

Chapter 15

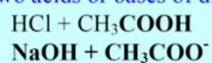
TITRATION CURVES FOR COMPLEX ACID/BASE SYSTEMS

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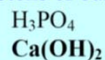
1. Treating Complex Acid-Base Systems

Complex systems are defined as solutions made up of:

- 1) Two acids or bases of different strengths

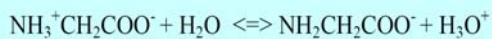


- 2) An acid or base that has two or more acidic protons or basic functional groups



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- 3) An amphiprotic substance that is capable of acting as both acid and base



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2. Equations for more than one equilibrium are required to describe the characteristics of any of these systems.

3. Applications

1) Systems in most biological and environmental matrices

2) To predict which species will be present (and in what amounts) is important in defining biological acid/base buffering.

3) To use the titration curve to examine how the species will change as we slowly add titrant (in other words, change the pH).

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4. Examples

A. Mixtures of Strong and Weak Acids or Strong and Weak Bases

B. Polyfunctional Acids and Bases

C. Buffer Solutions Involving Polyprotic Acids

D. Calculation of the pH of Solutions of Amphiprotic Salts (NaHA)

E. Titration Curves of Polyfunctional Acids.

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Questions:

(a) Can we titrate the two components (two acids or two bases, or different protons or hydroxide ions) separately?

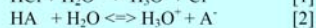
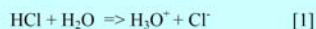
(b) If yes, in general, what conditions should be met in term of dissociation constants (K_{a1} or K_{b1}) and concentrations?

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Example A. Mixtures of Strong and Weak Acids or Strong and Weak Bases

Derive a titration curve for a titration of a 50.00 mL solution containing 0.1000 M strong acid, HCl, and 0.1000 M weak acid HA ($K_a = 1 \times 10^{-4}$) with 0.1000 NaOH.

The equilibria:



$$[\text{H}_3\text{O}^+] = C_{\text{HCl}} + [\text{A}^-] + [\text{OH}^-]$$

Since the HCl, which is completely dissociated, will repress the dissociation of HA and H_2O .

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Assume that $[\text{OH}^-]$ and $[\text{A}^-] \ll C_{\text{HCl}}$ so that $[\text{H}_3\text{O}^+] = C_{\text{HCl}}$.

1. $V_{\text{NaOH}} = 0$: The pH before the addition of titrant is determined by the concentration of HCl alone: $[\text{H}_3\text{O}^+] = C_{\text{HCl}}$

2. $0 < V_{\text{NaOH}} < 50.00 \text{ mL}$: After titrant has been added, the titration curve will be identical to that for the titration of the HCl alone and pH will be determined by the remaining HCl in the solution.

$$[\text{H}_3\text{O}^+] = \frac{\text{Moles of } [\text{H}_3\text{O}^+] - \text{Moles of } [\text{OH}^-]_{\text{added}}}{V_{\text{total}}}$$

3. $V_{\text{NaOH}} = 50.00 \text{ mL}$: When the HCl has been neutralized (the first equivalence-point), the presence of the weak acid must be considered. At this point, the equilibrium described in eq. [2]:

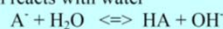
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad [\text{H}_3\text{O}^+] = \sqrt{C_{\text{HA}} K_a} \quad \frac{C_{\text{HA}}}{K_a} > 100$$

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4. $50.00 \text{ mL} < V_{\text{NaOH}} < 100.00 \text{ mL}$ HA is now reacting with the titrant and the titration curve will be identical to that of the titration of a weak acid and

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a + \log \frac{C_{\text{NaA}}}{C_{\text{HA}}}$$

5. $V_{\text{NaOH}} = 100.00 \text{ mL}$ At the point where both HCl and HA are neutralized (the second equivalence-point), the titration solution now contains A^- which reacts with water



and the pH at this equivalence point is determined by concentration of $[\text{A}^-]$ and K_b (1.0×10^{-10})

$$[\text{OH}^-] = \sqrt{C_b K_b} \quad \frac{C_b}{K_b} > 100$$

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6. $V_{\text{NaOH}} > 100.00 \text{ mL}$ After all of the acid has been neutralized, further addition of titrant results in a mixture of a weak and strong base. pH of the solution is determined by the concentration of the strong base.

$$[\text{OH}^-] = \frac{\text{Moles of } [\text{OH}^-]_{\text{added}} - \text{Moles of } [\text{H}_3\text{O}^+]}{V_{\text{total}}}$$

In summary, the titration curve includes a titration curve of HCl (a strong acid) with NaOH and a titration curve of HA (weak acid) with NaOH.

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EXAMPLE 15-1

HCl + HAc with KOH

Calculate the pH of a mixture that is 0.1200 M in hydrochloric acid and 0.0800 M in the weak acid HA ($K_a = 1.00 \times 10^{-4}$) during its titration with 0.1000 M KOH. Compute results for additions of the following volumes of base: (a) 0.00 mL and (b) 5.00 mL.

(Initial Volume = 25.00 mL)

Solution

$$C_{\text{HCl}} V_{\text{HCl}} = C_{\text{KOH}} V_{\text{KOH}} \quad V_{1\text{st Eq. KOH}} = 25.00 \times 0.1200 / 0.1000 = 30.00 \text{ mL}$$

$$C_{\text{HA}} V_{\text{HA}} = C_{\text{KOH}} V_{\text{KOH}} \quad V_{2\text{nd Eq. KOH}} = V_{1\text{st Eq. KOH}} + 25.00 \times 0.0800 / 0.1000 = 50.00 \text{ mL}$$

H_2O . In the presence of the two acids, however, we can be certain that the concentration of hydronium ions from the dissociation of water is extremely small. We, therefore, need to take into account only the other two sources of protons. Thus, we may write

$$[\text{H}_3\text{O}^+] = c_{\text{HCl}}^0 + [\text{A}^-] = 0.1200 + [\text{A}^-]$$

Note that $[\text{A}^-]$ is equal to the concentration of hydronium ions from the dissociation of HA.

Now, assume that the presence of the strong acid so represses the dissociation of HA that $[\text{A}^-] \ll 0.1200 \text{ M}$; then,

$$[\text{H}_3\text{O}^+] \approx 0.1200 \text{ M}, \text{ and the pH is } 0.92$$

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To check this assumption, the provisional value for $[\text{H}_3\text{O}^+]$ is substituted into the dissociation-constant expression for HA. When this expression is rearranged, we obtain

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-4}}{0.1200} = 8.33 \times 10^{-4}$$

This expression can be rearranged to

$$[\text{HA}] = [\text{A}^-] / (8.33 \times 10^{-4})$$

From the concentration of the weak acid, we can write the mass-balance expression

$$c_{\text{HA}}^0 = [\text{HA}] + [\text{A}^-] = 0.0800 \text{ M}$$

Substituting the value of $[\text{HA}]$ from the previous equation gives

$$[\text{A}^-] / (8.33 \times 10^{-4}) + [\text{A}^-] \approx (1.20 \times 10^3) [\text{A}^-] = 0.0800 \text{ M}$$

$$[\text{A}^-] = 6.7 \times 10^{-5} \text{ M}$$

We see that $[\text{A}^-]$ is indeed much smaller than 0.1200 M, as assumed.

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Before the 1st equivalence point: 5.00 mL < 30.00 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{Moles of } [\text{H}_3\text{O}^+] - \text{Moles of } [\text{OH}^-]_{\text{added}}}{V_{\text{total}}}$$

(b) 5.00 mL KOH

$$c_{\text{HCl}} = \frac{25.00 \times 0.1200 - 5.00 \times 0.100}{25.00 + 5.00} = 0.0833 \text{ M}$$

and we may write

$$[\text{H}_3\text{O}^+] = 0.0833 + [\text{A}^-] \approx 0.0833 \text{ M}$$

$$\text{pH} = 1.08$$

To determine whether our assumption is still valid, we compute $[\text{A}^-]$ as we did in part (a), knowing that the concentration of HA is now $0.0800 \times 25.00/30.00 = 0.0667$, and find

$$[\text{A}^-] = 8.0 \times 10^{-5} \text{ M}$$

which is still much smaller than 0.0833 M.

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EXAMPLE 15-2

Calculate the pH of the resulting solution after the addition of 29.00 mL of 0.1000 M NaOH to 25.00 mL of the solution described in Example 15-1.

Solution

Before the 1st equivalence point: 29.00 mL < 30.00 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{Moles of } [\text{H}_3\text{O}^+] - \text{Moles of } [\text{OH}^-]_{\text{added}}}{V_{\text{total}}}$$

As in the previous example, a provisional result based on the assumption that $[\text{H}_3\text{O}^+] = 1.85 \times 10^{-3} \text{ M}$ yields a value of $1.90 \times 10^{-5} \text{ M}$ for $[\text{A}^-]$. We see that $[\text{A}^-]$ is no longer much smaller than $[\text{H}_3\text{O}^+]$, and we must write

MBE $[\text{H}_3\text{O}^+] = c_{\text{HCl}} + [\text{A}^-] = 1.85 \times 10^{-3} + [\text{A}^-]$ (15-1)

In addition, from mass-balance considerations, we know that

MBE $[\text{HA}] + [\text{A}^-] = c_{\text{HA}} = 3.70 \times 10^{-2}$ (15-2)

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We rearrange the acid dissociation-constant expression for HA and obtain

$$[\text{HA}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{1.00 \times 10^{-4}}$$

Substitution of this expression into Equation 15-2 yields

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{1.00 \times 10^{-4}} + [\text{A}^-] = 3.70 \times 10^{-2}$$

$$[\text{A}^-] = \frac{3.70 \times 10^{-6}}{[\text{H}_3\text{O}^+] + 1.00 \times 10^{-4}}$$

Substitution for $[\text{A}^-]$ and c_{HCl} in Equation 15-1 yields

$$[\text{H}_3\text{O}^+] = 1.85 \times 10^{-3} + \frac{3.70 \times 10^{-6}}{[\text{H}_3\text{O}^+] + 1.00 \times 10^{-4}}$$

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Multiplying through to clear the denominator and collecting terms gives

$$[\text{H}_3\text{O}^+]^2 - (1.75 \times 10^{-3})[\text{H}_3\text{O}^+] - 3.885 \times 10^{-6} = 0$$

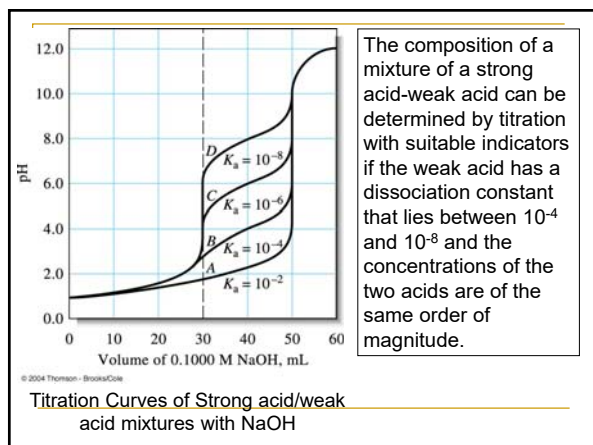
Solving the quadratic equation gives

$$[\text{H}_3\text{O}^+] = 3.03 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.52$$

Note that the contributions to the hydronium ion concentration from HCl ($1.85 \times 10^{-3} \text{ M}$) and HA ($3.03 \times 10^{-3} \text{ M} - 1.85 \times 10^{-3} \text{ M}$) are of comparable magnitude. Hence, we cannot make the assumption that we made in Example 15-1.

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B. Polyfunctional Acids:

These acids may donate two or more H^+ , and the bases may accept two or more H^+ .

An example of a polyfunctional acid is H_3PO_4 , with the following equilibria:

$$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$$

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3}$$

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

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.34 \times 10^{-8}$$

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

$$K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}$$

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Equilibria Constants for Overall Reactions

H₃PO₄ + H₂O ⇌ H₃O⁺ + H₂PO₄⁻ [Eq. 1]

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.1 \times 10^{-3}$$

H₂PO₄⁻ + H₂O ⇌ H₃O⁺ + HPO₄²⁻ [Eq. 2]

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.34 \times 10^{-8}$$

HPO₄²⁻ + H₂O ⇌ H₃O⁺ + PO₄³⁻ [Eq. 3]

$$K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}$$

[Eq. 1] + [Eq. 2] + [Eq. 3]: H₃PO₄ + 3H₂O ⇌ 3H₃O⁺ + PO₄³⁻

$$K_{a1}K_{a2}K_{a3} = \frac{[\text{H}_3\text{O}^+]^3[\text{PO}_4^{3-}]}{[\text{H}_3\text{PO}_4]} = 2.0 \times 10^{-22}$$

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Definition of K_a and K_b for Polyfunctional Acids

K_a

H₃PO₄ + H₂O ⇌ H₃O⁺ + H₂PO₄⁻ K_{a1}

H₂PO₄⁻ + H₂O ⇌ H₃O⁺ + HPO₄²⁻ K_{a2}

HPO₄²⁻ + H₂O ⇌ H₃O⁺ + PO₄³⁻ K_{a3}

K_b

PO₄³⁻ + H₂O ⇌ HPO₄²⁻ + OH⁻ K_{b1}

HPO₄²⁻ + H₂O ⇌ H₂PO₄⁻ + OH⁻ K_{b2}

H₂PO₄⁻ + H₂O ⇌ H₃PO₄ + OH⁻ K_{b3}

K_{a1}K_{b3} = K_{a2}K_{b2} = K_{a3}K_{b1} = [H₃O⁺][OH⁻] = K_w

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C. Buffer solutions Involving Polyprotic Acids:

(A) Three buffer systems can be described when using a weak diprotic acid, H₂A, and its salts, H₂A⁻, HA²⁻ and A³⁻.

➤ H₂A/H₂A⁻ pH = pK_{a1} + log $\frac{C_{\text{H}_2\text{A}^-}}{C_{\text{H}_2\text{A}}}$

➤ H₂A⁻/HA²⁻ pH = pK_{a2} + log $\frac{C_{\text{HA}^{2-}}}{C_{\text{H}_2\text{A}^-}}$

➤ HA²⁻/A³⁻ pH = pK_{a3} + log $\frac{C_{\text{A}^{3-}}}{C_{\text{HA}^{2-}}}$

When K_{a1}, K_{a2}, K_{a3} are well separated

$$\frac{K_{a1}}{K_{a2}} > 10^3 \quad \frac{K_{a2}}{K_{a3}} > 10^3$$

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(B) Two buffer systems can be described when using a weak diprotic acid, H_2A , and its salts, HA^- and A^{2-} .

$$\text{➤ } H_2A/HA^- \quad pH = pK_{a1} + \log \frac{C_{HA^-}}{C_{H_2A}}$$

$$\text{➤ } HA^-/A^{2-} \quad pH = pK_{a2} + \log \frac{C_{A^{2-}}}{C_{HA^-}}$$

When K_{a1} is well-separated from K_{a2} :

$$\frac{K_{a1}}{K_{a2}} > 10^3$$

We can treat these systems as separated one for calculation of pH and species present.

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EXAMPLE 15-4

Calculate the hydronium ion concentration for a buffer solution that is 2.00 M in phosphoric acid and 1.50 M in potassium dihydrogen phosphate.

Solution

The principal equilibrium in this solution is the dissociation of H_3PO_4 .



We assume that the dissociation of $H_2PO_4^-$ is negligible, that is, $[HPO_4^{2-}]$ and $[PO_4^{3-}] \ll [H_2PO_4^-]$ and $[H_3PO_4]$. Then,

$$\begin{aligned} [H_3PO_4] &\approx c_{H_3PO_4} = 2.00 \text{ M} \\ [H_2PO_4^-] &\approx c_{KH_2PO_4} = 1.50 \text{ M} \\ [H_3O^+] &= \frac{7.11 \times 10^{-3} \times 2.00}{1.50} = 9.49 \times 10^{-3} \text{ M} \end{aligned}$$

We now use the equilibrium constant expression for K_{a2} to see if our assumption was valid.

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We now use the equilibrium constant expression for K_{a2} to see if our assumption was valid.

$$K_{a2} = 6.34 \times 10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{9.48 \times 10^{-3}[HPO_4^{2-}]}{1.50}$$

Solving this equation yields

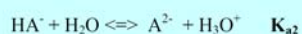
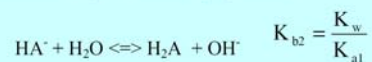
$$[HPO_4^{2-}] = 1.00 \times 10^{-5} \text{ M}$$

Since this concentration is much smaller than the concentrations of the major species, H_3PO_4 and $H_2PO_4^-$, our assumption is valid. Note that $[PO_4^{3-}]$ is even smaller than $[HPO_4^{2-}]$.

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D. Calculation of the pH of Solutions of Amphiprotic Salts (NaHA)

The pH is determined by the following equilibria:



At the first equivalence point, the solution will be either acidic or basic based upon the relative magnitude of the equilibrium constants (K_{b2} and K_{a2})

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Using the systematic method to solve for the $[\text{H}_3\text{O}^+]$:

1. Equilibrium Constants

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

$$K_{b2} = \frac{[\text{OH}^-][\text{H}_2\text{A}]}{[\text{HA}^-]}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

2. The mass balance equation:

$$C_{\text{NaHA}} = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]$$

3. The charge balance equation:

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HA}^-] + 2[\text{A}^{2-}]$$

$$[\text{Na}^+] = C_{\text{NaHA}}$$

$$\text{Hence } [\text{H}_3\text{O}^+] + C_{\text{NaHA}} = [\text{OH}^-] + [\text{HA}^-] + 2[\text{A}^{2-}]$$

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Subtracting the mass balance from the charge balance equation:

$$[\text{H}_3\text{O}^+] = [\text{A}^{2-}] + [\text{OH}^-] - [\text{H}_2\text{A}]$$

We can express all terms using $[\text{HA}^-]$, $[\text{H}_3\text{O}^+]$, K_{a1} , K_w and K_{a2}

$$[\text{H}_3\text{O}^+] = \frac{K_{a2}[\text{HA}^-]}{[\text{H}_3\text{O}^+]} + \frac{K_w}{[\text{H}_3\text{O}^+]} - \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{K_{a1}}$$

Multiplying both sides by $[\text{H}_3\text{O}^+]$:

$$[\text{H}_3\text{O}^+]^2 \left(1 + \frac{[\text{HA}^-]}{K_{a1}}\right) = K_{a2}[\text{HA}^-] + K_w$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a2}[\text{HA}^-] + K_w}{1 + \frac{[\text{HA}^-]}{K_{a1}}}}$$

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Assume $[HA^-] = C_{NaHA}$
(not true for HA^- very dilute, or K_{a2} or K_{b2} very large)

$$[H_3O^+] = \sqrt{\frac{K_{a2}C_{HA^-} + K_w}{1 + \frac{C_{HA^-}}{K_{a1}}}}$$

If $\frac{C_{HA^-}}{K_{a1}} \gg 1$ and $K_{a2}C_{NaHA} \gg K_w$

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

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EXAMPLE 15-6
Calculate the hydronium ion concentration of a 1.00×10^{-3} M Na_2HPO_4 solution.

Solution
The pertinent dissociation constants are K_{a2} and K_{a3} , which both contain $[HPO_4^{2-}]$. Their values are $K_{a2} = 6.32 \times 10^{-8}$ and $K_{a3} = 4.5 \times 10^{-13}$. In the case of a Na_2HPO_4 solution, Equation 15-15 can be written

$$[H_3O^+] = \sqrt{\frac{K_{a3}c_{Na_2HPO_4} + K_w}{1 + c_{Na_2HPO_4}/K_{a2}}}$$

Note that we have used K_{a3} in place of K_{a2} in Equation 15-15 and K_{a2} in place of K_{a1} since these are the appropriate dissociation constants when Na_2HPO_4 is the salt.

If we consider again the assumptions that led to Equation 15-16, we find that the term $c_{Na_2HPO_4}/K_{a2} = (1.0 \times 10^{-3})/(6.32 \times 10^{-8})$ is much larger than 1 so that the denominator can be simplified. In the numerator, however, $K_{a3}c_{Na_2HPO_4} = 4.5 \times 10^{-13} \times 1.00 \times 10^{-3}$ is comparable to K_w so that no simplification can be made there. We, therefore, use a partially simplified version of Equation 15-15:

$$[H_3O^+] = \sqrt{\frac{K_{a3}c_{Na_2HPO_4} + K_w}{c_{Na_2HPO_4}/K_{a2}}}$$

$$= \sqrt{\frac{(4.5 \times 10^{-13})(1.00 \times 10^{-3}) + 1.00 \times 10^{-14}}{(1.00 \times 10^{-3})/(6.32 \times 10^{-8})}} = 8.1 \times 10^{-10} \text{ M}$$

The simplified Equation 15-15 gave 1.7×10^{-10} M, which is in error by a large amount.

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EXAMPLE 15-7
Find the hydronium ion concentration of a 0.0100 M NaH_2PO_4 solution.

Solution
The two dissociation constants of importance (those containing $[H_2PO_4^{2-}]$) are $K_{a1} = 7.11 \times 10^{-3}$ and $K_{a2} = 6.32 \times 10^{-8}$. A test shows that the denominator of Equation 15-15 cannot be simplified, but the numerator reduces to $K_{a2}c_{NaH_2PO_4}$. Thus, Equation 15-15 becomes,

$$[H_3O^+] = \sqrt{\frac{(6.32 \times 10^{-8})(1.00 \times 10^{-2})}{1.00 + (1.00 \times 10^{-2})/(7.11 \times 10^{-3})}} = 1.62 \times 10^{-5} \text{ M}$$

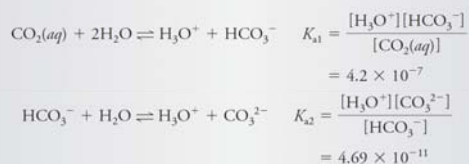
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EXAMPLE 15-8

Calculate the hydronium ion concentration of a 0.1000 M NaHCO_3 solution.

Solution

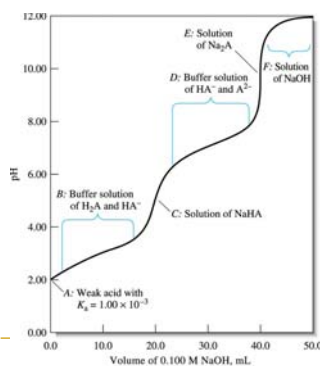
We assume, as we did earlier (page 353), that $[\text{H}_2\text{CO}_3] \ll [\text{CO}_2(aq)]$ and that the following equilibria describe the system:



We note that $c_{\text{NaHA}}/K_{a1} \gg 1$ so that the denominator of Equation 15-15 can be simplified. In addition, $K_{a2}c_{\text{NaHA}}$ has a value of 4.69×10^{-12} , which is substantially greater than K_w . Thus, Equation 15-16 applies, and

$$[\text{H}_3\text{O}^+] = \sqrt{4.2 \times 10^{-7} \times 4.69 \times 10^{-11}} = 4.4 \times 10^{-9} \text{ M}$$

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Titration Curves for Polyfunctional Acids

20 mL of 0.1000 M H_2A with 0.1000 M NaOH . $K_{a1} = 1.00\text{e-}3$ and $K_{a2} = 1.00\text{e-}7$

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E. Titration Curves of Polyfunctional Acids:

For the titration of a diprotic acid (H_2A) with a strong base, the $[\text{H}_3\text{O}^+]$ in the following regions of the titration curve are calculated as follows:

1) $V_{\text{Titrant}} = 0 \text{ mL}$

If $\frac{K_{a1}}{K_{a2}} > 10^4$, treat as monoprotic acid

$$\text{If } C_{\text{H}_2\text{A}}/K_{a1} > 100, \quad [\text{H}_3\text{O}^+] = \sqrt{C_{\text{H}_2\text{A}}K_{a1}}$$

2) $0 < V_{\text{Titrant}} < V_{\text{1st equivalence point}}$

$$\text{pH} = \text{p}K_{a1} + \log \frac{C_{\text{HA}^-}}{C_{\text{H}_2\text{A}}} \quad [\text{H}_3\text{O}^+] = \frac{K_{a1}[\text{H}_2\text{A}]}{[\text{HA}^-]}$$

3) $V_{\text{Titrant}} = V_{\text{1st equivalence point}}$

If $\frac{C_{\text{HA}^-}}{K_{a1}} \gg 1$, $K_{a2}C_{\text{NaHA}} \gg K_w$, $K_{a2} < 10^{-3}$, $K_{b2} < 10^{-3}$

$$[\text{H}_3\text{O}^+] = \sqrt{K_{a1}K_{a2}}$$

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4) $V_{1st\ equivalence\ point} < V_{Titrant} < V_{2nd\ equivalence\ point}$

$$pH = pK_{a2} + \log \frac{C_{A^{2-}}}{C_{HA^-}} \quad [H_3O^+] = \frac{K_{a2}[HA^-]}{[A^{2-}]}$$

5) $V_{Titrant} = V_{2nd\ equivalence\ point}$

$$\text{If } C_b/K_{b1} > 100 \quad [OH^-] = \sqrt{C_b K_{b1}} = \sqrt{C_b \frac{K_w}{K_{a2}}}$$

$$C_b = \frac{\text{moles of acid (H}_2\text{A) before titration}}{\text{total volume}} = \frac{C_{H_2A} V_{\text{acid before titration}}}{V_{\text{acid}} + V_{\text{titrant}}}$$

6) $V_{Titrant} > V_{2nd\ equivalence\ point}$

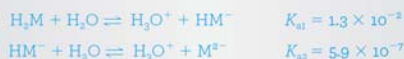
$$[OH^-] = \frac{\text{Moles of } [OH^-]_{\text{added}} - \text{Moles of } [H_3O^+]}{V_{\text{total}}}$$

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EXAMPLE 15-9

Construct a curve for the titration of 25.00 mL of 0.1000 M maleic acid, $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$, with 0.1000 M NaOH.

We can write the two dissociation equilibria as



Because the ratio K_{a1}/K_{a2} is large (2×10^{-4}), we can proceed using the techniques just described.

Solution

Initial pH

Initially, the solution is 0.1000 M H_2M . At this point, only the first dissociation makes an appreciable contribution to $[H_3O^+]$; thus,

$$[H_3O^+] \approx [HM^-] \quad \boxed{C_{H_2M}/K_{a1} < 100}$$

$[H^+] = \text{sqrt}(K_a c)$ cannot be used

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Mass balance requires that

$$c_{H_2M}^0 = [H_2M] + [HM^-] + [M^{2-}] = 0.1000 \text{ M}$$

Since the second dissociation is negligible, $[M^{2-}]$ is very small so that

$$c_{H_2M}^0 \approx [H_2M] + [HM^-] = 0.1000 \text{ M}$$

or

$$[H_2M] = 0.1000 - [HM^-] = 0.1000 - [H_3O^+]$$

Substituting these relationships into the expression for K_{a1} gives

$$K_{a1} = 1.3 \times 10^{-2} = \frac{[H_3O^+][HM^-]}{[H_2M]} = \frac{[H_3O^+]^2}{0.1000 - [H_3O^+]}$$

Rearranging yields

$$[H_3O^+]^2 + 1.3 \times 10^{-2}[H_3O^+] - 1.3 \times 10^{-3} = 0$$

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Because K_{a1} for maleic acid is relatively large, we must solve the quadratic equation or find $[\text{H}_3\text{O}^+]$ by successive approximations. When we do so, we obtain

$$[\text{H}_3\text{O}^+] = 3.01 \times 10^{-2} \text{ M}$$

$$\text{pH} = 2 - \log 3.01 = 1.52$$

First Buffer Region **First Buffer Region: $0 < V_{\text{NaOH}} < 25.00 \text{ mL}$**

The addition of base, for example 5.00 mL, results in the formation of a buffer consisting of the weak acid H_2M and its conjugate base HM^- . To the extent that dissociation of HM^- to give M^{2-} is negligible, the solution can be treated as a simple buffer system. Thus, applying Equations 9-27 and 9-28 (page 220) gives

$$c_{\text{NaHM}} \approx [\text{HM}^-] = \frac{5.00 \times 0.1000}{30.00} = 1.67 \times 10^{-2} \text{ M}$$

$$c_{\text{H}_2\text{M}} \approx [\text{H}_2\text{M}] = \frac{25.00 \times 0.1000 - 5.00 \times 0.1000}{30.00} = 6.67 \times 10^{-2} \text{ M}$$

Substitution of these values into the equilibrium-constant expression for K_{a1} yields a tentative value of $5.2 \times 10^{-2} \text{ M}$ for $[\text{H}_3\text{O}^+]$. It is clear, however, that the approximation $[\text{H}_3\text{O}^+] \ll c_{\text{H}_2\text{M}}$ or c_{HM^-} is not valid; therefore, Equations 9-25 and 9-26 must be used, and

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$$[\text{HM}^-] = 1.67 \times 10^{-2} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$$

$$[\text{H}_2\text{M}] = 6.67 \times 10^{-2} - [\text{H}_3\text{O}^+] - [\text{OH}^-]$$

Because the solution is quite acidic, the approximation that $[\text{OH}^-]$ is very small is surely justified. Substitution of these expressions into the dissociation-constant relationship gives

$$K_{a1} = \frac{[\text{H}_3\text{O}^+](1.67 \times 10^{-2} + [\text{H}_3\text{O}^+])}{6.67 \times 10^{-2} - [\text{H}_3\text{O}^+]} = 1.3 \times 10^{-2}$$

$$[\text{H}_3\text{O}^+]^2 + (2.97 \times 10^{-2})[\text{H}_3\text{O}^+] - 8.67 \times 10^{-4} = 0$$

$$[\text{H}_3\text{O}^+] = 1.81 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log(1.81 \times 10^{-2}) = 1.74$$

Additional points in the first buffer region are computed in a similar way until just prior to the first equivalence point.

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Just Prior to First Equivalence Point

Just prior to the first equivalence point, the concentration of H_2M is so small that it becomes comparable to the concentration of M^{2-} , and the second equilibrium must also be considered. Within approximately 0.1 mL of the first equivalence point, we have a solution of primarily HM^- with a small amount of H_2M remaining and a small amount of M^{2-} formed. For example, at 24.90 mL of NaOH added,

$$[\text{HM}^-] \approx c_{\text{NaHM}} = \frac{24.90 \times 0.1000}{49.90} = 4.99 \times 10^{-2} \text{ M}$$

$$c_{\text{H}_2\text{M}} = \frac{25.00 \times 0.1000}{49.90} - \frac{24.90 \times 0.1000}{49.90} = 2.00 \times 10^{-4} \text{ M}$$

Mass balance gives

$$c_{\text{H}_2\text{M}} + c_{\text{NaHM}} = [\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}]$$

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Charge balance gives

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{HM}^-] + 2[\text{M}^{2-}] + [\text{OH}^-]$$

Since the solution consists primarily of the acid HM^- at the first equivalence point, we can safely neglect $[\text{OH}^-]$ in the previous equation and replace $[\text{Na}^+]$ with c_{NaHM} . After rearranging, we obtain

$$c_{\text{NaHM}} = [\text{HM}^-] + 2[\text{M}^{2-}] - [\text{H}_3\text{O}^+]$$

Substituting this equation into the mass-balance expression and solving for $[\text{H}_3\text{O}^+]$ give

$$[\text{H}_3\text{O}^+] = c_{\text{HM}} + [\text{M}^{2-}] - [\text{H}_2\text{M}]$$

If we express $[\text{M}^{2-}]$ and $[\text{H}_2\text{M}]$ in terms of $[\text{HM}^-]$ and $[\text{H}_3\text{O}^+]$, the result is

$$[\text{H}_3\text{O}^+] = c_{\text{HM}} + \frac{K_2[\text{HM}^-]}{[\text{H}_3\text{O}^+]} - \frac{[\text{H}_3\text{O}^+][\text{HM}^-]}{K_{a1}}$$

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Multiplying through by $[\text{H}_3\text{O}^+]$ gives, after rearrangement,

$$[\text{H}_3\text{O}^+]^2 \left(1 + \frac{[\text{HM}^-]}{K_{a1}} \right) - c_{\text{HM}}[\text{H}_3\text{O}^+] - K_2[\text{HM}^-] = 0$$

Substituting $[\text{HM}^-] = 4.99 \times 10^{-2}$, $c_{\text{HM}} = 2.00 \times 10^{-4}$, and the values for K_{a1} and K_2 leads to

$$4.838 [\text{H}_3\text{O}^+]^2 - 2.00 \times 10^{-4} [\text{H}_3\text{O}^+] - 2.94 \times 10^{-8} = 0$$

The solution to this equation is

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 1.014 \times 10^{-4} \text{ M} \\ \text{pH} &= 3.99 \end{aligned}$$

The same reasoning applies at 24.99 mL of titrant, where we find

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 8.01 \times 10^{-5} \text{ M} \\ \text{pH} &= 4.10 \end{aligned}$$

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$$V_{\text{NaOH}} = 25.00 \text{ mL}$$

First Equivalence Point

At the first equivalence point,

$$[\text{HM}^-] \approx c_{\text{NaHM}} = \frac{25.00 \times 0.1000}{50.00} = 5.00 \times 10^{-2} \text{ M}$$

Our simplification of the numerator in Equation 15-15 is certainly justified. On the other hand, the second term in the denominator is not $\ll 1$. Hence,

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{\frac{K_2 c_{\text{NaHM}}}{1 + c_{\text{NaHM}}/K_{a1}}} = \sqrt{\frac{5.9 \times 10^{-7} \times 5.00 \times 10^{-2}}{1 + (5.00 \times 10^{-2})/(1.3 \times 10^{-2})}} \\ &= 7.80 \times 10^{-5} \text{ M} \\ \text{pH} &= -\log(7.80 \times 10^{-5} \text{ M}) = 4.11 \end{aligned}$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_2 C_{\text{HM}^-} + K_w}{1 + \frac{C_{\text{HM}^-}}{K_{a1}}}}$$

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Just after the First Equivalence Point

Prior to the second equivalence point, we can obtain the analytical concentrations of NaHM and Na₂M from the titration stoichiometry. At 25.01 mL, for example, the values are

$$c_{\text{NaHM}} = \frac{\text{mmol NaHM formed} - (\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}}$$

$$= \frac{25.00 \times 0.1000 - (25.01 - 25.00) \times 0.1000}{50.01} = 0.04997 \text{ M}$$

$$c_{\text{Na}_2\text{M}} = \frac{(\text{mmol NaOH added} - \text{mmol NaHM formed})}{\text{total volume of solution}} = 1.9996 \times 10^{-5} \text{ M}$$

In the region a few tenths of a milliliter beyond the first equivalence point, the solution is primarily HM⁻ with some M²⁻ formed as a result of the titration. The mass balance at 25.01 mL added is

$$c_{\text{Na}_2\text{M}} + c_{\text{NaHM}} = [\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}] = 0.04997 + 1.9996 \times 10^{-5}$$

$$= 0.04999 \text{ M}$$

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and the charge balance is

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{HM}^-] + 2[\text{M}^{2-}] + [\text{OH}^-]$$

Again, the solution should be acidic, and so, we can neglect OH⁻ as an important species. The Na⁺ concentration equals the number of millimoles of NaOH added divided by the total volume, or

$$[\text{Na}^+] = \frac{25.01 \times 0.1000}{50.01} = 0.05001 \text{ M}$$

Subtracting the mass balance from the charge balance and solving for [H₃O⁺] gives

$$[\text{H}_3\text{O}^+] = [\text{M}^{2-}] - [\text{H}_2\text{M}] + (c_{\text{Na}_2\text{M}} + c_{\text{NaHM}}) - [\text{Na}^+]$$

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Expressing the [M²⁻] and [H₂M] in terms of the predominant species HM⁻, we have

$$[\text{H}_3\text{O}^+] = \frac{K_2[\text{HM}^-]}{[\text{H}_3\text{O}^+]} - \frac{[\text{H}_3\text{O}^+][\text{HM}^-]}{K_{a1}} + (c_{\text{Na}_2\text{M}} + c_{\text{NaHM}}) - [\text{Na}^+]$$

Since [HM⁻] ≈ c_{NaHM} = 0.04997. Therefore, if we substitute this value and numerical values for c_{Na₂M} + c_{NaHM} and [Na⁺] into the previous equation, we have, after rearranging, the following quadratic equation:

$$[\text{H}_3\text{O}^+] = \frac{K_2(0.04997)}{[\text{H}_3\text{O}^+]} - \frac{[\text{H}_3\text{O}^+](0.04997)}{K_{a1}} - 1.9996 \times 10^{-5}$$

$$K_{a1}[\text{H}_3\text{O}^+]^2 = 0.04997K_{a1}K_2 - 0.04997[\text{H}_3\text{O}^+]^2 - 1.9996 \times 10^{-5}K_{a1}[\text{H}_3\text{O}^+]$$

$$(K_{a1} + 0.04997)[\text{H}_3\text{O}^+]^2 + 1.9996 \times 10^{-5}K_{a1}[\text{H}_3\text{O}^+] - 0.04997K_{a1}K_2 = 0$$

This equation can then be solved for [H₃O⁺].

$$[\text{H}_3\text{O}^+] = 7.60 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.12$$

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Second Buffer Region $25.00 < V_{\text{NaOH}} < 50.00 \text{ mL}$

Further additions of base to the solution create a new buffer system consisting of HM^- and M^{2-} . When enough base has been added so that the reaction of HM^- with water to give OH^- can be neglected (a few tenths of a milliliter beyond the first equivalence point), the pH of the mixture may be calculated from K_{a2} . With the introduction of 25.50 mL of NaOH, for example,

$$[\text{M}^{2-}] \approx c_{\text{Na}_2\text{M}} = \frac{(25.50 - 25.00)(0.1000)}{50.50} = \frac{0.050}{50.50} \text{ M}$$

and the molar concentration of NaHM is

$$[\text{HM}^-] \approx c_{\text{NaHM}} = \frac{(25.00 \times 0.1000) - (25.50 - 25.00)(0.1000)}{50.50} = \frac{2.45}{50.50} \text{ M}$$

Substituting these values into the expression for K_{a2} gives

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{M}^{2-}]}{[\text{HM}^-]} = \frac{[\text{H}_3\text{O}^+](0.050/50.50)}{2.45/50.50} = 5.9 \times 10^{-7}$$

$$[\text{H}_3\text{O}^+] = 2.89 \times 10^{-5} \text{ M}$$

$K_{a2} = 5.9 \times 10^{-7}$
 $\text{pH} = \text{p}K_{a2} + \log \frac{C_{\text{M}^{2-}}}{C_{\text{HM}^-}}$

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Just Prior to Second Equivalence Point

Just prior to the second equivalence point (49.90 mL and more), the ratio $[\text{M}^{2-}]/[\text{HM}^-]$ becomes large, and the simple buffer equation no longer applies. At 49.90 mL, $c_{\text{HM}^-} = 1.335 \times 10^{-4} \text{ M}$, and $c_{\text{M}^{2-}} = 0.03324$. The primary equilibrium is now

$$\text{M}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HM}^- + \text{OH}^-$$

We can write the equilibrium constant as

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{[\text{OH}^-][\text{HM}^-]}{[\text{M}^{2-}]} = \frac{[\text{OH}^-](1.335 \times 10^{-4} + [\text{OH}^-])}{(0.03324 - [\text{OH}^-])}$$

$$= \frac{1.00 \times 10^{-14}}{5.9 \times 10^{-7}} = 1.69 \times 10^{-8}$$

In this case, it is easier to solve for $[\text{OH}^-]$ than for $[\text{H}_3\text{O}^+]$. Solving the resulting quadratic equation gives

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$$[\text{OH}^-] = 4.10 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.39$$

$$\text{pH} = 14.00 - \text{pOH} = 8.61$$

The same reasoning for 49.99 mL leads to $[\text{OH}^-] = 1.80 \times 10^{-5} \text{ M}$, and $\text{pH} = 9.26$.

Second Equivalence Point $V_{\text{NaOH}} = 50.00 \text{ mL}$

After the addition of 50.00 mL of 0.1000 M sodium hydroxide, the solution is 0.0333 M in Na_2M (2.5 mmol/75.00 mL). Reaction of the base M^{2-} with water is the predominant equilibrium in the system and the only one that we need to take into account. Thus,

$$\text{M}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HM}^-$$

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{[\text{OH}^-][\text{HM}^-]}{[\text{M}^{2-}]} = 1.69 \times 10^{-8}$$

$$C_b = \frac{\text{moles of acid (H}_2\text{M)}}{\text{total volume}} = \frac{C_{\text{H}_2\text{M}} V_{\text{acid before titration}}}{V_{\text{acid}} + V_{\text{titrant}}}$$

$$= 0.0333 \text{ M}$$

$$[\text{OH}^-] = \sqrt{C_b K_{b1}} = \sqrt{C_b \frac{K_w}{K_{a2}}} = 2.38 \times 10^{-5}$$

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$$[\text{OH}^-] = 2.37 \times 10^{-5} \text{ M, and } \text{pOH} = -\log(2.37 \times 10^{-5}) = 4.62$$

$$\text{pH} = 14.00 - \text{pOH} = 9.38$$

$$C_b = \frac{\text{moles of acid (H}_2\text{M) before titration}}{\text{total volume}} = \frac{C_{\text{H}_2\text{M}} V_{\text{acid before titration}}}{V_{\text{acid}} + V_{\text{titrant}}} = \frac{0.1000 \times 25.00}{25.00 + 50.00}$$

$$= 0.0333 \text{ M}$$

$$[\text{OH}^-] = \sqrt{C_b K_{b1}} = \sqrt{C_b \frac{K_w}{K_{a2}}} = 2.38 \times 10^{-5}$$

pH Just beyond Second Equivalence Point

In the region just beyond the second equivalence point (50.01 mL, for example), we still need to take into account the reaction of M^{2-} with water to give OH^- since not enough OH^- has been added in excess to suppress this reaction. The analytical concentration of M^{2-} is the number of millimoles of M^{2-} produced divided by the total solution volume:

$$c_{\text{M}^{2-}} = \frac{25.00 \times 0.1000}{75.01} = 0.03333 \text{ M}$$

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The OH^- now comes from the reaction of M^{2-} with water and from the excess OH^- added as titrant. The number of millimoles of excess OH^- is then the number of millimoles of NaOH added minus the number required to reach the second equivalence point. The concentration of this excess is the number of millimoles of excess OH^- divided by the total solution volume, or

$$[\text{OH}^-]_{\text{excess}} = \frac{(50.01 - 50.00) \times 0.1000}{75.01} = 1.333 \times 10^{-5} \text{ M}$$

The concentration of HM^- can now be found from K_{b1} .

$$[\text{M}^{2-}] = c_{\text{M}^{2-}} - [\text{HM}^-] = 0.03333 - [\text{HM}^-]$$

$$[\text{OH}^-] = 1.3333 \times 10^{-5} + [\text{HM}^-]$$

$$K_{b1} = \frac{[\text{HM}^-][\text{OH}^-]}{[\text{M}^{2-}]} = \frac{[\text{HM}^-](1.3333 \times 10^{-5} + [\text{HM}^-])}{0.03333 - [\text{HM}^-]} = 1.69 \times 10^{-8}$$

Solving the quadratic equation for $[\text{HM}^-]$ gives

$$[\text{HM}^-] = 1.807 \times 10^{-5} \text{ M}$$

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and

$$[\text{OH}^-] = 1.3333 \times 10^{-5} + [\text{HM}^-] = 1.33 \times 10^{-5} + 1.807 \times 10^{-5} = 3.14 \times 10^{-5} \text{ M}$$

$$\text{pOH} = 4.50 \text{ and } \text{pH} = 14.00 - \text{pOH} = 9.50$$

The same reasoning applies to 50.10 mL where the calculations give $\text{pH} = 10.14$

pH beyond the Second Equivalence Point

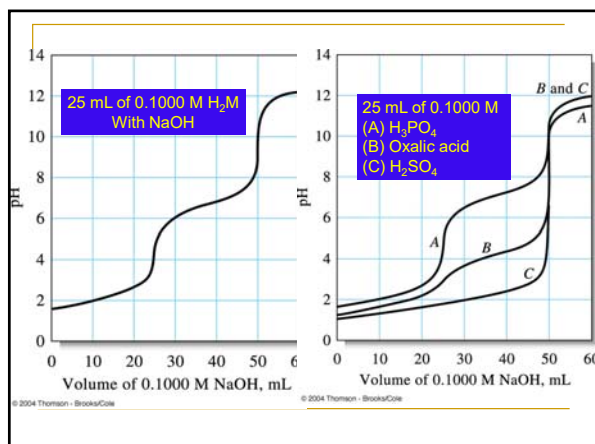
Addition of more than a few tenths of a milliliter of NaOH beyond the second equivalence point gives enough excess OH^- to repress the basic dissociation of M^{2-} . The pH is then calculated from the concentration of NaOH added in excess of that required for the complete neutralization of H_2M . Thus, when 51.00 mL of NaOH have been added, we have 1.00-mL excess of 0.1000 M NaOH, and

$$[\text{OH}^-] = \frac{1.00 \times 0.100}{76.00} = 1.32 \times 10^{-3} \text{ M}$$

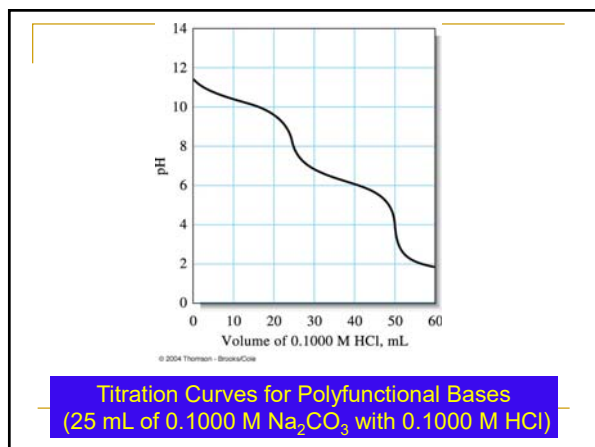
$$\text{pOH} = -\log(1.32 \times 10^{-3}) = 2.88$$

$$\text{pH} = 14.00 - \text{pOH} = 11.12$$

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The composition of solution of a polyprotic acid as a function of pH

$$\text{H}_2\text{M} \rightleftharpoons \text{H}^+ + \text{HM}^- \quad K_{a1} = \frac{[\text{H}^+][\text{HM}^-]}{[\text{H}_2\text{M}]}; \quad \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} = \frac{K_{a1}}{[\text{H}^+]}$$

$$\text{HM}^- \rightleftharpoons \text{H}^+ + \text{M}^{2-} \quad K_{a2} = \frac{[\text{H}^+][\text{M}^{2-}]}{[\text{HM}^-]}$$

$$\text{H}_2\text{M} \rightleftharpoons 2\text{H}^+ + \text{M}^{2-} \quad K_{a1}K_{a2} = \frac{[\text{H}^+]^2[\text{M}^{2-}]}{[\text{H}_2\text{M}]}; \quad \frac{[\text{M}^{2-}]}{[\text{H}_2\text{M}]} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2}$$

MBE: $c_T = [\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}]$

$$\alpha_0 = \frac{[\text{H}_2\text{M}]}{c_T} = \frac{[\text{H}_2\text{M}]}{[\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}]} = \frac{1}{1 + \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} + \frac{[\text{M}^{2-}]}{[\text{H}_2\text{M}]}}$$

$$= \frac{1}{1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}$$

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For a diprotic acid (H₂M):

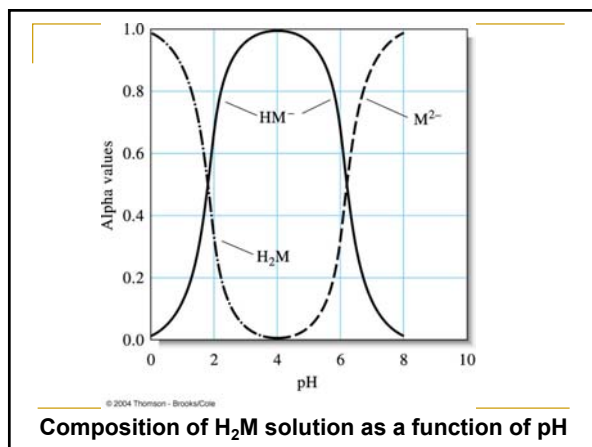
$$\alpha_0 = \frac{[\text{H}_2\text{M}]}{C_T} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_3\text{O}^+]^2 + K_{a1}[\text{H}_3\text{O}^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{[\text{HM}^-]}{C_T} = \frac{K_{a1}[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^2 + K_{a1}[\text{H}_3\text{O}^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{[\text{M}^{2-}]}{C_T} = \frac{K_{a1}K_{a2}}{[\text{H}_3\text{O}^+]^2 + K_{a1}[\text{H}_3\text{O}^+] + K_{a1}K_{a2}}$$

$$\alpha_0 + \alpha_1 + \alpha_2 = 1$$

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F. General Expression for α Values of a Polyprotic Acid (H_nA)
(Fraction of species when pH is fixed and known)

For the denominator:

$$D = C_T = [\text{H}_3\text{O}^+]^n + K_{a1}[\text{H}_3\text{O}^+]^{(n-1)} + K_{a1}K_{a2}[\text{H}_3\text{O}^+]^{(n-2)} + \dots + K_{a1}K_{a2}\dots K_n$$

where n = number of acidic protons in formula

$$\alpha_0 = \frac{[\text{H}_3\text{O}^+]^n}{D}$$

$$\alpha_1 = \frac{K_{a1}[\text{H}_3\text{O}^+]^{n-1}}{D}$$

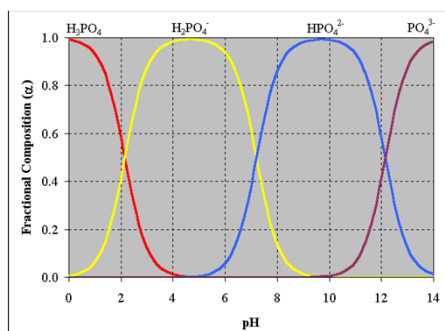
$$\alpha_2 = \frac{K_{a1}K_{a2}[\text{H}_3\text{O}^+]^{n-2}}{D}$$

...

$$\alpha_0 + \alpha_1 + \alpha_2 + \dots = 1$$

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Phosphoric Acid Species Composition Distribution



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CHE311 Assignment (due in 7 days):

Use Excel or other software to construct the composition curves of phosphoric acid solution as a function of pH. H_3PO_4 : $K_{a1} = 7.25 \times 10^{-3}$, $K_{a2} = 6.31 \times 10^{-8}$, $K_{a3} = 4.80 \times 10^{-13}$. You are required to email the instructor your Excel spreadsheet. Please make sure to label the plot properly, and use the file name of "CHE311_Assignment 7_ your name".

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Chapter 15 Summary

- Find the pH of mixtures of strong and weak acids and strong and weak bases
- Construct titration curves of mixtures with NaOH
- Calculate the pH in solutions of polyfunctional acids and bases, such as phosphoric and carbonic acid
- Calculate the pH of buffer solutions made from polyfunctional acids
- Determine the pH of amphiprotic salts
- Construct titration curves of polyfunctional acids and bases
- Compute alpha values for polyprotic acid solutions

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Important Equations	
For $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$	$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3}$
For $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$	$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8}$
For $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^+$	$K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}$
	$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_{a1}[\text{HA}^-] + K_w}{1 + [\text{HA}^-]/K_{a1}}}$
	$[\text{H}_3\text{O}^+] \approx \sqrt{\frac{K_{a2}c_{\text{NaHA}} + K_w}{1 + c_{\text{NaHA}}/K_{a1}}}$
	$\alpha_0 = \frac{[\text{H}_2\text{M}]}{c_T} \quad \alpha_1 = \frac{[\text{HM}^-]}{c_T} \quad \alpha_2 = \frac{[\text{M}^{2-}]}{c_T}$
Alpha values: $\alpha_0 = [\text{H}_3\text{O}^+]^n/D$, $\alpha_1 = K_{a1}[\text{H}_3\text{O}^+]^{n-1}/D$, and so forth, where	
$D = [\text{H}_3\text{O}^+]^n + K_{a1}[\text{H}_3\text{O}^+]^{n-1} + K_{a1}K_{a2}[\text{H}_3\text{O}^+]^{n-2} + \dots + K_{a1}K_{a2} \dots K_{an}$	

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