Student Learning Objectives

As a way to review most of the principles of acid-base chemistry, let us calculate the solution pH for various volumes of added strong base in the titration of the diprotic weak acid, maleic acid (cis-butenedioic acid). The focus will be on the set up of the appropriate calculation, so activities will not be used.

Problem: Titrate 25.0 mL of 0.10 M maleic acid (H₂M) with 0.10 M NaOH. Calculate the pH of the solution at various titrant volumes.

(Note: For maleic acid, H₂M, \( K_{a1} = 1.20 \times 10^{-2} \) and \( K_{a2} = 5.96 \times 10^{-7} \))

At this point it is instructive to note the volume of base needed to reach the first equivalence point and the second equivalence point. Because the acid and base concentrations are equal, the first equivalence point volume of titrant is 25.0 mL, and 50.0 mL is needed to reach the second equivalence point.

The titration reaction up to the first equivalence point is:

\[
H_2M + OH^- \rightarrow HM^- + H_2O
\]

As is the custom, this reaction is not written as an equilibrium because it has such a large equilibrium constant and can be effectively considered to proceed only in the forward direction. The equilibrium constant (\( K_1 \)) for this reaction can be calculated from known quantities by noting that the reverse reaction is simply the base hydrolysis of HM⁻. Thus,

\[
K_1 = \frac{1}{K_b} = \frac{1}{K_w/K_{a1}} = \frac{1.20 \times 10^{-2}}{1.0 \times 10^{-14}} = 1.2 \times 10^{12}
\]

The titration reaction from the first equivalence point to the second equivalence point is:

\[
HM^- + OH^- \rightarrow M^{2-} + H_2O
\]

This reaction also has a very large equilibrium constant.
At each point in the titration it is convenient (and justified) to assume that the added base will react completely with any available H₂M or HM⁻. This neutralization reaction should be accounted for before deciding what chemical species are present in solution.

**0.00 mL titrant**

At this point no base has been added so you have a solution of a diprotic weak acid.

\[ \text{H}_2\text{M} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HM}^- \quad \text{Ka}_1 = 1.20 \times 10^{-2} \]

\[ \text{HM}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{M}^{2-} \quad \text{Ka}_2 = 5.96 \times 10^{-7} \]

Since Ka₂ << Ka₁, we can neglect the effects of the second dissociation and treat this as a solution of a monoprotic weak acid. We will check this assumption later.

The concentration table for the first acid dissociation looks like

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Equilibrium 1</th>
<th>Equilibrium 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂M</td>
<td>0.10 M</td>
<td>~10⁻⁷ M</td>
<td>0</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>~x</td>
<td>x</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td></td>
<td>~x</td>
<td>x</td>
</tr>
</tbody>
</table>

where x equals the increase in HM⁻ concentration. Note that the equilibrium concentration of H₃O⁺ is also approximated by x. This assumes that x >> 10⁻⁷ M.

Substituting these equilibrium quantities into the reaction quotient and equating to Ka₁ gives

\[ \text{Ka}_1 = 1.20 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HM}^-]}{[\text{H}_2\text{M}]} = \frac{(x)(x)}{0.10 - x} = \frac{(x)(x)}{0.10} \]

The approximation made in the denominator assumes that x << 0.10 M.

Solving this gives x = 0.0346 M. This value for x is not at least a factor of 10 smaller than 0.10 M, so the simplification made in the denominator is not valid and the more complex quadratic equation must be solved. Recall that quadratic equations in
the form \( ax^2 + bx + c = 0 \) have the two solutions given by:

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

The exact solution using the quadratic formula is \( x = 0.029_2 \) M (a difference of nearly 20%). However, one must be careful when using the quadratic formula because it is easy to make a mistake in substituting the various quantities. Alternatively, it is sometimes possible to use the method of successive approximations. Since the original value of \( x \) is close to satisfying the simplifying assumption that \( x \ll 0.10 \) M, one can use this value as a first estimate for \( x \) in the denominator term and solve the simpler quadratic equation for another estimate of \( x \). This process is then repeated again and again until successive values of \( x \) are acceptably close. Although this calculation is repeated many times, it is much simpler to do and avoids the pitfalls of using the quadratic formula.

Substituting \( x = 0.034_6 \) into the denominator and solving for \( x \) gives

\[
1.20 \times 10^{-2} \approx \frac{(x)(x)}{0.10 - 0.034_6} \implies x = 0.028_0
\]

Repeating this process gives

\[
1.20 \times 10^{-2} \approx \frac{(x)(x)}{0.10 - 0.028_0} \implies x = 0.029_4
\]

Repeating this process gives

\[
1.20 \times 10^{-2} \approx \frac{(x)(x)}{0.10 - 0.029_4} \implies x = 0.029_1
\]

At this point the successive values calculated for \( x \) are sufficiently close (~1% variation) that we can stop and use 0.029, as our estimate for \( x \). Note that one additional calculation will produce the exact solution of 0.029₂. Thus, \( [H_3O^+] = 0.029_2 \) M and \( pH \approx 1.54 \).
The calculated equilibrium concentrations for H$_3$O$^+$ and HM$^-$ can be used to check the assumption that the second dissociation can be neglected. The concentration table for the second dissociation is

<table>
<thead>
<tr>
<th></th>
<th>HM$^-$ + H$_2$O $\rightleftharpoons$ H$_3$O$^+$ + M$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.029 M</td>
</tr>
<tr>
<td>equil</td>
<td>0.029 - x, 0.029 + x, x</td>
</tr>
</tbody>
</table>

Substituting gives

$$K_{a2} = 5.96 \times 10^{-7} = \frac{[H_3O^+][M^{2-}]}{[HM^-]} = \frac{(0.029 - x)(x)}{0.029 - x} = \frac{(0.029)(x)}{0.029}$$

The approximations in the numerator and denominator were made because $K_{a2}$ is so small and very little dissociation is expected ($x << 0.029$). Solving this gives $x = 5.96 \times 10^{-7}$ M = [M$^{2-}$]. This confirms our assumption that very little HM$^-$ dissociates.

### 5.00 mL titrant

Since 25.0 mL is needed to reach the first equivalence point, the 5.00 mL mark is 20% of the way along. This means that 20% of the weak acid H$_2$M has been converted to its conjugate base HM$^-$ and we have a H$_2$M/HM$^-$ buffer solution. In order to assess the concentrations of H$_2$M and HM$^-$ after the base has reacted, it is convenient to prepare a “mole table” for the titration reaction. The initial moles of weak acid and moles of added base are gotten by multiplying concentration times volume.

- initial moles of H$_2$M = (0.0250 L)(0.10 mol/L) = 0.00250 mol
- moles of NaOH added = (0.0050 L)(0.10 mol/L) = 0.00050 mol

The mole table then looks like

<table>
<thead>
<tr>
<th></th>
<th>H$_2$M       +     OH$^-$ $\rightarrow$ HM$^-$ + H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.00250 mol, 0.00050 mol, 0</td>
</tr>
<tr>
<td>after rxn</td>
<td>0.00205 mol, 0, 0.00050 mol</td>
</tr>
</tbody>
</table>
Since the total solution volume is now 30.0 mL,

\[[H_2M]_{init} = \frac{(0.00200 \text{ mol})}{(0.0300 \text{ L})} = 0.0667 \text{ M}\]

\[[HM^-]_{init} = \frac{(0.00050 \text{ mol})}{(0.0300 \text{ L})} = 0.0167 \text{ M}\]

The concentration table for the buffer then becomes

<table>
<thead>
<tr>
<th></th>
<th>(H_2M)</th>
<th>(H_3O^+)</th>
<th>(HM^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.0667 M</td>
<td>~10^{-7} M</td>
<td>0.0167 M</td>
</tr>
<tr>
<td>equil</td>
<td>~0.066_7 M</td>
<td>x</td>
<td>~0.016_7 M</td>
</tr>
</tbody>
</table>

The usual buffer assumption is to use the initial weak acid and conjugate base concentrations for their equilibrium concentrations, however, one of the “10^{-3} rules” does not hold for this buffer (\(K_a\) is not \(< 10^{-3}\)). Consequently we must adjust these initial concentrations. How they are adjusted depends on which way this reaction must shift in order to reach equilibrium. Since this is an acidic buffer (pK_a = 1.92), the \([H_3O^+]\) must increase over the initial \(10^{-7}\) M value so the reaction shifts to the right.

Let \(x\) equal the increase in \([HM^-]\). Then

\[
\begin{align*}
\text{H}_2\text{M} & + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^- + \text{HM}^- \\
n\text{initial} & : 0.066_7 \text{ M} \quad ~10^{-7} \text{ M} \quad 0.016_7 \text{ M} \\
n\text{equil} & : 0.066_7 - x \quad ~x \quad 0.016_7 + x
\end{align*}
\]

This assumes that \(x \gg 10^{-7}\) M.

Substituting these equilibrium quantities into the reaction quotient and equating to \(K_{a_1}\) gives

\[
K_{a_1} = 1.20 \times 10^{-2} = \frac{[H_3O^+][HM^-]}{[H_2M]} = \frac{(0.016_7 + x)(x)}{0.066_7 - x}
\]

This quadratic equation cannot be simplified because, as noted above, we cannot use the initial weak acid and conjugate base concentrations for the equilibrium values, nor can we use the method of successive approximations here. Consequently, one must solve the quadratic equation using the quadratic formula. The exact solution is \(x = 1.74 \times 10^{-2}\) M. Thus, \([H_3O^+] = 0.0174\) M and \(pH = 1.76\).
**12.5 mL titrant**

At this stage exactly half the base needed to reach the first equivalence point has been added and half the $\text{H}_2\text{M}$ has been converted to $\text{HM}^-$. Thus, a buffer in which $[\text{H}_2\text{M}] \approx [\text{HM}^-]$ is formed and $\text{pH} \approx \text{pK}_{a1} = 1.92$.

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**Check for Understanding 10.2**

1. Calculate the pH at the 12.5 mL mark following the approach used for the 5.00 mL point, including use of the quadratic formula.

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**Solution**