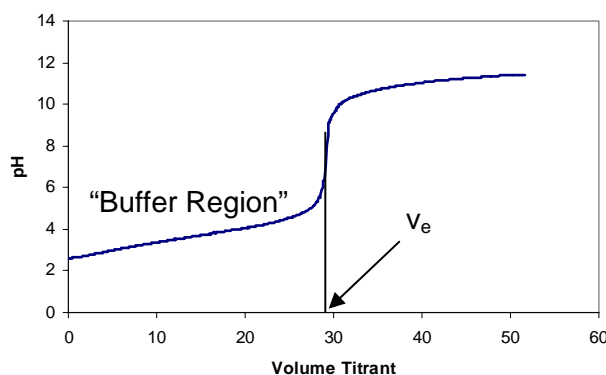


Determination of pKa's from titration curves.



Consider the titration curve above. Let's identify what we know to be true about the system:

1. Before we initiate the titration, there is a fixed amount of HA (and we'll assume only HA) in solution. Let's call this amount "mol HA_i"
2. At the equivalence point, we have converted all of the HA to A⁻, mathematically,

$$\text{mol A}^- = \text{mol HA}_i$$
3. After the equivalence point, we are simply adding excess titrant.
4. Between the start of the titration and the equivalence point, we have a buffer solution that contains both HA and A⁻. We'll call this the "Buffer Region".
 - a. Because of mass balance, the total amount of HA and A⁻ in solution has to sum to what was originally introduced:

$$\text{mol HA} + \text{mol A}^- = \text{mol HA}_i$$
 - b. The pH of the solution in this region depends on the relative amounts of HA and A⁻

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

We've measured pH as a function of *volume of titrant*. If we can convert the volume into a ratio of moles A⁻ to moles HA, we can calculate a pK_a.

Where do we go from here? Let's consider the point one third of the way to the equivalence point. At this point we have converted 1/3 of the HA we started with to A⁻ so that:

$$\text{mol HA} = 2/3 \text{ mol HA}_i, \text{ and } \text{mol A}^- = 1/3 \text{ mol HA}_i$$

By substituting these expressions into the Henderson Hasselbach equation, we can solve for pK_a:

$$\text{pH} = \text{pK}_a + \log \frac{1/3 \text{ mol HA}_i}{2/3 \text{ mol HA}_i} \quad (\text{after canceling mol HA}_i) \quad \text{pH} = \text{pK}_a + \log \frac{1}{2}$$

Note that only the *ratio* of moles is critical. It is not necessary to know the initial number of moles of HA in solution! We can use this same logic to find a pK_a value at any point** prior to the equivalence point. We can also translate this to polyprotic acids if we treat each proton as an independent "titration".

**Well, not quite any point. The H-H equation doesn't work well near the beginning or equivalence point of the titration. It is best to use values in the middle of the buffer region instead.