Chem 321 Lecture 15 - Acid-Base Equilibria & Titrations

10/17/13

Student Learning Objectives

Continuing Problem: Titrate 25.0 mL of 0.10 M maleic acid (H_2M) with 0.10 M NaOH and calculate the pH of the solution at various titrant volumes.

25.0 mL titrant (first equivalence point)

At the first equivalence point, all the H_2M has been converted to NaHM(aq) and there is a solution of the amphiprotic species HM^-. Since the volume has doubled, the concentration of NaHM at this point is half the original $[H_2M]$, or 0.050 M.

HM^- can react with water in two ways.

$$HM^- + H_2O \rightleftharpoons H_3O^+ + M^{2-} \qquad K_{a2} = 5.96 \times 10^{-7}$$

$$HM^- + H_2O \rightleftharpoons H_2M + OH^- \qquad K_b = K_w/K_{a1} = 8.33 \times 10^{-13}$$

We expect the solution to be acidic because $K_{a2} >> K_b$. If we ignore the base hydrolysis reaction and treat HM^- solely as a weak acid, $[H_3O^+]_{equil} = 1.7 \times 10^{-4}$ M and pH ≈ 3.76.

Check for Understanding 10.3 **Solution**

1. Calculate the pH of a 0.050 M HM^- solution assuming it acts solely as a weak acid.

However, it turns out that the base hydrolysis reaction proceeds to nearly the same extent as the acid dissociation process because it is driven to the right by the H_3O^+ produced in the acid dissociation reaction. If one is doing careful calculations, one should consider both reactions and both equilibria.

$$K_{a_2} = \frac{[H_3O^+][M^{2-}]}{[HM^-]}$$

$$K_b = \frac{[H_2M][OH^-]}{[HM^-]}$$

In these two equations there are 5 unknowns and in order to solve this problem exactly we need 3 additional equations. One equation comes from the water self-ionization equilibrium.

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

Another condition that must hold is charge balance. Since the solution is electrically neutral, the concentration of positive charges must equal the concentration of negative charges. In terms of the cations and anions in this titration solution this becomes

$$[Na^+] + [H_3O^+] = [HM^-] + [OH^-] + 2[M^{2-}]$$

Notice that the concentration of M^{2-} is doubled because its charge is 2-. Since $[Na^+]$ can be determined at any point in the titration, no new unknowns have been introduced in this additional equation.

The final relationship is based on mass conservation. Regardless of where you are in this titration, the maleic acid must exist as either H_2M, HM^- or M^{2-}. This can be expressed as:

$$M_{NaHM} = [HM^-] + [H_2M] + [M^{2-}]$$

Again, no new unknowns are involved. These 5 equations with 5 unknowns can be combined and solved exactly to get the $[H_3O^+]$. The rigorous solution gives

$$[H_3O^+] = \left[\frac{[HM^-]K_{a_1}K_{a_2} + K_{a_1}K_w}{K_{a_1} + [HM^-]}\right]^{1/2}$$

Since the equilibrium constants for the acid dissociation and the base hydrolysis reactions are both very small, it is a reasonable assumption that neither reaction will alter $[HM^-]$ significantly, thus $[HM^-] \sim M_{NaHM}$. Consequently, the $[H_3O^+]$ and pH can be evaluated.

This rather complex expression for $[H_3O^+]$ can be greatly simplified if certain conditions hold. Factoring out K_{a1} in the numerator gives

$$[H_3O^+] = \left[\frac{K_{a_1}([HM^-]K_{a_2} + K_w)}{K_{a_1} + [HM^-]}\right]^{1/2}$$

If K_{a2} $[HM^-]$ >> K_w then K_w can be dropped in the numerator and the numerator becomes ($[HM^-]$ K_{a1} K_{a2}). If [HM-] >> K_{a1}, then K_{a1} can be dropped in the denominator and the overall expression becomes

$$[H_3O^+] = \left[\frac{[HM^-]K_{a_1}K_{a_2}}{[HM^-]}\right]^{1/2} = \left[K_{a_1}K_{a_2}\right]^{1/2}$$

Taking the negative log of this equation gives:

$$pH \simeq \frac{pK_{a_1} + pK_{a_2}}{2}$$

This rather simple expression for determining the pH of the amphiprotic substance (HM^-) present at the first equivalence point is the basis for the method of estimating the equivalence point pH as an average of the pH plateaus before and after the equivalence point.

Using these simple expressions, one calculates $[H_3O^+] \simeq 8.5 \times 10^{-5}$ M and pH ≃ 4.07 for the solution at the first equivalence point. However, since $[HM^-] \simeq 0.050$ M it is not >> K_{a1} (= 0.012), so the denominator cannot be simplified and the more rigorous expression gives $[H_3O^+] \simeq 7.6 \times 10^{-5}$ M and **pH ≃ 4.12**. This value for $[H_3O^+]$ differ by more than a factor of 2 from the result obtained by neglecting the base hydrolysis reaction.

Check for Understanding 10.4

Solution

1. Take into account both possible reactions of $H_2PO_4^-$ with water and calculate the pH of a 0.10 M KH_2PO_4 solution. Compare this to the previously calculated value assuming only weak acid behavior.

30.0 mL titrant

This is 5.00 mL past the first equivalence point and 20% of the way to the second equivalence point. This means that 20% of the weak acid HM^- has been converted to its conjugate base M^{2-} and we have a HM^-/M^{2-} buffer solution. In order to assess the concentrations of HM^- and M^{2-} after the base has reacted, again prepare a mole table.

initial moles of HM^- = initial moles of H_2M = (0.0250 L)(0.10 mol/L) = 0.0025_0 mol

moles of NaOH added after 1st equiv point = (0.0050 L)(0.10 mol/L) = 0.00050 mol

The mole table then looks like

	HM^-	+	OH^-	→	M^{2-}	+	H_2O
initial	0.0025_0 mol		0.00050 mol		0		
after rxn	0.0020_0 mol		0		0.00050 mol		

Since the total solution volume is now 55.0 mL,

$[HM^-]_{init}$ = (0.0020_0 mol)/(0.0550 L) = 0.036_4 M

$[M^{2-}]_{init}$ = (0.00050 mol)/(0.0550 L) = 0.0090_9 M

The concentration table for the buffer then becomes:

	HM-	+	H_2O	⇌	H_3O^+	+	M^{2-}
initial	0.036_4 M				$\sim 10^{-7}$ M		0.0090_9 M
equil	$\sim 0.036_4$ M				x		$\sim 0.0090_9$ M

where x is the equilibrium $[H_3O^+]$.

Substituting gives

$$K_{a_2} = 5.96 \times 10^{-7} \simeq \frac{[H_3O^+][M^{2-}]}{[HM^-]} = \frac{(x)(0.0090_9)}{0.036_4}$$

Solving this gives x = 2.4×10^{-6} M = $[H_3O^+]$ and **pH ≃ 5.62**.

50.0 mL titrant (second equivalence point)

At the second equivalence point, all the HM^- has been converted to $Na_2M(aq)$ and there is a solution of the weak base M^{2-}. The total volume is now 75.0 mL, so the concentration of Na_2M at this point is one third the original $[H_2M]$, or 0.033_3 M. Base hydrolysis is the predominant reaction.

$$\begin{array}{lccccccc} & M^{2-} & + & H_2O & \rightleftharpoons & HM^- & + & OH^- \\ \text{initial} & 0.033_3\ M & & & & 0 & & \sim 10^{-7}\ M \\ \text{equil} & 0.033_3 - x & & & & x & & \sim x \end{array} \qquad K_b = K_w/K_{a2} = 1.68 \times 10^{-8}$$

where x is the increase in the $[HM^-]$ and is it assumed that $x >> 10^{-7}$ M.

Substituting gives

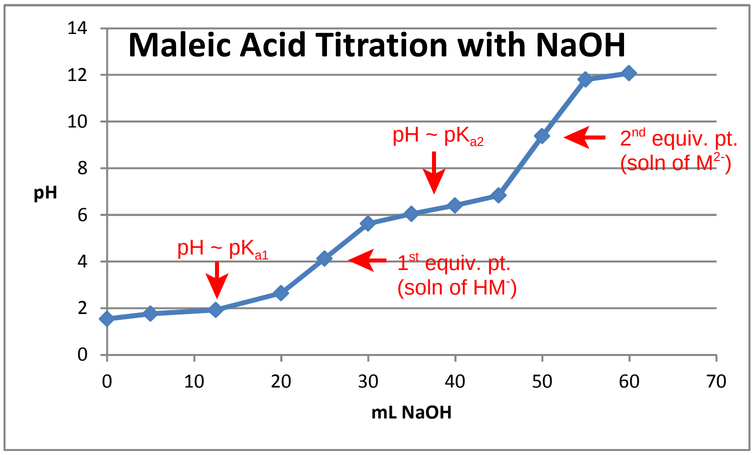
$$K_b = 1.68\,x\,10^{-8} \simeq \frac{[HM^-][OH^-]}{[M^{2-}]} = \frac{(x)(x)}{0.033_3 - x} \simeq \frac{x^2}{0.033_3}$$

Solving this gives $x = 2.4 \times 10^{-5}$ M = $[OH^-]$ and pOH ≃ 4.63. Thus, **pH ≃ 9.37**. Note that the two assumptions regarding the value of x are valid.

Maleic Acid Titration Curve

The approaches discussed above can be used to make additional calculations of pH at various points for this maleic acid titration. A plot of pH versus titrant volume constitutes a titration curve, as shown below. Note the key points labeled on the titration curve. Determination of the pH halfway to the first equivalence point and halfway between the first and second equivalence points allows one to estimate pK_{a1} and pK_{a2}, respectively, for the diprotic weak acid.

mL NaOH	pH
0.00	1.54
5.00	1.76
12.5	1.92
20.0	2.64
25.0	4.12
30.0	5.62
35.0	6.04
40.0	6.40
45.0	6.83
50.0	9.37
55.0	11.80
60.0	12.07



Exercises for Acid-Base Equilibria & Titrations