

Chemistry 201

Interpretation of a Titration Curve

NC State University

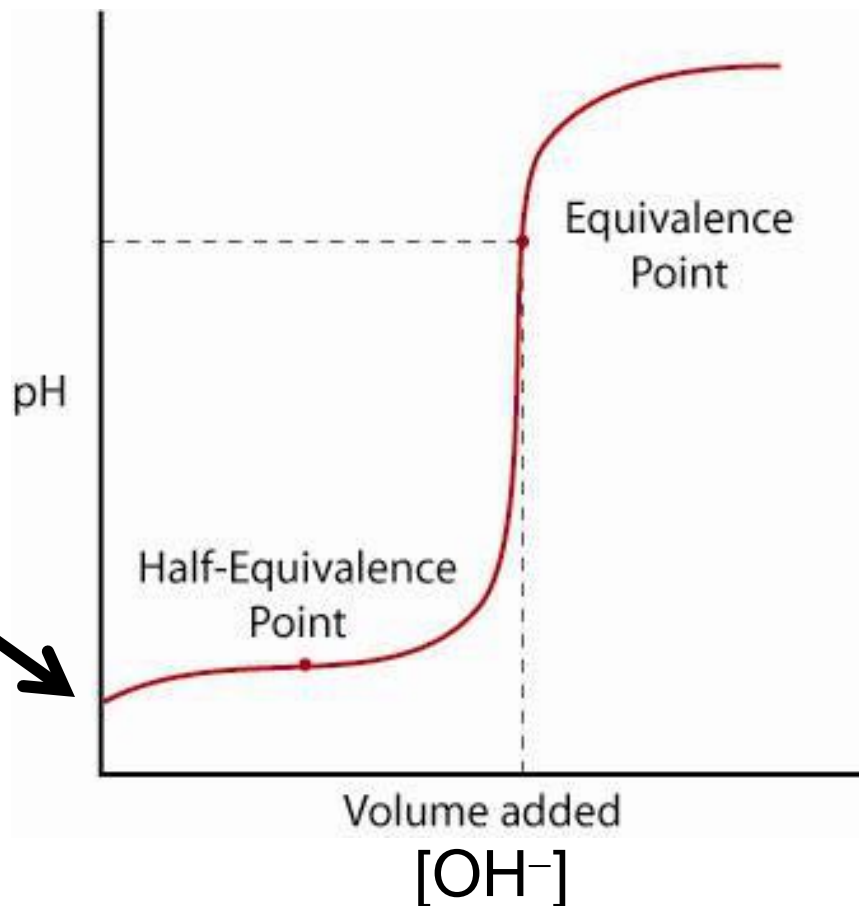
Starting point use K_a to calculate pH

Suppose we want to make a buffer by titrating $[\text{OH}^-]$. We cannot use the H-H equation initially since it does not suggest a way to calculate $[\text{A}^-]$. Instead at this initial point we will use the equilibrium constant and make an ICE table.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Starting point $[\text{HA}] = [\text{HA}]_0$

Added $[\text{OH}^-] = 0$



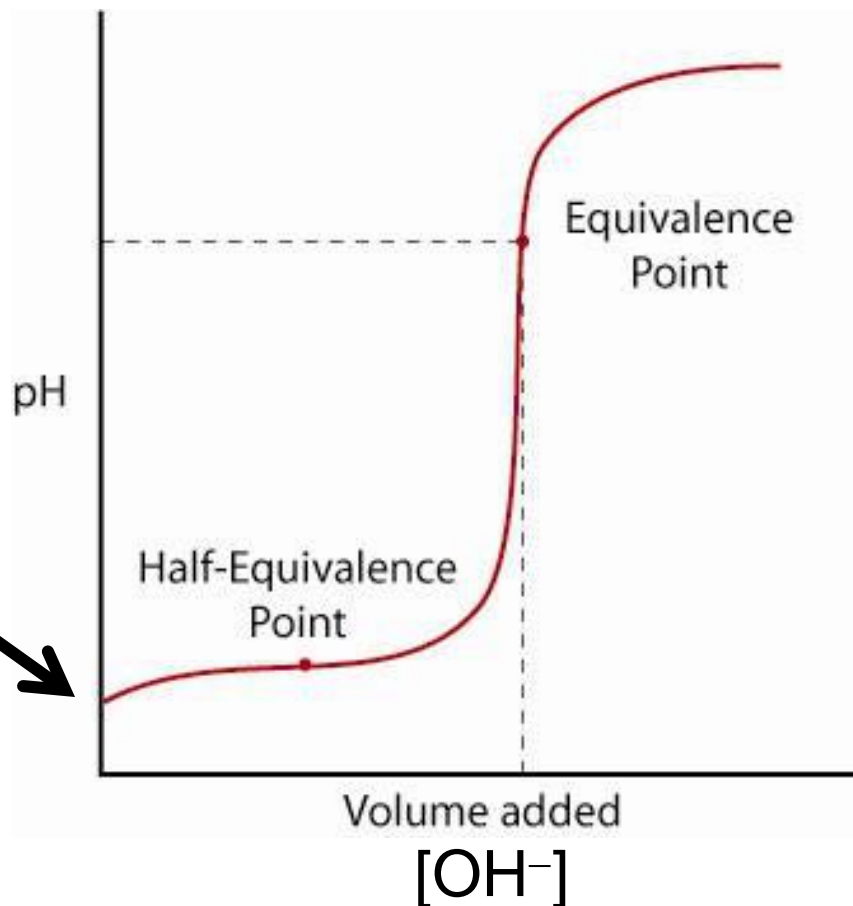
Starting point use K_a to calculate pH

Suppose we want to make a buffer by titrating $[\text{OH}^-]$. We cannot use the H-H equation initially. We do not know the concentration of $[\text{A}^-]$. Instead at this initial point we will use the other form of the equilibrium constant and make an ICE table.

$$K_a = \frac{x^2}{[\text{HA}]_0 - x}$$

Starting point $[\text{HA}] = [\text{HA}]_0$

Added $[\text{OH}^-] = 0$



Starting point use K_a to calculate pH

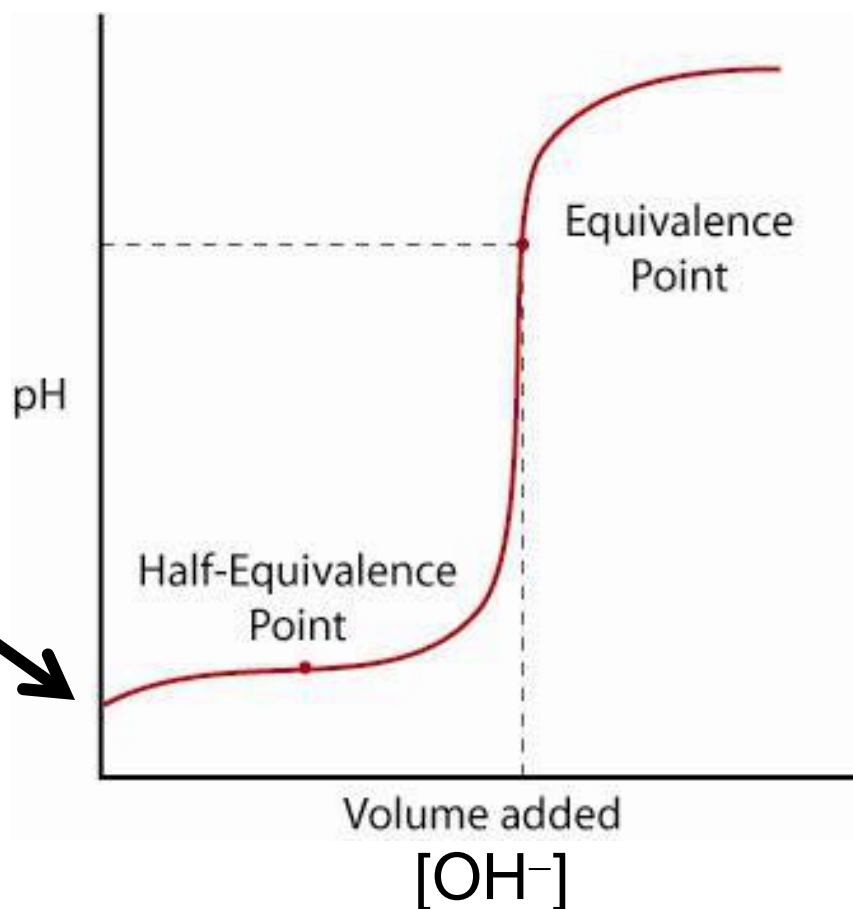
$$x^2 + K_a x - K_a [HA]_0 = 0$$

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a [HA]_0}}{2}$$

We can calculate $x = [H^+]$ and therefore the pH from the equilibrium constant.

Starting point $[HA] = [HA]_0$

Added $[OH^-] = 0$



Starting point use K_a to calculate pH

If $K_a \ll [HA]_0$ then we can use the approximate method

$$K_a \approx \frac{x^2}{[HA]_0}$$

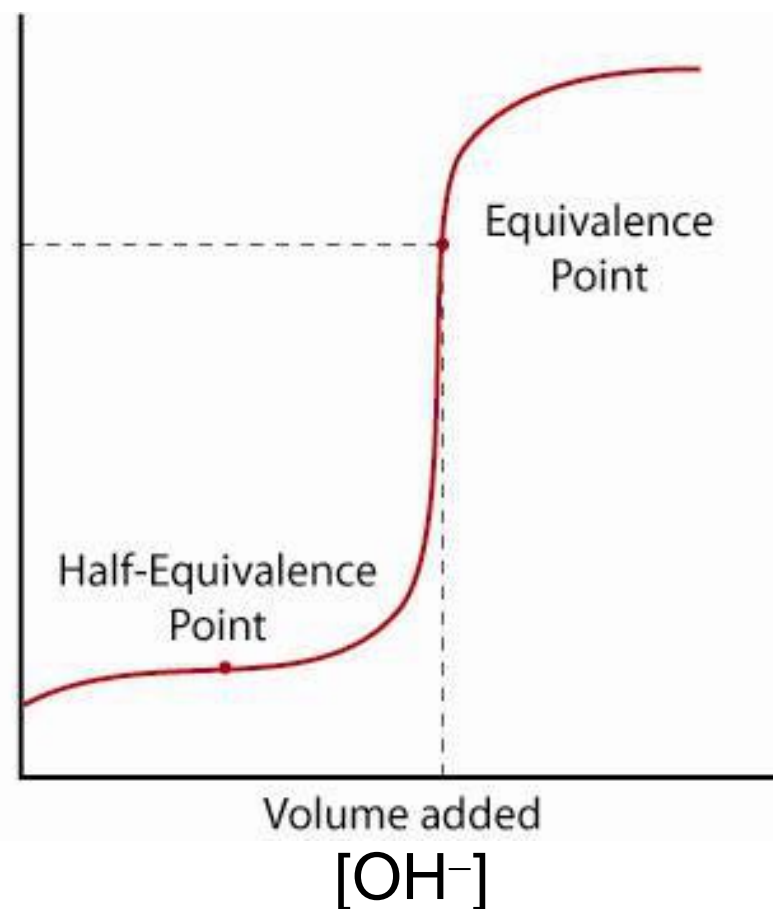
Therefore $x \approx \sqrt{[HA]_0 K_a}$

We can calculate $[H^+] = x$
and therefore the pH.

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

Starting point $[HA] = [HA]_0$

Added $[OH^-] = 0$



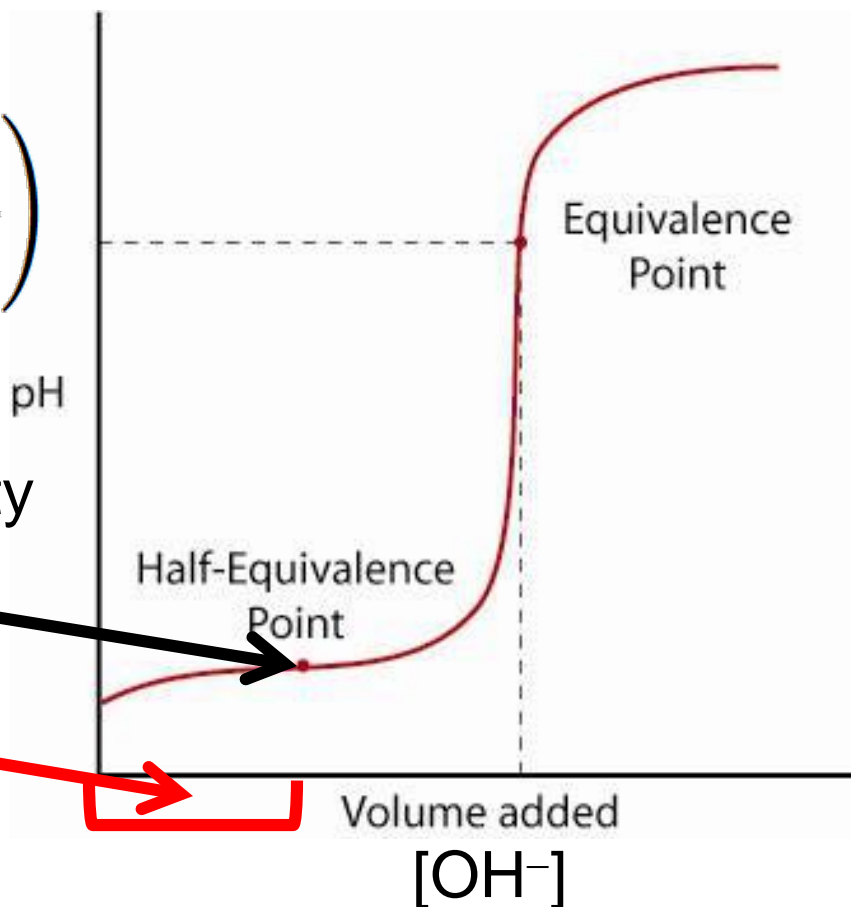
Use Hendersen-Hasselbach in the buffer region

When we have a buffer we can use the Hendersen-Hasselbach equation. In the case shown we have $\text{pH} = \text{pK}_a$.

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]}} \right)$$

Maximum buffer capacity
 $[\text{HA}] = [\text{A}^-]$.

Added $[\text{OH}^-] = 1/2 [\text{HA}]_0$



Limits of the buffer region

The buffer range is defined as approximately from:

$$\text{pH} = \text{pK}_a - 1 \quad R = [\text{A}^-]/[\text{HA}] = 0.1 \quad [\text{OH}^-] \sim 0.091 [\text{HA}]_0$$

to

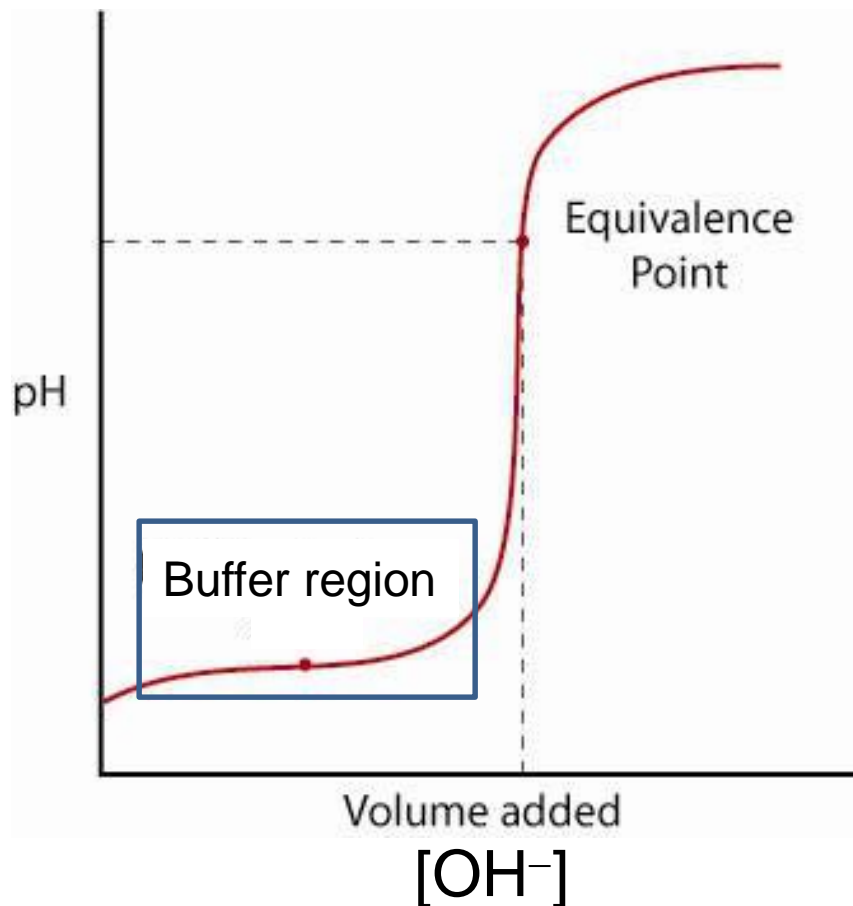
$$\text{pH} = \text{pK}_a + 1 \quad R = [\text{A}^-]/[\text{HA}] = 10 \quad [\text{OH}^-] \sim 0.91 [\text{HA}]_0$$

$$[\text{A}^-] = \frac{R}{1 + R} [\text{HA}]_0$$

Maximum buffer capacity

$[\text{HA}] = [\text{A}^-]$ when

$[\text{OH}^-] \sim 0.5 [\text{HA}]_0$



The equivalence point

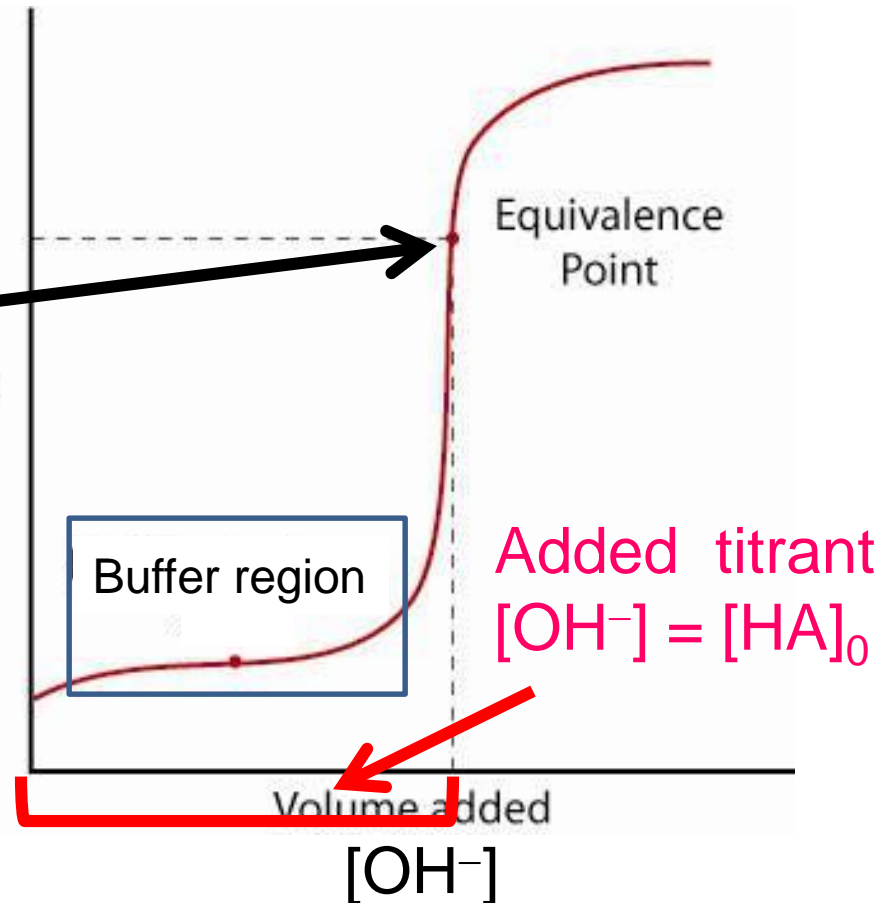
Once the solution moves outside the buffer range the pH shoots up. The equivalence point is reached when the added is equal to the original acid concentration, i.e. $[\text{OH}^-] \sim [\text{HA}]_0$

At this point one can no longer use the H-H equation. Instead, we assume that $[\text{A}^-] \sim [\text{HA}]_0$. Then we use the base equilibrium:



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Note that $\text{p}K_b = 14 - \text{p}K_a$



Using the approximate method to solve for pH using K_b

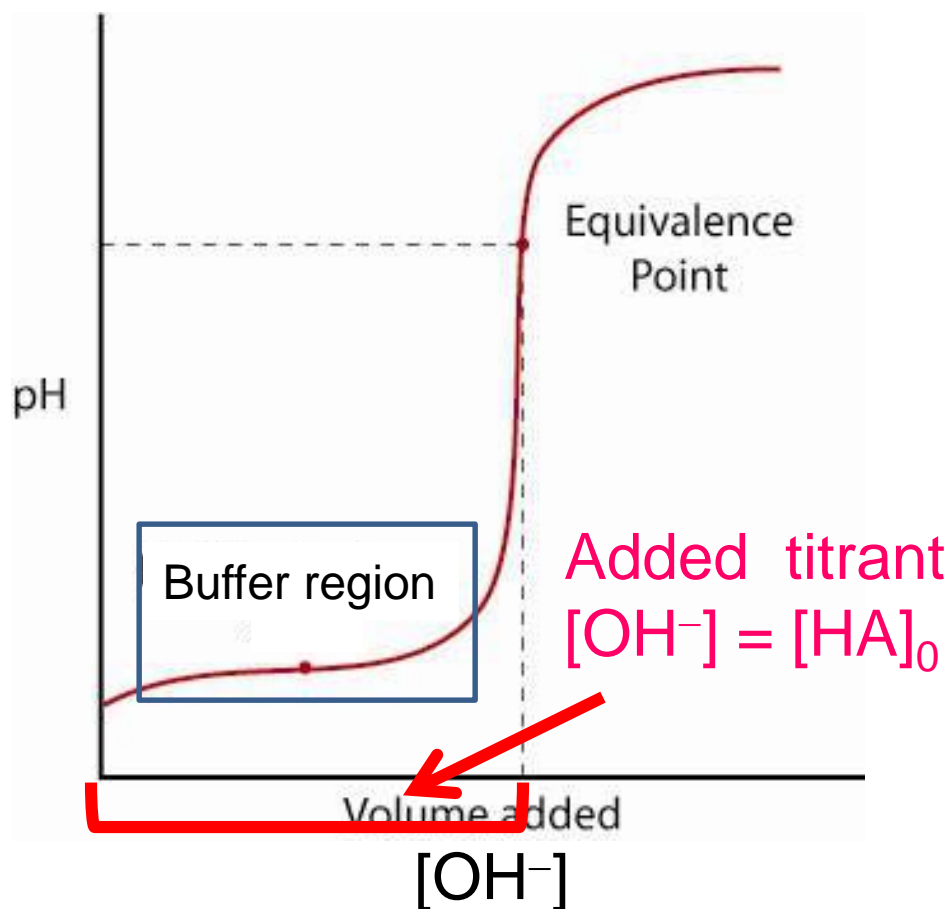
For most acids $K_b < K_a$. This means that the probability that one can use an approximate method to obtain pOH using pK_b is quite large. Thus, one can calculate the hydroxide concentration using

$$[OH^-] \approx \sqrt{[A^-]_0 K_b}$$

Keeping in mind that

$$[A^-]_0 = [HA]_0$$

Note that $pK_b = 14 - pK_a$



Titration curve summary

