



09
ACIDS & BASES

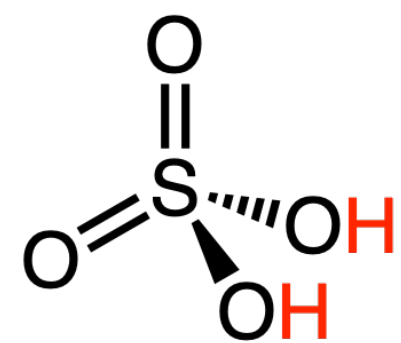
POLYPROTIC ACID & WEAK BASE TITRATIONS

CHEMISTRY 136L // FALL 2019

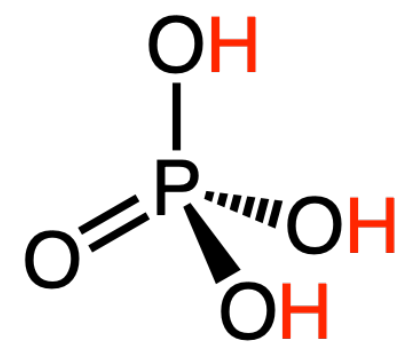
POLYPROTIC ACIDS

General ideas

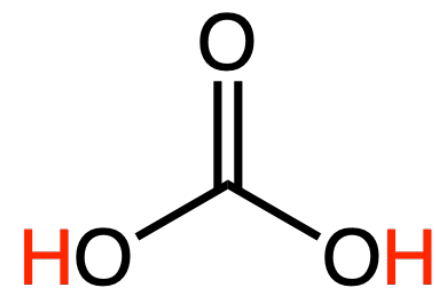
Polyprotic acids contain two or more ionizable protons (H^+).



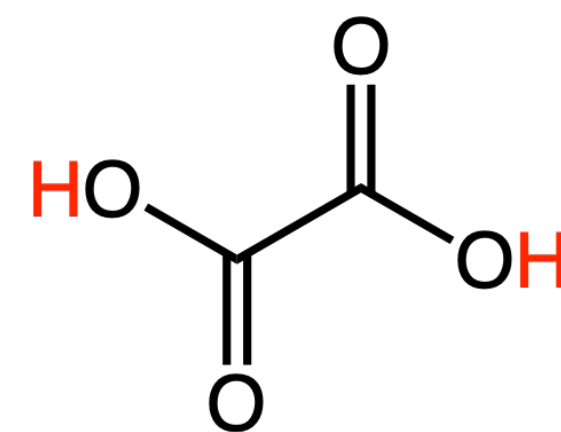
Sulfuric Acid



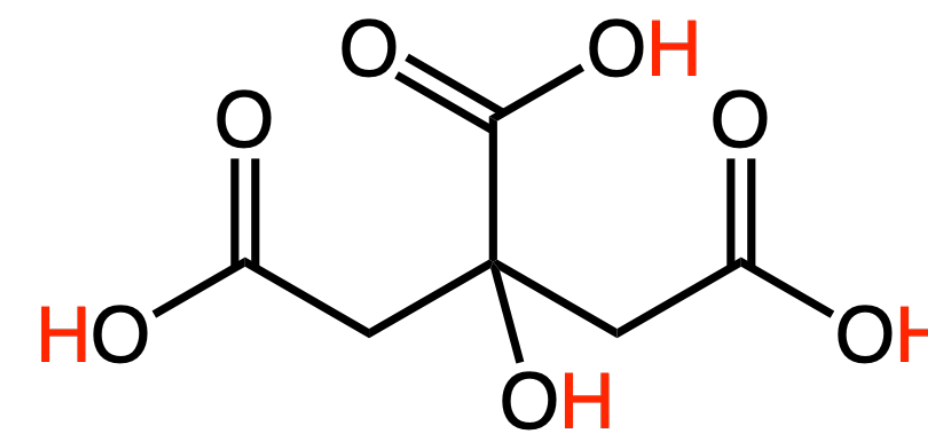
Phosphoric Acid



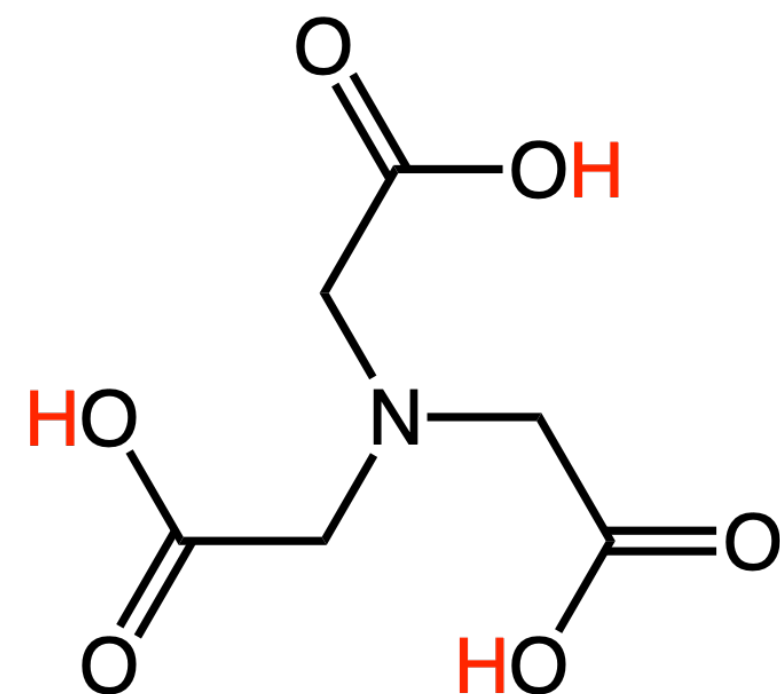
Carbonic Acid



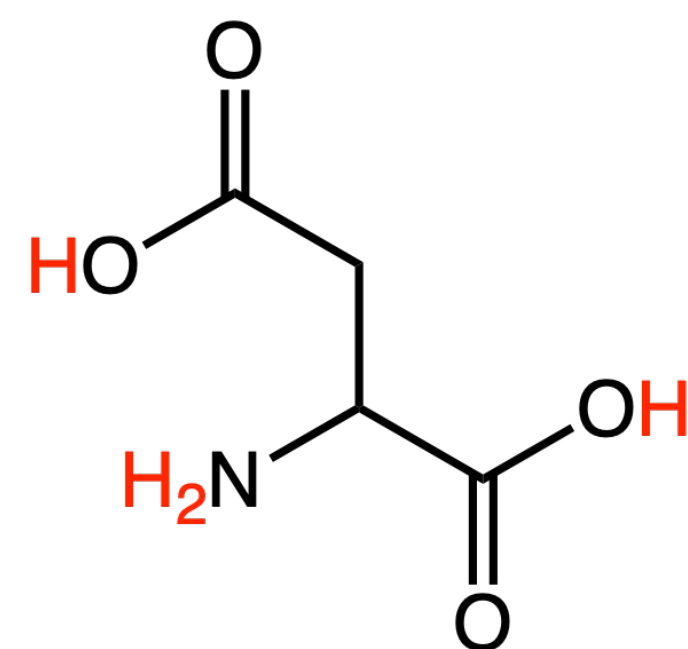
Oxalic Acid



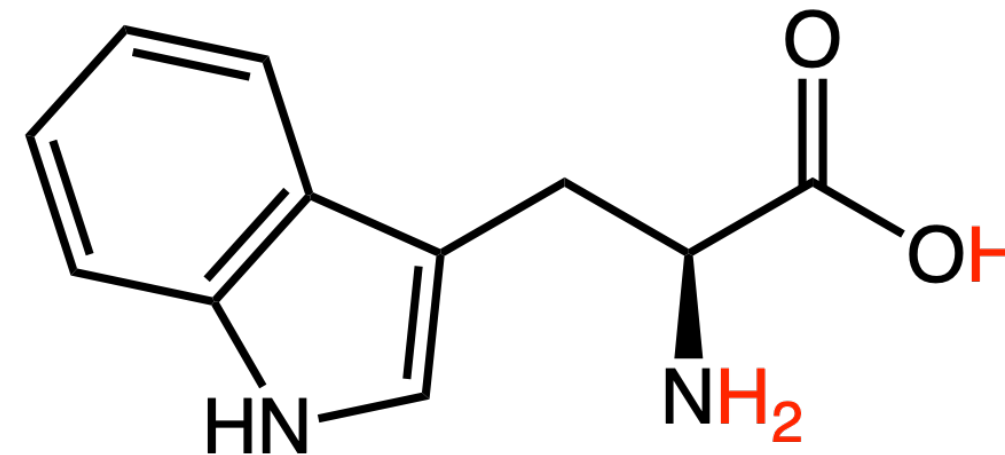
Citric Acid



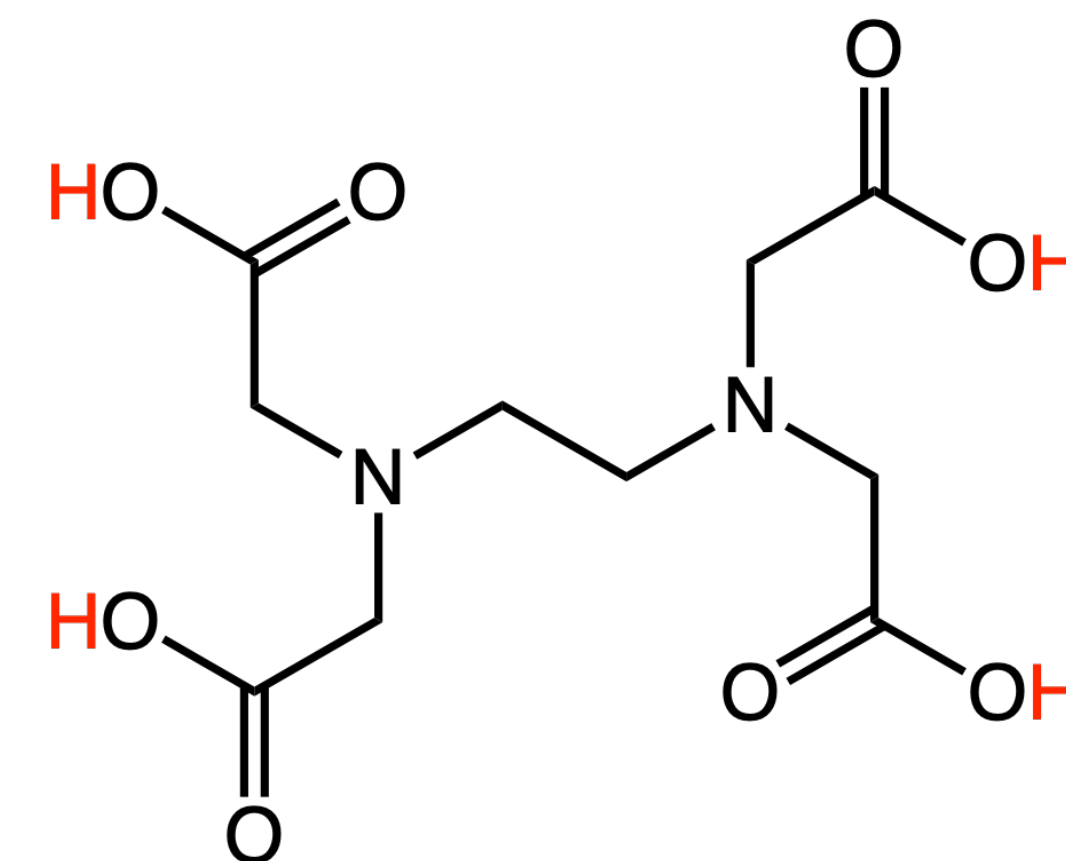
Nitrilotriacetic Acid



Aspartic Acid



Tryptophan



EDTA
(Ethylenediaminetetraacetic acid)

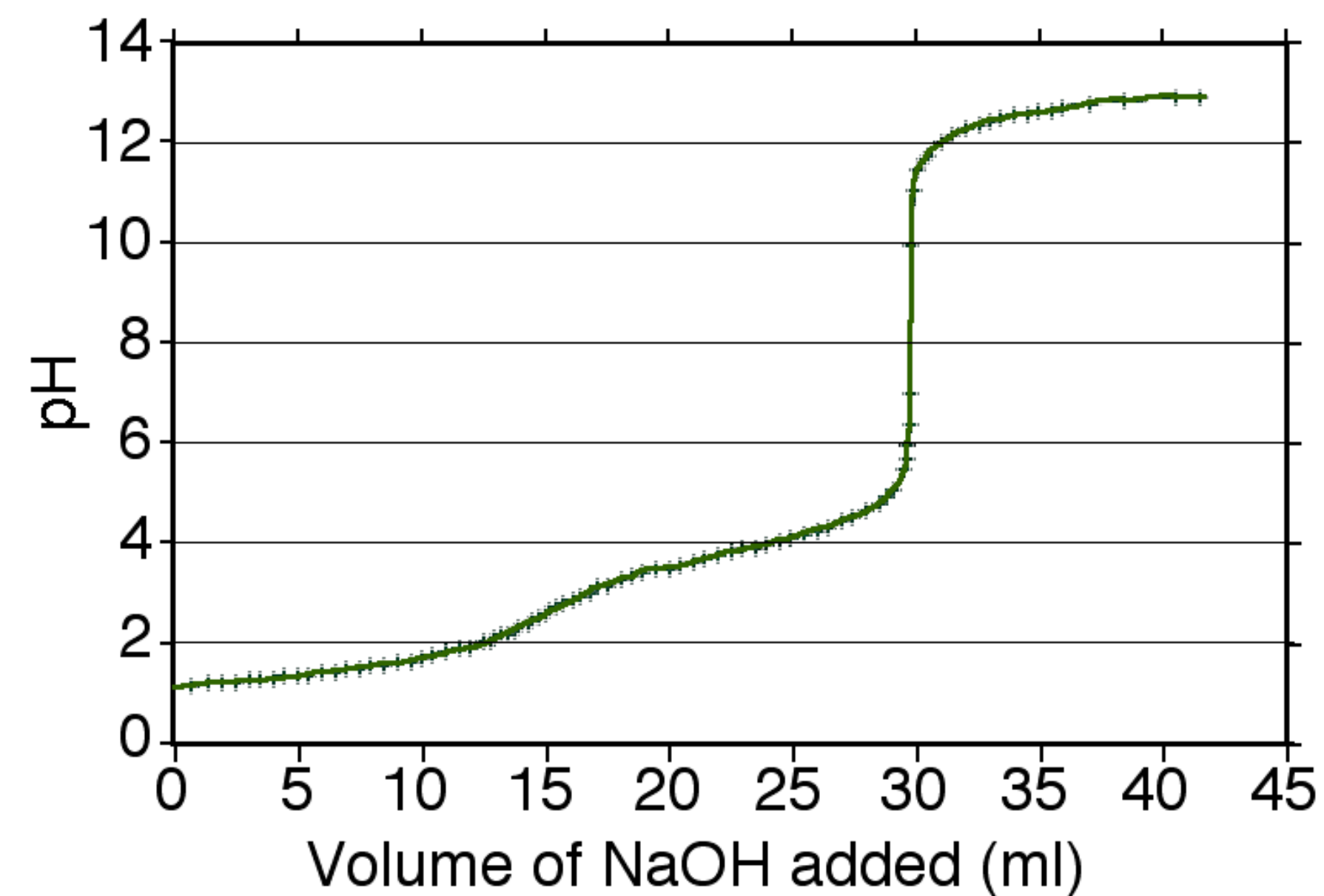
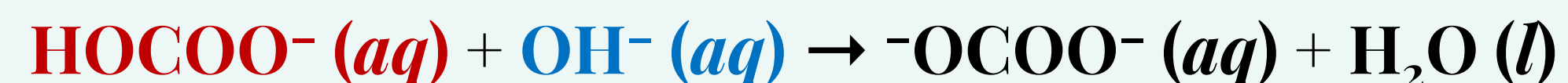
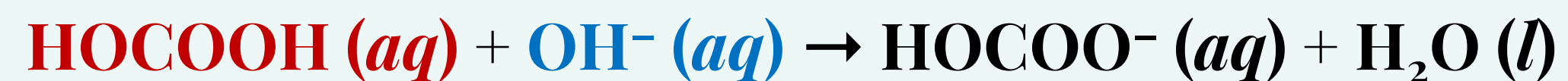
POLYPROTIC ACID TITRATION

Multiple equivalence points

In principle, when a **diprotic acid** is titrated with **NaOH** (a monoprotic strong base), two steep rises (equivalence points) are expected.

But, in practice, if the two K_a values are close together, the two steep rises overlap.

The titration curve for **oxalic acid** with **NaOH** has two overlapping steps.



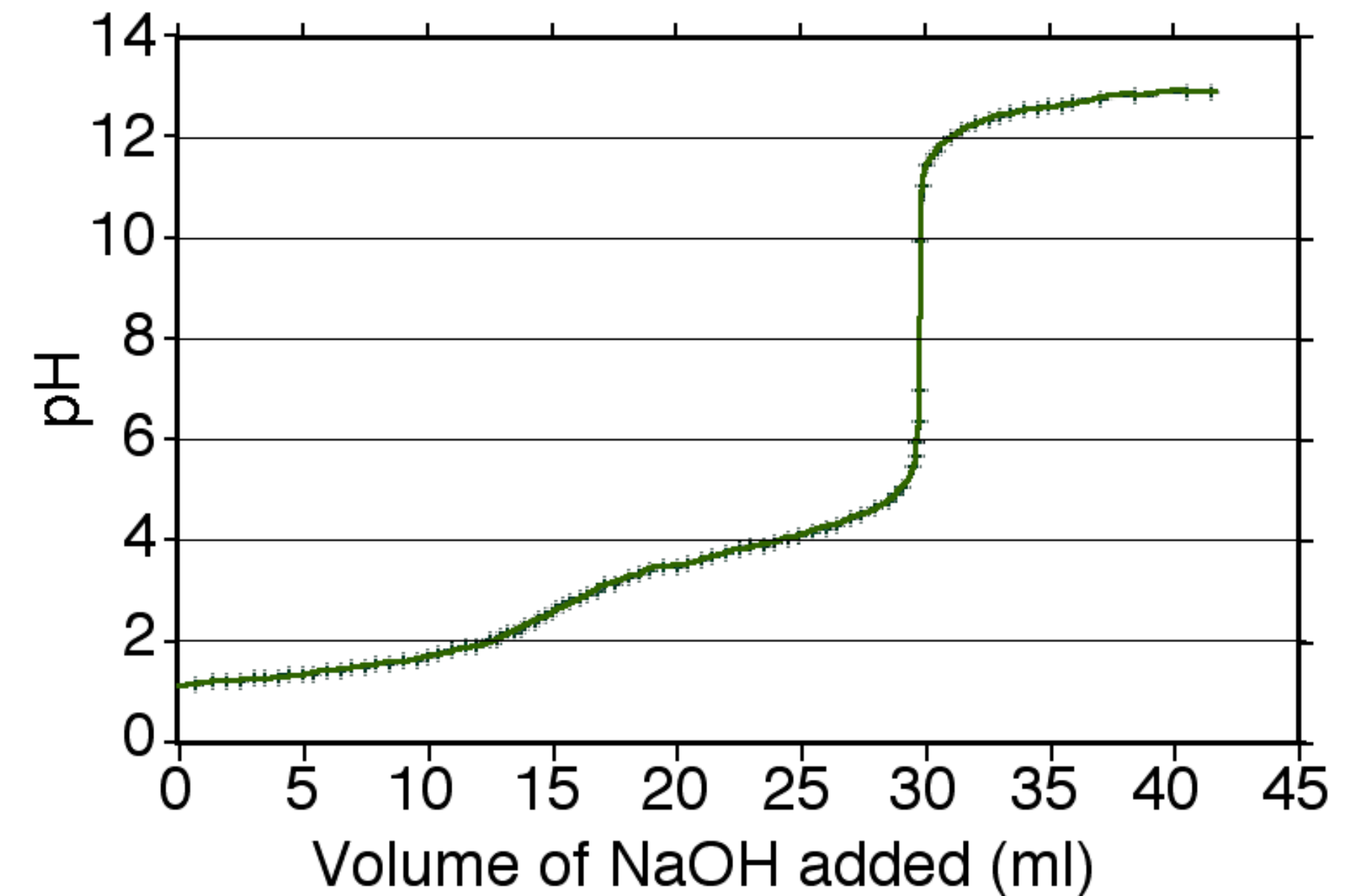
EQUIVALENCE POINT #1

Multiple equivalence points

In a **diprotic (polyprotic) acid** versus **NaOH** titration:

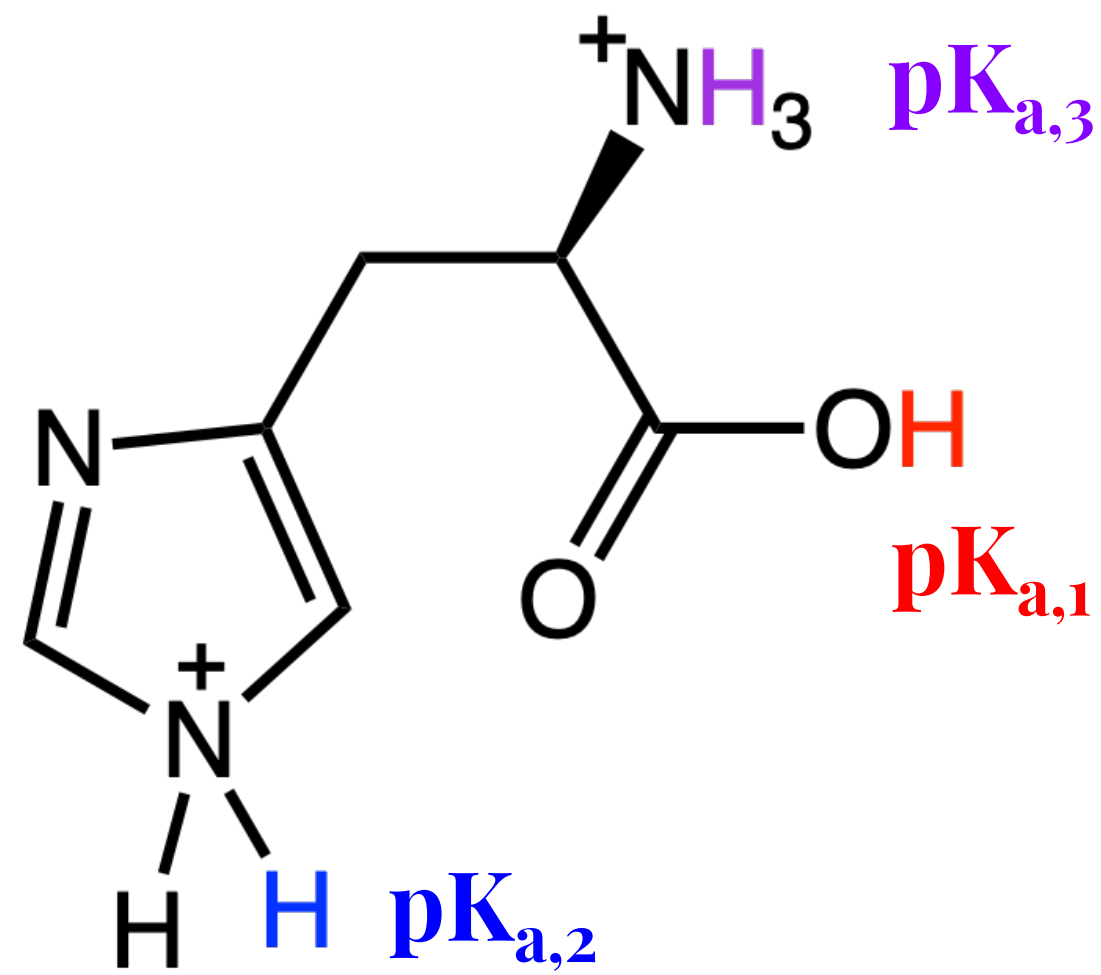
How is the volume at the 2nd equivalence point related to the volume at the first equivalence point?

Total volume of **NaOH** added to reach
the 2nd equivalence point
=
2× [Total volume of **NaOH** added to reach
the 1st equivalence point]



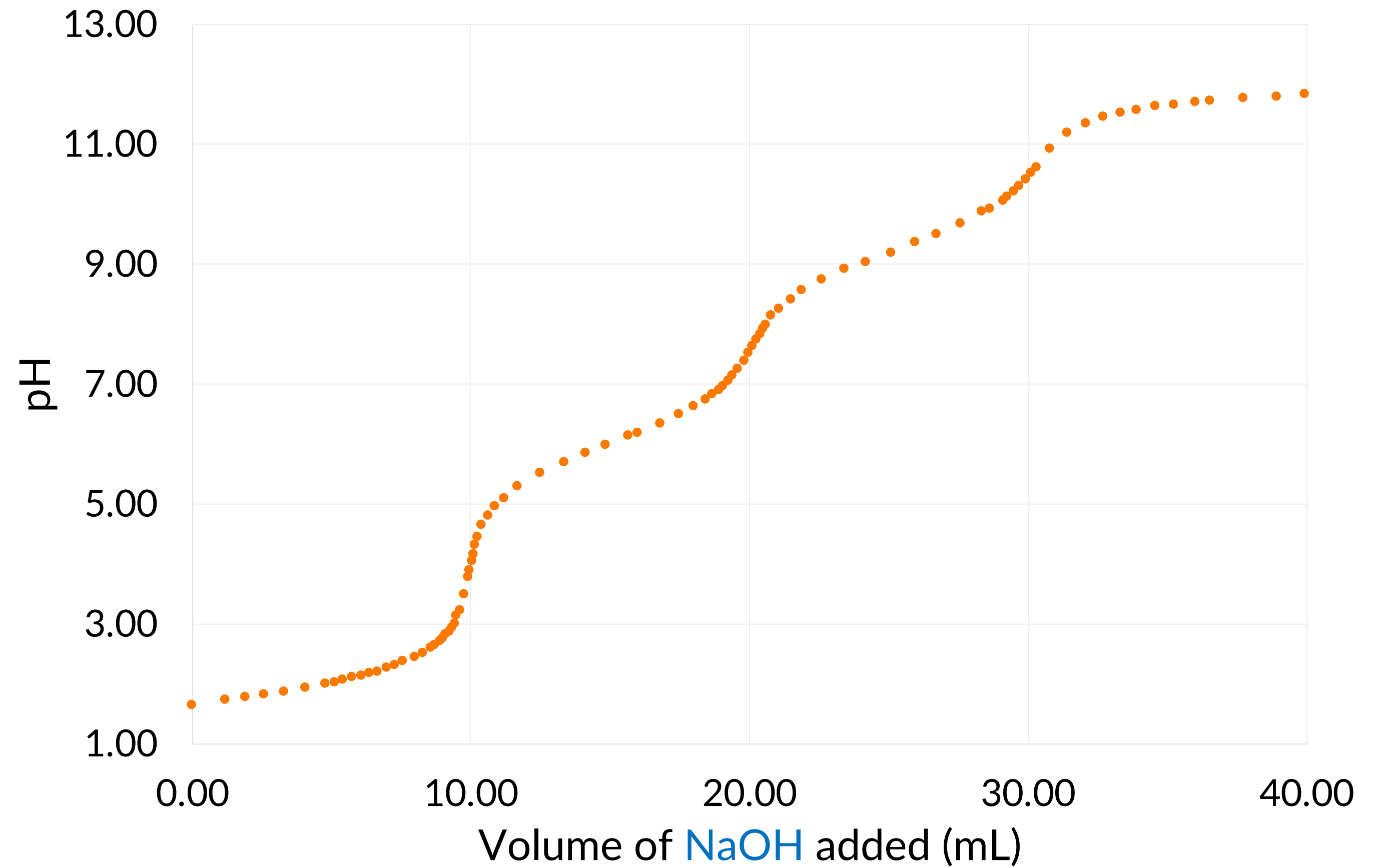
HISTIDINE (HIS, H)

An amino acid



Histidine is a triprotic amino acid, where

$$\begin{array}{ll} K_{a,1} = 3.0 \times 10^{-2} & pK_{a,1} = 1.52 \\ K_{a,2} = 1.1 \times 10^{-6} & pK_{a,2} = 5.96 \\ K_{a,3} = 5.2 \times 10^{-10} & pK_{a,3} = 9.28 \end{array}$$



HALF-EQUIVALENCE POINT

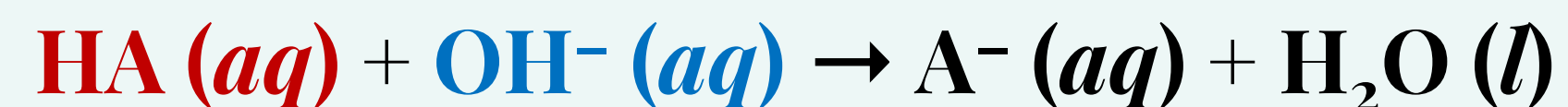
Significance

At the half-equivalence point:

$$\text{p}K_a = \text{pH}$$

Why?

In a **weak acid (HA)**-**strong base** titration, at the half-equivalence point:



$$n_{\text{HA}} = \frac{1}{2} \times n_{\text{HA,initial}} \quad n_{\text{A}^-} = \frac{1}{2} \times n_{\text{HA,initial}}$$

In other words, we have a buffer at the half-equivalence point because $[\text{HA}]_{\text{eq}} = [\text{A}^-]_{\text{eq}}$.

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

Notes

The pH electrode is delicate, so handle with care.
To work well, it needs to be well-immersed in the solution.

Plot both pH and its first derivative ($\partial\text{pH}/\partial V$).

Use $\partial\text{pH}/\partial V$ to choose **NaOH** increments during titration.

Near equivalence points, you must use very small increments of **NaOH** (i.e., one drop at a time).

If not, you will **NOT** be able to determine the equivalence point.