

An **acid–base titration** is the determination of the **concentration** of an acid or base by exactly neutralizing the acid or base with an acid or base of known concentration.

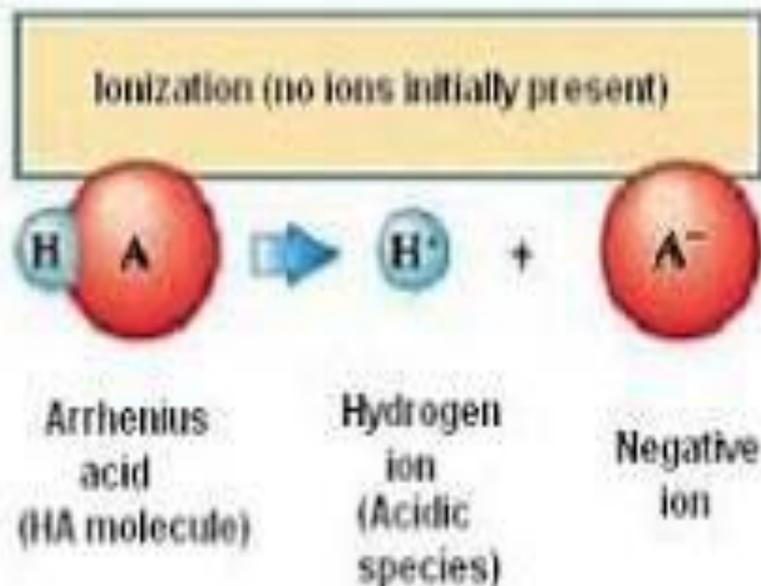
The Arrhenius Theory of acids and bases

The theory

- Acids are substances which produce hydrogen ions in solution.
- Bases are substances which produce hydroxide ions in solution.



Many scientists contributed to the theories of acid and bases describing acid base properties. **Arrhenius theory**, introduced in 1887 by the Swedish scientist Svante Arrhenius, that acids are substances that **dissociate** in water to yield electrically charged atoms or molecules, called ions, one of which is a hydrogen ion (H^+), and that bases **ionize** in water to yield hydroxide ions (OH^-).



Electrolyte Ions

Neutralization happens because hydrogen ions and hydroxide ions react to produce water.

Limitations of the theory

Hydrochloric acid is neutralised by both sodium hydroxide solution and ammonia solution. In both cases, you get a colourless solution which you can crystallise to get a white salt - either sodium chloride or ammonium chloride. These are clearly very similar reactions. The full equations are:

In the sodium hydroxide case, hydrogen ions from the acid are reacting with hydroxide ions from the sodium hydroxide - in line with the Arrhenius theory.

However, in the ammonia case, there don't appear to be any hydroxide ions. But if you look at the equations carefully, the ammonia is in solution - $\text{NH}_3(\text{aq})$. Ammonia reacts with water like this:

This is a reversible reaction, and in a typical dilute ammonia solution, about 99% of the ammonia remains as ammonia molecules. Nevertheless, there are hydroxide ions there and those react with hydrogen ions in just the same way as hydroxide ions from sodium hydroxide.

So you can just about justify ammonia as being a base on the Arrhenius definition - it does produce hydroxide ions in solution. But most of the reaction is going to be a direct reaction between ammonia molecules and hydrogen ions - which doesn't fit the Arrhenius definition.

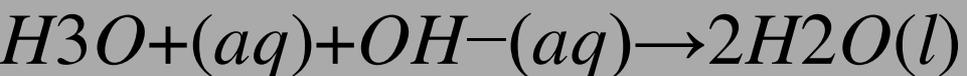
The Bronsted-Lowry Theory of acids and bases

- An acid is a proton (hydrogen ion) donor.
- A base is a proton (hydrogen ion) acceptor.

The Brønsted-Lowry theory does not go against the Arrhenius theory in any way - it just adds to it. Hydroxide ions are still bases because they accept hydrogen ions from acids and form water. An acid produces hydrogen ions in solution because it reacts with the water molecules by giving a proton to them. When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule. A **coordinate (dative covalent) bond** is formed between one of the lone pairs on the oxygen and the hydrogen from the HCl . **Hydronium ions**, $H_3O^+(aq)$, are produced.

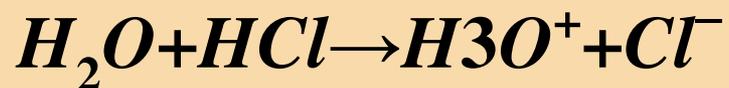


When acid in solution reacts with a base, what is actually functioning as the acid is the hydronium ion. For example, a proton is transferred from a hydronium ion to a hydroxide ion to make water.

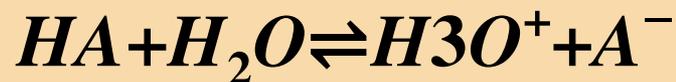


Conjugate pairs

When hydrogen chloride dissolves in water, almost 100% of it reacts with the water to produce **hydronium ions and chloride ions**. Hydrogen chloride is a strong acid, and we tend to write this as a one-way reaction:



In fact, the reaction between HCl and water is reversible, but only to a very minor extent. To generalize, consider an acid HA and think of the reaction as being reversible.



Thinking about the forward reaction:

- The HA is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the HA.

However, there is also a back reaction between the hydronium ion and the A^- ion:

➤ The H_3O^+ is an acid because it is donating a proton (hydrogen ion) to the A^- ion.

The A^- ion is a base because it is accepting a proton from the H_3O^+ .

The reversible reaction contains two acids and two bases. We think of them in pairs, called *conjugate pairs*.

When the acid, HA , loses a proton it forms a base, A⁻ , which can accept a proton back again to reform the acid, HA . These two are a *conjugate pair*. Members of a conjugate pair differ from each other by the presence or absence of the transferable hydrogen ion.

- If you are thinking about HA as the acid, then A⁻ is its conjugate base.
- If you are thinking about A⁻ as the base, then HA is its conjugate acid. **Second ex.**

The Lewis Theory of acids and bases

This theory extends well beyond the things you normally think of as acids and bases.

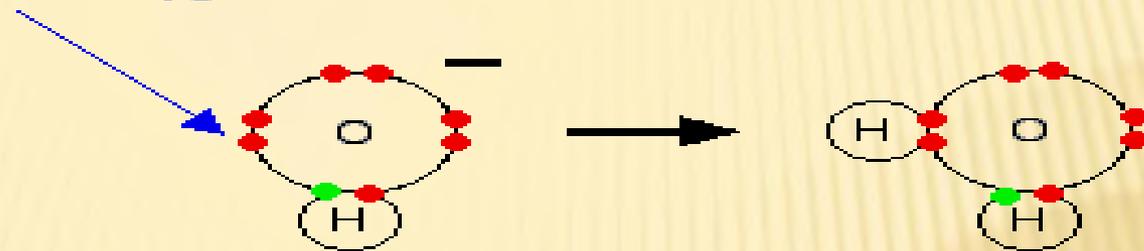
An acid is an electron pair acceptor.

A base is an electron pair donor.

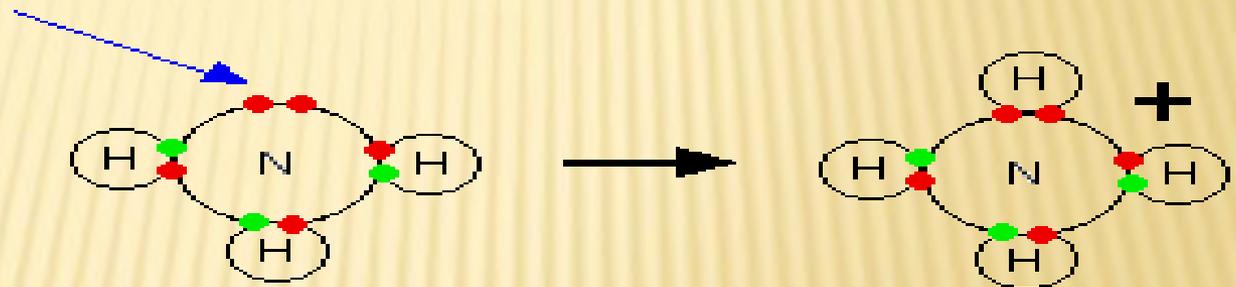
Lewis bases

It is easiest to see the relationship by looking at exactly what Brønsted-Lowry bases do when they accept hydrogen ions. Three Brønsted-Lowry bases we've looked at are hydroxide ions, ammonia and water, and they are typical of all the rest.

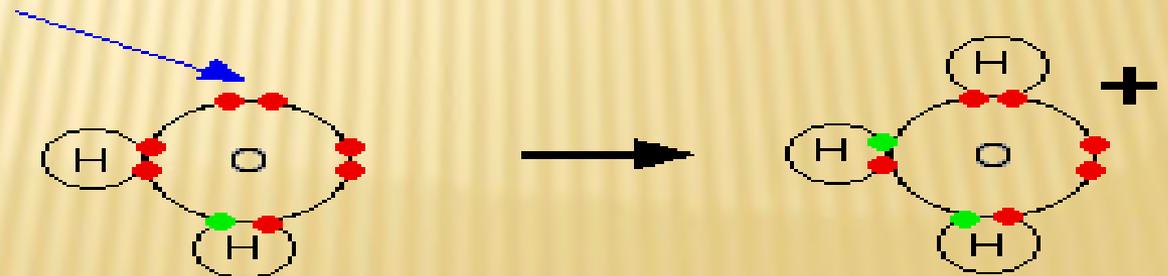
A hydroxide ion picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



Ammonia picks up a hydrogen ion by attaching it to the lone pair on the nitrogen.

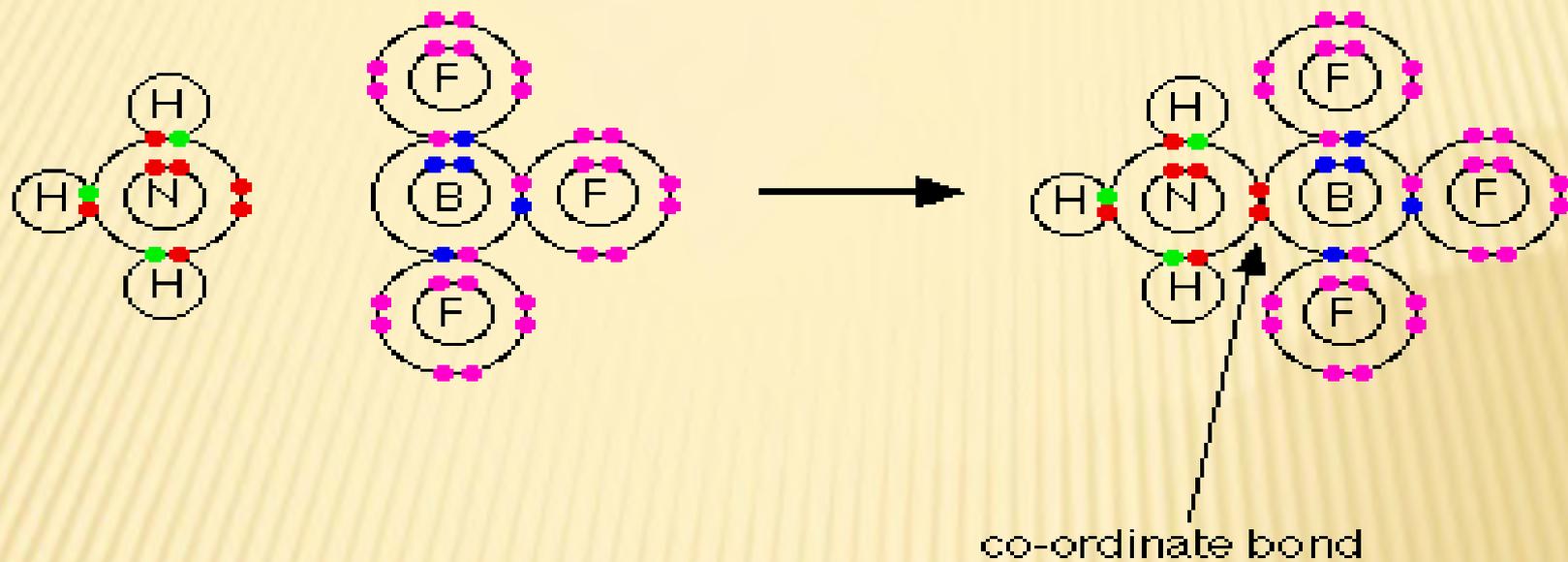


Water picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



The Brønsted-Lowry theory says that they are acting as bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pairs of electrons - which is what the Lewis theory says. The two are entirely consistent. So how does this extend the concept of a base?

But what about other similar reactions of ammonia or water, for example? On the Lewis theory, any reaction in which the ammonia or water used their lone pairs of electrons to form a co-ordinate bond would be counted as them acting as a base. Here is a reaction which you will find talked about on the page dealing with co-ordinate bonding. Ammonia reacts with BF_3 by using its lone pair to form a co-ordinate bond with the empty orbital on the boron.



Lewis acids

Lewis acids are electron pair acceptors. In the above example, the BF₃ is acting as the Lewis acid by accepting the nitrogen's lone pair. On the Brønsted-Lowry theory, the BF₃ has nothing remotely acidic about it. This is an extension of the term acid well beyond any common use.

What about more obviously acid-base reactions - like, for example, the reaction between ammonia and hydrogen chloride

The lone pair on the nitrogen of an ammonia molecule is attracted to the slightly positive hydrogen atom in the HCl. As it approaches it, the electrons in the hydrogen-chlorine bond are repelled still further towards the chlorine. Eventually, a coordinate bond is formed between the nitrogen and the hydrogen, and the chlorine breaks away as a chloride ion.

The whole HCl molecule is acting as a Lewis acid. It is accepting a pair of electrons from the ammonia, and in the process it breaks up.

CLASSIFICATION-

These are normal titration between acids and base dissolved in water. Hence the name aqueous titration

Strong acid V/s strong base: Here are strong acid reacts with a strong base to form **salt and water**. The reaction of this type is very fast and also complete. The reaction happens in **stoichiometric** means i.e. each molecule of acid reacts with corresponding molecule of base. At the end of reaction no molecule of acid or base exists as every molecule in the reaction has completely reacted to form **salt**. Hence the end point or equivalenc epoint is **precise and sharp** Reaction .



The pH at end point is neutral i.e. 7

Strong Acid v/s Weak Base: Here a strong acid reacts with weak base to form salt and water. But since the reaction uses strong acid, the pH at end point will be towards acidic i.e. **below 7**.



During reaction, known concentration of strong acid is taken in a burette and allowed to react drop by drop with the base in a beaker.

Weak Acid V/s Strong Base: Here the reaction happens between a weak acid and strong base. The weak acid is taken in a beaker and known quantity of strong base is dropped from a burette till the end point.



The salt formed is slightly **basic** in nature so the pH at end point is **above 7**

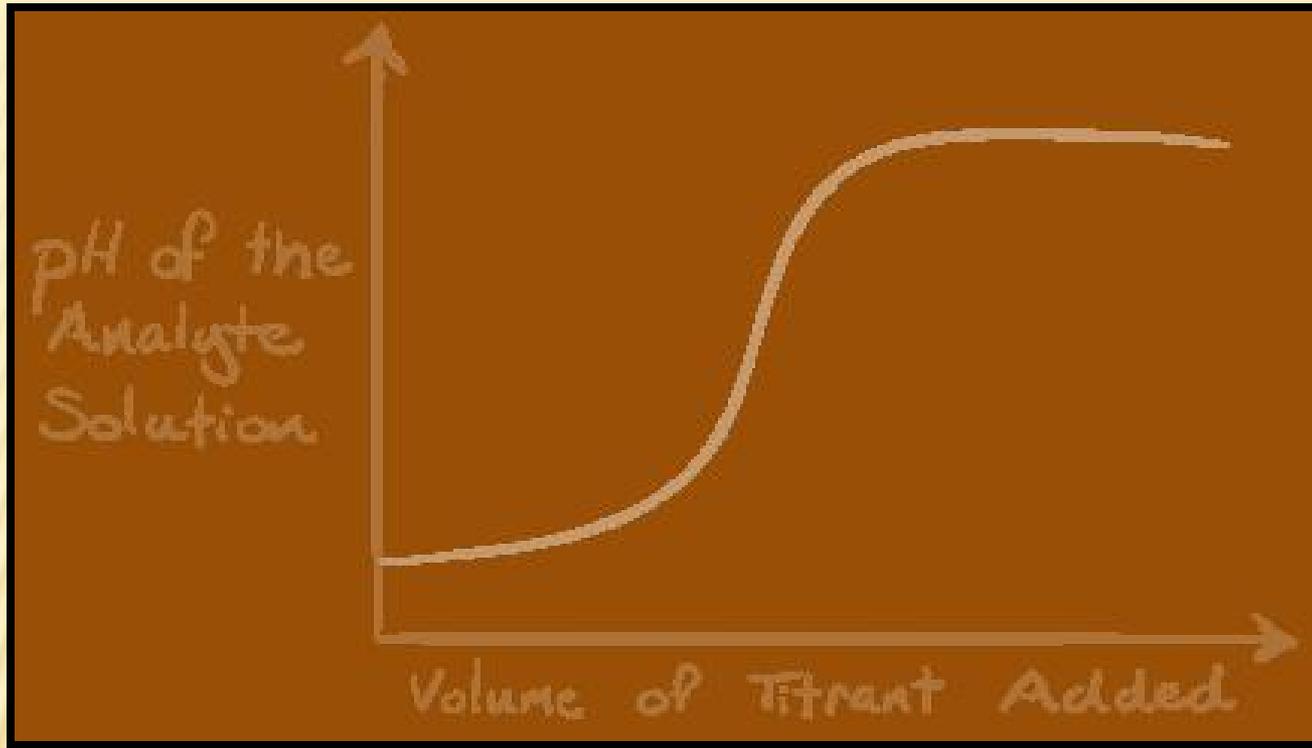
Weak Acid V/s Weak Base: Here both acid and base are **weak**. So mostly they are **avoided** due to **imprecise** end points. At the end point, the pH will be **7 theoretically**. But cannot be measured precisely .



pH TITRATION CURVE/NEUTRALIZATION CURVE

When you carry out a simple acid-base titration, you use an **indicator** to tell you when you have the acid and alkali mixed in exactly the right proportions to "**neutralise**" each other. When the **indicator changes colour**, this is often described as the *end point* of the titration.

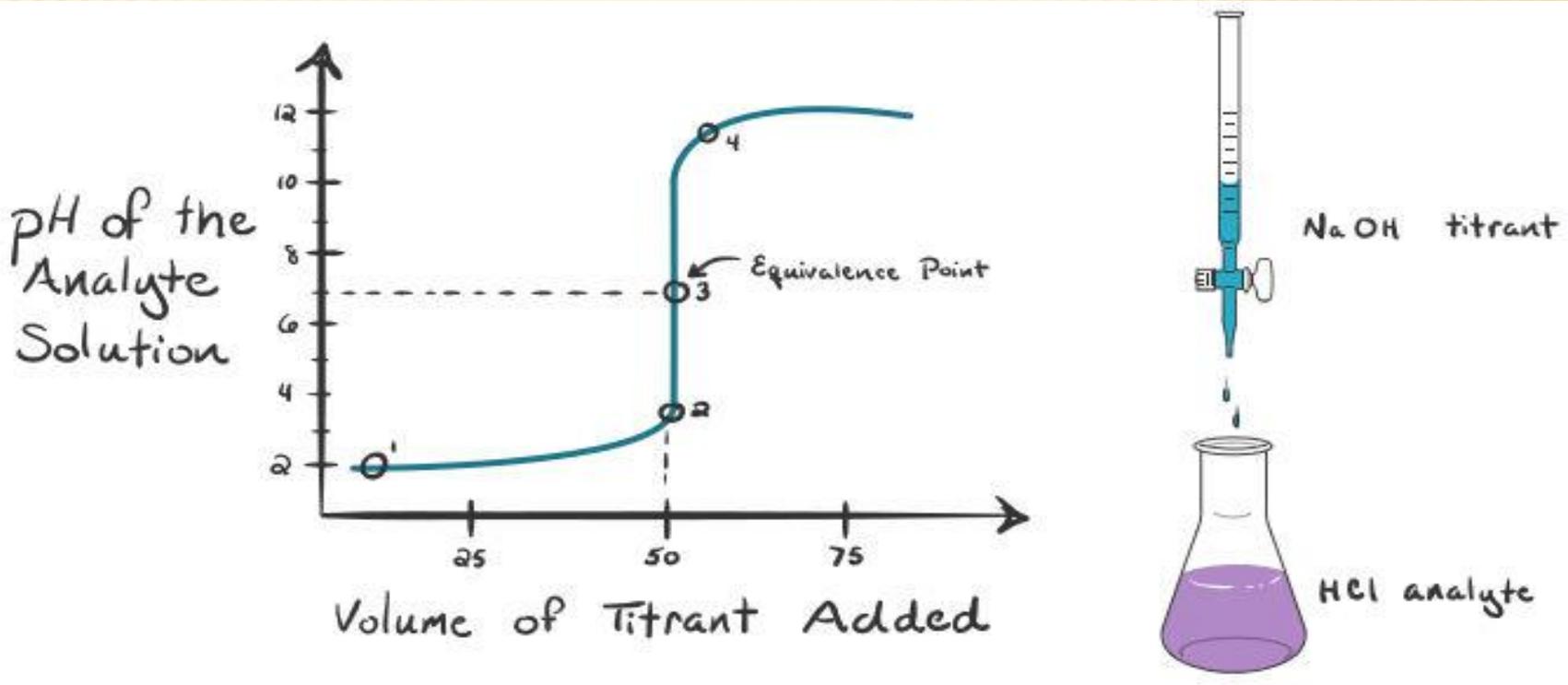
The **colour** change would happen when you **mix the two solutions** together in exactly **equation proportions**. That particular mixture is known as the *equivalence point*.



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, we will get a **titration curve** as shown below.



Point 1: No NaOH added yet, so the pH of the analyte is low. As NaOH is added dropwise,

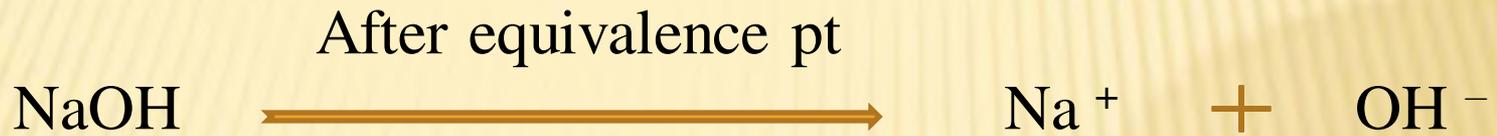


As NaOH is added dropwise, H_3O^+ slowly starts getting consumed by OH^- produced by dissociation of NaOH, Analyte is still acidic due to predominance H_3O^+

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 HCl in the analyte. At this point, H_3O^+ ions are completely neutralized by OH^- . The solution only has salt (NaCl) and water and therefore the pH is neutral i.e. pH = 7.



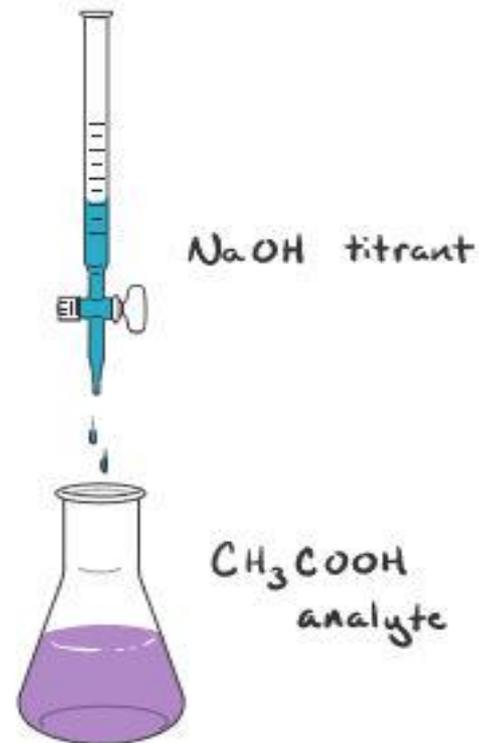
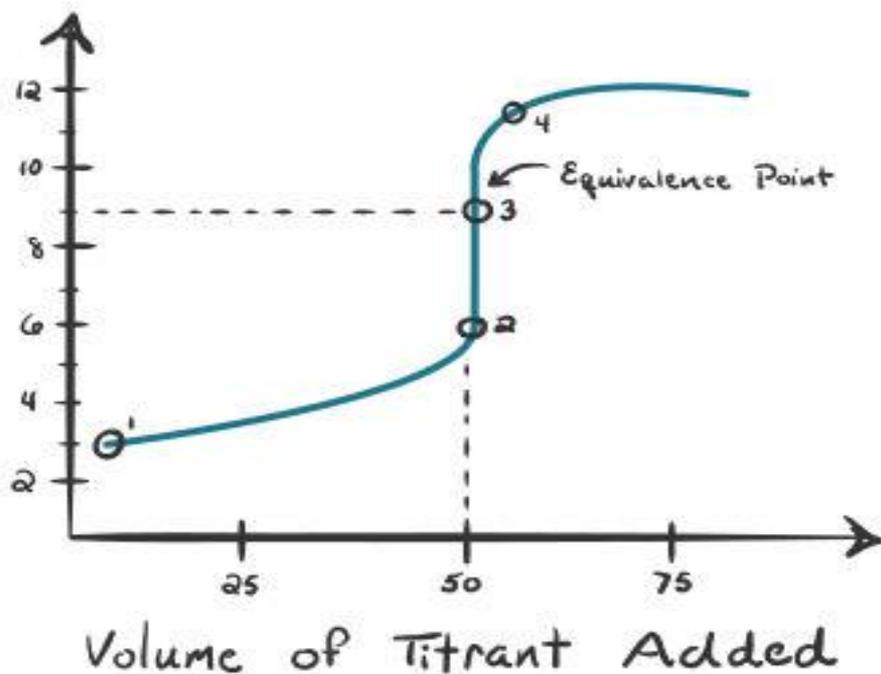
Point 4: Addition of NaOH continues, pH starts becoming basic because HCl has been completely neutralized and now excess of OH⁻ ions are present in the solution (from dissociation of NaOH).



2) Titration of a weak acid with a strong base

Assume analyte is **acetic acid CH₃COOH** (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

pH of the Analyte Solution



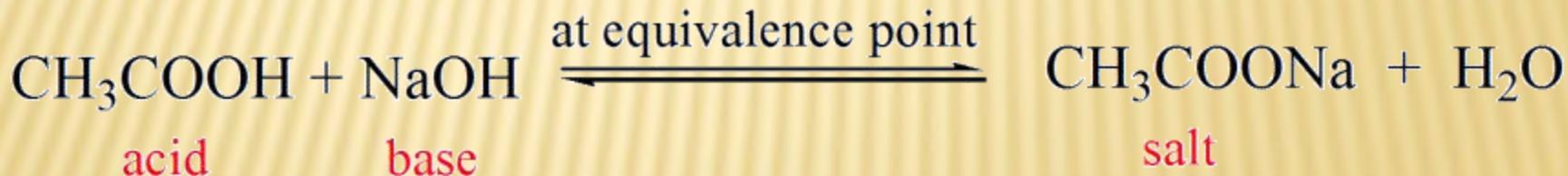
Point 1: No NaOH added yet, so the pH of the analyte is low (it predominantly contains H₃O⁺ from dissociation of CH₃COOH). But acetic acid is a weak acid, so the starting pH is higher.



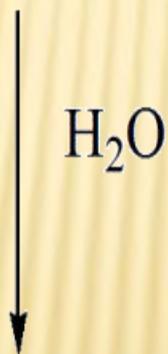
As NaOH is added drop wise, H₃O⁺ slowly starts getting consumed by OH⁻ (produced by dissociation of NaOH). But analyte is still acidic due to predominance of H₃O⁺ ions.

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 CH₃COOH in the analyte. The H₃O⁺ ions are completely neutralized by OH⁻ ions. The solution contains only CH₃COONa salt and H₂O.



at the equivalence point the solution contains CH_3COONa salt. This dissociates into acetate ions CH_3COO^- and sodium ions Na^+ , CH_3COO^- is the conjugate base of the weak acid CH_3COOH . So, CH_3COO^- a strong base (weak acid CH_3COOH has a strong conjugate base), and will thus react with H_2O to produce hydroxide ions (OH^-) thus increasing the pH to ~ 9 at the equivalence point.

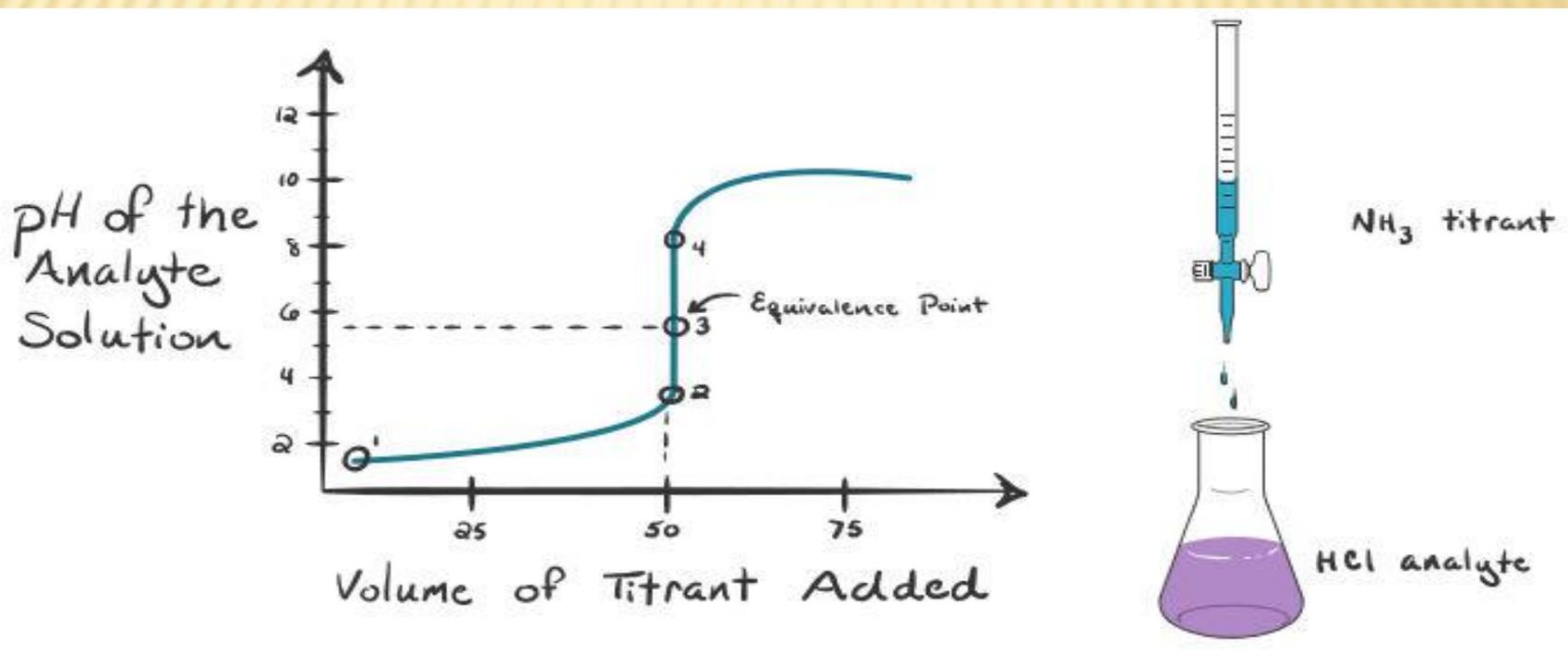


makes solution basic
at equivalence point

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 . If we start plotting the pH of the analyte against the volume of NH_3 that we are adding from the burette, we will get a titration curve as shown below.



Point 1: No NH₃ added yet, so the pH of the analyte is low



As NH₃ is added dropwise, H₃O⁺ slowly starts getting consumed by NH₃. Analyte is still acidic due to predominance of H₃O⁺ ions.



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

Point 3: This is the equivalence point. At this point, moles of NH₃ added = moles of HCl in the analyte. The H₃O⁺ ions are completely neutralized by NH₃. In this case *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.

At the equivalence point, the solution only has ammonium ions NH₄⁺ and chloride ions Cl⁻, the ammonium ion NH₄⁺ is the conjugate acid of the weak base NH₃. So NH₄⁺ is a relatively strong acid (weak base NH₃ strong conjugate acid), and thus NH₄⁺ will react with H₂O to produce hydronium ions making the solution acidic.



makes solution acidic
at equivalence point

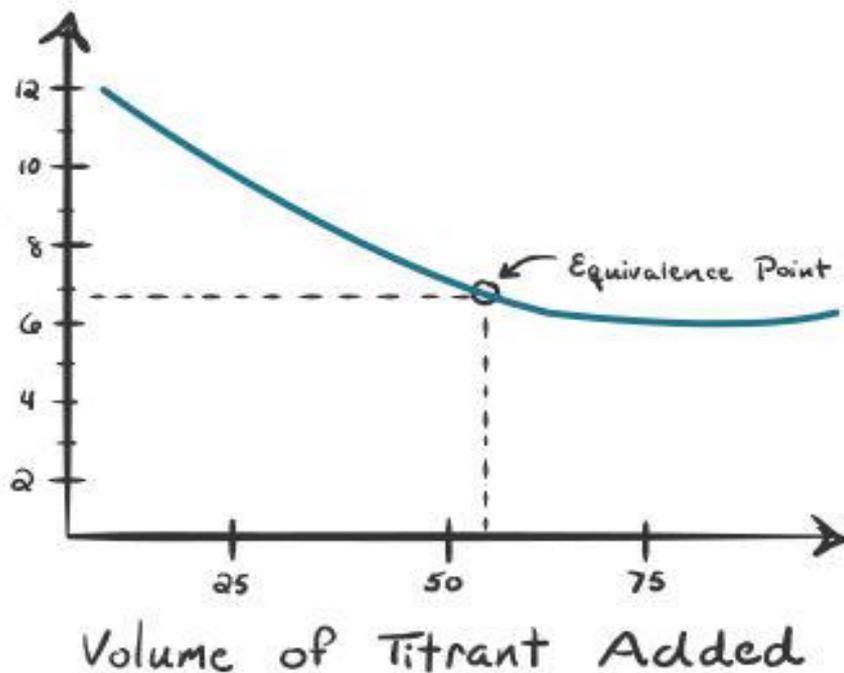


Point 4: After the equivalence point, NH_3 addition continues and is in excess, so the pH increases. NH_3 is a weak base so the pH is above 7, but is lower than what we saw with a strong base NaOH

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 as shown below.

pH of the
Analyte
Solution



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

ACKNOWLEDGEMENT

This power point presentation is part of following sites

- ❑ https://en.wikipedia.org/wiki/Acid%E2%80%93base_titration
- ❑ <https://www.khanacademy.org/test-prep/mcat/chemical-processes/titrations-and-solubility-equilibria/a/acid-base-titration-curves>
- ❑ <https://opentextbc.ca/chemistry/chapter/14-7-acid-base-titrations/>
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