ACID BASE TITRATION

Titrant: solution of a known concentration, which is added to another solution whose concentration has to be determined.

Titrand or analyte: the solution whose concentration has to be determined.

Equivalence point: point in titration at which the amount of titrant added is just enough to completely neutralize the analyte solution. *At the equivalence point in an acid-base titration, moles of base = moles of acid and the solution only contains salt and water*.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \xrightarrow{\text{at equivalence point}} \underset{\text{salt}}{NaCl} + H_2O$$

Acid-base titrations are monitored by the change of pH as titration progresses

Indicator: It is a weak acid or base that is added to the analyte solution, and it changes color when the equivalence point is reached i.e. the point at which the amount of titrant added is just enough to completely neutralize the analyte solution. The point at which the indicator changes color is called the endpoint. So the addition of an indicator to the analyte solution helps us to visually spot the equivalence point in an acid-base titration.

Endpoint: refers to the point at which the indicator changes color in an acid-base titration.

What is a titration curve?

A titration curve is the plot of the pH of the analyte solution versus the volume of the titrant added as the titration progresses.

1) Titration of a strong acid with a strong base

Suppose our analyte is hydrochloric acid HCl (strong acid) and the titrant is sodium hydroxide NaOH (strong base). If we start plotting the pH of the analyte against the volume of NaOH that we are adding from the burette.

<u>Point 1</u>: No NaOH added yet, so the pH of the analyte is low (it predominantly contains H_3O^+ from dissociation of HCl).

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

<u>Point 2</u>: This is the pH recorded at a time point just before complete neutralization takes place.

<u>Point 3</u>: This is the equivalence point (halfway up the steep curve). At this point, moles of NaOH added = moles of HCl in the analyte. At this point, H_3O^+ ions are completely neutralized by OH^- ions. The solution only has salt (NaCl) and water and therefore the pH is neutral i.e. pH = 7.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \xrightarrow{\text{at equivalence point}} \underset{\text{salt}}{NaCl} + H_2O$$

<u>Point 4</u>: Addition of NaOH continues, pH starts becoming basic because HCl has been completely neutralized and now excess of OH^- ions are present in the solution (from dissociation of NaOH).

$$NaOH \xrightarrow{\text{after equivalence point}} Na^+ + OH^-$$

2) Titration of a weak acid with a strong base

Let's assume our analyte is acetic acid CH_3COOH (weak acid) and the titrant is sodium hydroxide NaOH (strong base). If we start plotting the pH of the analyte against the volume of NaOH that we are adding from the burette, we will get a titration curve as shown below.

Point 1: No NaOH added yet, so the pH of the analyte is low (it predominantly contains H_3O^+ from dissociation of CH_3 COOH). But acetic acid is a weak acid, so the starting pH is higher than what we noticed in case 1 where we had a strong acid (HCl).

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

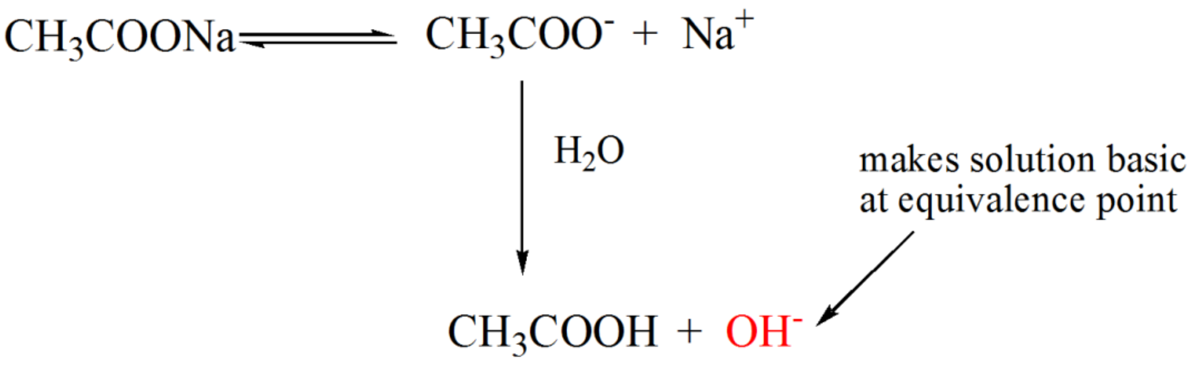
As NaOH is added dropwise, H_3O^+ slowly starts getting consumed by OH^- (produced by dissociation of NaOH). But analyte is still acidic due to predominance of H_3O^+

Point 2: This is the pH recorded at a time point just before complete neutralization takes place.

Point 3: This is the equivalence point (halfway up the steep curve). At this point, moles of NaOH added = moles of CH_3COOH in the analyte. The H_3O^+ are completely neutralized by OH^- ions. The solution contains only CH_3COONa salt and H_2O

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{NaOH} \xrightleftharpoons{\text{at equivalence point}} \underset{\text{salt}}{CH_3COONa} + H_2O$$

As you can see from the above equation, at the equivalence point the solution contains CH_3COONa salt. This dissociates into acetate ions CH_3COO^- and sodium ions Na^-. As you will recall from the discussion of strong/ weak acids in the beginning of this tutorial, CH_3COO^- is the conjugate base of the weak acid CH_3COOH. So CH_3COO^- is relatively a strong base (weak acid CH_3COOH has a strong conjugate base), and will thus react with H2O to produce hydroxide ions (OH^-) thus increasing the pH to ~ 9 at the equivalence point.



Point 4: Beyond the equivalence point (when sodium hydroxide is in excess) the curve is identical to HCl-NaOH titration curve.

3) Titration of a strong acid with a weak base

Suppose our analyte is hydrochloric acid HCl (strong acid) and the titrant is ammonia NH_3 (weak base). If we start plotting the pH of the analyte against the volume of NH_3 that we are adding from the burette

Point 1: No NH_3 added yet, so the pH of the analyte is low (it predominantly contains H_3O^+ from dissociation of HCl).

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

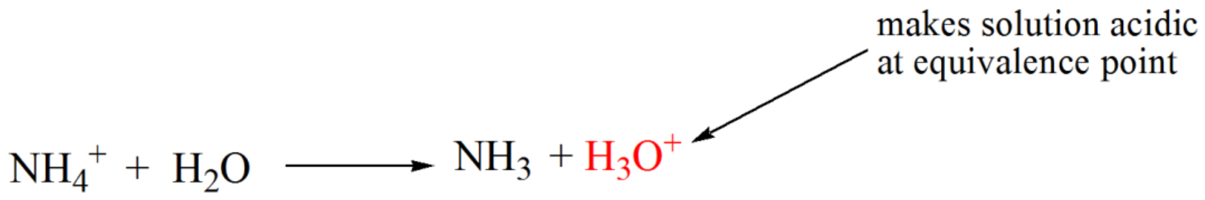
As $NH_3$is added dropwise, H_3O^+ slowly starts getting consumed by NH_3. Analyte is still acidic due to predominance of H_3O^+ ions.

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Point 2: This is the pH recorded at a time point just before complete neutralization takes place.

Point 3: This is the equivalence point (halfway up the steep curve). At this point, moles of NH_3 added = moles of HCl in the analyte. The H_3O^+ are completely neutralized by NH_3 . *In the case of a weak base versus a strong acid, the pH is not neutral at the equivalence point.* The solution is in fact acidic (pH ~ 5.5) at the equivalence point. Let's rationalize this.

At the equivalence point, the solution only has ammonium ions NH_4^+ and chloride ions Cl^-. But again if you recall, the ammonium ion NH_4^+ is the conjugate acid of the weak base NH_3. So NH_4^+ is a relatively strong acid (weak base NH_3 has a strong conjugate acid), and thus NH_4^+ will react with H_2O to produce hydronium ions making the solution acidic.



Point 4: After the equivalence point, NH_3 addition continues and is in excess, so the pH increases. NH_3 is a weak base so the pH is above 7, but is lower than what we saw with a strong base NaOH (case 1).

4) Titration of a weak base with a weak acid

Suppose our analyte is NH_3 (weak base) and the titrant is acetic acid CH_3COOH (weak acid). If we start plotting the pH of the analyte against the volume of acetic acid that we are adding from the burette, we will get a titration curve.

If you notice there isn't any steep bit in this plot. There is just what we call a 'point of inflexion' at the equivalence point. Lack of any steep change in pH throughout the titration renders titration of a weak base versus a weak acid difficult, and not much information can be extracted from such a curve.

To summarize

In an acid-base titration, a known volume of either the acid or the base (of unknown concentration) is placed in a conical flask.

The second reagent (of known concentration) is placed in a burette.

The reagent from the burette is slowly added to the reagent in the conical flask.

A titration curve is a plot showing the change in pH of the solution in the conical flask as the reagent is added from the burette.

A titration curve can be used to determine:

1) The equivalence point of an acid-base reaction (the point at which the amounts of acid and of base are just sufficient to cause complete neutralization).

2) The pH of the solution at equivalence point is dependent on the strength of the acid and strength of the base used in the titration.

-- For strong acid-strong base titration, pH = 7 at equivalence point
-- For weak acid-strong base titration, pH > 7 at equivalence point
-- For strong acid-weak base titration, pH < 7 at equivalence point