignments, the `MassBal` expression will be a lot cleaner.

```
> alpha[Y4]:= K[a1]*K[a2]*K[a3]*K[a4]/(10^(-4*pH)
  + K[a1]*10^(-3*pH) + K[a1]*K[a2]*10^(-2*pH) +
  K[a1]*K[a2]*K[a3]*10^(-pH) + K[a1]*K[a2]*K[a3]*K[a4]);
  alpha['Mg']:= 1/(1 + beta[1]*OH); alpha['Mg']:= algsubs(OH
  = 10^(pH - 14), alpha['Mg']);
```

$$\alpha_{Mg} := \frac{1}{1 + \beta_1\, 10^{pH - 14}}$$

```
> K[a1]:= 10^(-1.99); K[a2]:= 10^(-2.67); K[a3]:= 10^(-
  6.16); K[a4]:= 10^(-10.26); beta[1]:= 10^2.58; K[f]:=
  10^8.69; pH:= 8.8; 'alpha[Y4]'= alpha[Y4]; 'alpha['Mg']'=
  alpha['Mg']; Kpp[f,Mg]:= alpha[Y4]*alpha['Mg']*K[f];'MassB
  al' = MassBal;
```

$$K_{f,pp} := 1.6338\ 10^{7}$$

$$MassBal = \left(C_{Mg} = Mg2 + 0.5012\, C_{Mg} + 0.4988\, C_{EDTA} + 3.0530\, 10^{-8} - 3.0530\, 10^{-8} \left(2.6693\, 10^{14}\, C_{Mg}^2 - 5.3385\, 10^{14}\, C_{EDTA}\, C_{Mg} + 3.2676\, 10^{7}\, C_{Mg} + 2.6693\, 10^{14}\, C_{EDTA}^2 + 3.2676\, 10^{7}\, C_{EDTA} + 1 \right)^{1/2} \right)$$

5. b. Notice that K''_f has been calculated ($1.64\ 10^7$). With $C_{EqPt} = 0.0479$ (found below), we could show that indeed, $K''_f > 10^6 \div C_{EqPt}$. Also, V_{EqPt} is calculated so that the range for V_{EqPt} can be set.

   Appropriately, $[Mg^{2+}]$ in the MassBal expression depends only on C_{Mg} and C_{EDTA}, and these can now be expressed in terms of $C°_{Mg}$, $C°_{EDTA}$, V_{Mg} and $V°_{EDTA}$ (**7-2a** and **7-2b**). Then, we assign values for the C°s and V°. Remember that $C°_{EDTA}$ is *not* 0.100 because the Ba^{2+} has precipitated 15% of it as $BaSO_4$).

```
> C['Mg']:= V['Mg']*C°['Mg']/(V°[EDTA] + V['Mg']); C[EDTA]:=
  V°[EDTA]*C°[EDTA]/(V°[EDTA] + V['Mg']); 'MassBal'= MassBal;
> V°[EDTA]:= 10.0; C°[EDTA]:= 0.085; C°['Mg']:= 0.110;
  C[EqPt]:= C°[EDTA]*C°['Mg']/(C°[EDTA] + C°['Mg']);
  V[EqPt]:= C°[EDTA]*V°[EDTA]/C°['Mg']; 'MassBal' = MassBal;
```

$$C_{EqPt} := 0.0479$$
$$V_{EqPt} := 7.7273$$

$$MassBal = \left(\frac{0.1100\, V_{Mg}}{10.0000 + V_{Mg}} = Mg2 + \frac{0.0551\, V_{Mg}}{10.0000 + V_{Mg}} + \frac{0.4240}{10.0000 + V_{Mg}} + 3.0530\, 10^{-8} - 3.0530\, 10^{-8} \left(\frac{3.2298\, 10^{12}\, V_{Mg}^2}{\left(10.0000 + V_{Mg}\right)^2} - \frac{4.9915\, 10^{13}\, V_{Mg}}{\left(10.0000 + V_{Mg}\right)^2} + \frac{3.5943\, 10^{6}\, V_{Mg}}{10.0000 + V_{Mg}} + \frac{1.9285\, 10^{14}}{\left(10.0000 + V_{Mg}\right)^2} + \frac{2.7774\, 10^{7}}{10.0000 + V_{Mg}} + 1 \right)^{1/2} \right)$$

It is $[Mg^{2+}]$ from *MassBal* that we are seeking. We extract this as the solution to MassBal at any given V_{Mg}. We will call the solution FreeMg. For plotting purposes, we will take $-\log_{10}$ of that solution.

```
> MgFree:= solve(MassBal, Mg2);pMg:= -log[10](MgFree):
```

The expression is suitable for plotting, and could be plotted to fulfill **4a** and to assure that the expression is correct. But first we turn to characterizing the indicator. We will closely follow the treatment of the CuPAR system (page 81). We will presume that EBT exists only as H_2EBT^{-1}, $HEBT^{2-}$, EBT^{3-} and MgEBT. Again we will (only as an approximation) include $[MgEBT^{1-}]$ in the alpha expression. Also, we will assign values for K_{In1}, K_{In2} and $K_{f,In}$ first, so that the alpha will be rendered in terms of only the free Mg^{2+}. That is $[Mg^{2+}]$.

```
> K[In1]:= 10^(-6.3); K[In2]:= 10^(-11.5); K[f,In]:= 1e7;
  alpha[HEBT2]:= K[In1]*10^(-pH)/(10^(-2*pH) + K[In1]*10^(-
  pH) + K[In1]*K[In2] + K[In1]*K[In2]*MgFree*K[f,In]);
  alpha[MgEBT]:= K[In1]*K[In2]*MgFree*K[f,In]/
  (10^(-2*pH) + K[In1]*10^(-pH) + K[In1]*K[In2] +
  K[In1]*K[In2]*MgFree*K[f,In]);
```

The two alphas are not shown here because each contains MgFree and those are themselves large expressions in terms of V_{Mg}, but the reader should inspect these expressions to be sure that the only variable they contain is V_{Mg}. Again, we create expressions suitable for plotting, and then execute the plot.

```
> p_alpha_HEBT2:= -log(alpha[HEBT2]): p_alpha_MgEBT:=
  -log(alpha [MgEBT]):
> plot([pMg, p_alpha_HEBT2, p_alpha_MgEBT], V['Mg'] = 0..10,
  color = [black,blue,red], labels = ["mL of EDTA", "-log Mg
  or alpha"], axes= boxed);
```

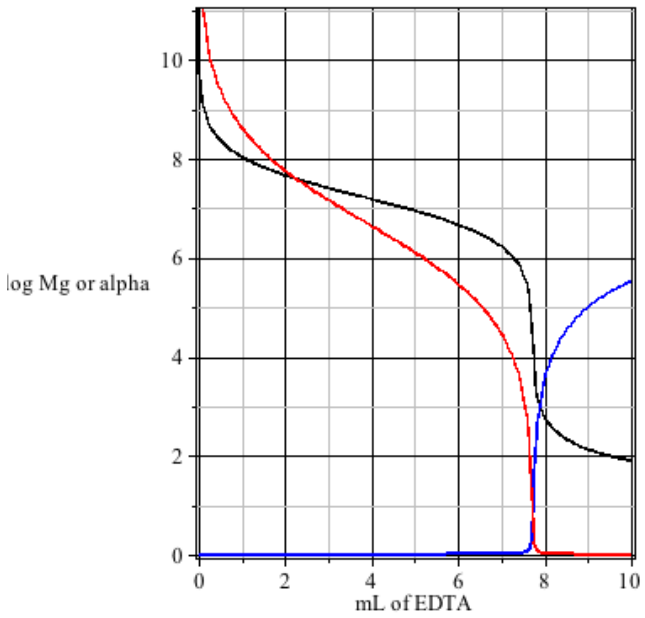

Fig 9-11

6. c. It is apparent, qualitatively, from Figure **9-11** that EBT will be an effective indicator, that α_{HEBT2-} is essentially 1.0 right up to the equivalence point and that immediately thereafter α_{MgEBT}- becomes 1.0. So a blue to pink change is expected very close to the equivalence point. To be quantitative, the relationship between these alphas must be quantified. Using the 10:1 criterion introduced in Chapter 7 (Part I, page 170), V_{Mg} can be calculated for what might be defined as an endpoint. That is, at what V_{Mg} will α_{MgEBT}- be ten times α_{HEBT2-}? This was in 4b above. With $V_{EndPoint}$ = 7.890 and V_{EqPt} = 7.727, we have:

```
> Error:= 100*(V[EndPoint] - V[EqPt])/V[EqPt];
```

$$Error := 2.10$$

This is not acceptable, but it is based on an arbitrary definition of endpoint. If α_{MgEBT^-} equals $\alpha_{HEBT^{2-}}$ had been used as the endpoint, $V_{EndPoint}$ would have been 7.734 mL, an error of only 0.088%. This is still late, but tolerably.

As an aside: the consequence of a late endpoint can be alleviated by performing a "blank" titration. In such a titration, no sample (in this case no $BaSO_4$) is added. The titration to the same endpoint would also be late. The analysis is based on the *difference* in volume required to reach the blank endpoint and the volume required to reach an endpoint with sample present.

Both endpoints are late by the same volume of titrant, and so the endpoint error is cancelled out. This technique is a natural part of the back titration, but it is also used in direct titrations where the endpoint is intrinsically late. This will be addressed in the precipitation titration in the next chapter.

10 Solubility Equilibrium

The final topic on chemical equilibrium includes reactions in which either the reactants or products are insoluble. It pertains either to the formation of solids from soluble reactants or to the dissolution of solids to form soluble products. It is a subject appropriately placed at the end of a text on ionic equilibrium because solubility is affected by the other types of equilibration, acid / base and complex formation, discussed in earlier chapters. These effects will be explored after presenting the most simple examples solubility equilibrium.

Consider the salt, potassium perchlorate. It is sparingly soluble in water. Its dissolution might be written:

$$KClO_4(s) \rightleftharpoons K^+ + ClO_4^-.$$

As long a *some* of the $KClO_4$ remains undissolved, the thermodynamic equilibrium expression[212] for this process might be written:

$$K°_{eq} = \frac{\{K^+\}\{ClO_4^-\}}{\{KClO_4\}}$$

But this form contains a hidden redundancy: if $KClO_4$ is a pure solid, as it should be in this example, its activity will be exactly 1. So the activity of the precipitate is never included in these equilibrium expressions. These equilibrium expression are given a name, solubility product, and this constant is expressed thermodynamically as

$$K°_{sp} = \{K^+\}\{ClO_4^-\}$$

There is also the concentration-based equilibrium expression for this reaction:

$$K_{eq} = \frac{[K^+][ClO_4^-]}{[KClO_4]}$$

This expression, too, contains a redundancy in that for a pure solid like $KClO_4$, the mass to volume ratio should be effectively a constant, and so $[KClO_4]$ is likewise a constant. This constant is *not* moved to the left hand side of the expression and combined with the constant K_{eq}; it is simply omitted giving:

$$K_{sp} = [K^+][ClO_4^-].$$

With this expression, it is easy to forget the proviso that this equilibration requires the presence of *some* solid $KClO_4$.

Recalling, from Equation **2-3**, the relationship between molarity and activity leads to:

$$K°_{sp} = \gamma_{K+}[K^+]\gamma_{ClO4}\text{-}[ClO_4^-]$$

so that

$$K°_{sp} = \gamma_{K+}\gamma_{ClO4\text{-}}K_{sp}$$

and

$$K_{sp} = K°_{sp}/\gamma_{K+}\gamma_{ClO4}\text{-}.$$

In general terms, consider the solubility equilibrium of the ionic solid M_xA_y as it dissolves to produce

$$M_xA_y(s) \rightleftharpoons xM^{m+} + yA^{a-}.$$

The thermodynamic solubility product could be expressed as

$$K°_{sp} = \{M^{m+}\}^x\{A^{a-}\}^y, \qquad \textbf{10-1}$$

$$K°_{sp} = (\gamma_{M^{m+}})^x(\gamma_{A^{a-}})^y[M^{m+}]^x[A^{a-}]^y \qquad \textbf{10-2}$$

or

$$K°_{sp} = (\gamma_{M\,m+})^x(\gamma_{A^{a-}})^y K_{sp}. \quad \textbf{10-3}$$

The concentration based solubility product might be expressed as

$$K_{sp} = [M^{m+}]^x[A^{a-}]^y, \quad \textbf{10-4}$$

or as

$$K_{sp} = K°_{sp} /((\gamma_{M^{m+}})^x(\gamma_{A^{a-}})^y). \quad \textbf{10-5}$$

Just as with thermodynamic acid dissociation constants, the thermodynamic solubility product is genuinely a constant (for a given solvent at a given temperature), but because the activity coefficients, γ_{Mm+} and γ_{Aa-}, for the soluble species vary profoundly with ionic strength, it is clear that the concentration based solubility product is *not* a real constant. Nevertheless, K_{sp} is commonly treated as a constant for approximation, and often this yields good approximations. Here, ionic strength effects will be taken into consideration in order to enhance the accuracy of most of the calculations presented. Admittedly, it is often difficult to know if a table of solubility products provides K_{sp} or $K°_{sp}$. The values in Appendix VII are presumed to be $K°_{sp}$ values.

Returning to the $KClO_4$ equilibrium, a calculation of molar solubility from $K°_{sp}$ and the effect of ionic strength on that solubility will be demonstrated. If $K°_{sp}$ for $KClO_4$ is taken as $1.1\ 10^{-2}$, what is the molar concentration of a solution saturated[213] with K^+ and ClO_4^-? This is carried out using Maple, perhaps in a more elaborate way than might be done on a calculator, but the example is intended to exercise Maple worksheet skills, not simply to find a solution. We begin with a statement of the equilibrium requirement, but presuming that the activities of K^+ and ClO_4^- can be approximated with their respective concentrations. That is `K` is taken as $[K^+]$, not $\{K^+\}$, and `ClO[4]` represents $[ClO_4^-]$, not $\{ClO_4^-\}$.

```
> restart; SolEq:= K°[sp]= K*ClO[4];
```

$$SolEq := K°_{sp} = K\ ClO_4$$

Mass balance would require that $[K^+]$ equals $[ClO_4^-]$ because both come in equal amount from the same source. So, the K and ClO[4] are set equal, and then *SolEq* can be solved for ClO[4]. This will effectively make $K°_{sp}$ equal to $[ClO_4^-]^2$ and that will mean two roots for $[ClO_4^-]$. So that the two roots can be isolated, they are listed, i.e. included in braces.

```
> K:= ClO[4]; Root:= solve (SolEq,{ClO[4]});
```

$$K := ClO_4$$

$$Root := \left\{ClO_4 = \sqrt{K°_{sp}}\right\}, \left\{ClO_4 = -\sqrt{K°_{sp}}\right\}$$

Only the first root has physical meaning because the second root, being less than zero, cannot be observed. Therefore,

```
> K°[sp]:= 1.1e-2; ClO[4]:= subs(Root[1], ClO[4]); 'K'= K;
```

$$K°_{sp} := 0.0110$$
$$ClO_4 := 0.1049$$
$$K = 0.1049$$

In order to achieve such concentrations, it is necessary that 0.105 mole of $KClO_4$ dissolve in each liter of water. There is, however, a bit of a paradox here. Notice that the concentrations are considerable, and that consequently, the ionic strength is appreciably greater than 0.001 where it can be ignored. To resolve this, the reiteration process introduced in Chapter 4 (Part I, page 74 *et seq.*) might be used, but, as illustrated in Chapter 7, this process will be automated. From Equation **2-5**, a calculation of ionic strength is made.

```
> μ:= 0.5*(K + ClO[4]);
```

$$\mu := 0.1049$$

This μ is then used to calculate γ_{K+} and γ_{ClO4}- by the Davies Equation (**2-8**). This, recall, will not discriminate between K^+ and ClO_4^-. So the two activity coefficients will be equal and called g. Because K = ClO_4, either of these is simply $\sqrt{K_{sp}}$. They will be called Solubility, and μ which is the sum of these two, equal concentrations times 0.5, μ = Solubility.

```
> for i to 3 do
> g:= 10^(-0.5*(1^2)*((sqrt(μ)/(1 + sqrt(μ)) - 0.15*μ)));
> Solubility[i]:= evalf(sqrt(K°[sp]/g^2)); μ:= Solubility[i];
> end;
```

$$Solubility_1 := 0.1365$$
$$Solubility_2 := 0.1398$$
$$Solubility_1 := 0.1400$$

Clearly, the largest adjustment comes when K_{sp} replaces $K°_{sp}$ where the solubility increases from 0.104_9 to 0.136_5; the final iteration makes little difference.

Before moving on to solubility equilibria which are affected by competing reactions like acid/base and complex formation, another type of problem will be addressed. It pertains to completeness of precipitation. This concept is crucial to gravimetric analyses which require two conditions: First the precipitation must be "complete" and by that, the 99.9% rule is implied; second, the precipitate must be of known stoichiometery so that the mass of the precipitate can be converted into the mass of analyte using its formula weight. This second issue will be addressed in the context of competing precipitation reactions.

Addressing the first issue, consider another simple system, $CsClO_4$, which is essentially the only insoluble salt of cesium. The $K°_{sp}$ is 4.0 10^{-3}. If one were to mix equal volumes of 0.25 **M** Cs^+ with 0.25 **M** ClO_4^-,[214] would a precipitate form, and if so, how complete would that precipitation be? The first step is to recognize that each solution will be diluted upon mixing. This will be addressed in the opening input of a new Maple worksheet using the dilution concept introduced in Equation **7-2**.

```
> restart; C[Cs]:= V°[Cs]*C°[Cs]/(V°[Cs] + V°[ClO[4]]); C[ClO[4]]:=
  V°[ClO[4]]*C°[ClO[4]]/(V°[Cs] + V°[ClO[4]]);
```

$$C_{Cs} := \frac{V°_{Cs}\, C°_{Cs}}{V°_{Cs} + V°_{ClO_4}}$$

$$C_{ClO_4} := \frac{V°_{ClO_4}\, C°_{ClO_4}}{V°_{Cs} + V°_{ClO_4}}$$

```
> V°[ClO[4]]:= V°[Cs]: 'C[Cs]'= C[Cs]; 'C[ClO[4]]'= C[ClO[4]];
```

$$C_{Cs} = \frac{1}{2} C°_{Cs}$$
$$C_{ClO_4} = \frac{1}{2} C°_{ClO_4}$$

For the reader who anticipated that this mix would dilute each reagent exactly in half, it would be tempting to enter $C_{Cs} := {}^1/_2 C°_{Cs}$ *etc.*, but with the strategy used here, one can experiment with different volumes and concentrations by modifying the `V°[ClO[4]]:= V°[Cs]:` input.

The next step is to invoke the conditions of a solubility equilibrium for

$$CsClO_4(s) \rightleftharpoons Cs^+ + ClO_4^-.$$

This requires that

$$K_{sp} = [Cs^+][ClO_4^-].$$

What is needed is the relationship between C_{Cs} and $[Cs^+]$ and between C_{ClO4} and $[ClO_4^-]$. The balanced equation above indicates that exactly as much Cs^+ will be lost from solution as ClO_4^- will be lost. This will be lost as precipitate which can be called `Prcp`. So,

$$[Cs^+] = C_{Cs} - Prcp$$

and,

$$[ClO_4^-] = C_{ClO4} - Prcp.$$

These can then be written into a solubility equilibrium expression.

```
> SolEq:= K[sp]= (C[Cs] - Prcp)*(C[ClO[4]] - Prcp);
```

$$SolEq := K_{sp} = \left(\frac{1}{2} C°_{Cs} - Prcp\right)\left(\frac{1}{2} C°_{ClO_4} - Prcp\right)$$

This allows for a calculation of the amount of $CsClO_4$ that will precipitate out of solution when *equal* volumes of Cs^+ and ClO_4^- are mixed.[215] Assigning values to the parameters and solving the equilibrium expression gives:

```
> K[sp]:= 4e-3: C°[Cs]:= 0.25: C°[ClO[4]]:= 0.25: Prcp_s:=
  solve(SolEq, {Prcp}); Prcp_f:= fsolve(SolEq, Prcp, 0.. C[Cs]);
```

$$Prcp\_s := \{Prcp = 0.0618\}, \{Prcp = 0.1882\}$$
$$Prcp\_f := 0.0618$$

`SolEq` is solved two ways here. The first method, `solve(SolEq`…, is general, and because `Prcp` is squared in the expression, two roots are expected. In previous chapters, the "physically impossible" root has been immediately recognizable because it has always been less than zero. But here, both roots are greater than zero. Nevertheless, one of the two is impossible: it is not possible to precipitate out more Cs^+ (or ClO_4^-) than exists in solution! $C_{Cs} = {}^1/_2 C°_{Cs} = 0.125$ **M**. *Prcp*, therefore, cannot exceed 0.125. So the first root, will be selected (below).

The second way to solve `SolEq` is for those who would rather not inspect the list of roots and decide which is the physically possible root; `fsolve` is a prudent strategy, but only if it is framed by the range of physically possible solutions. This would be 0 to C_{Cs} (or 0 to C_{ClO4}). Of course the solution from `fsolve` is contained in the list of roots given by `solve`. For those who pursue the solve route, the root of choice must be selected. *Solid* is used to denote this solution.

```
> Solid:= subs(Prcp_s[1], Prcp);
```

$$Solid := 0.0618$$

And finally, using either *Prcp_f* or *Solid*, the completeness of the precipitation can be computed.

```
> Completeness:= 100*Solid/C[Cs];
```

$$Completeness := 49.4036$$

This is not impressive, nor is it surprising.[216] This K_{sp} is too large to provide a thorough precipitation, especially with relatively dilute agents (0.125 **M**).[217] One could go *back* and use $^{1}/_{10}^{th}$ the volume of ClO_4^- at ten times its concentration (2.5 **M**). This would increase C_{Cs} and C_{ClO4} appreciably. Yet, this would increase completeness to only 72%, still unsatisfactory for quantitative work. Is it *not* possible to achieve "complete" precipitation? Maybe it is, but not if we require that $C_{Cs+} = C_{ClO4}$- in the mixture.

For a precipitation titration, it is expected that precipitation is ≥ 99.9% complete *at the equivalence point*. On the other hand, for gravimetric analyses one can certainly add an excess of ClO_4^- thereby making $C_{ClO4} > C_{Cs}$ to increase the completeness of the precipitation. We continue now with gravimetric issues using this $CsClO_4$ precipitation.

The solubility equilibrium expression is entered for reference. Then and C_{Cs} and C_{ClO4} are written in terms of V°s and C°s.

```
> restart; SolEq:= K[sp]= (C [Cs] - Prcp)*(C[ClO[4]] - Prcp):
  C[Cs]:= V°[Cs]*C°[Cs]/(V°[Cs] + V°[ClO[4]]); C[ClO[4]]:=
  V° [ClO[4]]*C°[ClO[4]]/(V°[Cs] + V°[ClO[4]]); "Solubility
  Expression"= SolEq;
```

$$C_{Cs} := \frac{V°_{Cs}\, C°_{Cs}}{V°_{Cs} + V°_{ClO_4}}$$

$$C_{ClO_4} := \frac{V°_{ClO_4}\, C°_{ClO_4}}{V°_{Cs} + V°_{ClO_4}}$$

$$\text{"Solubility Expression"} = \left(K_{sp} = \left(\frac{V°_{Cs}\, C°_{Cs}}{V°_{Cs} + V°_{ClO_4}} - Prcp \right) \left(\frac{V°_{ClO_4}\, C°_{ClO_4}}{V°_{Cs} + V°_{ClO_4}} - Prcp \right) \right)$$

Here we stipulate that it is Cs^+ that is to be "completely" precipitated. Given that, Prcp must be 99.9% of C_{Cs}. So,

```
> Prcp:= 0.999*C[Cs]: SolEq;
```

$$K_{sp} = \frac{0.001\ V°_{Cs}\ C°_{Cs}\left(\frac{V°_{ClO_4}\ C°_{ClO_4}}{V°_{Cs}+V°_{ClO_4}} - \frac{0.999\ V°_{Cs}\ C°_{Cs}}{V°_{Cs}+V°_{ClO_4}}\right)}{V°_{Cs}+V°_{ClO_4}}$$

This is the equilibrium expression that must be satisfied to "completely" precipitate Cs^+ using a ClO_4^- solution. Suppose now that we are using 10.00 mL of a 0.25 **M** Cs^+ and that a 4.0 **M** $NaClO_4$ solution is to be used to effect the precipitation. How much of this ClO_4^- solution is required? Values are assigned to each of the parameters. Then `SolEq` is inspected to show that only $V°_{ClO4}$ remains as a variable.

```
> K[sp]:= 4e-3: V°[Cs]:= 10.0: C°[Cs]:= 0.25: C°[ClO[4]]:= 4.0:
  'SolEq'= SolEq;
```

$$SolEq = \left(0.0040 = \frac{0.0025\left(\frac{4.0000\ V°_{ClO_4}}{10.0000+V°_{ClO_4}} - \frac{2.4975}{10.0000+V°_{ClO_4}}\right)}{10.0000+V°_{ClO_4}}\right)$$

Then, $SolEq$ is solved for $V°_{ClO4}$.

```
> Vol[Reqd]:= solve(SolEq, {V°[ClO[4]]});
```

$$Vol_{Reqd} := \left\{V°_{ClO_4} = -8.750 + 5.000\ I\right\}, \left\{V°_{ClO_4} = -8.750 - 5.000\ I\right\}$$

Both roots are complex numbers, indicating that there is no *real* solution to this problem! That is to say, there is no amount of 4.0 **M** $NaClO_4$ that can be added to a 0.25 **M** Cs^+ solution that will cause at least 99.9% of the Cs^+ to precipitate out. How can this be? It might seem that *some* very large volume of ClO_4^- solution would be effective, but look again at the expression for C_{ClO4} (in terms of $C°_{ClO4}$ and the two V°s).

$$C_{ClO_4} := \frac{V°_{ClO_4}\, C°_{ClO_4}}{V°_{Cs} + V°_{ClO_4}}$$

As $V°_{ClO4} \longrightarrow \infty$, $C_{ClO4} \longrightarrow C°_{ClO4}$. So adding more and more ClO_4^- solution cannot increase $[ClO_4^-]$ indefinitely; it can at best reach 4.0 **M**. At the same time as the volume of ClO_4^- solution is increased, C_{Cs} decreases, and this, of course reduces $[Cs^+]$ which works against the precipitation of $CsClO_4$.

$$C_{Cs} := \frac{V°_{Cs}\, C°_{Cs}}{V°_{Cs} + V°_{ClO_4}}$$

The problem here is that the K_{sp} is too large or the concentrations of Cs^+ or ClO_4^- are too small. The reader is invited to experiment with the previous worksheet to find just how thoroughly the Cs^+ can be precipitated.[218] Trial and error shows that 98.3% precipitation is about as well as one can do given the K_{sp}, $C°_{Cs}$ and $C°_{ClO4}$.

```
> Prcp:= 0.983*C[Cs]: SolEq: Vol983:= fsolve(SolEq, V°[ClO[4]]);
```

$$Vol983 := 10.578$$

If 99.9% cannot be achieved, what level of completeness is possible? For this, it is easier to start over. From the solubility equilibrium expression, *Prcp* is expressed in terms of C_{Cs}, C_{ClO4} and K_{sp}. Then, completeness (*i.e.* percent completeness), is expressed as the amount precipitated divided by the total amount[219] of Cs^+ in solution. Then, C_{Cs} and C_{ClO4} are expressed in terms of C°s and V°s as before. Enough of what follows has been shown in the previous worksheet that most of the output can be omitted.

```
> restart; SolEq:= K[sp]= (C[Cs] - Prcp)*(C[ClO[4]] - Prcp):
> P_roots:= solve(SolEq,{Prcp});
```

$$P\_roots := \left\{Prcp = \frac{1}{2} C_{Cs} + \frac{1}{2} C_{ClO_4} + \frac{1}{2} \sqrt{C_{Cs}^2 - 2 C_{Cs} C_{ClO_4} + C_{ClO_4}^2 + 4 K_{sp}}\right\},$$
$$\left\{Prcp = \frac{1}{2} C_{Cs} + \frac{1}{2} C_{ClO_4} - \frac{1}{2} \sqrt{C_{Cs}^2 - 2 C_{Cs} C_{ClO_4} + C_{ClO_4}^2 + 4 K_{sp}}\right\}$$

The two expressions for *Prcp* provide two values for *Prcp* at a single $V°_{ClO4}$. One of the values is larger than C_{Cs}, a physical impossibility. It will soon become apparent which of these two expressions is meaningless. Careful study of each expression might show that it is the first expression that provides unrealistic values for *Prcp*, but rather than eliminate the irrelevant expression here, we will continue until its irrelevance becomes obvious.

```
> P[1]:= subs(P_roots[1], Prcp): P[2]:=subs (P_roots[2], Prcp):
```

These are used in the calculation of completeness which would be $100P_1/C_{Cs}$ and $100P_2/C_{Cs}$. The simplify operation is not necessary, but it does clarify the expression.

```
> Comp[1]:= simplify(100*P[1] /C[Cs]); Comp[2]:= simplify
  (100*P[2]/C[Cs]);
```

$$Comp_1 := \frac{1}{C_{Cs}}\left(50\left(C_{Cs} + C_{ClO_4} + \sqrt{C_{Cs}^2 - 2 C_{Cs} C_{ClO_4} + C_{ClO_4}^2 + 4 K_{sp}}\right)\right)$$

$$Comp_2 := -\frac{1}{C_{Cs}}\left(50\left(-C_{Cs} - C_{ClO_4} + \sqrt{C_{Cs}^2 - 2\,C_{Cs}\,C_{ClO_4} + C_{ClO_4}^2 + 4\,K_{sp}}\right)\right)$$

With the expressions for completeness in order, it is now safe to expand them by expressing the analytical concentrations in terms of V°s and C°s. Then values can be assigned to the parameters. We continue as in the previous problem wherein 10.0 mL of 0.25 **M** Cs^+ is to be treated with 4.0 **M** $NaClO_4$ solution to effect the best possible precipitation of Cs^+.

```
> C[Cs]:= V°[Cs]*C °[Cs]/(V°[Cs] + V°[ClO[4]]); C[ClO[4]]:= V°
  [ClO[4]]*C°[ClO[4]]/(V°[Cs] + V°[ClO[4]]);
> V°[Cs]:=10.0: C°[Cs]:= 0.25: C°[ClO[4]]:= 4.0: K[sp]:= 4e-3:
  Comp[1]; Comp[2];
```

$Comp_1$ and $Comp_2$ are expressions in one variable only, namely $V°_{ClO4}$. They are very long and although they are called (with ;), they are not shown here. These expressions should increase with $V°_{ClO4}$ and then, as too much ClO_4^- is added, they should begin to decrease. This maximum is determined as the point at which $^{dComp}/_{dV} = 0$. Revisiting the differentiation operation introduced in Chapter 6 (Part I, page 139). Both $Comp_1$ and $Comp_2$ are differentiated with respect to $V°_{ClO4}$, but because of the complexity of these expressions, they are not shown.

```
> Der[1]:= diff(Comp[1], V°[ClO[4]]): Der[2]:=
  diff(Comp[2],V°[ClO[4]]):
```

Then, each is solved for the volume of ClO_4^- solution that will provide $^{dComp}/_{dV} = 0$.

```
> V[1]:= solve(Der[1] = 0, V°[ClO [4]]); V[2]:= solve(Der[2] =
  0,V°[ClO[4]]);
```

$$V_1 :=$$
$$V_2 := 11.229$$

Maple is unable to find a maximum or minimum to $Comp_1$, a sign that the function is inappropriate. So we look at $Comp_1$ and $Comp_2$ for completeness. At the same time, an option for plotting is revisited. It is the `thickness = n` specification, where increasing n increases the plot line thickness. The reader will notice that $Comp_1$ makes no sense: it implies more than 100% precipitation, even where no ClO_4^- has been added!

```
> plot([Comp[1], Comp[2]], V°[ClO[4]] = 0..3,color = [navy,
  orange], thickness = 3, labels = ["Vol of ClO4 Solution", "%
  Precipitated"], axes = boxed);
```

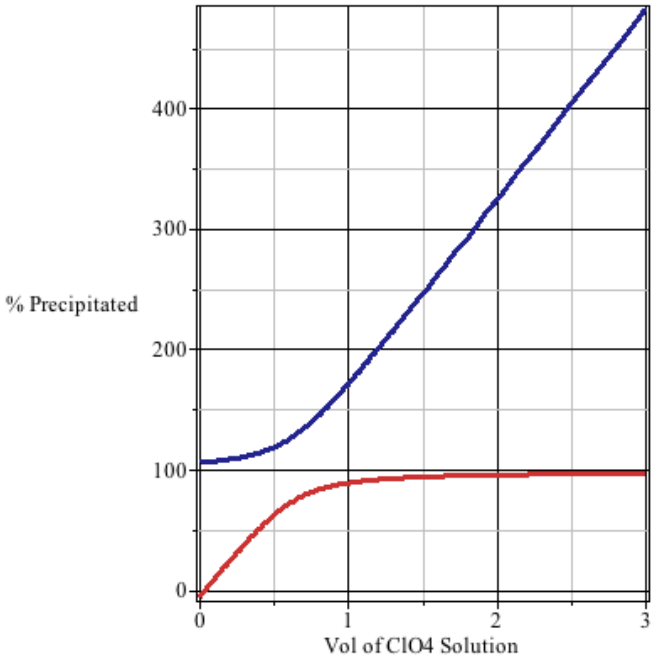

Figure 10-1

Clearly $Comp_1$ with > 100% precipitation makes no sense. $Comp_2$ is plotted alone, its form is easier to appreciate. An interesting segment of such a plot is found where the volume of ClO_4^- solution is much less than the optimum 11.229 mL.

```
> plot(Comp[2], V°[ClO[4]] = 0..1, labels = ["Vol of ClO4
  Solution","% Precipitated"], color = orange, axes = boxed);
```

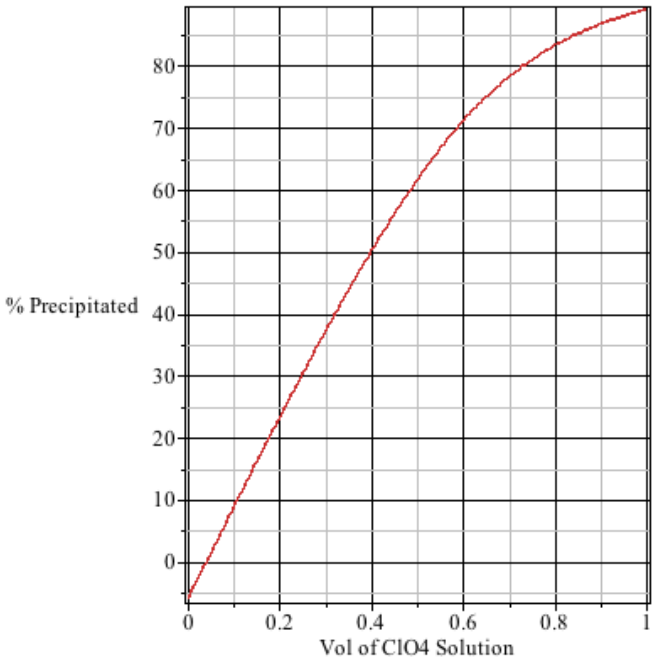

Figure 10-2

Notice that below $V_{ClO4} \approx 0.04$ mL, the percentage of Cs^+ precipitated is less than zero. *This is a manifestation of the requirement that there must be solid in equilibrium with the solution if solubility equilibrium conditions are invoked*. The volume of ClO_4^- at which *Prcp* reaches zero, represents the minimum volume required to *initiate* precipitation. At a volume less than that, the *SolEq* expression is invalid because there is no $CsClO_4(s)$.

To continue with the analysis of this $CsClO_4$ precipitation, $V°_{ClO4}$ is given the value of V_2 (11.229 mL) and out of curiosity, $Comp_1$ is computed. Then $V°_{ClO4}$ is set at zero.

```
> V°[ClO[4]]:= V[2]; Completeness[1] = Comp[1]; Completeness[2]
  = Comp[2]; V°[ClO[4]]:= 0; Completeness[1] = Comp[1];
  Completeness[2] = Comp[2];
```

$$V°_{ClO_4} := 11.229$$

$$Completeness_1 = 1798.302$$

$$Completeness_2 = 98.302$$

$$V°_{ClO_4} := 0$$

$$Completeness_1 = 106.036$$
$$Completeness_2 = -6.036$$

At 11.229 mL of 4.0 **M** $NaClO_4$, and 10.0 mL of 0.25 **M** CsCl, Cs^+ is precipitated as completely as possible, and that is at 98.3%. One more adjustment is required for precise work: the supernatant solution will have an ionic strength equal to C_{ClO4} (see Equation **3-13**).

```
> V°[ClO[4]]:= V[2]: μ:= C[ClO[4]];
```

$$\mu := 2.116$$

At this ionic strength even the Davies equation is inadequate for finding activity coefficients accurately, but any adjustment is likely to be better than none. K_{sp} would be adjusted with the activity coefficients and the problem solved again.

These problems pertaining to $KClO_4$ and $CsClO_4$ are the simplest possible examples of solubility equilibria, first because they involve 1:1 compounds and second because they do not entail competing reactions[220]. The most important competing reaction is between H^+ and M^{m+} for the anion that precipitates M^{n+}, and the next-most important is the competition between OH^- and A^{a-} for M^{m+}.

Consider the solubility of CaF_2. Its ionic dissolution would entail

$$CaF_2(s) \rightleftharpoons Ca^{2+} + 2\ F^-.$$

The equilibrium for this reaction is affected by reactions involving each of the product ions:

$$Ca^{2+} + OH^- \rightleftharpoons CaOH^+ \qquad \textbf{10-6}$$
$$H^+ + F^- \rightleftharpoons HF. \qquad \textbf{10-7}$$

So, at high pH, Ca^{2+} is removed from solution by the abundance of hydroxide ion, and at low pH, F^- is removed from solution by the abundance of hydronium ion. Either condition enhances the solubility of CaF_2. These adjustments to $[Ca^{2+}]$ and $[F^-]$ are addressed by replacing C_{Ca2+} with $\alpha_{Ca2+}C_{Ca2+}$ and C_F- with α_F-C_F-, and calculating the respective alphas.

The K_{sp} for the ionic dissolution of CaF_2 would be

$$K_{sp} = [Ca^{2+}][F^-]^2$$

In the previous examples [K^+] could be replaced with C_{K+} and [ClO_4^-] could be replaced with C_{ClO4}- because each alpha was exactly 1. Here, the alphas cannot be omitted. So

$$K_{sp} = \alpha_{Ca2+} C_{Ca2+} (\alpha_F\text{-} C_F\text{-})^2$$

In the worksheet that follows, [Ca^{2+}] will be denoted Sol_{Ca} meaning soluble Ca^{2+} and [F^-] will be Sol_F. This will avoid recursive error warnings when Ca and F are used as subscripts.

```
> restart; SolEq:= K[sp] = Sol[Ca]*Sol[F]^2:
> Sol[Ca] := alpha[Ca]*C[Ca]; Sol[F]:= alpha[F]*C[F]; 'SolEq'=
  SolEq;
```

$$SolEq = \left(K_{sp} = \alpha_{Ca} C_{Ca} \alpha_F^2 C_F^2 \right)$$

If the question is to determine the molar solubility of CaF_2, this can be determined simply from C_{Ca} because all of the Ca^{2+} *in solution* regardless of its form, originated from any CaF_2 that dissolved. This is true also for C_F, and from the stoichiometery of the salt, C_F must be $2 \times C_{Ca}$. Therefore, to find the molar solubility of CaF_2, one substitution and a rearrangement of *SolEq* is all that is necessary. *SolEq* being a 3° polynomial will have three roots (which will not be shown), but the only ~~the~~ first of the three is real. It is isolated and shown in the next step.

```
> C[F]:= 2*C[Ca]: Sol_roots:= solve(SolEq,{C[Ca]}):

> Solubility:= subs(Sol_roots[1], C[Ca]):
```

$$Solubility := \frac{1}{2} \frac{2^{1/3} \left(K_{sp} \alpha_{Ca}^2 \alpha_F \right)^{1/3}}{\alpha_{Ca} \alpha_F}$$

The `simplify` operation does not simplify the *Solubility* expression, but a little thought should make the relationship clearer: the solubility of CaF_2 goes as

$$(\alpha_{Ca+})^{-1/3} (\alpha_F\text{-})^{-2/3}.$$

So as either alpha approaches its maximum value of one, the solubility decreases, and as either alpha approaches zero, the solubility increases. This is consistent with Le Châtelier's Principle (Part I, page 9) as it would apply to Equations **10-6** and **10-7**. The dependence of solubility on pH comes as these alphas are written in terms of $[H^+]$ and then pH (actually *minus* $\log_{10}[H^+]$). α_{Ca} is taken from Chapter 9 (page 62 *et seq.*) α_F- is simply an application of Equation **4-21**, and taken directly from Part I, page 77. By first writing $[H^+]$ and $[OH^-]$ in terms of pH (as on page 71), the alphas will directly *substitute* into *Solubility* as a function of pH, K_a and K_{sp}.

```
> OH:= 10^(pH-14); H:= 10^(-pH); alpha[Ca]:= 1/(1 + OH*beta[1]);
  alpha[F]:= K[a]/(H + K[a]); Solubility;
```

$$\alpha_{Ca} := \frac{1}{1 + 10^{pH - 14}\,\beta_1}$$

$$\alpha_F := \frac{K_a}{10^{-pH} + K_a}$$

$$Solubility = \frac{1}{2}\frac{1}{K_a}\left(\left(1+10^{pH-14}\beta_1\right)\left(10^{-pH}+K_a\right)2^{1/3}\left(\frac{K_{sp}K_a}{\left(1+10^{pH-14}\beta_1\right)^2\left(10^{-pH}+K_a\right)}\right)^{1/3}\right)$$

And now, values can be assigned for equilibrium constants (Appendix IV, VI and VII, respectively).[221]

```
> K[a]:= 10^(-3.18); beta[1]:= 10^(1.46); K[sp]:= 10^(-8.28);
  'Solubility '= Solubility;
```

$$Solubility = 0.1145\left(1+28.8403\,10^{pH-14}\right)\left(10^{-pH}+0.0007\right)2^{1/3}\left(\frac{1}{\left(1+28.8403\,10^{pH-14}\right)^2\left(10^{-pH}+0.0007\right)}\right)^{1/3}$$

Now expression for solubility contains only one variable, pH. As pH changes from 0 to 14, the solubility of CaF_2 will change over several orders of magnitude. So, in order to make a plot of this solubility more meaningful, it will be expressed logarithmically, actually as $-\log_{10}$(Solubility), or "p(Solubility)." To do this, the `-log[10]` operation is carried out *within* the `plot` command.

```
> plot(-log[10](Solubility), pH = 0..14, axes = boxed, labels =
  ["-log[H+]", "p(Solubility)"], color = magenta);
```

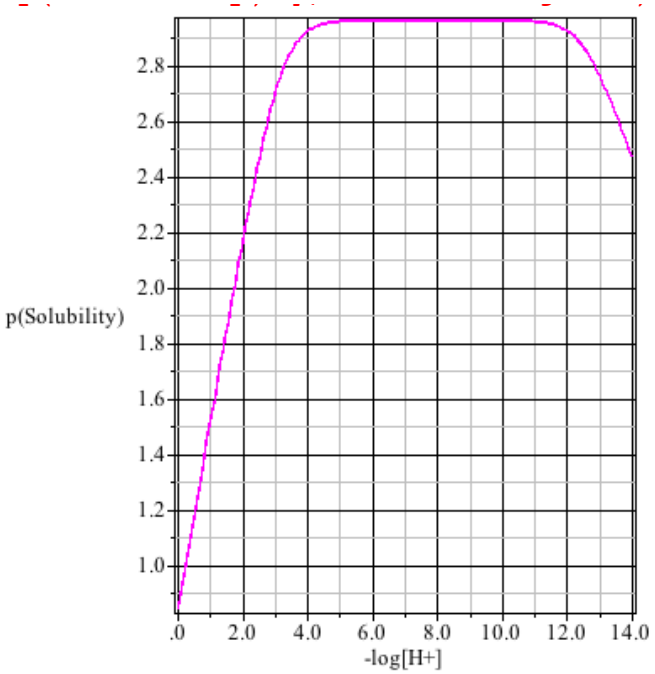

Figure 10-3

Apparently, CaF_2 becomes nearly soluble at $-\log_{10}[H^+] = 0$, or $[H^+] = 1.0$ **M**.

```
> pH:= 0: 'Solubility'= evalf[222](Solubility);
```

$$Solubility = 0.0284$$

At this concentration, $[H^+]$ would be 1.00 **M**, Ca^{2+} would be 0.028 **M**, and $[F^-]$ would be 2×0.0284 **M**. Charge balance would require an anion concentration of 1.00/z **M** where z is the charge on that anion (A^- from HA plus F^-). At any rate, even with z = 1, it should be apparent that the ionic strength at this pH would be considerable and it would require a substantial modification to K_a, β_1 and K_{sp} in order to compute the solubility accurately. We will not pursue the problem into ionic strength effects because the point has been made: the pH profoundly affects the solubility of CaF_2.

For gravimetric analysis, it is the region of minimum solubility that matters most. One might find $^{dSolubility}/_{dpH} = 0$, but from Figure **10-3** it is apparent that the region of minimum solubility is broad and flat (on a logarithmic scale). Indeed, assigning different values for the pH, between 5 and 11 shows that the solubility remains at $2.16\ 10^{-4} \pm 1\ 10^{-6}$.

Ca^{2+} like the Group IA and other Group IIA ions is not apt to form metal complexes with simple[223] anions, but consider what might look like a simple solubility equilibrium with a Group IB metal

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-.$$

While chloride ion offers the simplicity of being unaffected by pH because it is the anion of a strong acid, it brings a new complexity to the solubility equilibrium of all but a few metal ions: it is a sufficiently strong ligand to create multiple complexes with its cation.

$$\begin{aligned} Ag^+ + Cl^- &\rightleftharpoons AgCl(aq) \\ Ag^+ + 2\ Cl &\rightleftharpoons AgCl_2^- \\ Ag^+ + 3\ Cl^- &\rightleftharpoons AgCl_3^{2-} \\ Ag^+ + 4\ Cl^- &\rightleftharpoons AgCl_4^{3-} \end{aligned}$$

These provide for four more soluble forms of Ag^+ (in addition to Ag^+ itself). So, while increasing the chloride concentration might appear to drive the equilibrium toward the formation of solid AgCl, at the same time, the four competing reactions are driven so as to diminish $[Ag^+]$ which would enhance the dissolution of solid AgCl. Consequently, there will be an optimal $[Cl^-]$ that minimizes AgCl(s) solubility. This will be determined in the next example.

Before pursuing the effect of $[Cl^-]$ on AgCl(s) solubility, however, it would be timely to compare the two reactions

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-.$$

and

$$Ag^+ + Cl^- \rightleftharpoons AgCl(aq).$$

Their equilibria are represented as K_{sp} and K_{f1}, respectively. The sum of these reactions is:

$$AgCl(s) \rightleftharpoons AgCl(aq).$$

which would have the thermodynamic and concentration based equilibrium expressions

$$K°_{eq} = K°_{sp} \times K°_{f1} = \{AgCl(aq)\}$$

and

$$K_{eq} = K_{sp} \times K_{f1} = [AgCl(aq)],$$

respectively. The concentration based equilibrium expression says that the concentration of aqueous AgCl is a constant, and so as long as there is *some* solid AgCl in contact with the supernatant liquid, a *constant* amount of AgCl(s) will dissolve giving a constant AgCl(*aq*) concentration! Moreover, being a constant, it cannot be diminished by adding an excess of either Ag^+ or Cl^-. This phenomenon is known as intrinsic solubility. As the name implies, it is inherent to the solid and not alterable. It provides an upper limit to the completeness of precipitating that solid. This will become apparent in the example that follows here.

The existence of an intrinsic solubility is somewhat predictable. It requires a considerable degree of covalency in the substance. Generally, bonds between atoms on the right hand side of the periodic table are more covalent than bonds between atoms on opposite sides of the table. This is why the issue of intrinsic solubility was not raised with the CaF_2 example, but it would have been an issue had PbF_2 been addressed. Also, oxyanions have little covalent character in their bonds with metal ions. So, in terms of intrinsic solubility, chlorates are better than chlorides, sulfates are better than sulfides, *etc.*

A final point: because intrinsic solubility can be appreciable, using K_{sp} to estimate solubility can be precarious. Consider for example HgS with its K_{sp} of only $4.0\ 10^{-53}$. This implies that when this solid is in equilibrium with its supernatant solution, $[Hg^{2+}]$ and $[S^{2-}]$ are equal to 6.3×10^{-27} which is nominally one Hg^{2+} ion and one S^{2-} ion per thousand liters. One would, however, find a lot more mercury than that in the supernatant liquid because of the considerable presence of HgS(aq), and this because of the highly covalent Hg-S bond.

Returning to the AgCl(s) problem in terms of chloride ion effects, we begin with the solubility equilibrium requirement. The expression given earlier should be modified to

$$K_{sp} = \alpha_{Ag+} C_{Ag+} [Cl^-]$$

because C_{Ag+} represents the *total*, soluble component of AgCl(s). After all, if one is attempting to isolate Ag^+ by precipitating it out of solution, it doesn't matter how it escapes filtration, be it as Ag^+ or $AgCl_4^{3-}$. We can express this solubility with a simple rearrangement:

$$\text{Solubility} = C_{Ag+} = K_{sp}/\alpha_{Ag}+[Cl^-].$$

A cursory inspection of this expression might lead one to believe that increasing the chloride concentration will diminish the solubility of AgCl(s), but α_{Ag+} is itself a function of $[Cl^-]$.

```
> restart; SolEq:= K[sp] = alpha[Ag]*C[Ag]*Cl: Solubility:=
  solve(SolEq, C[Ag]);
```

$$Solubility := \frac{K_{sp}}{\alpha_{AG} CI}$$

The expression for α_{Ag+} is not derived here; rather, the reader is directed to page 55 *et seq.* or Example Problem 9-1 for details on its derivation. In the following step, it would be simple enough to enter $1/(1 + \beta_1 Cl + \beta_2 Cl^2 + \beta_3 Cl^3 + \beta_4 Cl^4)$ for $\alpha_{Ag}+$, but an analysis of the solution makeup will be interesting. So the more deliberate approach used in Chapter 9 is taken. With this approach all five alphas can be expressed so that they can be computed later in the worksheet. Showing only two of the alphas:

```
> Den:= 1 + beta[1]*Cl + beta[2]*Cl^2 + beta[3]*Cl^3 + beta
  [4]*Cl^4: alpha[Ag]:= 1/Den; alpha[AgCl]:= op(2,Den)/Den;
  alpha[AgCl[2]]:= op(3,Den)/Den; alpha[AgCl[3]]:= op(4, Den)/Den;
  alpha[AgCl[4]]:= op(5,Den)/Den; 'Solubility' = Solubility;
```

$$\alpha_{Ag} := \frac{1}{1 + \beta_1 Cl + \beta_2 Cl^2 + \beta_3 Cl^3 + \beta_4 Cl^4}$$

$$\alpha_{AgCl_4} := \frac{\beta_4 Cl^4}{1 + \beta_1 Cl + \beta_2 Cl^2 + \beta_3 Cl^3 + \beta_4 Cl^4}$$

$$Solubility = \frac{K_{sp}\left(1 + \beta_1 Cl + \beta_2 Cl^2 + \beta_3 Cl^3 + \beta_4 Cl^4\right)}{Cl}$$

From this expanded expression for *Solubility*, it is apparent that increasing [Cl^-] indefinitely might not continue to diminish the solubility of AgCl(s). From Appendix VIa and VII the constants are assigned next.

```
> K[sp]:= 10^(-9.75); beta[1]:= 10^3.04; beta[2]:= 10^5.04;
  beta[3]:= 10^5.04; beta[4]:= 10^5.30;
```

In order that [Cl^-] may be changed over several orders of magnitude and the result clearly plotted, *Solubility* will be expressed as a function of `pCl` and that requires the replacement of `Cl` with 10^{-pCl}.

```
> SOLUBILITY:= algsubs(Cl = 10^(-pCl), Solubility);
```

$$SOLUBILITY := \frac{1}{Cl}\left(1.780\ 10^{-10}\left(1.000 + 1.000\ 10^{6}\left(10^{-pCl}\right)^{4} + 63095.734\left(10^{-pCl}\right)^{2} + 3.162\ 10^{5}\left(10^{-pCl}\right)^{3} + 501.187\ 10^{-pCl}\right)\right)$$

Notice that the `alsubs` operation has not purged all of the *Cl*s from the expression. (This operation does not make all substitutions when *some* of the expressions to be substituted have negative exponents.) Here, *Cl* was expressed to the first, second, third, fourth and *minus* first power (*i.e. Cl* in the denominator). This can be cleaned up with a second application of `alsubs`. 1/Cl would be 10^{+pCl}. So,

```
> SOLUBILITY:= algsubs(1/Cl = 10^pCl, SOLUBILITY);
```

$$SOLUBILITY := 1.000\left(1.780\ 10^{-10} + 0.000\left(10^{-pCl}\right)^{4} + 0.000\left(10^{-pCl}\right)^{2} + 0.000\left(10^{-pCl}\right)^{3} + 8.921\ 10^{-8}\ 10^{-pCl}\right)10^{pCl}$$

Finally the logarithmic plot can be rendered. Again the command is built into the plot command, but recall that through **Plot > Axes > Properties...** it is a simple matter to change the vertical axis to a logarithmic scale, but the numbering will be different.

```
> plot(log[10](SOLUBILITY), pCl = 0..5, axes = boxed, labels =
  ["pCl","log of Solubility"], color = maroon);
```

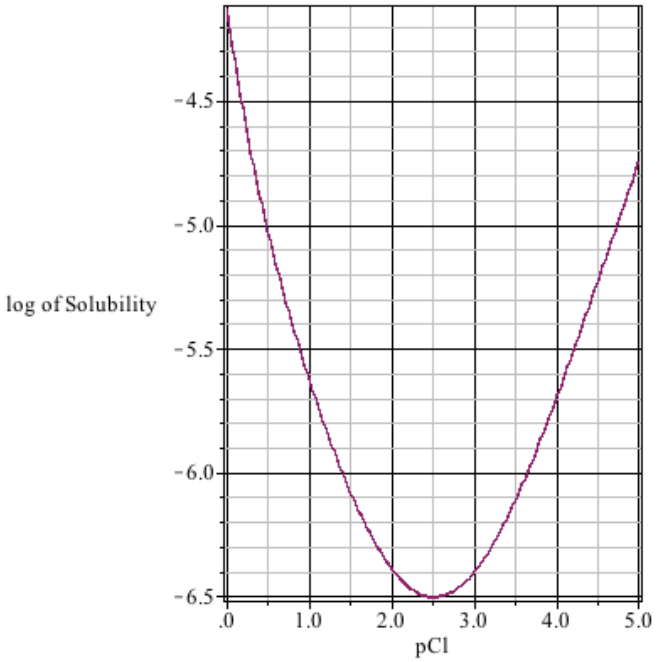

Figure 10-4

The point of minimum AgCl(s) solubility can be found quantitatively by finding the point at which $^{dSolubility}/_{dCl}$ is equal to zero. Unlike the work in Chapter 6 (Part I, page 139) we will combine two steps into one.

```
> Cl[optimum]:= solve(diff(Solubility, Cl) = 0, {Cl});
```

$$Cl_{optimum} := \{Cl = 0.0030\},$$
$$\{Cl = -0.1832 + 03868*I\}, \{Cl = -0.0030\},$$
$$\{Cl = -0.1832 - 03868*I\},$$

Only one physically possible root is found, the first root. After a change in numeric formatting:

```
> Cl:= subs(Cl[optimum][1], Cl);
```

$$Cl := 0.00301$$

With [Cl^-] assigned the value that gives minimal solubility, the nature of the solution can be analyzed by calling *Solubility* and the five alphas.

```
> 'Solubility'= Solubility; 'alpha[Ag]'= alpha[Ag]; 'alpha[AgCl]'=
  alpha[AgCl]; 'alpha[AgCl[2]]'=alpha[AgCl[2]]; 'alpha[AgCl[3]]'=alp
  ha[AgCl[3]]; 'alpha[AgCl[4]]'= alpha[AgCl[4]];
```

$$Solubility = 3.12931\ 10^{-7}$$

$$a_{Ag} = 0.18874$$

$$a_{AgCl} = 0.62309$$

$$\alpha_{AgCl_2} = 0.18760$$

$$\alpha_{AgCl_3} = 0.00056$$

$$\alpha_{AgCl_4} = 0.00000$$

The issue of intrinsic solubility emerges again: Notice that most (62.3%) of the silver in solution is in the form of AgCl(aq), and that less than one fifth exists as free Ag^+.

$[Cl^-] = 0.00301$ should not be confused with C_{Cl}, which is the *total* chloride concentration necessary to effect minimum solubility of AgCl(s). Each AgCl(s) will require one Cl^-, each $AgCl_2^-$ will require two Cl^-s *etc.*[224]

```
> C[Chloride, total]:= Cl + (alpha[AgCl] + 2*alpha[AgCl[2]] + 3*
  alpha[AgCl[3]] + 4*alpha[AgCl[4]])*Solubility;
```

$$C_{Chloride,total} := 0.00301$$

This is indistinguishable from Cl, but `C[Chloride, total] - Cl;` reveals a difference of (only) 3.1 10^{-7}. This is small because the total solubility is so small (3.1 10^{-7}).

The effect of ligand concentration on solubility is used more proactively by introducing strong ligands that can mask a cation from anions that cause it to precipitate. The principle is exactly the same as what was addressed in Chapter 9 (page 70) regarding the masking of metal cations from chelating agents. Indeed, ligands or more specifically chelating agents can be used to dissolve insoluble salts. This was the premise of Example Problem 4 in the previous chapter.

Consider the process of dissolving AgCl(s) in NH_3(aq). Because NH_3 is a much stronger ligand than Cl^-, it is much more effective at reducing α_{Ag+}. The solubility of AgCl(s) in water can be calculated by the process discussed on page 110 ($KClO_4$ example). What about the solubility of AgCl(s) or AgBr(s) in 6.0 **M** NH_3(aq)? The process will follow that of the $KClO_4$ example except that α_{Ag+} will be included in the solubility equilibrium expression. As AgCl(s) dissolves, Cl^- will be released, but the formation of $AgCl_n^{1-n}$ complexes will *not* be considered for the simple reason that [Cl^-] will not be able to exceed [Ag^+]. So there will not be enough chloride to form appreciable quantities of those chloro complexes, especially with their relatively small formation constants.

```
> restart; SolEq:= K[sp] = alpha[Ag]*C[Ag]*C[Cl];
```

$$SolEq := K_{sp} = a_{Ag} C_{Ag} C_{Cl}$$

Inasmuch as all of the Ag^+ and all of the Cl^- come from the same source, namely AgCl(s), C_{Ag} and C_{Cl} must be equal. (And this is why $AgCl_n^{1-n}$ with n >1 cannot form.) By the same reasoning, C_{Ag} and C_{Br} will be equal when AgBr(s) dissolves.

```
> C[Cl]:= C[Ag]: SolRoots:= solve(SolEq, {C[Ag]});
```

$$SolRoots := \left\{ C_{Ag} = \frac{\sqrt{\alpha_{Ag} K_{sp}}}{\alpha_{Ag}} \right\}, \left\{ C_{Ag} = -\frac{\sqrt{\alpha_{Ag} K_{sp}}}{\alpha_{Ag}} \right\}$$

The second root, with $C_{Ag} < 0$, can have no physical meaning. So,

```
> Solubility:= subs(SolRoots[1], C[Ag]);
```

$$Solubility := \frac{\sqrt{\alpha_{Ag} K_{sp}}}{\alpha_{Ag}}$$

Notice that the expression for solubility is no longer AgCl-specific. Indeed, it is applicable to any 1:1 AgX salt. The specificity comes from K_{sp} and that will be incorporated presently. But first, α_{Ag} will be expressed. The output is not shown because the operation has been performed several times in this and the previous chapters. α_{Ag} and α_{NH3} are defined here because they are going to be needed to convert C_{NH3} to $[NH_3]$ in a few input lines.

```
> Den:= 1 + beta[1]*NH[3] + beta[2]*NH[3]^2: alpha[Ag]:= 1/Den:
  alpha[AgNH3]:= op(2,Den)/Den; alpha[AgNH3[2]]:= op(3,Den)/Den:
  Solubility;
```

$$Solubility = \left(1 + \beta_1\, NH_3 + \beta_2\, NH_3^2\right) \sqrt{\frac{K_{sp}}{1 + \beta_1\, NH_3 + \beta_2\, NH_3^2}}$$

This expression for solubility shows that increasing $[NH_3]$, β_1, β_2, or K_{sp} will lead to an increase in solubility of the precipitate. Of course the latter three are constants that cannot be changed without changing the chemistry. Only the betas are assigned next.

```
> beta[1]:= 10^3.32: beta[2]:= 10^7.24:
```

Now, rather than simply assign one value to K_{sp} for AgCl and then another value for AgBr, the `subs` operation will be used. This will create two, compound-specific expressions from the same general expression.

```
> Sol[AgCl]:= subs(K[sp] = 1.78e-10, Solubility); Sol[AgBr]:=
  subs(K[sp] = 5.3e-13, Solubility);
```

The results (not shown) are two expressions that contain NH_3 as the only variable. One might wish to plot Sol_{AgCl} and Sol_{AgBr} as a function of $[NH_3]$, but the problem at hand is to calculate these solubilities at C_{NH3}. The best approximation that can be provided for $[NH_3]$ is C_{NH3}.

```
> NH[3]:= 6.0: AgCl_in_NH3:= Sol[AgCl]; AgBr_in_NH3:= Sol[AgBr];
```

$$AgCl\_in\_NH3 := 0.334$$
$$AgBr\_in\_NH3 := 0.018$$

This shows a considerable solubility of both silver salts despite their small solubility products. If 0.334 mole of AgCl were to dissolve in one liter of 6.0 **M** NH_3(aq) one should suspect a measurable NH_3 loss to the formation of $AgNH_3^+$ and $Ag(NH_3)_2^+$. That is to say, $[NH_3]$ will be measurably smaller than C_{NH3}. This adjustment is achieved with the reiteration, and as on page 114.

```
> for i to 4 do
> NH[3]:= 6-(alpha[AgNH3] + 2* alpha[AgNH3[2]])*Sol[AgCl];
> end;
```

$$NH_3 := 5.333$$
$$NH_3 := 5.407$$
$$NH_3 := 5.399$$
$$NH_3 := 5.399$$

Even after one iteration, [NH_3] settles in to within 1.2% of the "final" computation. Using this refined value for [NH_3] gives a reliable answer for AgCl solubility in C_{NH3} = 6.0 **M**, by using [NH_3] = 5.399.

```
> Solubility_of_AgCl = Sol[AgCl];
```

$$Solubility\_of\_AgCl = 0.300$$

An identical loop is executed for the AgBr solubility, using of course Sol[AgBr]. It yields:

$$NH_3 := 5.967$$
$$NH_3 := 5.964$$
$$NH_3 := 5.964$$
$$NH_3 := 5.964$$

Notice that NH[3] := 6 was not required. This is because the assignment of NH[3] in the loop effectively does that for us. Why did *this* loop settle on a concentration so quickly? Because so little AgBr dissolves that it barely perturbs the initial 6.0 **M** NH_3 concentration. Using the final [NH_3] gives:

```
> Solubility_of_AgBr = Sol[AgBr];
```

$$Solubility\_of\_AgBr = 0.018$$

Before leaving this problem, two comments are in order: first, ionic strength effects have, again, been ignored. They will be significant for both solids, especially the AgCl dissolution where C_{Ag+} and C_{Cl}- will be 0.300 **M**. This can be shown to equal the ionic strength. It would be simple enough to embed the μ calculation and γ calculations inside the for loops above. Even without this refinement, the calculation is useful in illustrating that AgCl is quite soluble in 6 **M** NH_3(aq) and that AgBr is not. The second point is that a more rigorous treatment of this problem would have [NH_3] represented as $\alpha_{NH3}C_{NH3}$. This is because, recall, NH_3 is a weak base and so its α_{NH3} is profoundly affected by pH. Indeed, adding H^+ to the AgCl/NH_3 solution will re-precipitate the AgCl as α_{NH3} is driven to zero.

The final topic in this chapter is the precipitation titration. The requirements of gravimetric methods have been enumerated (page 114), and they are crucial to a successful analysis. In addition to these, there must be enough analyte to provide a large enough mass of precipitate that it can be weighed with confidence. When this is not the case, the precipitation titration can be an attractive alternate to gravimetric methods. Moreover, volumetric techniques are almost always carried out more quickly than gravimetric techniques.

Consider the prospect of titrating OCN^- with Ag^+.[225] The nomenclature used in Chapters 7 and 9 will be continued here. So, the titrand will have a concentration $C°_{OCN}$ and will be delivered as volume $V°_{OCN}$, and the titrant will have a concentration $C°_{Ag}$ and a volume V_{Ag}. Because Ag^+ and OCN^- react 1:1, the equivalence point volume of Ag^+ can be determined from:

$$C°_{Ag}V_{EqPt} = C°_{OCN}V°_{OCN}.$$

At any point in the titration, C_{Ag+} and C_{OCN}- are calculated as in Equation 7-8, and the equivalence point, analytical concentrations of Ag^+ and Cl^- will be determined as in Equation **7-10**.

Finally, the solubility equilibrium condition follows what has been presented in earlier examples. That is

$$K_{sp} = (C_{Ag} - Prcp)(C_{OCN} - Prcp).^{226}$$

Applying these principles to a new Maple worksheet might look like:

```
> restart; SolEq:= K[sp] = (C[Ag] - Prcp)*(C[OCN] - Prcp);
> C[Ag]:= C°[Ag]*V[Ag]/(V°[OCN] + V[Ag]): C[OCN]:= C°[OCN]*V°
  [OCN]/(V°[OCN] + V[Ag]): SolEq;
```

$$K_{sp} = \left(\frac{C°_{Ag} V_{Ag}}{V°_{OCN} + V_{Ag}} - Prcp \right) \left(\frac{C°_{OCN} V°_{OCN}}{V°_{OCN} + V_{Ag}} - Prcp \right)$$

This expression is a quadratic in *Prcp*. Next, because there are no soluble forms of Ag^+ in solution other than Ag^+, $[Ag^+] = C_{Ag} - Prcp$. So it remains only to compute C_{Ag} and *Prcp* at each given V_{Ag} to acquire the $[Ag^+]$ at that point in the titration.[227]

```
> SolEq_Roots:= solve(SolEq, {Prcp});
```

Neither of the two roots is shown here. They are long, complicated, and neither is *clearly* the physically possible root (*i.e.* $Prcp \le C_{Ag+}$). So a guess is made. If the guess were wrong, it would be apparent in the plot and then the other root would be chosen. The correct guess, by the way, is the second root.

```
> Prcp:= subs(SolEq_Roots[2], Prcp);
```

$$Prcp := \frac{1}{V°_{OCN} + V_{Ag}} \left(\frac{1}{2} C°_{Ag} V_{Ag} + \frac{1}{2} C°_{OCN} V°_{OCN} - \frac{1}{2} \left(C°^2_{Ag} V^2_{Ag} - 2 C°_{Ag} V_{Ag} C°_{OCN} V°_{OCN} + C°^2_{OCN} V°^2_{OCN} + 4 K_{sp} V°^2_{OCN} + 8 K_{sp} V°_{OCN} V_{Ag} + 4 K_{sp} V^2_{Ag} \right)^{1/2} \right)$$

Finally, we use C_{Ag} and *Prcp* to compute the soluble Ag^+ from what is left of C_{Ag} after AgOCN precipitates out. The expression will be displayed after the appropriate constants are assigned. The K_{sp} is found in the literature and the other constants arbitrarily chosen to depict a routine titration. The final expression will show that only V_{Ag} is required for input.

```
> Sol[Ag]:= C[Ag] - Prcp;
> C°[Ag] := 0.25; C°[OCN]:= 0.20; V°[OCN]:= 10.00; K[sp]:= 2.3e-7;
  'Sol[Ag]'= Sol[Ag];
```

$$Sol_{Ag} = \frac{0.250\ V_{Ag}}{10.000 + V_{Ag}} - \frac{1}{10.000 + V_{Ag}}\left(0.125\ V_{Ag} + 1.000 - \frac{1}{2}\sqrt{0.063\ V_{Ag}^2 - 1.000\ V_{Ag} + 4.000}\right)$$

```
> plot(-log[10](Sol[Ag]), V[Ag] = 0..12, labels = ["mL of Ag+","-
  log[Ag+]"], axes = boxed);
```

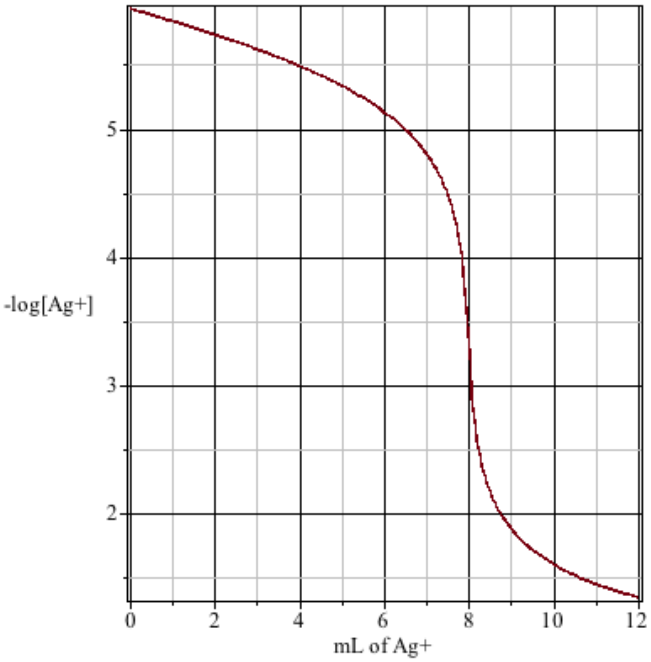

Figure 10-5

The equivalence point should occur at 8.00 mL of Ag^+. So points were plotted to 12 mL (50% excess) to make the $^{\Delta pAg}/_{\Delta V}$ at the equivalence point especially clear, but the $^{\Delta pAg}/_{\Delta V}$ is not particularly sharp. This is due to the relatively large K_{sp} for the C_{Ag+} at the equivalence point, a problem precisely like what was seen for the titration of weak acids at low concentrations.[228] This K_{sp} does not quite yield the requisite ≥ 99.9% completion at the equivalence point. To illustrate this the completeness is calculated with V_{Ag} = 8.00 mL.

```
> V[Ag]:= 8.00: EqPt[Ag]:= Sol[Ag]; EqPt[Precip]:= Prcp;
```

$$EqPt_{Ag} := 0.00048$$
$$EqPt_{Precip} := 0.11063$$

Before continuing with the calculation for completeness, a few comments might be useful: The value computed for `Sol[Ag]` will be needed in subsequent calculations, but care was taken not to assign `Sol[Ag]` to that value. Doing that would have made it a constant, no longer an expression and so later in the worksheet, one could not compute a new Sol_{Ag} from a new V[Ag], nor compute a V_{Ag} from an assigned `Sol[Ag]`. Notice, also, the subtle change to the *EqPt* subscript; *Prcp* currently has a value. So calling $EqPt_{Prcp}$ would have given $EqPt_{0.11063}$. This is done in lieu of protecting `Prcp`.

Completeness will be the "concentration" of precipitated Ag^+ divided by the analytical concentration of Ag^+, times one hundred, of course.

```
> Completeness:= 100*Prcp/C[Ag];
```

$$Completeness := 99.568$$

How can this equivalence point be observed? A potentiometric titration would require measurement of $\{Ag^+\}$ which will track $[Ag^+]$ closely, and both $\{Ag^+\}$ and $[Ag^+]$ will show a rapid change at the equivalence point. Another way to detect the equivalence point in a precipitation titration is by adding a small amount of a second anion that forms a precipitate with the metal ion being precipitated. The concentration of this second anion can be chosen so that it will *not* precipitate until the equivalence point is reached. For example, CrO_4^{2-} will precipitate Ag^+ as $Ag_2CrO_4(s)$. It is much less soluble than AgOCN(s) having a K_{sp} of only $1.1\ 10^{-12}$. From the previous output, the equivalence point $[Ag^+]$ is 0.00048 **M**. What $[CrO_4^{2-}]$ is necessary to cause the initial formation of $Ag_2CrO_4(s)$ at *this* $[Ag^+]$? Given that

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

the worksheet is continued with definitions, a K_{sp} (from Appendix VII) and a numeric formatting change for C_{CrO4}:

```
> IndicatorEq:= K[spCrO4] = EqPt[Ag]^2*C[CrO4];
```

$$IndicatorEq := K_{spCrO4} = 2.30000$$

```
> K[spCrO4]:= 10^(-11.95): C[CrO4]:= fsolve(IndicatorEq, C[CrO4]);
```

$$4.88 \times 10^{-6}$$

So, the titrand must be made to $4.9\ 10^{-6}$ **M** in CrO_4^{2-} *at the equivalence point.* This would be at a total volume of 18 mL, plus the volume of the chromate solution. The volume of chromate indicator can be rendered insignificant by preparing the indicator at a high concentration. Suppose that one drop is taken as 0.05 mL, and one wishes to achieve $4.9\ 10^{-6}$ **M** CrO_4^{2-} by adding one drop of $C°_{CrO4}$ solution to the titrand. Then, $C°_{CrO4}$ can be calculated from its initial volume, 0.05 mL, and final volume (at the equivalence point).

```
> Ind_Con:= solve(0.05*C°[CrO4] = (10 + 8 + 0.05)*C[CrO4]);
```

$$Ind\_Con := 0.00176$$

The procedure would require the preparation of a 0.0018 **M** CrO_4^{2-} solution, probably as K_2CrO_4 and adding one drop of this to the titrand. This would impart a pale yellow color to the solution which would persist until the silver ion concentration reaches 0.00048 **M**. At this point, which coincides with the equivalence point, Ag_2CrO_4, a brick red precipitate would form, constituting an endpoint. But suppose that a drop is 0.04 or 0.06 mL. What, then, is the titration error? Considering the use of 0.04 mL of indicator solution, C_{CrO4} is unassigned and then calculated.

```
> C[CrO4]:= 'C[CrO4]': C[CrO4]:= solve(0.04*Ind_Con = (10 + 8 +
  0.04)*C[CrO4]);
```

$$C_{CrO4} := 0.0000039048$$

Adding too little indicator makes the chromate concentration too small by a factor of 0.8 (*i.e.* $^{3.9E\text{-}6}/_{4.9E\text{-}6}$). What will $[Ag^+]$ be at the onset of Ag_2CrO_4 precipitation? *IndicatorEq* is rewritten in terms of EndPt[Ag]. Because $EndPt_{Ag}$ will be squared in this expression, two roots are anticipated, and therefore they are to be listed by using braces in the `solve` command.

```
> IndicatorEq:= K[spCrO4] = EndPt[Ag]^2*C[CrO4]; Ind_Roots:=
solve(IndicatorEq, {EndPt[Ag]});
```

$$IndicatorEq := 1.1000\ 10^{-12} = 0.0000\ EntPt^2_{Ag}$$
$$Ind\_Roots := \{EndPt_{Ag} = -0.00054\}, \{EndPt_{Ag} = 0.00054\}$$

Clearly, it is the second root that has meaning. So it is selected.

```
> EndPt[Ag]:=subs(Ind_Roots[2], EndPt[Ag]);
```

$$EndPt_{Ag} := 0.00054$$

Next, V_{Ag} is unassigned so that, again, it becomes a variable in Sol_{Ag}. It can be determined when Sol_{Ag} has been given a value. Sol_{Ag} will equal the *end*point $[Ag^+]$.

```
> V[Ag]:= 'V[Ag]'; V[EndPoint]:= solve(Sol[Ag] = EndPt[Ag], V[Ag]);
```

$$V_{EndPoint} := 8.00771$$

The volume of Ag^+ solution needed to reach the endpoint (onset of Ag_2CrO_4 precipitation) exceeds the volume necessary to reach the equivalence point. This is to be expected because by using too little CrO_4^{2-} indicator solution, $[CrO_4^{2-}]$ is too low, and so $[Ag^+]$ must be too large to offset this error. Notice that making $[CrO_4^{2-}]$ 20% too small does not translate into a 20% error. Indeed, because $\Delta[Ag^+]/\Delta V_{Ag}$ is appreciable at the equivalence point, the $5.6\ 10^{-5}$ **M** $\Delta[Ag^+]$ produces only a 0.0077 mL ΔV. Taking the equivalence point as 8.00 mL,

```
> Rel_Error:= 100*(V[EndPoint] - 8)/8;
```

$$Rel\_Error := 0.09631$$

A similar analysis would show that had 0.06 mL of indicator been used, the $V_{EndPoint}$ would have preceded the V_{EqPt} by about the same relative error.

In closing, the reader should be aware that for precipitation titrations there are several indicator strategies. Some indicators are sensitive to the net charge on a precipitate; that charge changes as the equivalence point is passed.[229] Other indicators respond to the change in the oxidation-reduction potential of the titrand as analyte is precipitated out of the titrand.[230] Calculating $V_{EndPoint}$ in these indicators requires more information than is provided here, but the principle of titration error remains the same, nevertheless.

Example Problems

1. Suppose that 10.00 mL of 0.15 **M** $Ca(NO_3)_2$ were mixed with 20.00 mL of 0.15 **M** HIO_3. Given that the $K°_{sp}$ for $Ca(IO_3)_2(s)$ is 7.1 10^{-7}, and considering ionic strength effects
   a) would a precipitate form?
   b) If so, what percent of the Ca^{2+} would be precipitated?
   c) If that percentage is less than 99.9%, how complete can the precipitation of Ca^{2+} be made given the $V°_{Ca}$, $C°_{Ca}$ and $C°_{IO3}$ allowing an increase in V_{IO3}.

4. One of the most important applications of pH control of precipitation pertains to the selective precipitation of sulfides. Consider a solution which is 0.10 **M** in Pb^{2+}, Ni^{2+}, and Fe^{2+}. Suppose that this solution could be made 0.20 **M** in *total* S^{2-} (*i.e.* $C_{S2-} = 0.20$). Could the pH of the solution be adjusted so that one or more might be precipitated completely (≥99.9%) without at all (≤0.1%) precipitating one or more of the others? Presume that the ionic strength of the solution is 0.3 and use Debye-Hückel to adjust for ionic strength effects.

5. $Zn(OH)_2$ is insoluble ($K_{sp} = 1.2\ 10^{-17}$), but it forms four hydroxy complexes as seen in Chapter 9 (page 61 *et seq.*). Ignoring ionic strength effects, what is the optimum $[H^+]$ for precipitating Zn^{2+} as its hydroxide?

6. In Chapter 9, Example Problem 4, $BaSO_4(s)$ was dissolved in 10.00 mL of 0.100 **M** EDTA at pH 8.8. Would that much $BaSO_4$ have dissolved and what is the maximum solubility of $BaSO_4$ there?

7. Recreate the Ag^+ / OCN^- titration begun on page 138, except calculate $\{Ag^+\}$ and plot pAg rather than $-\log_{10}[Ag^+]$.

Solutions to Example Problems

1. a. This problem follows the form of the work given on page 111, but with some important differences: this is a 1:2 compound, and it is a 1:2 mixture of solutions. This will change the solubility equilibrium expression and the relationship between C and C° for each agent.

   Because HIO_3 is taken as a strong acid (see Table **3-1**), α_{IO3} can be taken as 1.00, even at a high $[H^+]$, and because HIO_3 is being added to the Ca^{2+} solution, the solution will be distinctly acidic and no $CaOH^+$ will be formed. This will allow α_{Ca2+} to be taken as 1.00 also.

   The calculations are begun taking $K_{sp} \approx K°_{sp}$. After *Prcp* is calculated and subtracted from C_{Ca} and C_{IO3}, the soluble $[Ca^{2+}]$ and $[IO_3^-]$ can be calculated and used to find μ, then the γs and finally K_{sp}. This correction is not necessary for part **a**.

```
> restart; SolEq:= K[sp] = (C[Ca] - Prcp)*(C[IO3] -
2*Prcp)^2;
```

$$SolEq := K_{sp} = \left(C_{Ca} - Prcp\right)\left(C_{IO3} - 2\,Prcp\right)^2$$

SolEq is a cubic polynomial in *Prcp*. Following the approach used in the $CsClO_4$ example, `solve(SolEq, Prcp);` would be used and from the output, the one, physically relevant root would be selected for the computation of *Prcp*. A simpler, although less illustrative approach will be taken here: `fsolve` will be used because it can be guided to the only physically relevant root by setting the range over which roots are sought to 0 to C_{Ca}. The advantage is that, with `solve`, it can be difficult to select the appropriate root from the many lines of output, each line containing the many parameters. Also, `fsolve`, if it does not miss the root, provides "one-stop-shopping." With a 0 to C_{Ca} range, only a physically real root can be found

C_{Ca} and C_{IO3} are expressed in terms of the volumes and initial concentrations of these solutions,

```
> C[Ca]:= V°[Ca]*C°[Ca]/(V°[Ca] + V°[IO3]): C[IO3]:= V°[IO3]*
  C°[IO3]/(V°[Ca] + V°[IO3]):
```

and values are assigned to these parameters.

```
> V°[Ca]:= 10.0: V°[IO3]:= 20.0: C°[Ca]:= 0.15: C°[IO3]:=
  0.15: K[sp]:= 7.1e-7: Precipitate:= fsolve(SolEq, Prcp,
  0..C[Ca]);
```

$$Precipitate := 0.04438$$

Yes a precipitate will form. Because this calculation does not make adjustments for the considerable ionic strength of the solution, it will require a reiteration for part **b**.

1. b. The ionic strength will be

$$\mu = {}^1/_2\{[Ca^{2+}](2)^2 + [H^+](1)^2 + [IO_3^-](-1)^2 + [NO_3^-](-1)^2\}.$$

Because $[H^+]$ from H_2O is much less than $[H^+]$ from HIO_3 (see Part I, page 44) we can safely say that

$$[H^+] = C_{IO3}.$$

Because $Ca(NO_3)_2$ is a strong electrolyte,

$$[NO_3^-] = 2C_{Ca}$$

Mass balance requires that the concentration of soluble Ca^{2+} will be diminished by the amount of Ca^{2+} lost to precipitate formation.[231] So,

$$[Ca^{2+}] = C_{Ca} - Precipitate.$$

Likewise, mass balance for iodate will require that the concentration of soluble IO_3^- will be diminished, but by *twice* the amount that is lost to precipitate formation because each $Ca(IO_3)_2$ obviously contains two IO_3^-'s.

$$[IO_3^-] = C_{IO3} - 2\times Precipitate.$$

This allow the expression of μ in fewer terms:

```
> μ:= 0.5*((C[Ca] - Precipitate)*2^2 + C[IO3] + (C[IO3] -
  2*Precipitate) + 2*C[Ca]);
```

$$\mu := 0.117$$

Using Equation **2-13** with ionic radii from Appendix II provides the necessary activity coefficients.

```
> a[Ca]:= 6; a[IO3]:= 4; Gamma[Ca]:=
  10^(-0.511*(2^2)*sqrt(μ)/(1 + (0.329*a[Ca]*sqrt(μ))));
  Gamma[IO3]:= 10^(-0.511*sqrt(μ)/(1 +
  (0.329*a[IO3]*sqrt(μ))));
```

Now, for the correction of $K°_{sp}$ to K_{sp}.

```
> K[sp]:= K[sp]/(Gamma[Ca]*Gamma[IO3]^2);
```

$$3.23 \times 10^{-6}$$

This represents a substantial change in K_{sp}. It is almost five times larger than $K°_{sp}$ (7.1×10^{-7}) and that will substantially reduce the completeness of the precipitation.

```
> Precipitate:= fsolve(SolEq, Prcp, 0..C[Ca]);
```

$$Precipitate := 0.04069$$

This constitutes a ten percent decrease in *Precipitate* from what was found in part **a**.

```
> Completeness:= 100*Precipitate/C[Ca];
```

$$Completeness := 81.37$$

1. c. This completeness is far from adequate and it will likely require a substantial excess of HIO_3 solution to drive this precipitation to completion.

   There are several strategies to finding an optimum volume of HIO_3 solution. It might appear that one could return to *SolEq* and assign `Prcp:= 0.999*V°[Ca]* C°[Ca]/(V°[Ca] + V[IO3])`, assign the two concentrations, $V°_{Ca}$ and K_{sp} and then solve for V_{IO3}. But this gives V_{IO3} = 8.47 mL, an obviously incorrect answer! (V_{IO3} must be at least $2 \times V°_{Ca}$ to provide enough IO_3^- to precipitate $V°_{Ca} \times C°_{Ca}$ moles of Ca^{2+}.) The problem is a misguided use of `Precp` which contains IO_3^-. We will see shortly that 99.9% precipitation is not possible (page 151). An entirely new approach is necessary.

   We will solve this problem by revisiting the mass balance requirements, and rewriting the equilibrium expression *without Prcp*. This new strategy will create an expression that Maple can handle.

   Consider the Ca^{2+} and IO_3^- mass balance requirements that were introduced in the ionic strength calculation. `Sol[Ca]` pertains to $[Ca^{2+}]$ which is the soluble portion of Ca^{2+} in solution; likewise `Sol[IO3]` represents the *soluble* IO_3^-.

```
> restart; CaMassBal:= C[Ca] - Prcp = Sol[Ca]; IO3MassBal:=
  C[IO3] - 2*Prcp = Sol[IO3];
```

$$CaMassBal := C_{Ca} - Prcp = Sol_{Ca}$$
$$IO3MassBal := C_{IO3} - 2\,Prcp = Sol_{IO3}$$

Prcp can be removed from this pair of expressions and a more general mass balance expression can be written.

```
> MassBal:= 2*CaMassBal - IO3MassBal;
```

$$MassBal := 2*C_{Ca} - C_{IO3} = 2*Sol_{Ca} - Sol_{IO3}$$

The solubility equilibrium requirement remains as it was, but it is expressed in newer terms: Sol_{xx} instead of $C_{xx} - Prcp$.

```
> SolEq:= K[sp]= Sol[Ca]*Sol[IO3]^2;
```

$$SolEq := K_{sp} = Sol_{Ca}\,Sol_{IO3}^2$$

This is used to express Sol_{IO3} in terms of Sol_{Ca}.

```
> IO3Roots:= solve(SolEq, {Sol[IO3]});
```

$$IO3Roots := \left\{Sol_{IO3} = \frac{\sqrt{Sol_{Ca}\,K_{sp}}}{Sol_{Ca}}\right\}, \left\{Sol_{IO3} = -\frac{\sqrt{Sol_{Ca}\,K_{sp}}}{Sol_{Ca}}\right\}$$

The second root can have no physical meaning. So,

```
> Sol[IO3]:= subs(IO3Roots[1], Sol[IO3]):
```

For inspection,

```
> 'MassBal'= MassBal;
```

$$MassBal = \left(2\,C_{Ca} - C_{IO3} = 2\,Sol_{Ca} - \frac{\sqrt{Sol_{Ca}\,K_{sp}}}{Sol_{Ca}}\right)$$

The concentrations are expressed in terms of *unmixed* concentrations and solution volumes, and *MassBal* is again inspected.

```
> C[Ca]:= V°[Ca]*C°[Ca]/(V°[Ca] + V[IO3]): C[IO3]:= V[IO3]*
  C°[IO3]/(V°[Ca] + V[IO3]): 'MassBal'=MassBal;
```

$$MassBal = \left(\frac{2\, V°_{Ca}\, C°_{Ca}}{V°_{Ca} + V_{IO3}} - \frac{V_{IO3}\, C°_{IO3}}{V°_{Ca} + V_{IO3}} = 2\, Sol_{Ca} - \frac{\sqrt{Sol_{Ca}\, K_{sp}}}{Sol_{Ca}} \right)$$

The parameters from Parts **a** and **b** are assigned. $K°_{sp}$ is not given here because we will not correct for ionic strength effects as we did in Part **b**. `MassBal` is called but will not be shown here for one more, critical step.

```
> V°[Ca]:= 10.00: C°[Ca]:= 0.150: C°[IO3]:= 0.150: K[sp]:=
  7.1e-7: 'MassBal'= MassBal:
```

This is the implicit expression for the concentration of *soluble* Ca^{2+} in terms of the volume of HIO_3 added. To write it explicitly:

```
> Soluble[Ca]:= solve(MassBal, {Sol[Ca]});
```

The three roots are too long to be displayed meaningfully. An inspection of the output would show that the second and third roots yield complex numbers. So the first root is selected. This solubility might be expressed as a *relative* solubility because *absolute* solubility is meaningless.[232] So:

```
> Solubility:= 100*subs( Soluble [Ca][1],Sol[Ca])/ C[Ca]:
```

And finally a plot, but the plot shown required a bit of trial and error to create the clear display. The V_{IO3} that produces the minimum *relative* solubility is not obvious. So experimenting with the range for `V[IO3]` was required. This optimum volume might be found by plotting a narrower and narrower region.

```
> plot(Solubility, V[IO3] = 50..100, axes = boxed, color
  = blue, labels = ["Vol of HIO3","% Ca in Solution"],
  gridlines = true);
```

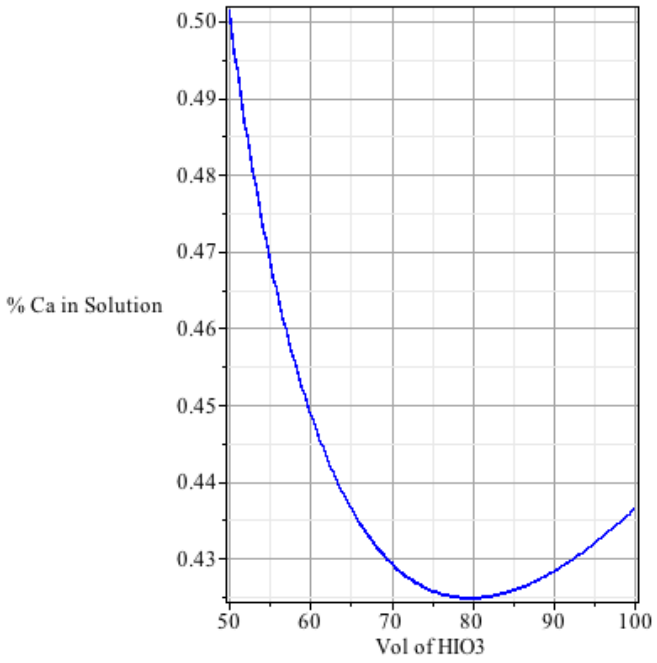

Figure 10-6

The scale here is a bit misleading: note that between 50 and 80 mL of HIO_3 the percentage of Ca^{2+} that remains in solution decreases from only 0.500% to 0.425%. The optimum V_{IO3} can be found where $^{dSolubility}/_{dV} = 0$. `fsolve` requires the V_{IO3} = 50 to 100 range; without a range, the operation fails to return a value.

```
> DerSol:= diff(Solubility, V[IO 3]): V[Min Sol]:= fsolve
  (DerSol, V[IO3]=50..100);
```

$$V_{MinSol} := 79.745$$

And what is that minimum solubility, and what percentage of Ca^{2+} is precipitated at this volume?

```
> V[IO3]:= %: MinSol:= evalf(Solubility); PercentPrecip:= 100
- %;
```

$$MinSol := 0.425$$
$$PercentPrecip := 99.575$$

Before leaving this problem, it is worth noting that substituting 20.0 mL for V_{IO3} into the `Solubility` expression will produce:

```
> V[IO3]:= 20.0: Sol[EqPt]:= evalf(Solubility);
  PercentPrecip:= 100 - %; P:= C[Ca]*%/100;
```

$$Sol_{EqPt} := 11.23991$$
$$PercentPrecip := 88.76009$$
$$P := 0.04438$$

P is the amount of precipitate found in part **a** of this problem; it agrees exactly with the output obtained from the cubic polynomial expression used to solve directly for `Precipitate`. So that expression was correct, but only very near the equivalence point (20 mL of HIO_3). The lesson is that it is sometimes necessary to present Maple with a different formulation of a problem in order to extract correct answers. In Part **a** and in the resolution of 1:1 precipitates like AgOCN, it is acceptable to solve for *Prcp*, the amount of an agent that is precipitated from solution. In Part **c**, however, it became evident that it is necessary to solve for *Sol* the amount of agent *not* precipitated and then to subtract *Sol* from the total concentration, *C*, to get *Prcp*. Only by careful inspection of the two strategies does it become apparent that they yield different results, and inasmuch as only one can be correct, always check the results to see if they are reasonable.

2. "Complete precipitation" would require that ≤ 0.1% of the metal cation remains in solution. Given that $C°_{M2+}$ is 0.10 **M**, this implies $[M^{2+}] \leq 1\ 10^{-4}$ **M** or pM ≥ 4. "No precipitation" requires that ≥ 99.9% of the metal cation remains in solution so that $[M^{2+}] \geq 9.99\ 10^{-2}$ **M** or pM ≥ 1. Plotting pM *vs.* pH should illustrate the feasibility of this separation.

   Because H_2S is a weak acid ($pK°_{a1}$ = 6.97 and $pK°_{a2}$ = 12.92), α_{S2-} must be calculated for each pH. A rigorous calculation would also necessitate the computation of each α_{M2+} because all three are susceptible to $M(OH)_n^{2-n}$ formation. But it will be shown that this question can be answered at pH ≤ 6 where the formation of hydroxy complexes is negligible. So α_{M2+} will be taken as 1.000 in this work.

   The strategy here will be to write a single expression for Pb^{2+}, Ni^{2+} and Fe^{2+} addressing ionic strength effects, and then to distinguish the three cations by substituting the appropriate $K°_{sp}$ into the general expression. Because we are seeking the activity, not concentration, of each cation, the activity coefficients will not need to be calculated. Also, it will turn out that γ_{H+} will not need to be calculated, because it cancels out of the general expression. We begin with the familiar solubility equilibrium expression, but in terms of $K°_{sp}$ rather than K_{sp}. This requires the use of the activity of M^{2+} and S^{2-} in place of their respective molarities.

```
> restart; SolEq:= K°[sp] = Act[M]*Act[S]:
```

From Equation **2-3**:

```
> Act[S]:= Gamma[S]*Sol[S]: Sol[S] := alpha[S]*C[S]:
'SolEq'=SolEq;
```

$$SolEq := (K°_{sp} = Act_M \Gamma_S a_S C_s)$$

From page 11:

```
> alpha[S]:= K[a1]*K[a2]/(H^2 + H*K[a1] + K[a1]*K[a2]);
  'SolEq'= SolEq;
```

$$\alpha_S := \frac{K_{a1} K_{a2}}{H^2 + H K_{a1} + K_{a1} K_{a2}}$$

$$SolEq = \left(K°_{sp} = \frac{Act_M \Gamma_S K_{a1} K_{a2} C_S}{H^2 + H K_{a1} + K_{a1} K_{a2}} \right)$$

Now to address ionic strength effects. See Equations **8-3a – 8-3c** for the effects on the dissociation constants of a polyprotic acid. The effects on solubility constants were discussed early in this chapter. Notice that `Gamma[Hyd]` is used for γ_{H+}. This is because "H" is used in an expression and is later assigned a new expression. This new expression would then be incorporated in `Gamma[H]`. Then $[H^+]$ will be expressed as pH.

```
> K[a1]:= K°[a1]/(Gamma[Hyd]*Gamma[HS]); K[a2]:=
  Gamma[HS]*K°[a2]/ (Gamma[Hyd]*Gamma[S]); H := 10^(-pH)/
  Gamma [Hyd];
```

$$K_{a1} := \frac{K°_{a1}}{\Gamma_{Hyd} \Gamma_{HS}}$$

$$K_{a2} := \frac{\Gamma_{HS} K°_{a2}}{\Gamma_{Hyd} \Gamma_S}$$

$$H := \frac{10^{(-pH)}}{\Gamma_{Hyd}}$$

An expression for $\{M^{2+}\}$ is extracted from the solubility equilibrium expression by solving it for Act_M. This is why γ_M was never required.

```
> Act[M]:= solve(SolEq, Act[M]);
```

$$Act_M := \frac{K^\circ_{sp}\left(\left(10^{-pH}\right)^2 \Gamma_{HS}\Gamma_S + 10^{-pH} K^\circ_{a1}\Gamma_S + K^\circ_{a1}K^\circ_{a2}\Gamma_{HS}\right)}{K^\circ_{a1}K^\circ_{a2}\Gamma_{HS}\Gamma_S C_S}$$

Notice that the activity coefficient for H^+ (Γ_{Hyd}) has cancelled out. This Act_M is converted into a logarithmic form for plotting. Yes, this operation can be carried out within the `plot` command, but remember that we are going to break this general expression into three, metal ion-specific expressions. So we convert to -log here.

```
> pM:= -log[10](Act[M]):
```

The two activity coefficients, γ_{HS^-} and γ_{S2-} are constants because μ has been set at 0.3. Constants are taken from Appendix II, and γs are calculated with Equation **2-13**.

```
> μ:= 0.3; a[HS]:= 3.5; a[S]:=5; Gamma[HS]:=
  10^(-0.511*sqrt(μ)/ (1 + (0.329*a[HS]*sqrt(μ))));
  Gamma[S]:= 10^(-0.511*((-2)^2)* sqrt(μ)/(1 +
  (0.329*a[S]*sqrt(μ))));
```

$$\Gamma_{HS} := 0.6735$$
$$\Gamma_S := 0.2577$$

Finally, values are assigned to the dissociation constants and to C_S and then pM is called, for one final inspection.

```
> K°[a1]:= 10^(-7.00): K°[a2]:= 10^(-12.92): C[S]:= 0.20:
'pM'= pM;
```

$$pM = -\frac{1}{\ln(10)}\left(\ln\left(2.396230\,10^{21}\,K^\circ_{sp}\left(0.173557\left(10^{-pH}\right)^2 + 2.576777\,10^{-8}\,10^{-pH} + 8.097755\,10^{-21}\right)\right)\right)$$

Only two variables remain, $K°_{sp}$ which distinguishes Pb^{2+} from Ni^{2+} from Fe^{2+} and pH which of course drives pH effects. Each pM is now created using the `subs` operation. (Fe^{2+} is designated `Fe2` to distinguish it from Fe^{3+}.)

```
> pPb:= subs(K°[sp] = 10^(-26.60),pM): pNi:= subs(K°[sp] =
  10^ (-18.49), pM): pFe2:= subs(K°[sp] = 10^(-17.30), pM):
```

The output is predictable: it looks like the previous output but without the $K°_{sp}$ parameter. This leaves the three expressions that will be plotted. Here we add two "pseudo expressions." These are constants that will produce horizontal lines on the plot; they will delineate the pM above which M is "completely" soluble and below which M is "completely" insoluble.[233]

```
> soluble:= 1: insoluble:= 4:
```

The three expressions and two pseudo expressions are plotted.

```
> plot([pPb, pNi, pFe2, soluble, insoluble], pH = 0..7, axes
  = boxed, color = ["DarkOrchid", "DarkGreen", "DarkBlue",
  black, black], labels = ["pH", "pM"], gridlines = true);
```

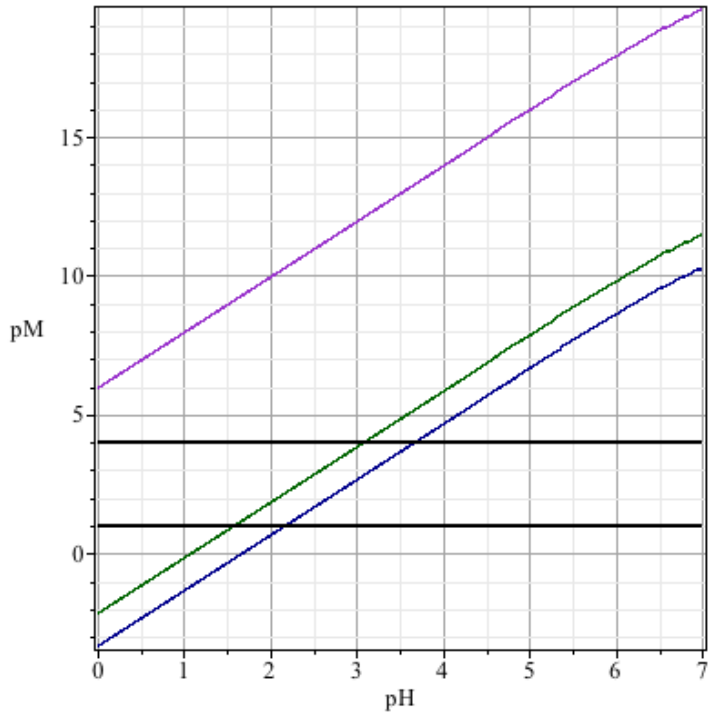

Figure 10-7

The solubility line for Pb^{2+} (orchid) lies entirely above the completely insoluble boundary indicating that even at pH zero, α_{S2-} cannot be made sufficiently small to provide a measurable solubility of PbS. Even for Ni^{2+} and Fe^{2+}, green and blue respectively, the pH must be maintained below 1.6 and 2.2, respectively, to effect complete dissolution.

To answer the question regarding the separation of these metals, it is evident that Pb^{2+} can be selectively precipitated from Ni^{2+} and Fe^{2+} using a 0.2 **M** S^{2-} solution if it is maintained below pH 1.6 (and above ≈ *minus* 2). The Ni^{2+} and Fe^{2+} solubility lines never separate by more than 1.5. This means that over this pH range, one sulfide (FeS) is constantly $10^{1.5}$ (= 32) times as soluble as the other (NiS). To effect a clean separation, one must be 999 times as soluble as the other at some pH. Such a pH does not exist.

3. This is a variation on the AgCl problem of page 129. It is an illustration that if a little Cl^- (or OH^-) is good, more is not necessarily better. The principle follows from the equilibrium requirement that:

$$K_{sp} = [Zn^{2+}][OH^-]^2$$

that

$$[Zn^{2+}] = \alpha_{Zn2+}C_{Zn2+},$$

and that α_{Zn2+} *decreases* with increasing $[OH^-]$. The solubility of Zn^{2+} is not $[Zn^{2+}]$ alone; it is C_{Zn2+} because this represents *all* soluble forms of zinc in solution. So the solubility of zinc becomes

$$C_{Zn2+} = K_{sp} \div (\alpha_{Zn2+}[OH^-]^2).$$

The expression for α_{Zn2+} was derived in Chapter 9 (page 61 *et seq.*), but its derivation will be recreated here because with the $[OH^-]^2$ term, the final expression for C_{Zn2+} takes on a different look that might not be appreciated by simply cutting and pasting the work from Chapter 9. Nevertheless, a lot of output that is called (;) but not shown because it should be familiar.

```
> restart; SolEq:= K[sp] = Zn2*OH^2;
```

$$SolEq := K_{sp} = Zn2\ OH^2$$

Zn2 is used to represent $[Zn^{2+}]$ rather than Zn as we have been using. This is to preclude a recursive assignment error in the next step where Zn is used as a subscript.

```
> Zn2:= alpha[Zn]*C[Zn]; SolEq;
```

Still another designation for $[Zn^{2+}]$ will be necessary for the expression of α_{Zn2+}. $Free_{Zn}$ is used. The concentrations of the four hydroxy complexes are contained in the denominator with obvious representations.

```
> alpha[Zn]:= Free[Zn]/(Free [Zn]+Zn(OH)[1]+Zn(OH)[2]+ Zn(OH)
  [3]+Zn(OH)[4]);
```

$$\alpha_{Zn} := \frac{Free_{Zn}}{Free_{Zn} + Zn(OH)_1 + Zn(OH)_2 + Zn(OH)_3 + Zn(OH)_4}$$

From the definition of β_n (Equations **9-1** and **9-2**), and showing only a couple of the $Zn(OH)_n^{2-n}$ expressions and the solubility equilibrium expression

```
> Zn(OH)[1]:= beta[1]*Free [Zn]*OH; Zn(OH)[2]:= beta
  [2]*Free[Zn]*OH^2; Zn(OH)[3] := beta[3]*Free[Zn]*OH^3;
  Zn(OH)[4]:= beta[4]*Free[Zn] *OH^4; 'SolEq'= SolEq;
```

$$Zn(OH)_1 := \beta_1 Free_{Zn} OH$$
$$Zn(OH)_4 := \beta_4 Free_{Zn} OH^4$$

$$SolEq = \left(K_{sp} = \left(Free_{Zn}\, C_{Zn}\, OH^2\right) \Big/ \left(Free_{Zn} + \beta_1\, Free_{Zn}\, OH + \beta_2\, Free_{Zn}\, OH^2 + \beta_3\, Free_{Zn}\, OH^3 + \beta_4\, Free_{Zn}\, OH^4\right)\right)$$

$[Zn^{2+}]$ or $Free_{Zn}$ can be cancelled out of the numerator and denominator.

```
> SolEq:= simplify(SolEq);
```

$$SolEq := K_{sp} = \frac{C_{Zn}\, OH^2}{1 + \beta_1\, OH + \beta_2\, OH^2 + \beta_3\, OH^3 + \beta_4\, OH^4}$$

Using concepts from Chapter 3 and applied in Chapter 9 (*e.g.* page 61) we express $[OH^-]$ in terms of pH (actually $-\log_{10}[H^+]$). K_w is taken to be $1.00\ 10^{-14}$.

```
> SolEq:= algsubs(OH = K[w]/H, SolEq); SolEq:= algsubs(H =
  10^(-pH), SolEq);
```

$$SolEq := K_{sp} = \frac{C_{Zn}\, K_w^2\, H^2}{\beta_4\, K_w^4 + H\,\beta_3\, K_w^3 + H^4 + H^3\,\beta_1\, K_w + H^2\,\beta_2\, K_w^2}$$

Now C_{Zn}, the concentration of all soluble species of zinc, can be extracted from the solubility equilibrium expression. This, C_{Zn}, represents all the zinc that is in solution; appropriately it is shown to increase as K_{sp} or any of the betas increase, because these increases lead to a decrease in $Zn(OH)_2(s)$ and increases in $Zn(OH)_n^{2-n}$.

```
> C[Zn]:= solve(SolEq, C[Zn]);
```

$$C_{Zn} := \frac{1}{\left(10^{pH-14}\right)^2}\left(K_{sp}\left(1+\beta_4\left(10^{pH-14}\right)^4 + \beta_2\left(10^{pH-14}\right)^2+\beta_3\left(10^{pH-14}\right)^3+\beta_1\,10^{pH-14}\right)\right)$$

Assigning values to each of the four betas and K_{sp} produces an expression for the solubility of zinc as a function of only pH.

```
> K[w]:= 1.01E-14:beta[1]:= 10^4.40: beta[2]:= 10^11.3:
  beta[3]:= 10^13.14: beta[4]:= 10^14.66: K[sp]:= 10^(-
  16.92): 'C[Zn]'= C[Zn];
```

$$C_{Zn} = \frac{1}{\left(10^{-pH}\right)^2}\left(1.179\,10^{11}\left(4.756\,10^{-42}+\left(10^{-pH}\right)^4 + 2.035\,10^{-17}\left(10^{-pH}\right)^2+2.537\,10^{-10}\left(10^{-pH}\right)^3 + 1.422\,10^{-29}\,10^{-pH}\right)\right)$$

For a qualitative answer to this question, the expression will be plotted.

```
> plot(-log[10](C[Zn]), pH = 0..14, axes = boxed, labels =
["-log[H+]","-log[Zinc]"], thickness = 2, gridlines = true);
```

The plot (below) shows that at pH < 6, zinc is freely soluble ($-\log_{10}$[Zinc] ≤ 0 implies C_{Zn} is ≥1 **M**). It should be realized that $-\log_{10}$[Zinc] ≤ -1 is *in practice* unachievable as this implies concentrations in excess of 10 **M**; this requires more than 650 g of zinc in a liter of solution! From the plot, an optimum pH, that is a pH of minimum C_{Zn} is not apparent, only a pH range. To compute this optimum pH, $^{dC[Zn]}/_{dpH} = 0$ might be found, but instead we introduce a special Maple package for directly finding a maximum or minimum. It is the non-linear program solver, `NLPSolve` which first must be called using the `with` command.

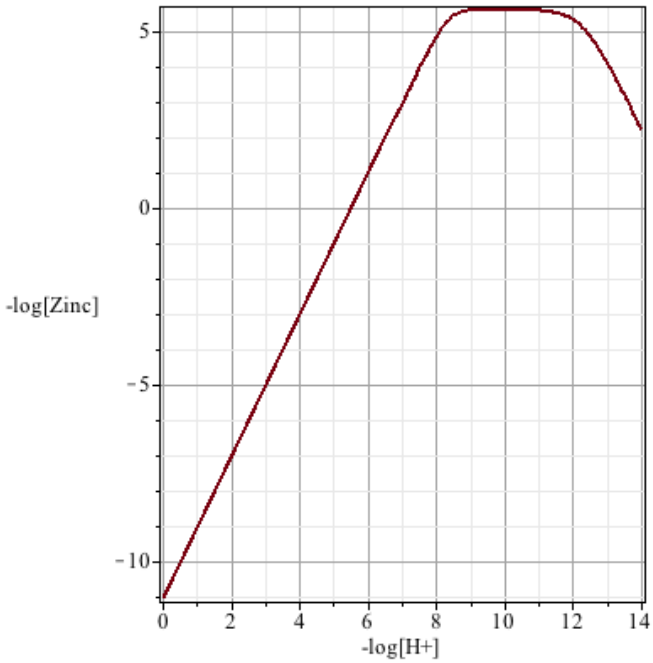

Figure 10-8

```
> with(Optimization);
```

[*ImportMPS, Interactive, LPSolve, LSSolve, Maximize, Minimize, NLPSolve, QPSolve*]

```
> NLPSolve(C[Zn],pH=6..12);
```

$$[2.42 \times 10^{-6}, [pH = 9.805]]$$

This represents the pH at which zinc is least soluble and the solubility at that pH. It *might* require a numeric reformatting to see that $C_{Zn} = 2.42\ 10^{-6}$.

4. The specification of a pH 8.8 in Problem #4, Chapter 9 was made so that α_{Y4-} could be calculated. That relatively high pH also assured that α_{SO42-} would be very close to 1.000 (minimal HSO_4^- and of course zero H_2SO_4, a strong acid). This pH is likewise sufficiently low that we can ignore the formation of $BaOH^+$.[234]

   We begin with the familiar solubility equilibrium expression, but with a novel representation of $[Ba^{2+}]$ and $[SO_4^{2-}]$. This is because still another representation for $[Ba^{2+}]$ will be needed later in an expression for α_{Ba2+}. Again, output should be inspected by the reader but is sparsely shown here.

```
> restart; SolEq:= K[sp] = Ba2*SO[4]:
```

The solubility of $BaSO_4$ in a solvent that does not itself contain Ba^{2+} or SO_4^{2-} will allow that the total barium concentration will equal the total sulfate concentration because each comes exclusively from the same source, namely the solid $BaSO_4$.

```
> Ba2:= alpha[Ba]*C[Ba]; SO[4]:= C[Ba]; SolEq;
```

Next, α_{Ba2+} is expressed in terms of $[Ba^{2+}]$ and $[BaY^{2-}]$ (but ignoring $[BaOH^+]$).

```
> alpha[Ba]:= Free[Ba]/(Free[Ba] + BaY); 'SolEq'= SolEq;
```

$$SolEq = \left(K_{sp} = \frac{Free_{Ba}\, C_{Ba}^2}{Free_{Ba} + BaY} \right)$$

$[BaY^{2-}]$ (= *BaY*) can be extracted from an expression for the formation equilibrium. That expression includes $[Y^{4-}]$, the free Y^{4-} concentration. In Chapter 9 (page 56) it was shown that it is inappropriate to represent $[Y^{4-}]$ as $\alpha_{Y4-}\times C_Y$ because the alpha does not include MY^{n-4} (BaY^{2-} here). The correct expression is $\alpha_{Y4-}\times(C_Y - [BaY^{2-}])$. However, using this correct expression for $[Y^{4-}]$ (*Free*$_Y$ below) will leave *Free*$_{Ba}$ in the formation equilibrium expression, and this value is unknown. We will use $\alpha_{Y4-}\times C_Y$ for *Free*$_Y$ and *correct it later*. The penultimate form of *SolEq* will contain *Free*$_{Ba}$ in the numerator and denominator such that it can be factored out with the `simplify` command, but this is carried out on a subsequent command line to avoid a warning message.

```
> FormEq:= K[f] = BaY/(Free[Ba]*Free[Y4]): Free[Y4]:= alpha
  [Y4]*C[Y]: BaY:= solve(FormEq , BaY); 'SolEq'= SolEq;
```

$$SolEq = \left(K_{sp} = \frac{Free_{Ba}\, C_{Ba}^2}{Free_{Ba} + K_f Free_{Ba}\, \alpha_{Y4}\, C_Y} \right)$$

```
> SolEq:= simplify(SolEq);
```

$$SolEq := K_{sp} = \frac{C_{Ba}{}^2}{1 + K_f\, \alpha_{Y4}\, C_Y}$$

All of the barium in solution, *i.e.* C_{Ba}, comes from the dissolution of $BaSO_4$(s). So the solubility of $BaSO_4$ *is* C_{Ba}.

```
> Sol_Roots:= solve(SolEq, {C[Ba]});
```

$$Sol\_Roots := \left\{ C_{Ba} = \sqrt{K_{sp} + K_{sp} K_f \alpha_{Y4} C_Y} \right\},$$
$$\left\{ C_{Ba} = -\sqrt{K_{sp} + K_{sp} K_f \alpha_{Y4} C_Y} \right\}$$

Only the first root gives C_{Ba} greater than zero. So it is chosen, and appropriately named *Solubility*.

```
> Solubility:= subs(Sol_Roots[1], C[Ba]);
```

$$Solubility := \sqrt{K_{sp} + K_{sp} K_f \alpha_{Y4} C_Y}$$

This expression for the solubility of an insoluble salt in a complexing agent makes perfect sense: Solubility increases as K_{sp} increases, as K_f increases, as the fraction (α) of free complexing agent increases and as the concentration of complexing agent increases. Moreover, *when* no complexing agent is present ($C_Y = 0$), the solubility depends only on K_{sp} as it should. Remember, however, that it is based on a presumption that C_Y is approximately C_Y - $[BaY^{2-}]$. This will be addressed after *Solubility* has been calculated, and that requires providing values for the four parameters. α_{Y4-} could be calculated from the four K_as for EDTA and the given pH, but this has already been done on page 104 as part of solving Problem #4 in Chapter 9. It will be copied from that work.

```
> K[sp]:= 1.1e-10; K[f]:= 10^7.8; alpha[Y4]:= 0.03344; C[Y]:=
  0.10; 'Solubility' = Solubility;
```

$$Solubility := 0.00482$$

So, the solubility of $BaSO_4$ in 0.100 **M** EDTA at pH 8.8 is 4.8 mmole per liter, but this is artificially high because we presumed an artificially large $[Y^{4-}]$; we presumed $[Y^{4-}]$ to be $\alpha_{Y4-} \times C_Y$ *not* $\alpha_{Y4-} \times (C_Y - BaY^{2-}])$. How large can $[BaY^{2-}]$ possibly be? Not larger than C_{Ba}. So the smallest $[Y^{4-}]$ is $\alpha_{Y4-} \times (C_Y - 0.00481_5)$. So, to simulate this, C_Y can be adjusted downward.

```
> C[Y]:= C[Y] - Solubility; 'Solubility'= Solubility;
```

$$C_Y := 0.095182$$
$$Solubility := 0.004700$$

The difference of 2.5% is acceptable for the problem at hand. That is, to decide if indeed the 35 mg of $BaSO_4$ added to 10.00 mL (0.01 L) of 0.100 **M** EDTA at pH 8.8 would dissolve completely. Using the 0.00482 **M** solubility and the formula weight of $BaSO_4$:

```
> Mass[BaSO[4]]:= 0.01*Solubility*(137.327 +
32.066*4*15.9994);
```

$$Mass_{BaSO_4} := 0.01029$$

This is more than 100 mg implying that the 35 mg of $BaSO_4$ from the problem would certainly dissolve completely.

5. Although this problem has been addressed (page 138 *et seq.*), it will be approached here in a different manner: as in Example Problem 1 part **c**, the concentration of free, soluble cation will be determined directly, rather than by subtracting the "concentration" of precipitated cation from its analytical concentration. It will be apparent that the results are the same as those illustrated in Figure **10-5**. And by calculating both [Ag^+] and {Ag^+} in this problem, we can show the difference between the two titration curves, one in *minus* $\log_{10}${Ag^+} (*i.e.* pAg) and the other in *minus* $\log_{10}$[Ag^+].

   The details of calculating the activity of Ag^+ from its molarity, at each point in the titration, will be presented later, after an expression for [Ag^+] as a function of V_{AgNO3} has been developed. In order to make ionic strength effects specific, counter ions for Ag^+ and OCN^- are assigned. For this we assign NO_3^- to Ag^+ and K^+ to OCN^-, and so the titrant becomes $AgNO_3$ and the titrand becomes KOCN.

   Using this more specific nomenclature, we follow the process described in Example Problem 1, that is where we remove *Prcp* from the mass balance expression.

```
> restart; MassBal[Ag]:= C[AgNO3] = Sol[Ag] + Prcp;
  MassBal[OCN] := C[KOCN] = Sol[OCN] + Prcp;
```

$$MassBal_{Ag} := C_{AgNO3} = Sol_{Ag} + Prcp$$
$$MassBal_{OCN} := C_{KOCN} = Sol_{OCN} + Prcp$$

The *Prcp* term is removed by subtracting one expression from the other.

```
> MassBal[Total]:= MassBal[Ag] - MassBal[OCN];
```

$$MassBal_{Total} := C_{AgNO3} - C_{KOCN} = Sol_{Ag} - Sol_{OCN}$$

The solubility equilibrium requirement is used to express Sol_{OCN} in terms of Sol_{Ag}. $K°_{sp}$ is used in anticipation of addressing ionic strength effects later in the problem.

```
> Sol[OCN]:= solve(K°[sp] = Sol[Ag]*Sol[OCN], Sol[OCN]);
  'MassBal[Total]'= MassBal[Total];
```

$$MassBal_{Total} = \left(C_{AgNO3} - C_{KOCN} = Sol_{Ag} - \frac{K°_{sp}}{Sol_{Ag}} \right)$$

The analytical concentrations for the mixed solution are now expressed in terms of unmixed analytical concentrations and volumes for the titrand and titrant. Keeping the tradition of using V° for the titrand (because it does not change throughout the titration) and V for the titrant (because it *does* change), the expressions are:

```
> C[AgNO3]:= C°[AgNO3]*V[AgNO3]/(V°[KOCN] + V[AgNO3]):
  C[KOCN]:= C°[KOCN]*V°[KOCN]/(V°[KOCN] + V[AgNO3]): 'MassBal
  [Total]' = MassBal[Total];
```

$$MassBal_{Total} = \left(\frac{C°_{AgNO3} V_{AgNO3}}{V°_{KOCN} + V_{AgNO3}} - \frac{C°_{KOCN} V°_{KOCN}}{V°_{KOCN} + V_{AgNO3}} = Sol_{Ag} - \frac{K°_{sp}}{Sol_{Ag}} \right)$$

Solving for the two roots:

```
> AgRoots:= solve(MassBal[Total], {Sol[Ag]});
```

Either by trial and error or by careful inspection, the first root is chosen as the expression that will provide physically possible ($C_{AgNO3} > Sol_{Ag} > 0$) values for [Ag^+]. This expression will be called `Conc°[Ag]` to denote that it derives from $K°_{sp}$.

```
> Conc°[Ag]:= subs(AgRoots[1], Sol[Ag]):
```

$$Conc°_{Ag} := \frac{1}{2}\,\frac{1}{V°_{KOCN} + V_{AgNO3}}\left(C°_{AgNO3}\,V_{AgNO3} - C°_{KOCN}\,V°_{KOCN} + \left(C°^{2}_{AgNO3}\,V^{2}_{AgNO3} - 2\,C°_{AgNO3}\,V_{AgNO3}\,C°_{KOCN}\,V°_{KOCN} + V°^{2}_{KOCN} + 8\,V°_{KOCN}\,K°_{sp}\,V_{AgNO3} + 4\,K°_{sp}\,V^{2}_{AgNO3}\right)^{1/2}\right)$$

The compliment to Conc°[Ag] is Conc[Ag] which will derive from K_{sp}. Recalling that K_{sp} would be $K°_{sp}/(\gamma_{Ag}+\gamma_{OCN}-)$, the `algsubs` operation can be used to effect this new definition.

```
> Conc[Ag]:= algsubs(K°[sp] = K°[sp]/(Gamma[Ag]*Gamma[OCN]),
  Conc°[Ag]);
```

Appropriately, the new expression contains activity coefficients. In order to clear out the clutter of the many parameters, they will be assigned values before continuing. All of these come directly from the initial approach to this problem (page 139). For that reason, the output is not shown.

```
> C°[AgNO3]:= 0.25: C°[KOCN]:= 0.20: V°[KOCN]:= 10.00:
  K°[sp]:= 2.3e-7:
```

For inspection:

```
> 'Conc[Ag]'= Conc[Ag];
```

$$Conc_{Ag} = \frac{1}{2}\,\frac{1}{10.000 + V_{AgNO3}}\left(0.250\,V_{AgNO3} - 2.000 + \left(0.063\,V^{2}_{AgNO3} - 1.000\,V_{AgNO3} + 4.000 + \frac{9.200\,10^{-7}\left(100.000 + 20.000\,V_{AgNO3} + V^{2}_{AgNO3}\right)}{\Gamma_{Ag}\,\Gamma_{OCN}}\right)^{1/2}\right)$$

Clearly $Conc_{Ag}$ changes with V_{AgNO3}, but the two activity coefficients change with V_{AgNO3} also. This is because, as we know, γ changes with μ, and μ will change with C_{KOCN} and C_{AgNO3} which, of course change with V_{AgNO3}. We develop this relationship here.

```
> a[Ag]:= 2.5; a[OCN]:= 3.5; Gamma[Ag]:= 10^(-0.511*sqrt
  (μ)/(1 + (0.329*a[Ag]*sqrt(μ)))); Gamma[OCN]:=
  10^(-0.511*sqrt(μ)/(1 + (0.329*a[OCN]*sqrt(μ))));
```

Now, $Conc_{Ag}$ is an expression in terms of V_{AgNO3} and μ.

Finally, to address the relationship between μ and V_{AgNO3} consider the expression for ionic strength as it would pertain to this titration.

$$\mu = {}^1/_2\{[K^+] + [OCN^-] + [Ag^+] + [NO_3^-]\}$$

In the true spirit of being spectator ions, $[K^+]$ and $[NO_3^-]$ exactly equal the analytical concentration of their parent compound. So,

$$\mu = {}^1/_2\{C_{KOCN} + [OCN^-] + [Ag^+] + C_{AgNO3}\}$$

The concentrations of OCN^- and Ag^+ are regulated by the solubility equilibrium expression; $[Ag^+]$ *is* $Conc_{Ag}$ which, for simplification, can be closely approximated with $Conc°_{Ag}$.[235] $[OCN^-]$ can be expressed in terms of $Conc°_{Ag}$ by considering the charge balance requirement:

$$[K^+] + [Ag^+] = [OCN^-] + [NO_3^-]$$

So,

$$[OCN^-] = [K^+] + [Ag^+] - [NO_3^-]$$

and then,

$$[OCN^-] = C_{KOCN} + Conc°_{Ag} - C_{AgNO3}.$$

Rewriting the expression for μ with all of these substitutions gives a very simple expression:

$$\mu = C_{KOCN} + Conc°_{Ag}.$$

Using this expression for μ which will implicitly contain V_{AgNO3} we have:

```
> μ:= C[KOCN] + Conc°[Ag];
```

$$\mu := \frac{2.000}{10.000 + V_{AgNO3}} + \frac{1}{2}\frac{1}{10.000 + V_{AgNO3}}\left(0.250\, V_{AgNO3} - 2.000 + \sqrt{0.063\, V_{AgNO3}^2 - 1.000\, V_{AgNO3} + 4.000}\right)$$

Expressions for $[Ag^+]$ regarding *and* disregarding ionic strength effects are now complete. A "for loop" will be used to compute each of these from 0.10 to 10 mL of $AgNO_3$ titrant. We begin at a volume measurably greater than 0 mL because at a very small volume of titrand, no precipitate will form and that will make the solubility equilibrium condition irrelevant (*i.e.* non binding).

```
> V[AgNO3]:= 0.10:
```

$$V_{AgNO3} := 0.100$$

```
> for i to 100 do
> pAg_Con[i] := -log[10](Conc°[Ag]): pAg_Act[i]:= -log [10]
  (Gamma [Ag]*Conc[Ag]): V[i]:= V[AgNO3]:
```

```
> V[AgNO3]:= V[AgNO3] + 0.10:
> end:
```

We can quickly compare {Ag^+} and [Ag^+] at the equivalence point by calling these values at `i` = 80, which corresponds to V_{AgNO3} = 8.00 mL.

```
> 'V'=V[80]; '-log_Ag_conc' = pAg_Con[80]; '-log_Ag_act' =
  pAg_Act[80];
```

$$V = 8.000$$
$$-log\_Ag\_conc = 3.319$$
$$-log\_Ag\_conc = 3.324$$

There is not much difference between the molarity and activity of Ag^+. Notice also that there is *no* difference between the molarity of Ag^+ calculated here and what was calculated from $C_{Ag} - Prcp$ on page 140.[236]

For a thorough comparison, the data are packaged for plotting (Part I, page 192). There is no need to show that output.

```
> ConcData:= [seq([V[i], pAg_Con[i]], i = 1..100)]: ActData:=
  [seq([V[i], pAg_Act[i]], i = 1..100)]:
```

Then, the plot structures are set. Recall that because the two structures will be plotted together there is no need to include label or axis specifications in both structures. Again, there is no value in displaying the output from this input line. The Ag^+ concentration results are plotted as a red line because they should exactly replicate what was calculated for Figure **10.5** and shown there as a red line. The reader might notice that we have not attempted a simpler approach, using `plots[pointplot]([ConcData,ActData],.....)`. Point plotting does not allow plotting multiple data sets. So each plot structure is stored and then combined for plotting with `plots[display]`.

```
> ConcPlot:= plots[pointplot](ConcData, style = line, labels
  = ["Vol of AgNO3","-logAg"], axes = boxed, color = red):
  ActPlot := plots[pointplot](ActData, symbol = circle, color
  = blue):
```

Finally, the plot is generated.

```
> plots[display]({ConcPlot, ActPlot});
```

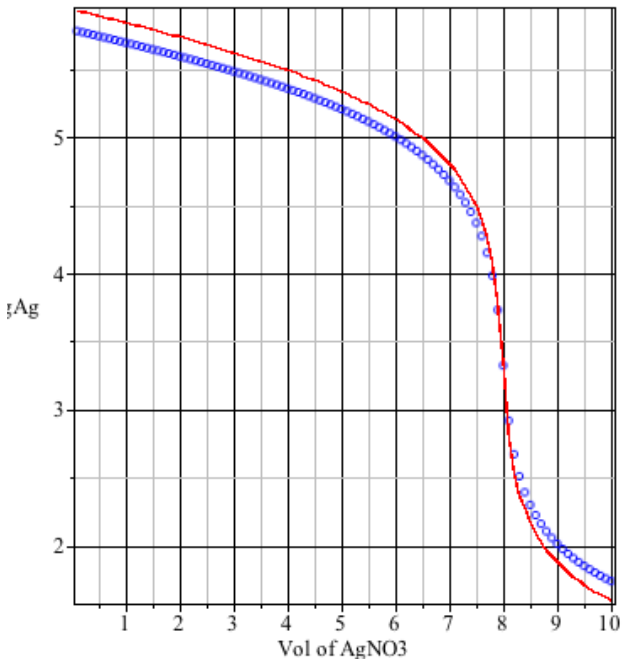

Figure 10-9

The difference between concentration and activity is not significant, especially near the equivalence point. This phenomenon was seen with the acid base titration of (Figure **7-6**). It might seem surprising that with ionic strength *exceeding* C_{KOCN}, γ_{Ag+} would not make $\{Ag^+\}$ appreciably different from $[Ag^+]$ or $K°_{sp}$ different from K_{sp}. In fact γ_{Ag+} changes both of these significantly, but in opposite ways. So the changes offset and effectively $\{Ag^+\} \approx [Ag^+]$. At the end of the titration (10 mL of KOCN), for example:

```
> 'μ'= μ; 'Gamma[Ag]'= Gamma [Ag]; 'Gamma[OCN]'= Gamma
  [OCN]; 'V_of_KOCN'= V[100]; 'p[Ag_Conc]'= pAg_Con[100];
  'p[Ag_Act]'= pAg_Act[100]; 'Conc_of_KOCN'= C[KOCN];
```

$$\mu = 0.126$$
$$\Gamma_{Ag} = 0.724$$
$$\Gamma_{OCN} = 0.744$$
$$V\_of\_KOCN = 10.000$$
$$p[Ag\_Conc] = 1.602$$
$$p[Ag\_Act] = 1.742$$
$$Conc\_of\_KOCN = 0.100$$

The calculation of activity is important in potentiometric titrations because it is the activity of a titrand or titrant ion that is monitored. In automated systems, it is $^{\Delta Activity}/_{\Delta Volume}$ or more correctly $^{\Delta pActivity}/_{\Delta Volume}$ that is monitored. This can be recreated from the data at hand with a very short "for loop." What we do here is simply find the difference between adjacent pAg's (i and i+1) from the previous "for loop."

```
> for i to 99 do
> delta_pAg[i]:= (pAg_Act[i + 1] - pAg_Act[i])/(V[i+1] -
V[i]):
> end:
```

Packaging and plotting the data follow. Notice that there is no need to create a plot structure for `plots[display]` because `plots[pointplot]` can be used directly.

```
> Delta_Data := [seq([V[i], delta_pAg[i]], i = 1..99)]:
> plots[pointplot](Delta_Data, style = line, color = navy,
axes = boxed, labels = ["mL of AgNO3","ΔpAg"]);
```

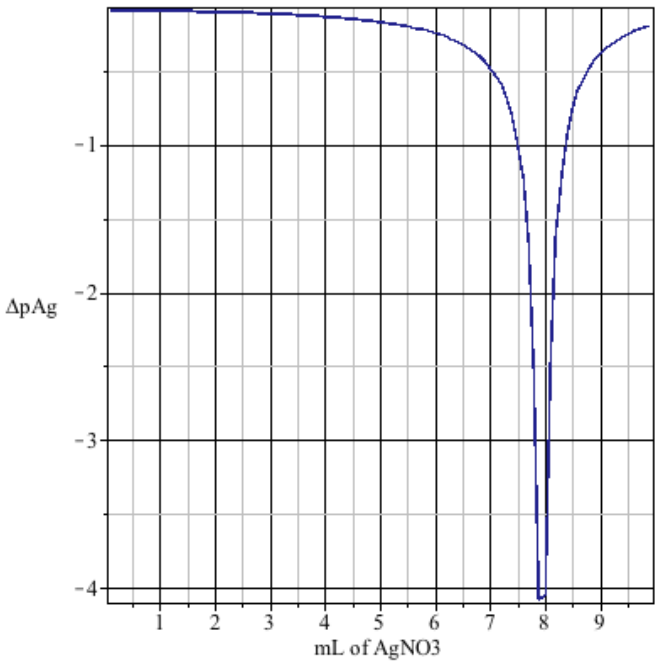

Figure 10-10

The equivalence point is marked by the greatest change in pAg per change in volume of titrant. But a caution is in order: the coincidence of *this* endpoint and equivalence point pertains *only* to 1:1 precipitates. The endpoint for a titration in which $M_2A(s)$ or $MA_2(s)$ is produced will not coincide with the equivalence point.[237]

Appendix I

Solvent Parameters for Calculations of Aqueous Solutions Using Extended Debye-Hückel Theory

$-\log_{10}\gamma = (Az_1^2\sqrt{\mu})/(1 + Ba\sqrt{\mu})$

z is the charge of ion, *i*.

a is the effective ionic radius of ion i expressed in Å. See Appendix II.

Temp. °C	A	B
0	0.4918	0.3248
5	0.4952	0.3256
10	0.4989	0.3264
15	0.5028	0.3273
20	0.5070	0.3282
25	0.5115	0.3291
30	0.5161	0.3301
35	0.5211	0.3312
40	0.5262	0.3323
45	0.5317	0.3334
50	0.5373	0.3346
55	0.5432	0.3358
60	0.5494	0.3371
65	0.5558	0.3384
70	0.5625	0.3397
75	0.5695	0.3411
80	0.5767	0.3426
85	0.5842	0.3440
90	0.5920	0.3456
95	0.6001	0.3471
100	0.6086	0.3488

Appendix II

Constants for Calculating Activity Coefficients

The estimated values for the a parameter for selected inorganic ions.[238]

Ag^{+}	2.5	$[Fe(CN)_6]^{4-}$	5	Ni^{2+}	6
Al^{3+}	9	Fe^{2+}	6	NO_2^{-}	3
Ba^{2+}	5	Fe^{3+}	9	NO_3^{-}	3
Be^{2+}	8	H^{+}	9	OH^{-}	3.5
BrO_3^{-}	3.5	$H_2AsO_4^{-}$	4-4.5	Pb^{2+}	4.5
Ca^{2+}	6	$H_2PO_4^{-}$	4-4.5	PO_4^{3-}	4
Cd^{2+}	5	HCO_3^{-}	4-4.5	Pr^{3+}	9
$CdCl^{+}$	4-4.5	Hg^{2+}	5	Ra^{2+}	5
Ce^{3+}	9	Hg_2^{2+}	4-4.5	Rb^{+}	2.5
Ce^{4+}	11	HPO_4^{2-}	4	S^{2-}	5
Cl^{-}	3	HS^{-}	3.5	$S_2O_3^{2-}$	4
ClO_2^{-}	3.5	HSO_3^{-}	4-4.5	$S_2O_4^{2-}$	5
ClO_3^{-}	4-4.5	I-	3	Sc^{3+}	9
ClO_4^{-}	3.5	In^{3+}	9	SeO_4^{2-}	4
CN^{-}	3	IO_3^{-}	4-4.5	Sm^{3+}	9
CNO^{-}	3.5	IO_4^{-}	3.5	Sn^{2+}	6
$[Co(en)_3]^{3+}$	6	K^{+}	3	Sn^{4+}	11
$[Co(NH_3)_6]^{3+}$	4	La^{3+}	9	SO_3^{2-}	4.5
Co^{2+}	6	Li^{+}	6	SO_4^{2-}	4
CO_3^{2-}	4.5	Mg^{2+}	8	Sr^{2+}	5
$[Cr(NH_3)_6]^{3+}$	4	Mn^{2+}	6	Th^{4+}	11
Cr^{3+}	9	MnO_4^{-}	3.5	Tl^{+}	2.5
CrO_4^{2-}	4	MoO_4^{2-}	4.5	WO_4^{2-}	5
Cs^{+}	2.5	Na^{+}	4-4.5	Y^{3+}	9
Cu^{2+}	6	NCS^{-}	3.5	Zn^{2+}	6
F^{-}	3.5	Nd^{3+}	9	Zr^{4+}	11
$[Fe(CN)_6]^{3-}$	4	NH_4^{+}	2.5		

The estimated values for the a parameter for selected organic ions.[239]

Acetate	4.5	$HC_6H_5O_7^{2-}$	4.5
Benzoate	6	$CH_3NH_3^+$	3.5
$C_6H_4CH_2COO^-$	6	$HCOO^-$	3.5
$C_6H_4ClCOO^-$	6	$N(C_2H_5)_2H_2^+$	4.5
$C_6H_4OHCOO^-$	6	$NH(C_2H_5)_3^+$	5
$(C_6H_5)_2CHCOO^-$	8	$N(C_3H_7)_2H_2^+$	6
$C_6H_5COO^-$	6	$NH(C_3H_7)_3^+$	7
$C_6H_5O^-$	5	$N(C_3H_7)H_3^+$	5
CCl_3COO^-	5	$NH(CH_3)_3^+$	4
$CH_2(NH_2)COO^-$	4.5	Hydrogen Citrate	4.5
CH_2ClCOO^-	4.5	Methyl Ammonium	3.5
CH_3COO^-	4.5	$N(C_2H_5)_4^+$	6
$CH_3OC_6H_4COO^-$	7	$N(C_3H_7)_4^+$	8
$CHCl_2COO^-$	5	$N(CH_3)_4^+$	4.5
Chloroacetate	4.5	$NH_2CH_2COO^-$	4.5
Citrate	5	$(NO_2)_3C_6H_2O^-$	7
$(COO)_2^{2-}$	4.5	Oxalate	4.5
Dichloroacetate	5	Phenylacetate	6
Diethyl Ammonium	4.5	Picrate	7
Dihydrogen Citrate	3.5	Propyl Ammonium	5
Dimethyl Ammonium	3.5	Tetraethyl Ammonium	4.5
Dipropyl Ammonium	6	Tetraethyl Ammonium	6
Ethyl Ammonium	3.5	Tetrapropyl Ammonium	8
Formate	3.5	Trichloroacetate	5
$CH_2(NH_3^+)COOH$	4	Triethyl Ammonium	5
$(CH_3)_2NH_2^+$	3.5	Trimethyl Ammonium	4
$H_2C_6H_5O_7^-$	3.5	Tripropyl Ammonium	7
$C_2H_5NH_3^+$	3.5		

Appendix III

Autoprotolysis Constants for Water

Temp. °C	pK_w	K_w
0	14.994	1.0139E-15
5	14.734	1.8450E-15
10	14.535	2.9174E-15
15	14.346	4.5082E-15
20	14.167	6.8077E-15
25	13.996	1.0093E-14
30	13.833	1.4689E-14
35	13.680	2.0893E-14
40	13.535	2.9174E-14
45	13.396	4.0179E-14
50	13.262	5.4702E-14
55	13.137	7.2946E-14
60	13.017	9.6161E-14
65	12.90	1.2589E-13
70	12.80	1.5849E-13
75	12.69	2.0417E-13
80	12.60	2.5119E-13
85	12.51	3.0903E-13
90	12.42	3.8019E-13
95	12.34	4.5709E-13
100	12.26	5.4954E-13

Appendix IV

Acid Dissociation Constants for Some Common Weak Acids

Name	Formula	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
Acetic Acid	$HC_2H_3O_2$	4.756			
Ammonium	NH_4^+	9.24			
2-Ammoniumbenzoic acid	$H_2C_7H_7NO_2^+$	2.09	4.79		
3-Ammoniumbenzoic acid	$H_2C_7H_7NO_2^+$	3.07	4.79		
4-Ammoniumbenzoic acid	$H_2C_7H_7NO_2^+$	2.41	4.85		
2-Ammoniumbutanoic Acid	$H_2C_4H_{10}NO_2^+$	2.286	9.38		
Anilinium	$HC_6H_7N^+$	4.596			
Arsenic Acid	H_3AsO_4	2.22	6.98	11.5	
Arsenous Acid	$HAsO_2$	9.18			
Benzoic Acid	$HC_7H_5O_2$	4.204			
Boric Acid (ortho)	H_3BO_3	9.24	12.74	13.8	
Boric Acid (tetra)	$H_2B_4O_7$	4	9		
Bromoacetic Acid	$HC_2H_2O_2$	2.902			
Bromoacetic Acid	$HC_2H_2BrO_2$	2.902			

Name	Formula	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
2-Bromobenzoic Acid	$HC_7H_4BrO_2$	2.85			
3-Bromobenzoic Acid	$HC_7H_4BrO_2$	3.81			
4-Bromobenzoic Acid	$HC_7H_4BrO_2$	3.99			
3-Bromophenol	HC_6H_4BrO	9.031			
4-Bromophenol	HC_6H_4BrO	9.34			
Butanoic Acid	$HC_4H_9O_2$	4.817			
Carbonic Acid	H_2CO_3	6.36	10.33		
Chloric Acid	$HClO_3$	-2.7			
Chloroacetic Acid	$HC_2H_2ClO_2$	2.867			
2-Chlorobenzoic Acid	$HC_7H_4ClO_2$	2.877			
3-Chlorobenzoic Acid	$HC_7H_4ClO_2$	3.83			
4-Chlorobenzoic Acid	$HC_7H_4ClO_2$	3.986			
2-Chlorophenol	HC_6H_4ClO	8.55			
3-Chlorophenol	HC_6H_4ClO	9.1			
4-Chlorophenol	HC_6H_4ClO	9.43			
Chlorous Acid	$HClO_2$	1.94			
Chromic Acid	H_2CrO_4	-0.98	6.5		
Citric Acid	$H_3C_6H_5O_7$	3.128	4.761	6.396	
Cyanic Acid	HOCN	3.46			
Cyanoacetic Acid	$HC_3H_2NO_2$	2.46			
1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid **DCYTA**	$H_4C_{14}H_{18}N_2O_8$	2.43	3.54	6.10	11.70
Dibromoacetic Acid	$HC_2HBr_2O_2$	1.39			
Dichloroacetic Acid	$HC_2HCl_2O_2$	1.26			
Diethylammonium	$HC_4H_{11}N^+$	10.8			
Difluoroacetic Acid	$HC_2HF_2O_2$	1.33			
Dimethylammonium	$HC_2H_7N^+$	10.77			
2,4-Dinitrophenol	$HC_6H_7N_2O_4$	4.08			
Ethylammonium	$HC_2H_6N^+$	10.63			
Ethylenediamine-N,N,N′,N′-tetraacetic Acid (μ=0.1) **EDTA**	$H_4C_{10}H_{12}N_2O_8$	1.99	2.67	6.16	10.26
Ethylenediammonium	$H_2C_2H_6N^{2+}$	6.85	9.93		
Ethyleneglycol bis(oxyethylenenitrilo) tetraacetic acid **EGTA**	$H_4C_{14}H_{20}N_2O_{10}$	2.00	2.65	8.85	9.46
Fluoroacetic Acid	$HC_2H_2FO_2$	2.586			
2-Fluoroanilinium	$HC_6H_6NF^+$	3.2			

Name	Formula	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
3-Fluoroanilinium	$HC_6H_6NF^+$	3.58			
4-Fluoroanilinium	$HC_6H_6NF^+$	4.65			
3-Fluorobenzoic Acid	$HC_7H_5FO_2$	3.865			
3-Fluorophenol	HC_6H_5FO	9.29			
Formic Acid	$HCHO_2$	3.751			
Fumaric Acid	$H_2C_4H_2O_2$	3.1	4.6		
Glutaric Acid	$H_2C_5H_6O_4$	3.77	6.08		
Glycine	$H_2C_2H_4NO_2^+$	2.351	9.78		
Hydrazinium	$H_2N_2H_4^{2+}$	0.27	7.94		
Hydrazoic Acid	HN_3	4.72			
Hydrocyanic Acid	HCN	9.21			
Hydrofluoric Acid	HF	3.18			
Hydrogen Peroxide	H_2O_2	11.65			
Hydrosulfuric Acid	H_2S	6.97	12.92		
Hydroxylammonium	HNH2OH+	5.95			
Hypobromous Acid	HBrO	8.6			
Hypochlorous Acid	HClO	7.54			
Hypoiodous Acid	HIO	10.64			
Hyponitrous Acid	$H_2N_2O_2$	7.05	11.4		
Hypophosphorous Acid	$H_4P_2O_6$	2	2.19	6.77	9.48
Iodic Acid	HIO_3	0.804			
Iodoacetic Acid	$HC_2H_2IO_2$	3.175			
Maleic Acid	$H_2C_4H_2O_2$	1.91	6.33		
Malonic Acid	$H_2C_3H_2O_4$	2.826	5.696		
Methylammonium	HCH_3N^+	10.62			
Nitrilotriacetic Acid	$H_3C_6H_6NO_6$	1.65	2.94	10.33	
Nitroacetic Acid	$HC_2H_2NO_4$	1.68			
2-Nitrophenol	$HC_6H_4NO_3$	7.222			
3-Nitrophenol	$HC_6H_4NO_3$	8.36			
4-Nitrophenol	$HC_6H_4NO_3$	7.15			
Nitrous Acid	HNO_2	3.14			
Oxalic Acid	$H_2C_2O_4$	1.271	4.272		
Periodic Acid	HIO_4	1.55			
Phosphoric Acid	H_3PO_4	2.15	7.2	12.38	
o-Phthalic Acid	$H_2C_8H_4O_4$	2.95	5.408		

Name	Formula	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}
Propanoic Acid	$HC_3H_5O_2$	4.874			
Pyridinium	$HC_5H_5N^+$	5.17			
Salicylic Acid	$H_2C_7H_4O_3$	2.98	12.38		
Selenous Acid	H_2SeO_3	2.64	8.27		
Sulfurous Acid	H_2SO_3	1.89	7.21		
t-Butylammonium	$HC_4H_{11}N^+$	10.685			
Thiosulfuric Acid	$H_2S_2O_3$	0.6	1.6		
Tribromoacetic Acid	$HC_2Br_3O_2$	-0.147			
Trichloroacetic Acid	$HC_2Cl_3O_2$	0.52			
Triethylammonium	$HN(C_2H_5)_3^+$	10.72			
Triethylenetetraammonium	$H_4C_6H_{16}N_4^{4+}$	3.32	6.67	9.2	9.92
Trifluoroacetic Acid	$HC_2F_3O_2$	0.5			
Trimethylammonium	$HN(CH_3)_3^+$	9.8			
Uric Acid		5.4	5.53		
Water	H_2O	15.74			

Appendix V

Properties of Some Common Acid / Base Indicators

Indicator	**pK_{In}** [240]	**Transition pH** [241]	**Color of [HIn]**	
Cresol Purple	1.5	1.2–2.8	Red	Yellow
Thymol Blue	1.65	1.2–2.8	Red	Yellow
Tropeoline OO	2.0	1.3–3.0	Red	Yellow
Methyl Yellow	3.2	2.9–4.0	Red	Yellow
Methyl Orange	3.4	3.1–4.4	Yellow	Orange
Bromophenol Blue	3.9	3.0–4.6	Yellow	Purple
Bromocresol Green	4.9	3.8–5.4	Yellow	Blue
Methyl Red	5.0	4.2–6.2	Red	Yellow
Chlorophenol Red	6.1	5.4–6.8	Yellow	Red
Bromothymol Blue	7.2	6.2–7.6	Yellow	Blue
Phenol Red	7.5	6.4–8.4	Yellow	Red
Cresol Red	8.2	7.2–8.8	Yellow	Red
Cresol Purple	8.3	7.4–9.0	Yellow	Purple
Thymol Blue	8.9	8.0–9.6	Yellow	Blue
Phenolphthalein	9.4	8.1–9.9	Colorless	Red
Thymolphthalein	9.9	9.3–10.5	Colorless	Blue
Alizarine Yellow	11.2	10.0–12.0	Colorless	Yellow
Nitramine	11.9	10.8–13.0	Colorless	Orange
Tropeoline O	12	11.0–13.0	Yellow	Orange

Appendix VI

Formation Constants of Some Metal Complexes

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Ammonia	**NH_3**					
Ag^+	3.32	7.24				
Au^+		≈27				
Au^{3+}				30		
Cd^{2+}	2.51	4.47	5.77	6.56	6.26	4.56
Co^{2+}	1.99	3.5	4.43	5.07	5.13	4.39
Co^{3+}	7.3	14.00	20.1	25.7	30.8	35.21
Cu^+	5.93	10.86				
Cu^{2+}	3.99	7.33	10.06	12.03	11.43	8.9
Fe^{2+}	1.4	2.2	?	3.7		
Hg^{2+}	8.8	17.5	18.5	19.3		
Mg^{2+}	0.23	0.08	-0.34	-1.04	-1.99	-3.29
Mn^{2+}	0.8	1.3	?	?	?	≈9
Ni^{2+}	2.67	4.79	6.4	7.47	8.1	8.0
Tl^{3+}				≈17		
Zn^{2+}	2.18	4.43	6.74	8.700		
Bromide	**Br^-**					
Ag^+	4.38	7.34	8.00	8.73		
Au^+		12.46				
Au^{3+}				31.5		
Bi^{3+}	2.26	4.45	6.33	7.84	9.42	9.52
Cd^{2+}	2.23	3.001	2.83	2.93		
Ce^{3+}	0.38					
Co^{2+}	-2.30					
Cu^+		5.92				
Cu^{2+}	-0.03					
Fe^{3+}	0.55	0.82				
Hg^{2+}	9.05	17.33	19.74	21.00		
In^{3+}	1.20	1.78	2.48	3.33		
Ni^{2+}	-0.12	-3.24	?	-8.12		
Pb^{2+}	2.23	3.00	2.83	2.93		

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Pt^{2+}				20.5		
Sn^{2+}	0.73	1.14	1.35			
Tl^{+}	0.95	1.01	0.6	-0.2		
Tl^{3+}	9.7	16.6	21.2	23.9	25.5	26.2
Zn^{2+}	-0.8	-2.2	-2.9	-2.5		
Chloride	Cl^-					
Ag^{+}	3.04	5.04	5.04	5.30		
Au^{+}		9.42				
Au^{3+}				21.30		
Bi^{3+}	2.43	4.7	5.0	5.6	6.1	6.42
Cd^{2+}	2.05	2.60	2.4	2.9		
Ce^{3+}	0.22					
Cr^{3+}	0.60	-0.11				
Cu^{+}		5.35	5.63			
Cu^{2+}	0.07	-0.57	-2.1			
Fe^{2+}	0.36	0.401				
Fe^{3+}	1.45	2.10	1.10	-0.85		
Hg^{2+}	6.74	13.22	14.07	15.07		

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
In^{3+}	1.01	1.5	1.55	1.35		
Pb^{2+}	1.62	2.44	2.04	1.01		
Pt^{2+}		11.5	14.00	16.00		
Sn^{2+}	1.51	2.24	2.03	1.48		
Tl^{+}	0.52	0.09	-0.8			
Tl^{3+}	8.14	13.60	15.78	18.00	17.47	
Zn^{2+}	0.43	0.61	0.53	0.20		
Cyanide CN^-						
Ag^{+}		19.85	20.55	19.42		
Au^{+}		38.3				
Au^{3+}				≈56		
Cd^{2+}	5.18	9.60	13.92	17.11		
Co^{2+}						19.09
Co^{3+}						≈64
Cu^{+}		24.0	28.6	30.3		
Fe^{2+}					15.7	≈24
Fe^{3+}						≈31
Hg^{2+}	18.0	34.70	38.53	41.51		
Ni^{2+}				31.0	30.3	
Tl^{3+}				≈35		
Zn^{2+}			≈17	≈19		

DCYTA

	$\log_{10}\beta_1$
Al^{3+}	17.6
Ba^{2+}	8.
Bi^{3+}	24.1
Ca^{2+}	12.5
Cd^{2+}	19.2
Co^{2+}	18.9
Cu^{2+}	21.3
Fe^{2+}	18.2
Fe^{3+}	29.3
Hg^{2+}	24.3
Mg^{2+}	10.3
Mn^{2+}	16.8
Ni^{2+}	19.4
Pb^{2+}	19.7
Sr^{2+}	10.0
Th^{2+}	23.2
Zn^{2+}	18.7

EDTA

	$\log_{10}\beta_1$
Ag^{+}	7.3
Al^{2+}	16.1
Ba^{2+}	7.8
Bi^{3+}	22.8
Ca^{2+}	10.7
Cd^{2+}	16.5
Co^{2+}	16.3
Cr^{3+}	23
Cu^{2+}	18.8
Fe^{2+}	14.4
Fe^{3+}	25.1
Hg^{2+}	21.8
In^{3+}	24.95
Mg^{2+}	8.7
Mn^{2+}	14.0
Ni^{2+}	18.6
Pb^{2+}	18.0
Sn^{2+}	22.1
Sr^{2+}	8.6
Th^{4+}	23.2
Tl^{3+}	21.3
Zn^{2+}	16.5

EGTA

Ba^{2+}	8.4
Ca^{2+}	11.0
Cd^{2+}	15.6
Co^{2+}	12.3
Cu^{2+}	17.0
Hg^{2+}	23.2
Mg^{2+}	5.2
Mn^{2+}	11.5
Ni^{2+}	12.0
Pb^{2+}	13.0
Sr^{2+}	8.5
Sn^{2+}	12.8
Th^{4+}	23.2
Tl^{3+}	21.3
Zn^{2+}	16.5

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Ethylenediamine	**$H_2NCH_2CH_2NH_2$**					
Ag^+	4.701	7.70				
Cd^{2+}	5.47	10.09	12.09			
Co^{2+}	5.91	10.64	13.94			
Co^{3+}	18.7	34.9	48.69			
Cr^{2+}	5.15	9.19				
Cu^+		10.8				
Cu^{2+}	10.67	20.00	21.01			
Fe^{2+}	4.34	7.65	9.70			
Hg^{2+}	14.3	23.3				
Mn^{2+}	2.73	4.79	5.67			
Ni^{2+}	7.52	13.84	18.33			
Zn^{2+}	5.77	10.83	14.11			
Fluoride	**F^-**					
Ag^+	0.36					
$Al3^+$	7.10	11.98	15.83	18.53	20.20	20.67
Ca^{2+}	≈1					
Cd^{2+}	0.46	0.53				
Ce^{3+}	3.99					
Cr^{3+}	5.201	8.54	11.02			
Cu^{2+}	1.23					
Fe^{3+}	6.04	10.74	13.74	15.74	16.10	≈16
Hg^{2+}	1.56					
In^{3+}	4.63	7.41	10.23			
Mg^{2+}	1.82					
Mn^{2+}	5.76					
Sc^{3+}	7.08	12.88	17.33	20.81		
Sn^{2+}	4.85	?	≈10			
Th^{4+}	7.65	13.46	17.97			
Tl^+	0.10					
Zn^{2+}	1.26					
Zr^{4+}	9.801	17.37	23.45			
Hydrazine	**N_2H_4**					
Cd^{2+}	2.25	2.40	2.78	3.89		
Ni^{2+}	2.76	5.20	7.35	9.20	10.75	11.99
Zn^{2+}	3.40	3.70	3.78	3.88		
Hydroxide	**OH^-**					
Ag^+	2.301	4.0	5.2			
$Al3^+$	9.04	?	?	33.0		
As^{3+} (AsO^+)	14.33	18.73	20.60	21.2		
Ba^{2+}	0.85					
Bi^{3+}	12.4	15.8	?	35.2		

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Ca^{2+}	1.46					
Cd^{2+}	4.17	8.33	9.02	8.62		
Ce^{3+}	4.3					
Ce^{4+}	13.28	27.06				
Co^{2+}	4.4	4.6	10.5			
Cr^{3+}	10.1	17.8		29.9		
Cu^{2+}	7.0	13.68	17.0	18.5		
Fe^{2+}	5.56	9.77	9.67	8.56		
Fe^{3+}	11.87	21.17	30.67			
Hg^{2+}	10.30	21.70	21.20			
In^{3+}	9.9	19.8	?	28.7		
Li^{+}	0.17					
Mg^{2+}	2.58					
Mn^{2+}	3.9		8.3			
Ni^{2+}	4.97	8.55	11.33			
Pb^{2+}	6.9	10.8	13.3			
Sn^{2+}	11.86	20.64	25.13			
Th^{4+}	10.0	21.2	32.0	?	8.7	38.7
Tl+	0.82					
Tl^{3+}	12.86	25.37				
Zn^{2+}	4.4	11.3	13.14	14.66		
Zr^{4+}	14.32	28.26	41.91	55.27		

NTA	**$N(CH_2COOH)_3$**	
Al^{3+}	≈11	
Ba^{2+}	4.8	
Ca^{2+}	7.60	11.61
Cd^{2+}	9.80	15.2
Co^{2+}	10.38	14.5
Cr^{3+}	≈11	
Cu^{2+}	13.1	
Fe^{2+}	8.8	
Fe^{3+}	15.87	24.32
Hg^{2+}	12.7	
In^{3+}	≈15	
Mg^{2+}	5.36	10.2
Mn^{2+}	8.60	11.1
Ni^{2+}	11.26	16.0
Pb^{2+}	11.8	
Sr^{2+}	6.73	

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Th^{4+}	12.4					
Zn^{2+}	10.45	13.45				

Oxalate $C_2O_4^{2-}$

Ag^{+}	2.41					
Al^{3+}	7.3	≈13	16.3			
Ba^{2+}	2.3					
Ca^{2+}	≈3					
Cd^{2+}	4.00	5.77				
Ce^{3+}	6.52	10.48	11.30			
Co^{2+}	4.7	6.7	9.7			
Cu^{2+}	6.7	10.3				
Fe^{2+}	2.9	4.52	5.22			
Fe^{3+}	9.4	16.2	20.2			
Mg^{2+}	2.55	4.38				
Mn^{2+}	3.82	5.25				
Mn^{3+}	9.98	16.57	19.42			
Ni^{2+}	5.3	6.51	8.5			
Pb^{2+}		6.54				
Sr^{2+}	2.54					
Tl^{+}	2.03					

	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}\beta_4$	$\log_{10}\beta_5$	$\log_{10}\beta_6$
Zn^{2+}	5.00	7.36	8.15			
Tartrate	**$[(CHOH)_2(COO)]_2^{2-}$**					
Ba^{2+}	2.54					
Ca^{2+}	2.98					
Cd^{2+}	2.8					
Co^{2+}	2.1					
Cu^{2+}	3.1	5.11	4.8	6.3		
Fe^{2+}	4.8					
Fe^{3+}	7.49					
Mg^{2+}	1.36					
Pb^{2+}	3.78					
Sr^{2+}	1.59					
Zn^{2+}	2.68					
Thiocyanate	**SCN^-**					
Ag^+	4.75	8.23	9.45	9.67		
Au^+		≈24				
Au^{3+}				42.00	42.00	42.04
Bi^{3+}	1.15	2.26		3.41		4.23
Cd^{2+}	1.39	1.98	2.58	3.6		
Co^{2+}	-0.04	-0.7	0	3.00		
Cr^{3+}	1.87	2.98				
C^{u+}	12.11	5.18				
Cu^{2+}	2.30	3.65	5.19	6.52		
Fe^{2+}	0.95	0.07				
Fe^{3+}	3.01	4.66	4.63	4.23	3.23	
Hg^{2+}		17.47	19.15	19.77		
In^{3+}	2.58	3.60	4.63			
Ni^{2+}	1.18	1.64	1.81			
Pb^{2+}	1.09	2.52		0.85		-0.30
Th^{4+}	1.08		1.78			
Tl^+	0.8	0.65	0.2	0		
Zn^{2+}	1.7	2.1	2.2	3.7		

Appendix VII

Formation Constants of Some Metallochrome Indicators with Their pK_as

	CAL	CMG	EBT	HQS	MPT	MUR	NIN	PAN	PAR	PYV	QIN	XYO
	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a	pK_a
Hin	7.36			1.3	2.2	0	11.2	1.9	2.30	0.3	5.13	-1.74
H_2In	13.5	8.14	6.3	4.15	2.9	9.20		12.3	6.95	7.82	9.89	-1.09
H_3In		12.35	11.5	8.74	7.0	10.50			12.4	9.76		2.58
H_4In					7.8					12.50		3.23
H_5In					11.4							6.37
H_6In					12.01							10.46
H_7In												12.28
	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f	pK_f
Al^{3+}										19.13 Al_2In 4.95		
Ba^{2+}					6.2							
Bi^{3+}										27.07 Bi_2In 5.25		5.52
Ca^{2+}	5.58	6.05	5.4		7.8	5.0						
Cd^{2+}				7.6 $CdIn_2$ 5.9						8.13 CdHIn 5.86 Cd_2In 4.0	7.2 $CdIn_2$ 6.2	
Co^{2+}				9.2 $CoIn_2$ 7.6				> 12	CoHIn >12	9.01 CoHIn 6.53	9.1 $CoIn_2$ 8.1	
Cu^{2+}	21			12.5 $CuIn_2$ 10.6		17.9		16	10.3	16.47 CuHIn 11.18	12.2 $CuIn_2$ 11.2	
Fe^{2+}				8.4 $FeIn_2$ 6.7							8.0 $FeIn_2$ 7.0	5.70
Fe^{3+}				12.0							12.3 $FeIn_2$ 11.3	
Mg^{2+}	7.64	8.05	7.0		8.9		5.80 $MgIn_2$ 3.80			4.42 MgHIn 3.66 Mg_2In 4.6		
Mn^{2+}				6.6 $MnIn_2$ 4.9			7.10 $MnIn_2$ 5.50	8.5 $MnIn_2$ 7.9	MnHIn 9.7 $Mn(HIn)_2$ 9.2	7.13 MnHIn 5.36	6.8 $MnIn_2$ 5.8	
Ni^{2+}				10.0 $NiIn_2$ 8.1		11.3	10.70 $NiIn_2$ 9.20 $NiIn_3$ 5.9	12.7 $NiIn_2$ 12.6	NiHIn 13.2 $Ni(HIn)_2$ 12.8	9.35 NiHIn 6.85 Ni_2In 4.38	9.9 $NiIn_2$ 8.8	
Pb^{2+}										13.25 PbHIn 10.19	10.61 $PbIn_2$ 8.09	
Sc^{3+}									4.8			
Tl^{3+}								2.29	4.23			4.90
Zn^{2+}	12.5		13.5	8.4 $ZnIn_2$ 6.7	15.1		8.7 $ZnIn_2$ 7.00	11.2 $ZnIn_2$ 10.5	10.41 ZnHIn 7.21 Zn_2In 6.21	10.41 ZnHIn 7.21 Zn_2In 6.21	9.96 $ZnIn_2$ 8.90	6.15

CAL= Calcon, CMG = Calmagite, EBT = Eriochrome Black T, HQS = 8-hydroxy-5-quinolinesulfonic acid, MPT = Metalphthalein, MUR = Murexide, NIN = 2-nitroso-1-naphthol, PAN = 1-(2-pyridylazo)-2-naphthol, PAR = 4-(2-pyridylazo)resorcinol, PYV = Pyrocatechol violet, QIN = 8-quinolinol, XYO = Xylenol orange

Appendix VII

pK_{sp} Constants for Some Sparingly Soluble Substances

	Br^-	Cl^-	CN^-	CO_3^{2-}	CrO_4^{2-}	F^-	I^-	IO_3^-	OH^{-1*}	S^{2-}	SO_4^{2-}
Ag^+	12.28	9.75	15.84	11.09	11.95		16.08	7.51	7.71	49.2	4.8
Al^{3+}									32.0	6.7	
As^{3+}										21.68	
Ba^{2+}				9.26	9.93	6.0		8.82	2.3		9.97
Bi^{3+2**}							18.09		30.4	97	
Ca^{2+}				8.32	3.15	8.28		6.15	5.26		5.04
Cd^{2+}			8.0	11.28					13.06	26.1	
Ce^{3+}						15.1		9.50	19.8		
Ce^{4+}								16.3	47.7	10.22	
Co^{2+}				12.84				4.0	14.8	20.4α 24.7β	
Cr^{3+}						10.18			30.2		
Cu^+	8.28	6.73	19.49				11.96		14.0	47.6	
Cu^{2+}				9.86	5.44		6	7.13		35.2	
Fe^{2+}				10.50					15.1	17.2	
Fe^{3+}									37.4		
Hg_2^{2+}	22.24	17.88	39.3	16.05	8.70		28.35	13.71	23.7	47.0	6.13
Hg^{2+}								12.5	25.52	51.8 black	
In^{3+}									33.2	73.24 4	
Li^+				1.60		2.42					
Mg^{2+}				7.46		8.19		2.5	10.7 4		
Mn^{2+}				10.74						9.6	
Ni^{2+}				8.18				7.85	14.7	18.5α 24.0 β 25.7 γ	
Pb^{2+}	4.41	4.79		13.13	12.55	7.57	8.15	12.49	14.93	27.9	7.79
Sn^{2+}							4.0		27.85	25.0	
Th^{4+}						25.3		14.6	44.4		
Tl^+	5.47	3.76			12.00		7.19	5.51		20.3	
Tl^{3+}									45.20		
Zn^{2+}			12.59	10.84				5.4		23.8α 21.6 β	

Appendix VIII

Glossary of Maple Terms and Operations

Command	Page[242]	Comment
`:=`	18, 20	`x:=2` *assigns* x the value of 2. Until x is unassigned or the `restart` command is used, every time x is entered into the worksheet, it will be replaced with the value 2. This is *not* to be confused with the equal (=) symbol. While `x := x + 2` is possible; `x = x + 2` is not.
`{...}`	43, 50	These braces delineate a *set* of expressions, solutions, numbers or instructions. In a set, each element is unique (no repetitions) and the order of elements is *not* stored. One might solve two expressions for two variables with `solve({expr1, expr2},{x,y})`. The second set of braces yields two *independent* terms, one for x and the other for y. Using square brackets `[x,y]`, `solve` would produce a single, indivisible term for x *and* y.
`[...]`	19, 29, 181	These symbols enclose lists of numbers, variables, expressions or sets. Their order is preserved and replicates are allowed. When used inside commands like plot, if a list of expressions (to be plotted) is followed by a list of line colors, the order of line colors follows the order of the expressions. This is *not* the case when options are entered as sets. These brackets also create subscripts. See Subscripting below.
`:`	18	One of two characters required for separating or terminating statements in the Worksheet Mode. This causes Maple to execute that statement (command) *without* providing its output. See Semicolon below.

`;`	18	One of two required characters for terminating a command in the Worksheet Mode. This causes Maple to execute that command *with* output. *cf.* Colon above.
`%`	58	The ditto or nullary operator reevaluates the last expression computed (or defined). It allows an operation to be performed on the most recent output without having to reenter that output. `%%` reevaluates the second most recent output; `%%%` third most recent. Be advised that most recent pertains to time and *not* space. And so, if one were to scroll several command lines up a worksheet and enter `sqrt(%);`, the square root operation would be applied *not* to the output immediately above this command, but rather to the output most recently generated, *i.e.* at the bottom of the worksheet. Finally, there are "level" issues that complicate the use of this operator. Reference to the Maple Help menu is recommended.
`'...'`	52, 64, Part II, 101	Enclosing input between single quotation marks can (but not always) protect that input from being evaluated. That is, it is treated as an unassigned name. It allows its output without the quotation marks. For example `x:=2: SQRT['x']:=sqrt(x);` would yield $SQRT_x := \sqrt{2}$. Without the protection, $SQRT_2 := \sqrt{2}$. "" offers a defacto protection by disguising the string with quotation marks; this would produce $SQRT_{"x"} := \sqrt{2}$. The single quotation marks are useful for adding an unassigned name to an output. Continuing with the example above, `'answer'= sqrt(x);` would return $answer = \sqrt{2}$. The single quotation marks are used also to unassign a previously assigned name. (see Unassign below).

`algsubs`	55	`algsubs(x=y, exp)` replaces `y` with `x` in an *algebraic* expression, `exp`. So if exp is y+2 and `EXP := algsubs(x=y,exp)`, then EXP will become x+2.
Apply Globally	16	One of two options (buttons at bottom of the screen) on each page of the Preferences. This allows the user to direct changes to every worksheet opened or yet to be opened (Globally). The other option is [Apply to Session].
Apply to Session	58	One of two options (button at bottom of the screen) on each page of Preferences. This allows the user to direct changes only to the currently open worksheet. The other option is [Apply Globally].
Assignment operator =WZ	18, 20	`x:=2` assigns x the value of 2. Until x is unassigned or the `restart` command is used, every time x is entered into the worksheet, it will be replaced with the value 2. This is *not* to be confused with the equal (=) symbol. While `x := x + 2` is possible; `x = x + 2` is not.

`axes`	26, 132	One of several options for plotting, `axes = boxed`, `normal`, `frame` or `none`. If expr is the expression to be plotted, then `plot(expr, axes = boxed)` might be used. Using `axes = normal` is the equivalent of omitting this option. Right (or control) clicking on the plot and accessing the plot menu provides a simple way to effect this and other plot options.
Braces `{}`	43, 50	These delineate a *set* of expressions, solutions, numbers or instructions. In a set, each element is unique (no repetitions) and the order of elements is *not* stored. One might solve two expressions for two variables with `solve({expr1, expr2},{x,y})`. The second set of braces yields two *independent* terms, one for x and the other for y. Using square brackets `[x,y]`, `solve` would produce a single, indivisible term for x *and* y.
`collect`	71	`collect(expr, term)` This collects all of the terms in the polynomial, `expr` according to the power to which the named term is raised. For example if expr is $bx + ax^2 + cx$, then `collect(expr,x);` or `collect(bx + ax^2 + cx, x)` would return $bx + a\,x^2 + cx$. One can right (or control) click on the $bx + a\,x^2 + cx$ output to open a menu from which collect can be chosen. Within that menu is an-other option to collect the terms by a, b, c, or x.
Colon `:`	18	One of two characters required for separating or terminating statements in the Worksheet Mode. This causes Maple to execute that statement (command) *without* providing its output. See Semicolon below.

color	23, 44	One of several options for plotting. This dictates the color of any expression to be plotted. Without this option, default colors are provided. There are dozens of color choices, many with obvious names: green, red, blue; there are more esoteric names that require quotation marks like "Lime," "Maroon," and "HotPink." All color names are case-sensitive. When multiple colors are required, they should be listed in square brackets to correlate their order with the order of the expressions being plotted. `plot([expr1, expr2],color =[black,"Fuchsia"]);` Using the color option in `plot3d` paints the entire surface the specified color and overrides Maple's default which paints the surface in a gradient of colors to enhance the curvature of the surface. The color option is particularly useful in 3-D plotting when multiple expressions are plotted and they are to be articulated with multiple colors, in square brackets, of course.
coloring	142	One of several options for contour plotting. `coloring = [x,y]` dictates the range of the "z axis" in the contour plot. The lowest value is articulated by lines of color x and the maximum by lines of color y, where `x` and `y` are colors as described in `color`, above.
contourplot	142	Used to create a contour plot of a three dimensional function or expression in two dimensions. (It *might* be necessary to call it from Maple's plot package using `with(plots, contourplot);` before using it for the first time.) This command requires an expression (or list of expressions in square brackets) followed by a comma, then the identity and range for each of the two axes separated with a comma. (*cf.* `plot3d`) If options are listed, they follow the axis ranges. For example, a contour plot of sin(x*y) might be created with `contourplot (sin(x*y),x=-2..2,y=-2..2,` option$_1$, option$_2$...`);`. Options like coloring, contours and grid are described elsewhere in this Appendix.

`Contours`[243]	142	A `countourplot` option `contours = n` where n is an integer > 0. (The default value is 10.) As n is increased the number of lines articulating the plot is increased. *cf.* `grid`.
`diff`[244]	139, Part II, 121	This operator differentiates a function or expression in terms of any *one* of its variables. So if expr is $x^2+2y+z=0$, then `diff(expr, x);` yields $2x$. This operator can be accessed by right (or *control*) clicking on the $x^2+2y+z=0$ output. This will open a menu from which Differentiate can be chosen. Within that menu is another option to differentiate in terms of x, y or z.
`Digits`	20	`Digits:= n` where `n` is an integer > 0 sets the number of digits Maple uses in numerical calculations. This can also be set in the Precision tab of the Preferences window by checking ☑ Round calculations to [n] significant figures. `Digits := n` will *not* override the screen display setting. That too can be set in the Precision tab described above.

Display tab	17	One of six tabs found within Preferences. Here several default settings can be reset. All worksheets can be made to open with and use Maple Notation or 2-D Math Notation for input or output. One can also set Maple to show plots (Plot display) in line with output or as a separate window.
do	180	Precedes a sequence of statements (instructions) to be carried out more than once. It is *not* followed by a colon or semicolon, but rather with od or end or end do at the end of the sequence of command lines. The od or end or end do must be followed by : (for no output display) or ; to display the output. Each command *within* the sequence is followed with a colon. (A semicolon following commands *between* do and end does *not* yield an output.) It is only the semicolon following end or od or end do that produces an output display. The do command can be preceded with a for clause in order to define how many times the sequence is executed. Alternatively, a while clause (a Boolean expression) can be used to establish the condition at which the execution of the sequence will terminate.
Document mode	16	An alternate to the Worksheet mode (envi-ronment). Unless it is reset in Interface tab in Preferences, this is the default operating mode. In the document mode, the work area is a blank page, where input prompts (>) are replaced with a blinking, slanted cursor. The input operations are different because this mode uses Math input (see below). As in the Worksheet mode, a right (or Control) click on the *output* from a command line opens a menu of operations that can be performed on this expression. They include Differentiate, Integrate, Simplify and Solve.

done	168	The done command (synonyms with quit and stop) terminates the Command-Line Maple session and returns the user to the shell from which Maple was started. This does *not* quit Maple. This command *might* be disabled, and its use will cause a "Warning, done/ quit/stop disabled. Please use File->Close" output.
end	180	This is the terminal statement that follows the sequence of commands after the do command. It can be replaced with od or end do. A colon for suppressing output or semicolon for displaying output must follow end.
eval	57	This operator allows the evaluation of an ex-pression, say expr, at any point where its parameters are defined. For example if expr is defined as $x^2 + y^2$, then eval(expr, [x=3, y=4]); or eval(x^2+y^2, [x=3, y=4]); yields *25*, and eval(x^2+y^2, =3); yields $9 + y^2$. By right (or control) clicking on the output $x^2 + y^2$ a menu from which Evaluate at a point can be selected. This will contain a submenu for choosing the desired value of x and y. This operator can produce an ambiguous output. For example eval(sqrt(2)); yields $\sqrt{2}$, and eval(log[10](2)); yields $\ln(2)/\ln(10)$, legitimate but not useful outputs. For an unambiguous numeric output, evalf is recommended. However, one can also produce approximated numeric values by right (or *control*) clicking on the output and selecting *Approximate* from the menu that opens. Within that menu, the number of decimal places used to approximate the output can be chosen. This does not affect the number of places used to display the approximated output. For that see Numeric Formatting.

`evalf`	57	This command calls the math coprocessor and uses floating point arithmetic to provide a *numerical* calculation of an expression. *cf.* `eval` above. But where `eval` can have an algebraic output, `evalf` *must* be a purely numeric output. The number of decimal places used in the floating point approximation can be set in this command by enclosing that number in square brackets after the floating point evaluation command. For example `evalf[5] (sqrt(2));` returns 1.414 while `evalf[2] (sqrt(2));` returns 1.400.
`factor`		This returns the factors multivariate polynomial expression with integer, rational, (complex) numeric, or algebraic number coefficients. By right (or control) clicking on the output of an expression, a menu will appear from which Factor can be selected. This will execute the factor operation as `factor (expr)` where `expr` is the assigned polynomial. `factor (x^2-1);` returns $(x - 1)(x+1)$.

`for`	180	An *optional* clause that precedes the `do` com-mand. It defines how many times the sequence is executed. It does this by describing a counter, something like i. It *can* set the initial value of the counter with a `from` option (see below); it can set the increment size for the count with a `by` option; and it *must* set the final value of the counter with the `to` command. When `from` and `by` are omitted they are taken to be 1. The syntax might look like: `from j = 3 by 2 to 17 do`.
`from`	Part II, 15	An optional part of the `for` command that sets the initial value of the counter. Without it, that value is taken to be 1.

`fsolve`	22	As with the `evalf` command, this calls the math coprocessor and uses floating point arithmetic to solve an equation numerically, and so it provides only real, numeric solutions *unless* the `complex` option is included in the `fsolve` command as in `fsolve(expr, x, complex)`, where `expr` is an expression in x and `x` is the term to be solved for, and `complex` calls for complex solutions. If an option like `complex` is *not* included in the syntax, it is not necessary to stipulate the variable to be solved for, because in `fsolve` there can be only one variable if only one expression is to be solved for. (See below.) This command can be executed by right (or *control*) clicking on the output for `expr` and first selecting Solve from the menu and then selecting Numerically solve from the submenu. The range over which `fsolve` seeks roots can be set by stipulating the range as, for example `,x=0..13);`. While this is not required, providing a range increases the likelihood that `fsolve` will find a root as long as a root indeed exists within the stated range. See also `solve`. Multiple expressions can be solved simultane-ously by including the multiple expressions within braces, `{}`, as a set. If the variables to be solved for are to be specified, they must also be expressed as a set. For example `fsolve({x +2*y=3, x-y=0},{x,y});` returns $\{x = 1.000, y = 1.000\}$.
`grid`	132, 142	This is an option in `plot3d`. It is entered after the expression(s) to be plotted in the form `grid = [m,n]` where `m` is an integer stipulating the number of grid lines on the first of two axes required for the plot, and `n` is the integer stipulating grid lines on the second axis.

`gridlines`	26, 204	An option for the plot command. It is entered after the function to be plotted and activated with `gridlines = true`. The gridline properties are best set from the plot menu which is accessed by right (or *control*) clicking on the plot. That menu contains Axes which contains a Gridlines Properties... in its submenu which then leads to a screen for making adjustments.
Interface tab	16	One of six tabs found within Preferences. Here several default settings can be reset. The user can reset the default format for new worksheets from Document to Worksheet.

`labels`	26, 132	An option that can be applied to `plot`, `plot3d` or `countourplot`. This option follows the expression(s) to be plotted; the syntax for a 3-D plot would be `labels = [text_x,text_y, text_z]` where `text_x`, `text_y` and `text_z` are the text that will label the x, y and z axes, respectively. Note the use of square brackets. Right (or *control*) clicking on the plot will open the plot menu which contains an Axes option that contains a Labels sub-option. Within the Labels selection there are options to remove or edit each of the available axis titles.
`lhs`	71	An operation that calls the left hand side of an expression. The expression must contain an equal sign. So if `expr:= x^2 + 2 = y^2:`, then `lhs(expr);` returns $x^2 + 2$.
`line`	44	One of the options within the `style` option for `plot`, `plot3d` and `countourplot`. It is the *default* setting in lieu of `style=point`. So it need not be called, but if multiple expressions are plotted and not all are to be plotted with a line, then `style = [point, line]` would render the plots with the first expression listed using points and the second expression using a line. Several line options can be accessed within the plot menu. Right (or *control*) click on plot and scroll to Line. See also the `thickness` option.
`log`	21	This command returns the *natural* logarithm of an expression or real number. For a logarithm to a base other than *e*, that base must be specified in square brackets following the log command. For example `log[10](17);` returns the common log of 17. However, it is not displayed numerically: this requires the `evalf` command, see above.
Manipulator	133, Part II, 211	A menu item accessed by right (or *control*) clicking on a contour, two dimensional or three dimensional plot. Selecting Manipulator leads to a sub menu Point probe, Pan or Scale. The Manipulator for a three dimensional plot has a Rotate option.

Math input	17	The default mode of entry in the Document or Worksheet mode. Math / Text Input modes can be toggled by clicking on the Text or Math buttons at the left edge of the menu at the top of the worksheet. With Math input, mathematical operations are automatically interpreted, and the terminating command (a semicolon) is not required. So entering x^2 + 2x -14 would require the following keystrokes: x, then ^, then 2, then ⟶ (right arrow), then +, then 2, then x (note that there is no need for * between the 2 and x), then - ,then 1 then 4, and finally [return]. This returns $x^2 + 2\,x\,-14$.
Minimum exponent digits	34	Within the Numeric Formatting... menu there are options for displaying numbers, among these is Scientific. When this output format is selected, one can set the *minimum* number of digits, ***n***, used in the $x\,10^n$ part of the output.

`NLPSolve`	Part II, 160	A non-linear program solver that computes a minimum or maximum of an object function. If that function is Fnc, then `NLPSolve(Fnc);` would be called. The search (for a minimum or maximum) can be specified for each variable. If Fnc contains x, then `NLPSolve(Fnc,x = 0..2);` might be called, but note that `NLPSolve` finds a true maximum or minimum, *not* the greatest or smallest value within the cited range. (Before using this operator for the first time, it *might* be necessary to call it from Maple's plot package using `with(Optimization):`)
`normal`	70	This command can somewhat "clean up" a polynomial, especially those that contain a denominator. `normal((x^3-2*x^2+ 14*x)/x);` would return $x^2 - 2x + 14$.
Numeric Formatting	34	A menu item which is accessed by right (or *control*) clicking on an output. Clicking on Numeric Formatting... opens a window that allows the output display to be customized such as fixed decimal, scientific or engineering notation. A caution is in order here. If, for example `X := 0.0035;`, is entered, and $X = 0.0035$ is returned, adjusting the output to scientific notation as described above will change that output to 3.50×10^{-3}. The font and color are changed, and the $X =$ are lost irreversibly. Even restarting the worksheet will not recover this original output. See Protection (below) for a way to preserve output text with single quotation marks.
`od`	180	This is the terminator for a "do loop" used on earlier releases of Maple. It is still functional and can be used in lieu of `end` which is used on current releases.
`op`	175	`op(n,expr);` isolates the n^{th} operand in the expression expr for assignment or for manipulation. For example `D:= op(2, expr)-op(1,expr);`.

`orientation`	132	`orientation = [ψ,θ]` specifies the angles (in degrees) at which a three dimensional plot is rendered. The default values are 45° and 45°. Each value can be ≤ 0°.
Pan	133, Part II, 211	One of the options for the Manipulator. Select-ing Pan from the submenu turns the cursor into the image of a hand that allows one to slide the graph into uncharted regions of *x* and *y*.
Percent (`%`)	58	The ditto or nullary operator reevaluates the last expression computed (or defined). It allows an operation to be performed on the most recent output without having to reenter that output. `%%` reevaluates the second most recent output; the `%%%` third most recent. Be advised that most recent pertains to time and *not* space. And so, if one were to scroll several command lines up a worksheet and enter `sqrt(%);`, the square root operation would be applied *not* to the output immediately above this command, but rather to the output most recently generated, *i.e.* at the bottom of the worksheet. Finally, there are "level" issues that complicate the use of this operator. Reference to the Maple Help menu is recommended.

`plot`	23	The command for creating a two dimensional plot of an expression (or series of points). The expression can be explicitly included *e.g.* `plot(sin(x));` or predefined *e.g.* `expr := sin(x); plot(expr);`. The range over which the variable is to be plotted can (should) be dictated *e.g.* `plot( expr, x=-1..1);`. Following these parameters, several options can be added, each separated with a comma. These include (and are described in this Appendix): `axes, color, labels, gridlines, style, title and titlefont`. Multiple expressions can be plotted by separ-ating them with a comma and placing them in square brackets. *e.g.* `plot([expr1,expr2 ],x=0..4);`. If options are assigned individ-ually to each expression, they too should be in square brackets, assigned in the same order as the expressions. *e.g.* `color = [black, "Crimson"])`.
Plot menu	24	Found in the menu bar at the top of the work-sheet when a plot is "clicked on," or by right (or *control*) clicking on any plot. This opens a list of operations and options pertinent to the type of plot.
Plot structure	137	A record of all elements necessary to render a plot. This is achieved by assigning a name to the command used to create a plot. So if `plot(expr, x=-1..1, option`$_1$`, option`$_2$`,...);` creates a desired plot, then `Structure := plot(expr, x=-1..1, option`$_1$`, option`$_2$`,...);` will store that structure which can be rendered with the `plots[display](Structure);` command.

`plot3d`	132	The command for creating a three dimensional plot of an expression (or series of points). The expression can be explicitly included *e.g.* `plot(sin(x*y));` or predefined *e.g.* `expr := sin(x*y); plot(expr);`. The range over which the variable is to be plotted can (should) be dictated *e.g.* `plot( expr, x= -1..1, y=-1..1);`. Following these parameters, several options can be added, each separated with a comma. These include (and are described in this Appendix): `axes, color, labels, gridlines, orientation, style and title`.
`plots[display]`	138	`plots[display](X,Y,Z);` combines the plot and display commands to render, in a single plot, the plot structures (above) defined as X, Y, and Z. That is, the three plots, X, Y and Z are plotted on the same axes. Options like `title` are not required in every plot structure; indeed, if each has its own title, the title for the first structure listed (X here) will prevail.
`plots[pointplot]`	178	Creates a two dimensional plot of a sequence of ordered pairs. The points to be plotted may come from a set or list. The set of points can be entered directly as $\{[x_1,y_1],[x_2,y_2]...\}$ or indirectly by first assigning the set, `SET:={[1, 1],[2,4]...}:`. Multiple sets can be plotted and the options available for plot are available in addition to `connect = true` to connect the points. See also `pointplot`.
`point`	44	One of two options for the style option in plot. The other option is line. The syntax is `style = point`.
Point Probe	30	One of the options for the Manipulator. Selecting Point Probe from the submenu turns the cursor into a circle with crosshairs that allows one to find the x and y coordinates of any point within the plot. The coordinates are shown in a window at the top left of the worksheet that contains the plot.

Precision tab	20	One of six tabs found within Maple Preferences. Here the output can be adjusted to a prescribed number of decimal places; the significant figures used in calculations can be set, and digit truncation (elision) can be set. These can be set globally or to only the current session with the appropriate button at the bottom of the tab screen. The precision of any numeric output can also be set or altered by right (or *control*) clicking on the output and selecting Numeric Formatting... from the pop up menu. The output precision can be set for a command line and all subsequent command lines using `Digits:=n:`.
Preferences	16	Can be accessed from the menu bar at the top left of the screen by clicking on Maple *n* (where *n* is the release) and scrolling down to Preferences. Alternatively it can be opened with ⌘, keystrokes. This opens six tabs: General, Display, Export, Precision and Security.
Properties	Part II, 41 Part II, 66	One of several submenus among the Axes selection within the Plot menu (see above). The resulting tab is illustrated on page 8–23. It allows modifications to the horizontal and vertical axes (x, y and z for three dimensional plots).

Protection `'...'`	52, 64, Part II, 101	Enclosing input between single quotation marks can (but not always) protect that input from being evaluated. That is, it is treated as an unassigned name. It allows its output without the quotation marks. For example `x:=2: SQRT['x']:=sqrt(x);` would yield $SQRT_x := \sqrt{2}$. Without the protection, $SQRT_2 := \sqrt{2}$. "" offers a defacto protection by disguising the string with quotation marks; this would produce $SQRT_{"x"} := \sqrt{2}$. The single quotation marks are useful for adding an unassigned name to an output. Continuing with the example above, `'answer'= sqrt(x);` would return $answer = \sqrt{2}$. The single quotation marks are used also to un-assign a previously assigned name. (see Unassign below).
`restart`	18	This command is equivalent to starting a new Maple session: it clears Maple's internal memory thereby erasing all assignments and memory of all executions.
`rhs`	71	An operation that calls the right hand side of an expression. The expression must contain an equal sign. So if `expr:= x^2 + 2 = y^2:`, then `rhs(expr);` returns y^2.
Rotate manipulator	133	One of the options for the Manipulator in the three dimensional plot menu. Right (or control) clicking on a 3-D plot opens the plot menu; selecting Rotate from the submenu turns the cursor into a curved arrow that allows one to rotate a 3-D plot by depressing and moving the mouse.
Round calculations	20	A setting made from the Precision tab within Preferences (⌘,). *Setting this to an inappropriately small integer will cause errors in numeric computations.* For example `(1E-3)-(1E-7);` requires at least four significant digits to return the correct output, regardless of the precision of the screen display (below).

Round screen display	20	A setting made from the Precision tab within Preferences (⌘,). It is a purely cosmetic setting which does not affect calculations, although an output with too few decimal place can be misleading. This setting can also be made by right (or *control*) clicking on a numeric output, and selecting Numeric Formatting... from the submenu. See Numeric Formatting for cautions on this method of output management.
Scale	24, Part II, 211	One of the options for the Manipulator. Selecting Scale from the submenu turns the cursor into a double-headed arrow. Sliding the depressed mouse upward magnifies the scale; downward allow a greater range of the plot to be made visible.
Semicolon `;`	18	One of two required characters for terminating a command in the Worksheet Mode. This causes Maple to execute that command *with* output. See Colon above.
`seq`	181	This command constructs a sequence of values. The syntax might be `seq(x^2,x=0..3);` and would return 0, 1, 4, 9. (Note that this command can substitute for a `for` loop.) Ordered pairs might be created with something like `seq([x^2,x^3],x=0..3);` returning [0, 0], [1, 1], [4, 8], [9, 27]. Enclosing this command in square brackets, `[]`, will produce an output as a list. This creates input for a `plots[pointplot]`. Enclosing the `seq` command within braces, `{}`, will produce the sequence as a set.
Set	43	A special kind of list: it does not prescribe any order and does not allow replicate entries. The list of numbers, expressions or options is enclosed in braces like, `{a,b,c}`. *cf.* `[...]`.

`simplify`	25, 71	Simplification rules are applied to an expression, expr when `simplify(expr);` is called. Terms are collected and redundancies are removed. So `simplify(x^2+sin(x)^2+cos(x)^2-3*x^2);` returns $-2x^2 + 1$.
`solve`	22	`solve(expr,var);` *symbolically* solves the expression `expr` for the variable `var`. Multiple expressions can be solved simultaneously by including the multiple expressions within braces (`{}`, as a set). If the variables to be solved for are to be specified, they must also be expressed as a set. For example `solve({x+2*y=3, x-y=0},{x,y});` returns $\{x = 1, y = 1\}$. *cf.* `fsolve`. This command can be executed by right (or *control*) clicking on the output for `expr` and selecting Solve from the menu and then select-ing Solve from the submenu. If more than one variable appears in the expression, the submenu will allow one to select the variable to be solved for.
`sqrt`	21	This command extracts the square root of an argument. The syntax would be `sqrt(arg);` where `arg` is an expression, numerical value or variable. `sqrt(3);` returns $\sqrt{3}$; not 1.732; that would require `evalf(sqrt(3));`.
Square brackets (`[...]`)	19, 29, 181	These symbols enclose lists of numbers, variables, expressions or sets. Their order is preserved and replicates are allowed. When used inside commands like plot, if a list of expressions (to be plotted) is followed by a list of line colors, the order of line colors follows the order of the expressions. This is *not* the case when options are entered as sets. These brackets also create subscripts. See Subscripting below.

`style`	44	Pertains to a plot option. `style` can be stip-ulated in the plot command by including, for example `, style = point);` Without this stipulation, the default style is `line`. Including a `style =` is required where several styles are used in a single plot; these are listed in square brackets *e.g.* `style = [line, point]`. This plot option can be extracted from the plot menu with a right (or *control*) click on the plot to be modified to open the menu and select Style for the type of *plot* to be rendered The options include Line, Point, Polygon *etc.* When the menu for a 3-D plot is accessed, the style options also include Surface with Line, Surface, Surface with Contour and Contour among others.
`subs`	44	`subs(old = new, expr);` effects a sub-stitution of an old expression (`old`) for a new expression (`new`) in an expression `expr` or list of expressions (enclosed in square brackets). `expr:= x^2+2*x-14 = 6*x^3; subs (x=y, expr);` returns $y^2 + 2y - 14 = 6y^3$. Note that `expr` is *not* redefined as new expres-sion in y; that would require `expr := subs (...` . Also, `old` and `new` can be numeric values. See also `algsubs`.
Subscripting	19, 31	Subscripts can be appended to text or numbers by adding the desired subscript in square brackets. This operation is not allowed in the middle of text, as in `z[2]y` which will *not* return z_2y. Successive pairs of brackets, like `z[2[3]]` will produce a subscript 3 to the subscript 2.
Superscript (°)	21, Part II, 221	While there is no mechanism for effecting a superscript output from 1-D Maple Input, the superscript ° can be included in the input text and displayed in the output by simultaneously using the [*shift*] [*option*] [8] keys.

`symbol`	Part II, 23	An option available in any of the plotting formats (2-D, 3-D, contour) where `style = point` is called. symbol = XX is included in the string of parameters (see plot structure). XX can be asterisk, box, circle, cross, diagonalcross, diamond, point, solidbox, solidcircle, solid-diamond. See also `symbolsize` and `color` for 2-D and `coloring` for 3-D and contour plots.
`symbolsize`	Part II, 23	An option available in any of the plotting formats (2-D, 3-D, contour) where style = point is called. `symbolsize = n` sets the size of the symbol with the *integer* n. The default value is 10.
Text input	17	One of two entry modes in the Document or Worksheet mode. Unlike with the default Math input, mathematical operations are *not* automatically interpreted. And the terminating command (a semicolon) is required. See Document mode for more information on using Math input.
`thickness`	Part II, 50	One of several options for `contourplot` and `plot` commands. This dictates the thickness of lines used when lines are used (either by default or specified). The default thickness is 0, and "any" integer > 0 can be specified. For multiple plots, one might use `,thickness = [0,2]);` in the plot structure in order to differentiate the lines used for each plot.
`title`	26	One of several options for any of the plot packages. `title = "any text"` adds a title (any text) to the plot. Enclosing the title in single quotes, 'any text' adds the title in italics.

`titlefont`	59	This is an option that can be appended to the `title` option. The syntax `titlefont = [X,Y,Z]` specifies three characteristics of the title. `X` is the font which can be entered as TIMES, COURIER, HELVETICA, or SYMBOL. `Y` represents the style of the font which includes BOLD, ITALIC, or BOLDITALIC. These styles are not available for the SYMBOL font. `Z` represents the point size, 8,10,12 14 *etc.* to be used. This option can be accessed by right (or *control*) clicking on the plot and scrolling down to *Title* which leads to a submenu for adding or editing the title. There also exists a `labelfont` option that behaves exactly like `titlefont` except that it specifies the characteristics of any (axis) labels on the plot.
`to`	180	A required part of the `for` command that sets the final value of the counter. The syntax might look something like: `for i to 14`. Here Maple would presume that `i` begins at 1 (see `for` to alter this default), and would terminate the loop when i reaches 14.
Unassign	22	When a character or term is assigned after the `restart:` command, *e.g.* `x := sqrt (y);` anytime x is called or used in an expression, $\sqrt{y}$ will be returned and used in included in that expression until either the restart command or unassign operation is used. x can be unassigned with `x := 'x';`.
`with(Optimization)`	Part II, 161	A command that calls special, optimization packages within Maple.
`with(plots)`	142	A command that calls special, plotting packages within Maple.

Worksheet mode	16	One of two environments under which Maple can operate. One can open a worksheet mode page with ⌘N keystrokes[245] or by going to **File** in the menu bar and scrolling down to **New** and then over to **Worksheet Mode**. This will create a tab in the current Maple file. (Tabs are accessed just below the menu at the top of the worksheet.) This mode is intended for interactive use. It is characterized by the [> input prompt at the left edge of the worksheet. It requires the use of `:` or `;` at the end of a command line, and commands require normal programming syntax like `2*x` to enter "x multiplied by 2."

Endnotes for Part II

156. Like K_a these constants have a thermodynamic equivalent $K°_{an}$ which is expressed in terms of activities, $\{H^+\}$, $\{H_{n-1}A^{m-1}\}$, *etc.*
157. NH_2^- is a much stronger base than OH^-. Consequently:
$H_2O + NH_2^- \longrightarrow OH^- + NH_3$
will lie so far to the right that no NH_2^- is detected. This implies that K_{a2} (the dissociation of H^+ from NH_3) is less that 10^{-14} so that K_b for NH_2^- is greater than 1.
158. There are two important trends that should become apparent in the following pages: 1. For the acid H_nA, there will exist n + 1 congeners, and all but one will bear a charge, and 2. the charge balance expression will be an n + 2 degree polynomial in $[H^+]$.
159. Recall from Chapter 3 that the defining property of a strong base MOH is that M^+ is completely dissociated and remains inert in solution.
160. In **Preferences, Round calculations to…** has been set to 20 to preclude round off errors in computations to come.
161. This is done so that j = 0 coincides with pH = 0, which is convenient but not critical.
162. Of course, *only* because the Davies Equation is used to calculate the coefficients. Debye-Hückel would have produced a different γ for each of these, because each ion has a unique "a." (See Appendix II.)
163. If not, review the discussion in Part II page 11.
164. Notice the need to protect `H3A`, `H2A` *etc.* in the alpha subscripts by using single quotes. Without this protection, the subscripts will take on numerical values as soon as `H3A`, `H2A` *etc.* are evaluated.
165. "Right clicK" on the output.
166. Part I page 76.
167. Recall that `algsubs` allows only one substitution at a time, but one can string `algsubs` commands together. For example `ChBalC:= algsubs(K[a1]= K°[a1],algsubs(K[w] = K°[w], ChBal));`
168. Alternatively, we could also have set $K_{a1} = K°_{a1}$ *etc.* with K[a1] := K°[a1] *etc.* in place of g[1] := 1.0: g[2]:= 1.0: g[3] := 1.0:
169. This command is necessary because the plot was *not* skipped and at this point `H` would have a residual assignment from the final trip through the *j* loop.
170. The change in output font here is due to a change in the numeric formatting (right click on output and select Numeric Formatting… See Figure 2-10).
171. See Part I page 169 for the discussion on indicator choice.
172. Strictly speaking it is a hexaprotic acid, but because only four protons can be exchanged in the pH 2 to 14 range, it is traditionally treated as tetraprotic.

173. Notice the use of full quotation marks here to protect the subscript. Normally single quotations are sufficient, but if 'NH4' is used, an Error, recursive assignment warning is produced.
174. The reader should remember that the maximum value for an α is one, and that log(1) is zero.
175. The reader is welcome to verify this by creating an α vs. pH plot for this acid. The solution to this problem is found where the two α's cross.
176. This is not such a bold assumption. Looking at Figures **8-1** and **8-6** one sees that when $[H^+]$ approaches the "last" K_{an}, the totally deprotonated congener begins to dominate. That is α_{An^-} begins to approach 1.
177. K_w will not be required if our presumption about the pH of the solution and the alphas is correct.
178. The reader should be able to correct the equilibrium constants back to $\mu = 0$ conditions and then correct to the desired ionic strength. Because ionic radii data are rarely available, the Davies Equation (Equation **2-8**) would be required for this operation. The difference between $K°_{f,n}$ and $K_{f,n}$ can be substantial because, where n is large, some of the ionic charges can be substantial (*i.e.* $z = \pm 4$).
179. This is to say $[M^{p+}]$ and $[L^{q-}]$.
180. There is no need to report, for example, K_{f5} *and* β_5 because it can be shown that $K_{f5} = \beta_5 \div \beta_4$.
181. It is difficult to prepare *any* solution to a concentration more than *about* 10 **M**.
182. The logic of the coefficients is presented with Equations **3-7** and **3-8**. It should seem reasonable that to have a 1 **M** solution of $Fe(CN)_3$, it would be necessary to have *at least* 3 **M** *total* CN^- in solution.
183. These are taken from the Fe^{3+} complex with the oxalate ion, $C_2O_4^{2-}$ (Appendix VIa). A pH large enough to assure that α_{H2Ox} and α_{HOx} are negligible is presumed. The output here has been reformatted.
184. Recall how the placement of single quotation marks in the input will create the labels in the output above.
185. Three exceptions are Cl^-, Br^-, and I^-.
186. $\alpha_L q- \times K_{f,n}$ and $\alpha_L q- \times \beta_n$ are known as conditional formation constants, $K'_{f,n}$ and β'_n, respectively.
187. That is, there will be no need to look for β_1, β_2 *etc.*
188. The `gridlines = true` command is used here in lieu of the practice of adding gridlines from the plot menu.
189. Or in logarithmic terms, the sum of the logα's.
190. Recall (Problem 2, Chapter 8) that EDTA is so important that it has its own symbol, H_4Y.
191. This concept was introduced in Chapter 1 in the context of the reaction quotient, Q. It was discussed again in Chapter 4 (page 78) in the context of α_{A^-}, and it is most recently addressed as C_{EqPt} in Problem 3 in Chapter 7.
192. When a formation constant becomes this large, constants like β_3, β_2, and β_1 are unnecessary because $Ni(CN)_4^{2-}$ so dominates the solution makeup.

193. Even this alpha is incomplete because it ignores mixed complexes like $Ni(OH)_2(CN)_2^{2-}$. Such complexes are legitimate when the concentrations of the two ligands and formation constants favor their formation. Here, because CN^- is so strongly bound, these mixed complexes are insignificant.
194. There is a subtle flaw in this expression: Setting C_{KCN} equal to zero does not lead to the correct α_{Ni2+} expression for the cyanide-free solution. This is because the $1 + \beta_4[CN]^4 \approx \beta_4[CN]^4$ approximation is *un*-true when $[CN^-] < 1.88\ 10^{-9}$ **M**.
195. Some sources report a $Cu(NTA)_2^{4-}$ complex, but the K_f for this second complex is about 10^{-10} as strong as the $CuNTA^-$ complex. So it can be ignored without consequence.
196. Not as $\alpha_{NTA3} \times C_{NTA}$ for the reason described in Part II page 67.
197. Just as calculated by Equation **7-2b**, Part I page 164.
198. See the discussion in Part I page 190.
199. For an example where the titrand contains the complexing agent and the titrant contains the metal ion, see Example Problem 4 at the end of this chapter.
200. Although the rule is very general, the work from which it is taken, Flaschka, H., *Talanta*, **1**, 60 (1958), provides a rigorous derivation of more specific guidelines.
201. Aside: If $[MIn^{p-r}]$ is more than about 0.1% of $C_{Metal,}$ the titration error can be considerable. This issue was ignored in the Chapter 7 because $C_{Indicator}$ for acid / base titrations is routinely insignificant. So there, $[Hin^{1-r}]$ is taken to be negligible.
202. Reilley, C.N. and Schmid, R.W., *Anal. Chem.*, **31**, 887 (1959).
203. Charges are omitted for clarity.
204. The colors here do not represent the actual color change: it is a wine red to yellow that one sees. Note also that $\alpha_{H2PAR1-}$ and α_{HPAR2-} are not too different. So H_2PAR^{1-} might well contribute to the color of the titrand.
205. None of the necessary input is provided because it is essentially a rewrite of the worksheet begun in Part II page 76 but with several prudent shortcuts. First, the $pH_{optimum}$ calculation is not necessary. Second, constants, including `pH:= 8.5`, are assigned early so as to minimize the complexity of the output. In doing so, note that if K_{a1}, K_{a2} and K_{a3} are used for NTA, they cannot be used for PAR: K_{In1}, K_{In2} and K_{In3} make sense there. Also, the `alpha(n) := op(n,Den)/Den` command will not work, because with the constants pre-assigned, `Den` will not contain more than one operand.
206. In fact, if $C_{Indicator}$ is more that about 1% of C_{EqPt} the mass balance developed here is invalid because our mass balance made no allowances for $[MIn^{p-r}]$.
207. 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid. See Appendix VIa for the K_f values.
208. Only the excess is titrated because the K''_f for MgY^{2-} is not sufficient for Mg^{2+} to displace Ba^{2+} from BaY^{2-} until it has exhausted Y^{4-} and the In^{3-}.
209. Appendix VIb shows only two acid dissociation constants. So although H_2EBT^- is a congener, there is no H_3EBT; there is only H_2EBT^-, $HEBT^{2-}$ and EBT^{3-}.
210. H_2In^- is red. This too should be minimized so as not to impart its color to the titrand.

211. Recall that it is necessary to reassign MassBal because C_{Total} = 0.010 is embedded in MassBal.
212. See Chapter 2, especially Equation **2-2** for review. Also see Part II page 118 (and Endnote 215) for an example of how this expression fails if there is no solid in equilibrium with the solution.
213. Saturated would imply that some, even if only a trace, $KClO_4(s)$ would be present.
214. Of course counter ion are needed for the Cs^+ and ClO_4-. Because both are (or could be) members of Table **3-1**, any counter ion for each would do. So, CsCl and $NaClO_4$ would be reasonable.
215. Intuitively, one would expect that if $C°_{Cs}$ or $C°_{ClO4}$ = 0, there would be no precipitate (*i.e.* *Prcp* = 0). But the expression for *SolEq* does not produce that result! This is because the equilibrium expression that defines solution makeup is not binding (or even relevant) when there is no precipitate present.
216. This value will vary when ionic strength effects are considered, but because it is so much less than the desired 99.9%, there is little point is making that adjustment.
217. This is analogous to the discussion in Chapter 7 (page 205) regarding the relationship among C_{EqPt}, K_a, and α_A-. As C_{EqPt} approaches zero, K_a must become larger and larger to keep α_A- from approaching 1.
218. Also, see Example Problem 1 part c at the end of this chapter.
219. By amount, concentration is meant, but this is an awkward term for a material that has precipitated out of solution. Mathematically, however, it is as though this concentration has disappeared from solution.
220. Only the cations of Group IA do not bind OH^- to any measurable degree, and only the anions of strong acids do not measurably bind H^+. So salts of these cations and anions are not affected by pH. Also, oxyanions (perchlorate, sulfate *etc.*) are least likely to form complexes with metals as described in Chapter 9. And finally, oxyanion salts are highly ionic in nature, and that precludes a second mode of dissolution, the intrinsic solubility which will be discussed presently.
221. Note that just as $K_a = 10^{-pKa}$, $K_{sp} = 10^{-pKsp}$.
222. The `evalf` command is necessary; with `eval` one gets $0.1146\ 2^{1/3}$.
223. That is anions that are not chelating agents. Chelating agents like EDTA form complexes with Group IIA metal ions as demonstrated in Chapter 9.
224. If this point is not clear, see Part II page 56 and the discussion that follows or Example Problem 1, part d in Chapter 9.
225. Chloride in the previous examples has been replaced with cyanate here because cyanate, being an oxyanion is less inclined to form complexes $Ag(OCN)_n^{1-n}$ and also it will not have an intrinsic solubility (n=1). This is an important consideration when the metal ion M^{m+} is the *titrant* because M^{m+} falling into a "sea" of ligand anions (titrand) is likely to form many soluble complexes prior to forming a precipitate. Not only does this lead to an end point that *follows* the equivalence point, it complicates the mathematics of the precipitation titration.

226. See Example Problems 1c and 5 for a different approach to finding `C - Prcp`.
227. And then, if desired, to calculate the activity coefficient for Ag^+ at that point in the titration so that $[Ag^+]$ can be converted to $\{Ag^+\}$. Ignoring ionic strength effects allows one to create the titration curve with the `plot` command. This is the approach we will take here, deferring the calculation of $\{Ag^+\}$ to Example Problem 5 at the end of this chapter.
228. Part I page 173 and especially in Problem 4 of that chapter.
229. This principle derives from the Paneth-Fajans-Hahn adsorption rule.
230. An excellent example of this is the titration of Zn^{2+} with $Fe(CN)_6^{4-}$.
231. The soluble calcium is restricted to Ca^{2+} because the acid solution (from HIO_3) will preclude the formation of $CaOH^{1+}$ and $Ca(OH)_2$.
232. This is because the absolute solubility will decrease indefinitely, but C_{Ca} also decreases indefinitely with increasing V_{IO3}.
233. Recall the significance of the 1 and 4, described in problem 2 in Part II page 153.
234. The reader is invited to include $BaOH^+$ in the $\alpha_{Ba^{2+}}$ calculation and to calculate $\alpha_{HSO4^{1-}}$.
235. This might well seem like silliness: that we go to the trouble to create separate expressions for $Conc°_{Ag}$ and $Conc_{Ag}$ only to say $Conc°_{Ag} \approx Conc_{Ag}$. Indeed the two are close enough that when *either* is added to C_{KOCN}, approximately the same μ is found. Moreover, $Conc_{Ag}$ cannot be used in the expression for μ because it contains μ (see above) and one would produce a recursive assignment error.
236. $-\log_{10}(0.0004795832) = 3.319136082$.
237. Butler, James N., *Ionic Equilibrium A Mathematical Approach*, Addison-Wesley, Reading, MA, **1964**, p. 191.
238. Taken from J. Kielland, *J. Am. Chem. Soc.* **59**, 1675 (1937)
239. Taken from J. Kielland, *J. Am. Chem. Soc.* **59**, 1675 (1937)
240. At nominally $\mu = 0.1$.
241. This is $-\log_{10}\{H^+\}$ at $\mu = 0.1$ which gives $\gamma_{H^+} = 0.761$ so that this pH $\approx 0.12 + \log_{10}[H^+]$. This correction is rarely necessary. Indeed, K_{In} as it is determined from $K°_{In}$ requires a knowledge of the activity coefficients for H^+ and In^-. Moreover, some indicators are of the type $HIn^+ \rightleftharpoons H^+ + In$, and this entails a different correction procedure than $HIn \rightleftharpoons H^+ + In$. See Part I page 89.

    * In some cases, the insoluble product is an oxide like Ag_2O or oxyhydroxide like BiOOH.

    ** This does not include BiO^+ salts which have insoluble chlorides *etc*.
242. Part I unless otherwise noted. The page on which a term is first introduced. Subsequent page references are for significantly different applications of the term.
243. Note that `contour` (no `s`) is a style option in `plot3d`.
244. `Diff` executes a *partial* differentiation with respect to multiple variables.
245. This presumes that the Worksheet Mode has been chosen as the default mode under the Interface tab of the Preferences menu. Otherwise the ⌘**N** keystrokes will open a new tab in the Document mode.

Index for Part I

Index for Part II