APPLICATIONS OF TITRATIONS

I. Monoprotic Systems

\[ HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a = \frac{[H_3O^+][A^-]}{[HA]} \]

**MBE:**

\[
F = [HA] + [A^-] = [HA] + \frac{K_a [HA]}{[H_3O^+]} = [HA] \left( 1 + \frac{K_a}{[H_3O^+]} \right)
\]

\[
\alpha_{HA} = \frac{[HA]}{F} = \frac{[HA]}{[HA] \left( 1 + \frac{K_a}{[H_3O^+]} \right)} = \frac{1}{1 + \frac{K_a}{[H_3O^+]}} = \frac{[H_3O^+]}{[H_3O^+] + K_a}
\]

\[
\alpha_{A^-} = \frac{[A^-]}{F} = \frac{[A^-]}{[H_3O^+] \left[ A^- \right] / [H_3O^+] + [A^-] / K_a} = \frac{1}{1 + \frac{[H_3O^+]}{K_a}} = \frac{K_a}{K_a + [H_3O^+]}
\]

If \( \alpha_{HA} = \alpha_{A^-} \):

\[
\frac{[H_3O^+]}{[H_3O^+] + K_a} = \frac{K_a}{K_a + [H_3O^+]} \quad \Rightarrow \quad [H_3O^+] = K_a \quad \text{or} \quad pH = pK_a
\]

\[ H_2A + H_2O \rightleftharpoons H_3O^+ + HA^- \quad K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} \]
HA\(^-\) + H\(_2\)O ⇌ H\(_3\)O\(^+\) + A\(^2-\)

\[ K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} \]

**MBE:**

\[ F = [H_2A] + [HA^-] + [A^{2-}] = [H_2A] + \frac{K_{a1}[H_2A]}{[H_3O^+]} + \frac{K_{a2}K_{a1}[H_2A]}{[H_3O^+]^2} \Rightarrow \]

\[ F = [H_2A]\left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2}\right) \]

\[ \alpha_{H_2A} = \frac{[H_2A]}{F} = \frac{[H_2A]}{[H_2A]\left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2}\right)} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \]

\[ \alpha_{HA^-} = \frac{[HA^-]}{F} = \frac{K_{a1}[H_2A]/[H_3O^+]}{[H_2A]\left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2}\right)} = \frac{K_{a1}[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \]

\[ \alpha_{A^{2-}} = \frac{[A^{2-}]}{F} = \frac{K_{a1}K_{a2}[H_2A]/[H_3O^+]^2}{[H_2A]\left(1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2}\right)} = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \]

See picture below.
III. Common titration systems

1. Strong acid (SA) + Strong base (SB)
2. SB + SA
3. Weak acid (WA) + SB
4. SA + Weak base (WB)
5. WA + WB

Sample: 50 mL of 0.02 M KOH is titrated with 0.1M HBr.

There are three regions:

1. Before equivalence point
2. Equivalence point
3. Excess of H$_2$O$^+$

Equivalence point is 10 mL (of acid added):

\[ V_a M_a = V_b M_b \]

1. pH before the equivalence point. After 3 mL of the HBr are added.

\[ [OH^-] = \frac{10 - 3}{10} \cdot \frac{50}{50 + 3} = 0.0132 M \]

Fraction titrated \( DF \)

Initial concentration of the KOH

\[ [H_3O^+] = \frac{K_w}{[OH^-]} = 7.58 \cdot 10^{-13} M \quad \Rightarrow \quad pH = 12.12 \]

2. Equivalence point

\[ [H_3O^+] = [OH^-] \]

If \( [H_3O^+] = x \), then \( x^2 = 1 \cdot 10^{-14} \quad \Rightarrow \quad x = 10^{-7} \quad \Rightarrow \quad pH = 7 \]
3. Excess of the acid: assume 10.5 mL of the HBr is added.

Excess volume is \((10.5 - 10.0) \text{ mL} = 0.5 \text{ mL}\).

\[
[H_3O^+] = 0.1 \left( \frac{0.5}{50.0 + 10.5} \right) = 8.26 \cdot 10^{-4} \text{ M}
\]

Initial concentration of the HBr

pH = 3.08

When weak acid (MES: 50 mL, 0.02M, \(pK_a 6.15\)) is titrated with the strong base (0.1M NaOH).

The equivalence point is at:

\[
V_{\text{equiv}} = \frac{50 \cdot 0.02}{0.1} = 10.0 \text{ mL}
\]

The following four regions have to be considered:

1. Before base is added

\[
HA \rightleftharpoons H^+ + A^- \\
F-x \quad x \quad x
\]

\[
Ka = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x} = 10^{-6.15}
\]

\(x = 1.19 \cdot 10^{-4} \Rightarrow \text{pH} = 3.93\)

2. Before EP (\(V_b = 3 \text{ mL}\)). Buffer region:

\[
\text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) = 6.15 + \log \left( \frac{3/10}{7/10} \right) = 5.78
\]

3. At equivalence point:

All HA is converted into A\(^-\), so the following equilibria has to be considered:

\[
A^- + H_2O \rightleftharpoons HA + OH^- \\
F' - x \quad x \quad x
\]

\[
K_b = K_w \cdot \frac{F-x}{F-x} = \frac{x^2}{F-x}
\]

\[
F' = 0.02 \left( \frac{50}{50 + 10} \right) = 0.0167 \text{ M}
\]

Initial concentration of the HBr
of the HBr

\[ K_b = \frac{x^2}{F-x} = \frac{K_w}{K_a} = 1.43 \cdot 10^{-8} \Rightarrow x = 1.54 \cdot 10^{-5} \Rightarrow pH = 9.18 \]

4. After equivalence point: 0.1 mL of extra NaOH is added.

\[ [OH^-] = 0.1 \left( \frac{0.1}{50 + 10 \cdot 10} \right) = 1.66 \cdot 10^{-4} M \]

**Initial concentration of NaOH**

\[ pH = -\log \left( \frac{K_w}{[OH^-]} \right) = 10.22 \]