ACID-BASE TITRATION & CURVES

The Concept of a Weak/Strong Acid and Weak/Strong Base:

A strong acid dissociates (or ionizes) completely in aqueous solution to form hydronium ions (HO$_3$+)

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

Diagram of strong acid ionizing to form hydronium ions

A weak acid does not dissociate completely in aqueous solution to form hydronium ions (HO3+)

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

Diagram of weak acid not dissociating completely to form hydronium ions

A strong base dissociates completely in aqueous solution to form hydroxide ions (OH$^-$)

$$NaOH \longrightarrow Na^+ + OH^-$$

Diagram of strong base dissociating to form hydroxide ions

A weak base does not dissociate completely in aqueous solution to form hydroxide ions (OH$^-$).

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Diagram of weak base not dissociating completely to form hydroxide ions

Examples of weak/strong acids and bases

Type	**Examples**
Strong Acids	hydrochloric acid (HCl), sulfuric acid (H2SO4), nitric acid (HNO3).
Weak Acids	acetic acid (CH3COOH), hydrofluoric acid (HF), oxalic acid (COOH)2
Strong Bases	sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH)
Weak Bases	ammonium hydroxide (NH4OH), ammonia (NH3)

Weak acids and weak bases always exist as conjugate acid-base pairs in an aqueous solution as represented below

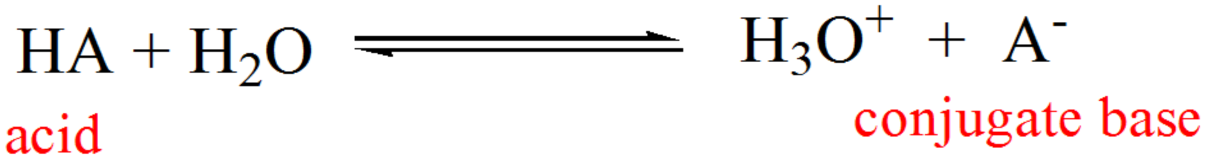


Diagram of HA acid and A- conjugate base

Here, HA is the acid and A- is termed as the conjugate base of HA

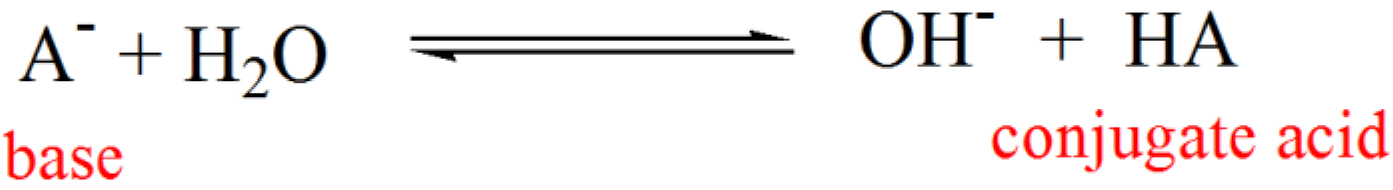
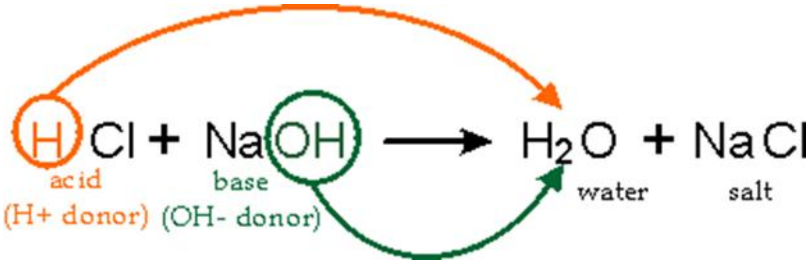


Diagram of A- base and HA conjugate base

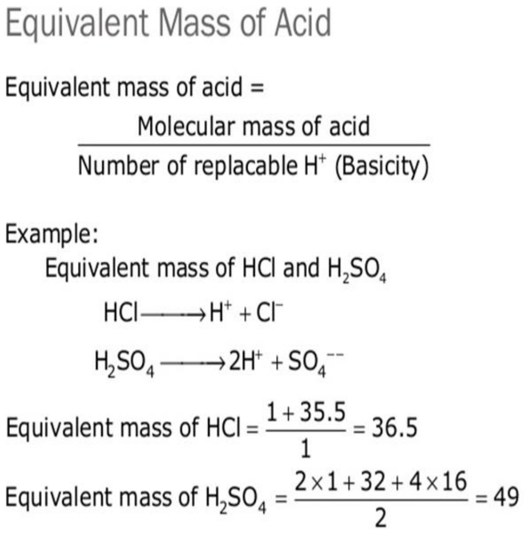
In the above reaction, A- is a base and HA is the conjugate acid of A-.

Rule of thumb is: Weak acids have strong conjugate bases, while weak bases have strong conjugate acids. As shown in the above two reactions, if HA is a weak acid, then its conjugate base A- will be a strong base. Similarly, if A- is a weak base, then its conjugate acid HA will be a strong acid.

The Concept of Equivalence:



- Molecular weight of HCl: 36.5 g, NaOH: 40.0g, NaCl: 58.5g, & H_2O is 18.0g respectively.
- 36.5 parts by weight of HCl are chemically equivalent to 40.0 parts by weight of NaOH.
- If to 36.5 g HCl, 100 g NaOH is added, only 40.0g alkali will react (which is chemically equivalent to 36.5 g HCl) and rest 60.0g will remain unreacted. This is the principle of CHEMICAL EQUIVALENCE.



Equivalent Mass of Acid

Equivalent mass of acid =

$$\frac{\text{Molecular mass of acid}}{\text{Number of replacable } H^+ \text{ (Basicity)}}$$

Example:

Equivalent mass of HCl and H_2SO_4

$$HCl \longrightarrow H^+ + Cl^-$$

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{--}$$

$$\text{Equivalent mass of HCl} = \frac{1+35.5}{1} = 36.5$$

$$\text{Equivalent mass of } H_2SO_4 = \frac{2\times1+32+4\times16}{2} = 49$$

Equivalent Mass of Base

Equivalent mass of base =

$$\frac{\text{Molecular mass}}{\text{Number of replacable OH}^{-}\text{ (Acidity)}}$$

Example:

Equivalent mass of NaOH and $Ca(OH)_2$

$$NaOH \longrightarrow Na^{+} + OH^{-}$$

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2OH^{-}$$

$$\text{Equivalent mass of NaOH} = \frac{23+16+1}{1} = 40$$

$$\text{Equivalent mass of } Ca(OH)_2 = \frac{40+2\times16+2\times1}{2} = 37$$

Equivalent mass of salt

Equivalent mass of salt =

$$\frac{\text{Molecular mass}}{\text{Total number of positive or negative charge}}$$

Example:

Equivalent mass of NaCl and $MgCl_2$

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

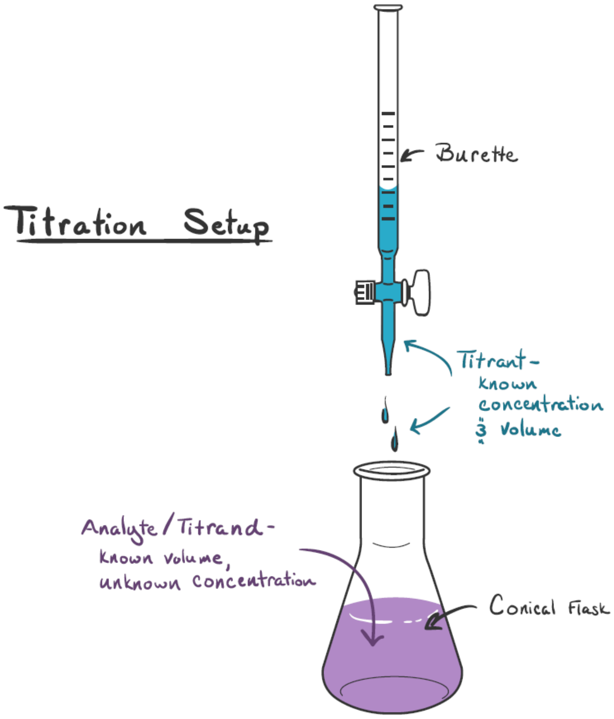
$$\text{Equivalent mass of NaCl} = \frac{23+35.5}{1} = 58.5$$

$$MgCl_2 \longrightarrow Mg^{++} + 2Cl^{-}$$

$$\text{Equivalent mass of } MgCl_2 = \frac{240+2\times35.5}{2} = 47.5$$

Titration

How do we define ‘titration’?



Titration setup with burette and conical flask

Titration is a technique to determine the concentration of an unknown solution. As illustrated in the titration setup above, a solution of known concentration (titrant) is used to determine the concentration of an unknown solution (titrand or analyte).

Typically, the titrant (the solution of known concentration) is added through a burette to a known volume of the analyte (the solution of unknown concentration) until the reaction is complete. Knowing the volume of titrant added allows us to determine the concentration of the unknown analyte. Often, an indicator is used to signal the end of the reaction, the endpoint. Titrant and analyte is a pair of acid and base. Acid-base titrations are monitored by the change of pH as titration progresses.

Terminologies Used in Titration/Titration Curves:

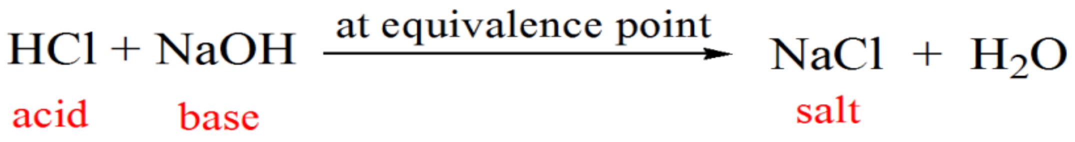
If you wish to find the concentration of an acid solution, you would titrate the acid solution with a solution of a base (alkai) of known concentration - **alkalimetry**

You titrate a base of unknown concentration with an acid of known concentration – **acidimetry.**

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.



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

Diagram of equivalence point

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

Indicator/Indicators:

- Chemists often use a chemical dye rather than a pH meter to detect the equivalence point of an acid-base titration.
- Chemical dyes whose colors are affected by acidic and basic solutions are called acid-base indicators.
- Many natural substances act as indicators. example(s):

If you use lemon juice in your tea, you might have noticed that the brown color of tea gets lighter when lemon juice is added.

Tea contains compounds called polyphenols that have slightly ionizable hydrogen atoms and therefore are weak acids.

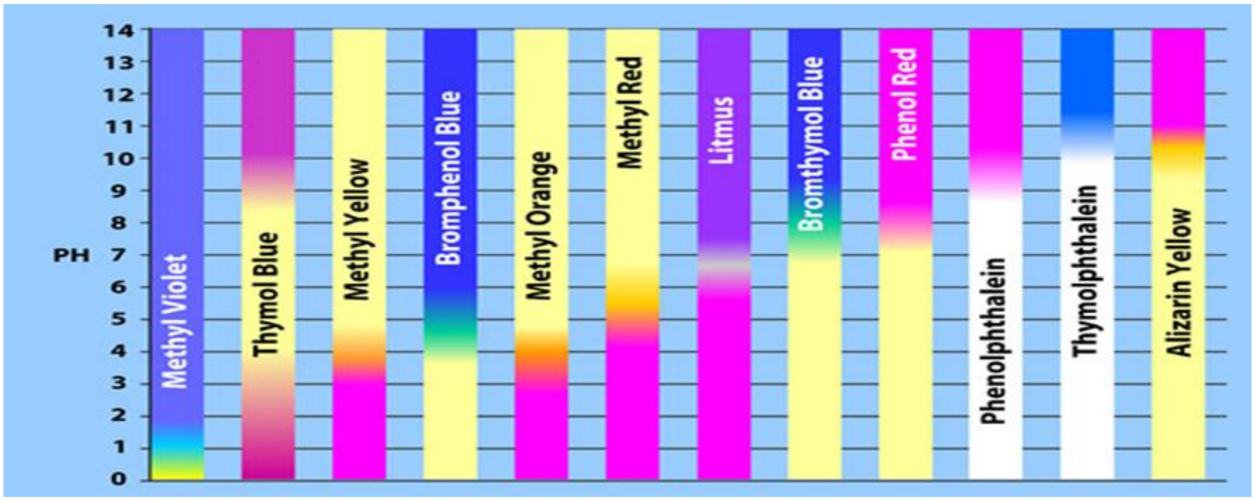
Adding acid in the form of lemon juice to a cup of tea lessens the degree of ionization, and the color of the un-ionized polyphenols becomes more apparent.

For the purposes of titration, it’s good enough to know that an indicator 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.

Chemists have several choices in selecting indicators: examples of indicators are

Properties of an indicator:

- Must have an easily observed colour change.
- Must change easily in the required pH range over the addition of ‘half’ a drop of reagent

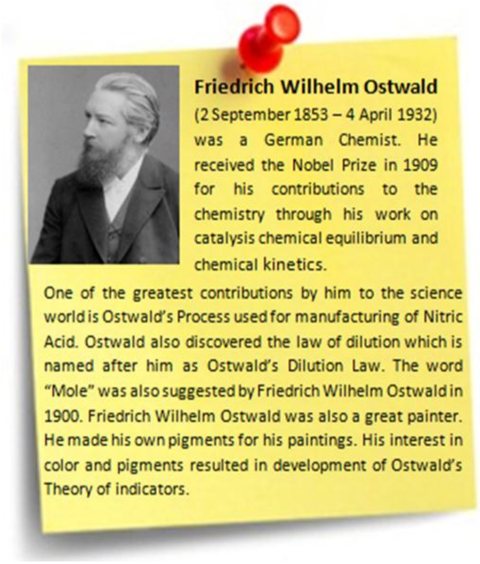


Theories of Acid Base Indicators

- **Ostwald’s theory**
- **Quinonoid theory**

Ostwald's theory:

- The colour change of any indicator is due to its ionisation. The unionised form of indicator has different colour than its ionised form.



Friedrich Wilhelm Ostwald

(2 September 1853 – 4 April 1932) was a German Chemist. He received the Nobel Prize in 1909 for his contributions to the chemistry through his work on catalysis chemical equilibrium and chemical kinetics.

One of the greatest contributions by him to the science world is Ostwald's Process used for manufacturing of Nitric Acid. Ostwald also discovered the law of dilution which is named after him as Ostwald's Dilution Law. The word "Mole" was also suggested by Friedrich Wilhelm Ostwald in 1900. Friedrich Wilhelm Ostwald was also a great painter. He made his own pigments for his paintings. His interest in color and pigments resulted in development of Ostwald's Theory of indicators.

Common-ion effect:

- If an indicator is a weak acid, its ionisation would be very much low in acids due to common H^+ ions while it is fairly ionised in alkalies.
- In the same way, if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Phenolphthalein Indicator:

- Represent as HPh is a weak acid.
- Undissociated form – colourless
- Ionised (Ph^- ion) form – *pink* colour

It is a weak acid, its ionisation would be very much low in acids due to common H^+ ions while it is fairly ionised in alkalies.

$$\begin{array}{ccccc} HPh & \rightleftharpoons & H^+ & + & Ph^- \\ HCl & \rightleftharpoons & H^+ & + & Cl^- \\ & & \downarrow & & \end{array}$$

Common ion

$$\begin{array}{ccccc} HPh & \rightleftharpoons & H^+ & + & Ph^- \\ NaOH & \rightleftharpoons & OH^- & + & Na^+ \\ & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ & & H_2O & & NaPh \\ & & & & \downarrow \\ & & & & \boxed{\text{Pink color } \bullet} \end{array}$$

Methyl Organe Indicator:

- Represent as MeOH is a weak base.
- Undissociated form – Yellow

- Ionised (Me$^+$ ion) form — Red colour

It is a weak base, its ionisation is large in acids and low in alkalies due to common OH$^-$ ions.

$$\mathrm{MeOH} \rightleftharpoons \mathrm{OH^-} + \mathrm{Me^+}$$
$$\mathrm{NaOH} \rightleftharpoons \mathrm{OH^-} + \mathrm{Na^+}$$

Common-ion

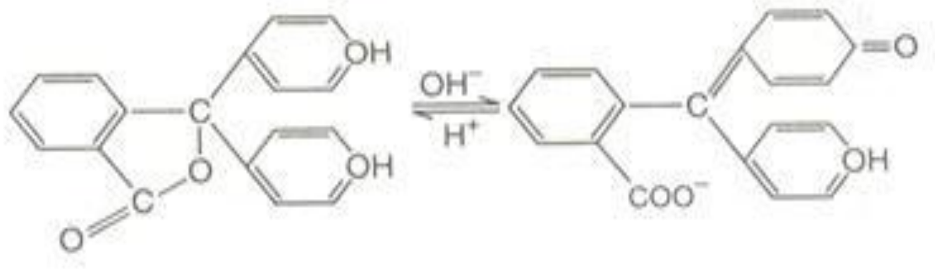
$$\mathrm{HCl} \rightleftharpoons \mathrm{H^+} + \mathrm{Cl^-}$$
$$\mathrm{MeOH} \rightleftharpoons \mathrm{OH^-} + \mathrm{Me^+}$$

Yellow $\rightleftharpoons$ H_2O Red colour

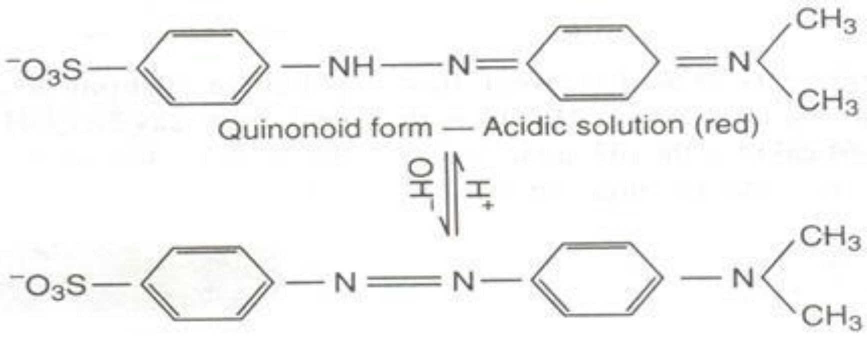
Quinonoid Theory:

- According to quinonoid theory, an **acid-base indicators** exist in two forms.
- One form is termed benzenoid form and the other quinonoid form.
- The two forms have different colors. The color change is due to the interconversation of one form into other.
- One form mainly exists in acidic medium and the other in alkaline medium.
-

Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.



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

Sorting Out Some Confusing Terms:

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.

In an ideal world, 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.

For example, if you were titrating sodium hydroxide solution with hydrochloric acid, both with a concentration of 1 mol dm-3, 25 cm3 of sodium hydroxide solution would need exactly the same volume of the acid - because they react 1 : 1 according to the equation.

In this particular instance, this would also be the neutral point of the titration, because sodium chloride solution has a pH of 7.

But that isn't necessarily true of all the salts you might get formed.

For example, if you titrate ammonia solution with hydrochloric acid, you would get ammonium chloride formed. The ammonium ion is slightly acidic, and so pure ammonium chloride has a slightly acidic pH.

That means that at the equivalence point (where you had mixed the solutions in the correct proportions according to the equation), the solution wouldn't actually be neutral. To use the term "neutral point" in this context would be misleading.

Similarly, if you titrate sodium hydroxide solution with ethanoic acid, at the equivalence point the pure sodium ethanoate formed has a slightly alkaline pH because the ethanoate ion is slightly basic.

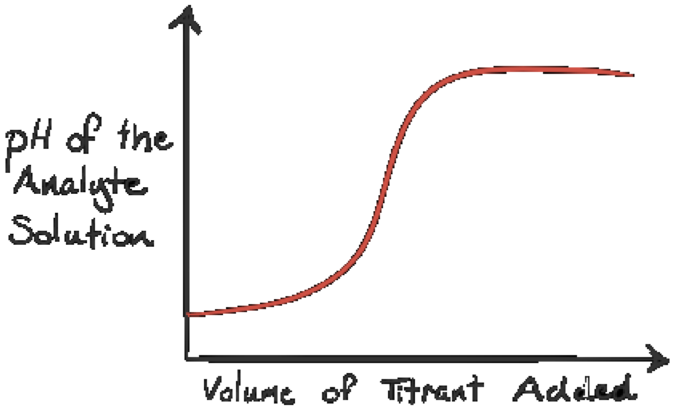
Types of Acid base Titrations

- **Titration of Strong acid – strong base titration**
- **Titration of Weak acid – strong base titration**
- **Titration of Strong acid – weak base titration**
- **Titration of Weak acid- weak base**
- **Titration of Polyprotic acid – strong base titration**
- **Titration of Polybasic base – strong acid titration**

Titration Curves

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.

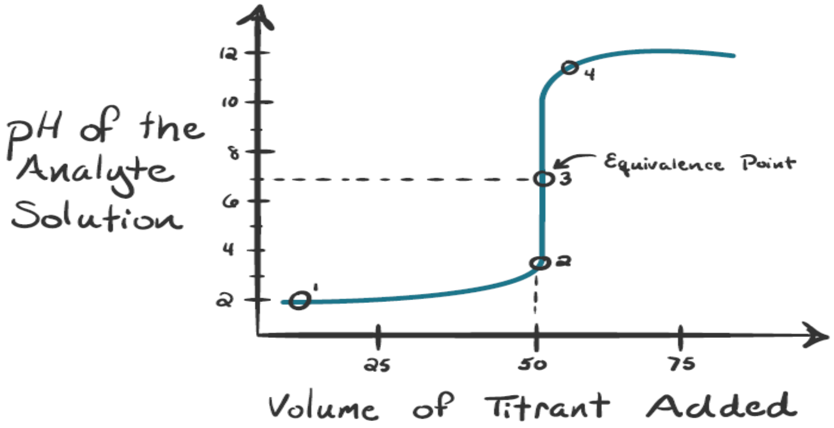


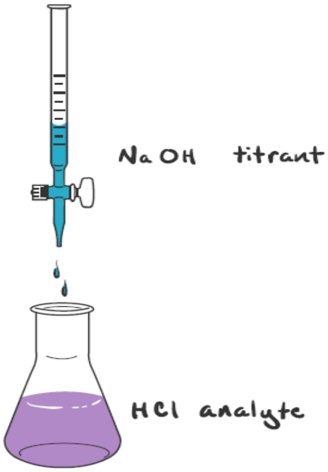
Titration curve chart

Let's attempt to draw some titration curves now.

1) TITRATION OF A STRONG ACID WITH A STRONG BASE (Strong-Strong Titration) (Running alkali into acid)

Here in this example 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 (it predominantly contains H3O+ from dissociation of HCl).

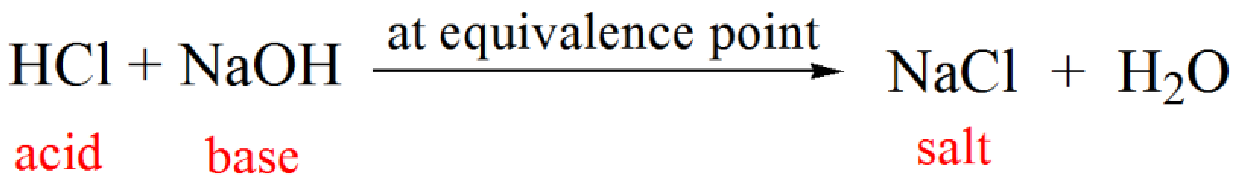
$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Diagram of solution transformation prior to titration

As NaOH is added dropwise, H_3O^+ slowly starts getting consumed by OH^- superscript produced by dissociation of NaOH. 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 HCl in the analyte. At this point, H_3O^+ are completely neutralized by OH^- ions. The solution only has salt (NaCl) and water and therefore the pH is neutral i.e. pH = 7.



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

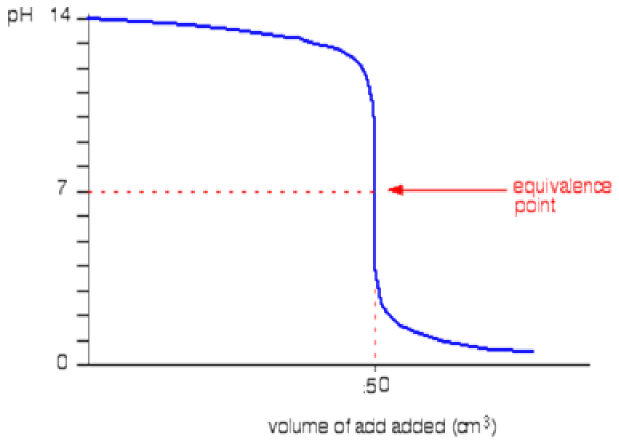
Diagram of solution transformation at equivalence point

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).

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

Diagram of solution transformation after equivalence point

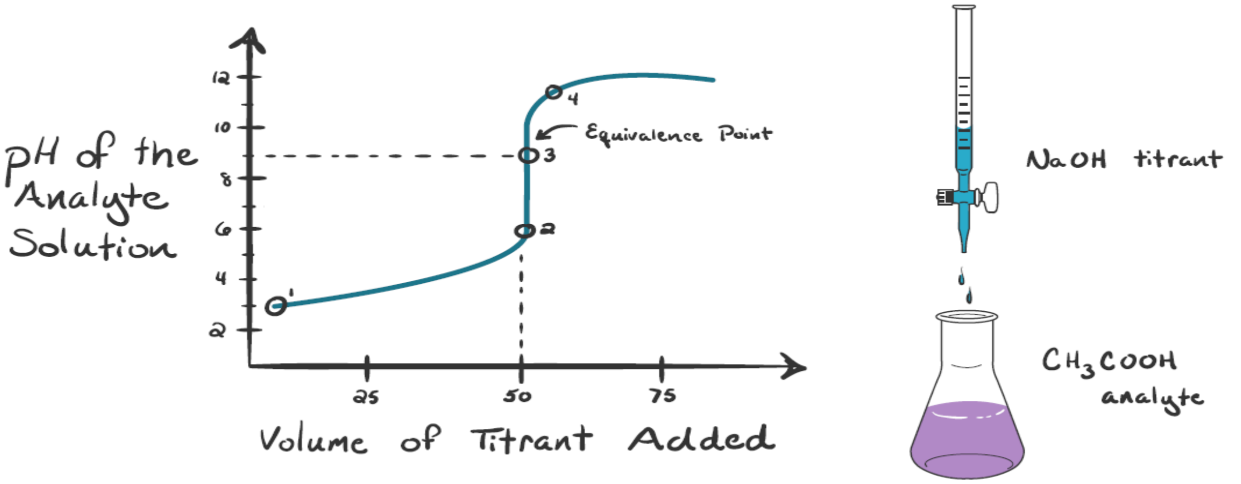
Running acid into the alkali



You can see that the pH only falls a very small amount until quite near the equivalence point. Then there is a really steep plunge. If you calculate the values, the pH falls all the way from 11.3 when you have added 49.9 ml to pH 2.7 when you have added 50.1 ml.

2) Titration of a weak acid with a strong base (Running alkali into acid):

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.



Titration curve of a weak acid with a strong base

<u>Point 1</u>: No NaOH added yet, so the pH of the analyte is low (it predominantly contains H3O+ from dissociation of CH_3COOH). 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).

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

Diagram of solution transformation as titration begins

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

<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 CH_3COOH in the analyte. The H_3O^+ ions are completely neutralized by OH^- ions. The solution contains only CH_3COONa salt and H_2O.

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

Diagram of solution transformation at equivalence point

Let me pause here for a second - can you spot a difference here as compared to case 1 (strong acid versus strong base titration)??? In the case of a weak acid versus a strong base, the pH is not neutral at the equivalence point. The solution is basic (pH ~ 9) at the equivalence point. Let's reason this out.

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 case 1, CH_3COO- is conjugate base of the weak acid CH_3COOH. So, CH_3COO^- is relatively a strong base (weak acid 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.

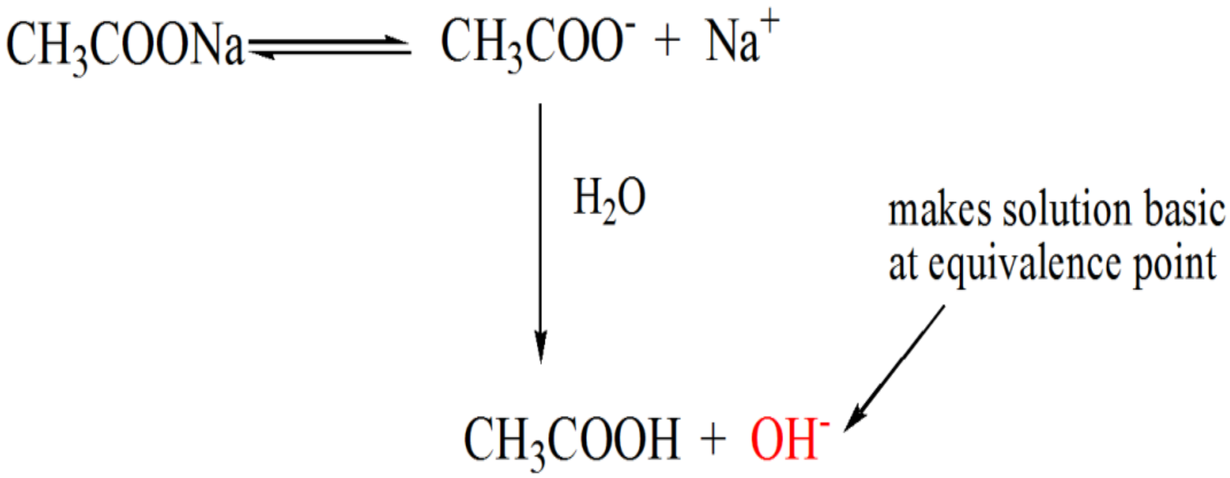
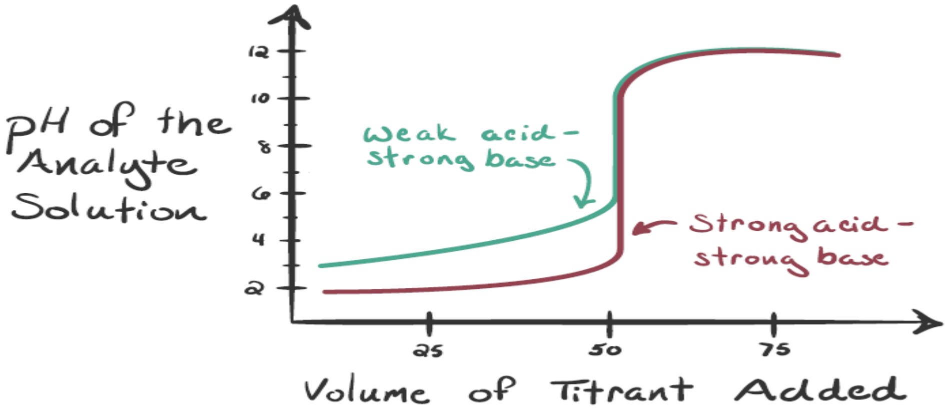


Diagram of CH_3COO^- reacting with H_2O to produce hydroxide ions (OH^-)

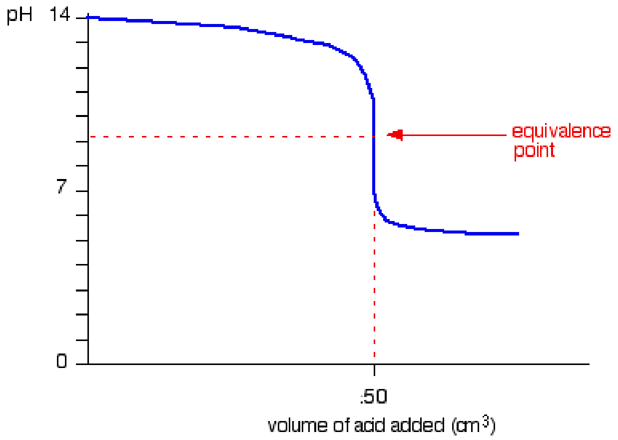
Point 4: Beyond the equivalence point (when sodium hydroxide is in excess) the curve is identical to HCl-NaOH titration curve (1) as shown below.



Titration curve of weak acid / strong base and strong acid / strong base

Running acid into alkali:

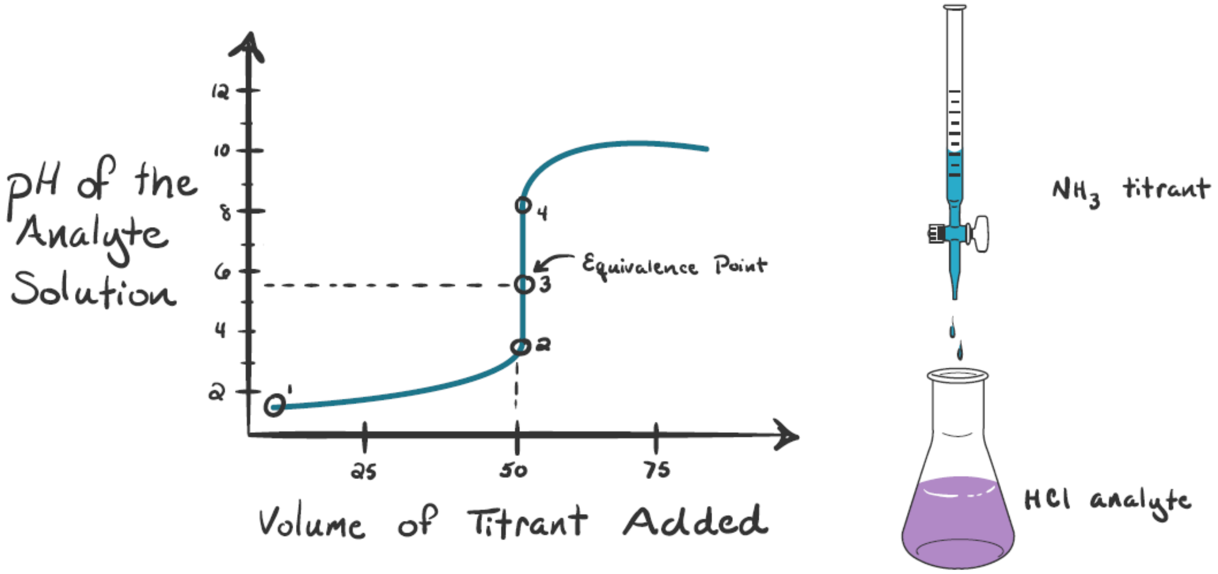
For the first part of the graph, you have an excess of sodium hydroxide. The curve will be exactly the same as when you add hydrochloric acid to sodium hydroxide. Once the acid is in excess, there will be a difference.



Past the equivalence point you have a buffer solution containing sodium ethanoate and ethanoic acid. This resists any large fall in pH.

3) Titration of a strong acid with a weak base (Running alkali into acid):

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, we will get a titration curve as shown below.



Titration curve of a strong acid with a weak base

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

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

Diagram of solution transformation prior to titration

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.

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

Diagram of solution transformation as titration begins

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^+ ions are completely neutralized by NH_3. But again do you spot a difference here??? 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.

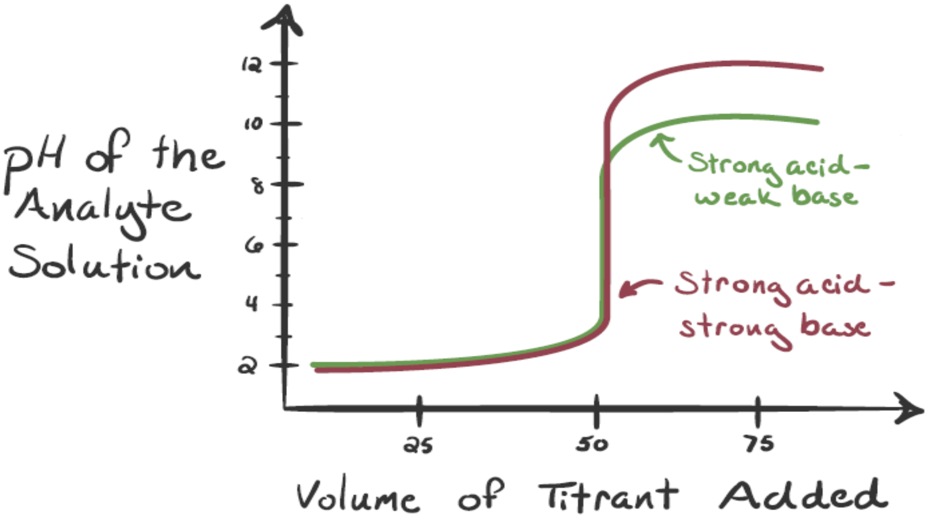
At the equivalence point, the solution only has ammonium ions NH_4^+ and chloride ions Cl^-. But again if you recall, the ammonium ion NH_4^+ is the conjugate acid of the weak base NH_3. So NH_4^+ is a relatively strong acid (weak base NH_3 has a strong conjugate acid), and thus NH_4^+ will react with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

makes solution acidic
at equivalence point

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

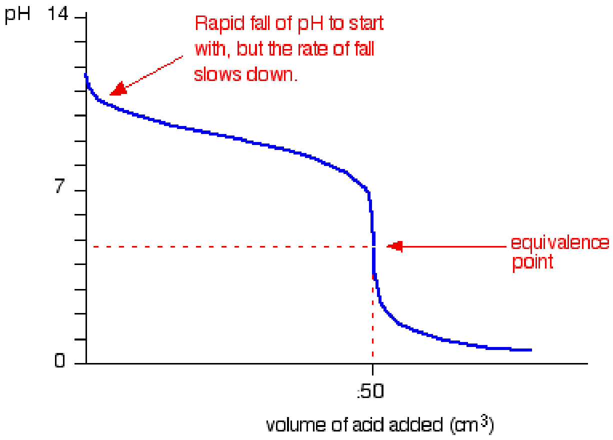
Diagram of NH_4^+ reacting with H_2O to produce hydronium ions

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).



Titration curve of strong acid / weak base and strong acid / strong base

Running acid into the alkali



Because you have got a weak base, the beginning of the curve is obviously going to be different. However, once you have got an excess of acid, the curve is essentially the same as before.

At the very beginning of the curve, the pH starts by falling quite quickly as the acid is added, but the curve very soon gets less steep. This is because a buffer solution is being set up - composed of the excess ammonia and the ammonium chloride being formed.

Notice that the equivalence point is now somewhat acidic (a bit less than pH 5), because pure ammonium chloride isn't neutral. However, the equivalence point still falls on the steepest bit of the curve. That will turn out to be important in choosing a suitable indicator for the titration.

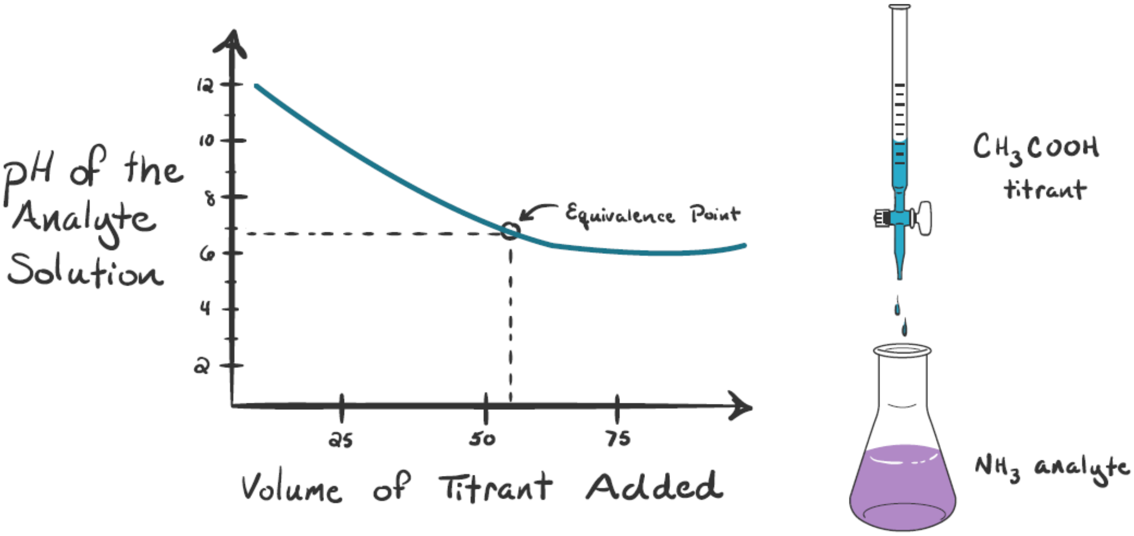
4) Titration of a weak base with a weak acid (Running acid into alkali):

The common example of this would be ethanoic acid (acetic acid) and ammonia.

$$CH_3COOH_{(aq)} + NH_{3(aq)} \longrightarrow CH_3COONH_{4(aq)}$$

It so happens that these two are both about equally weak - in that case, the equivalence point is approximately pH 7.

Here 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.



Titration curve of a weak base with a weak acid

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.

SUMMARY:

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

TITRATIONS IN NON-AQUEOUS MEDIA

Traditionally an important tool for the accurate determination of various pharmaceuticals & polymers.

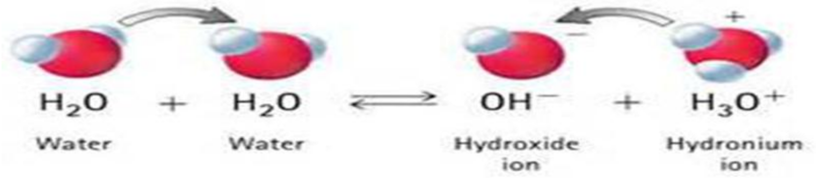
The success of this type of titrations are strongly depends on the solvent properties like:
- Acid base properties of the solvent relative to the solute.
- Autoprotolysis constant of the solvent, and
- Dielectric constant of the solvent.

Types of Solvents

The choice of the solvent for the titration of a specific sample is depends on:
- the solubility of the sample.
- the nature of the sample component(s) to be titrated (acidic or basic),
- the number of components in the sample and in case of a multicomponent sample, whether the titration should provide the result for all components separately or as their sum only.

Amphiprotic Solvents:

- Water can accept as well as donate protons hence are able to act as Bronted-Lowry acid or base.
- Other : Methanol (CH_3OH) & Ehtanol (C_2H_5OH) and works on the basis of AUTOPROTOLYSIS



Inert or Aprotic Solvents:

- Don not donate or accept protons
- Do not show acidic or basic properties
- E.g., Benzene & Carbon Tetrachloride

Polar Protic Solvents

Contains a hydrogen atom bound to an oxygen or a nitrogen
Contains a dissociable proton (H^+) and therefore can donate a proton

Formic acid, *n*-Butanol , Isopropanol (IPA), Ethanol (EtOH), Methanol (MeOH), Acetic acid (AcOH,) Water (H_2O)

Polar Aprotic Solvents

Does not contain a hydrogen atom bound to an oxygen or a nitrogen
Does not contain a dissociable proton (H^+) and therefore cannot donate a proton

Dichloromethane (DCM), Tetrahydrofuran (THF) Ethyl acetate (EtOAc) Acetone, Dimethylformamide (DMF), Acetonitrile (MeCN), Dimethyl sulfoxide (DMSO)

Protophilic Solvents:

- Basic character solvent – tendency to accept proton
- E.g., water, alcohol, liquid ammonia & amines

weak base

$$\underset{\text{weak base}}{NH_3} + H^+ \leftrightarrow \underset{\text{conjugate acid}}{NH_4^+}$$

or

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Protogenic Solvents:

- Acidic character
- Tendency to give protons
- E.g, water, alcohol pure formic, acetic and sulphuric acid

$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{2-}$ (HSO_4^- acting as an acid)

$HSO_4^- + H_2O \longrightarrow OH^- + H_2SO_4$ (HSO_4^- acting as a base)

Role of Solvent or Properties of Solvents

- Acidic or basic character(strong acid or weak acid) of substance are depends on the uses of appropriate solvent and/or relative tendancy to lose a proton!
- According to Bronsted Acid-base theory: Acid is proton donor and base is proton acceptor.

$$HB + S \longrightarrow HS^{+} + B^{-}$$

acid 1 base 2 acid 2 base 1

Conjugate acid base pair

e.g.
1. Acetic acid in water – weakly acidic but in NH_4 – strongly acidic
2. Perchloric acid in water – strongly acidic but in acetic acid – weakly acidic

$$HClO_4 + H_2O \longrightarrow H_3O+ + ClO_4-$$

In water complete Dissociate

$$HClO_4 + CH_3COOH \longrightarrow CH_3COOH_2+ + ClO_4-$$

Perchloric acid Acetic acid Protonated Acetic acid

In acetic acid partially dissociate

- According to Arrhenius acid-base theory: both are acids.
- According to Bronsted theory: even acetic acid a weak acid accept one proton by force from perchloric acid in order to maintain the pH. Hence, act as a base.
- The protonated acetic acid which is strong acid than hydronium ions ($H3O^+$) dissociate in the system to give enough H^+ ions thus, cause resistance to perchloric acid to dissociate and decrease the proton donor capability of HClO4.

$$CH_3COOH_2^{+} \longrightarrow CH_3COOH^{-} + H^{+}$$

Therefore, relative tendency to lose a proton are depends on the uses of appropriate solvent especially in non-aqueous titration.

Leveling Solvent/Effect:
e.g.: HClO4 & HCl dissociate 100% in water

Differentiating Solvent:
e.g.: HClO4 & HCl dissociate rate is less than 100% in acetic acid

Dielectric Constant

- Energy required in the separation of two oppositely charged ions or ion pair in the solvent.
- CH_3COOH in water – greater dissociation, strong acid
- CH_3COOH in ethanol (dissociate to ethoxy ions) – less dissociation, weak acid (CH_3COOH2^+)

$$HA + HS \rightleftharpoons [H_2S^{+}A^{-}] \rightleftharpoons H_2S^{+} + A^{-}$$

weak acid solvent Ion pair formation (Ionisation) Ion separation

Coulomb’s Law: Coulomb’s Force (F)

Electrostatic repulsion/attraction between two stationary charges separated by a distance.

$$\mathbf{F = (c^{+})(a^{-}) / D(r_1 + r_2)^2}$$

Where,

c^+: Charge on the cation
a^- : Charge on the anion
r_1: radius of the cation
r_2: radius of the anion
D: Dielectric constant

High value of ‘D’ – require a small amount of energy to separate the ions i.e., easy to dissolve an ionic solute/substance.

- ‘D’ value of water is 78.5 (25^oC)
- ‘D’ value of HF is 83.6 (0^oC)
- These two are best solvents for polar & ionic compounds.
- Other solvent like Ammonia (‘D’ value is 22 at 33^oC) reduced the tendency to dissolve ionic solute due to low value of ‘D’.

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

- The acidity of an ion NH_4^+ is not much affected by the dielectric constant.
- "The polarity & dielectric constant of a solvent are closely related properties”.

However, autoprotolysis properties of the solvent increased if it has a large dielectric constant.

Estimation of Ephedrine-Hydrochloride ($C_{10}H_{15}NO.HCl$)

Ephedrine: It is an alkaloid & weak organic base obtained from species of Ephedra. Halogen acid salt of ephedrine is freely soluble in water compare to plain form of it.

Therapeutic Uses: Bronchial Asthma, Nasal Decongestion, Hypotension, Mydriatic, CNS stimulant etc.

Theory: Titration of halogen acid salt of bases in acetic acid against perchloric acid includes, addition of mercuric acetate (which is undissociated in acetic acid solution) to a halide salt replaces the halide ion (they are too weakly basic to react quantitively with acetous perchloric acid) by an equivalent quantity of acetate ion, which is a strong base in acetic acid.

General mechanism/reaction:

$2R.NH_2.HCl$ (halogen acid salt of base) $\rightleftharpoons 2RNH_3^+ + 2Cl^-$

$(CH_3COO)_2$ Hg (undissociated) + $2Cl^- \rightarrow HgCl_2$ (undissociated) + $2CH_3COO^-$

$2CH_3COOH_2^+ + 2CH_3COO^- \rightleftharpoons 4CH_3COOH$

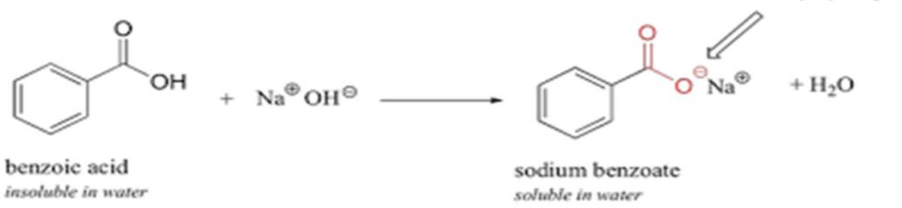
Assay: Dissolve about 500 mg of Ephedrine HCl accurately weighed in 25ml of acetic acid. Add 10 mL of mercuric acetate and 2 drops of crystal violet indicator and titrate with 0.1 N perchloric acid to an emerald-green (bluish-green) endpoint. Each ml of 0.1 N perchloric acid is equivalent to 20.17 mg of C10H15NO.HCl

Estimation of Sodium Benzoate

DESCRIPTION: White, odorless or nearly odorless granules, crystalline powder, or flakes. dissolves in water, and 90% alcohol.

Uses: Preservative in food products and pharmaceutical formulation including oral preparations in conc. up to 0.5% & in cough preparation and use as an Antimicrobial agent.

Preparation:



Assay:

- Transfer about 600 mg, accurately weighed, to a 250 ml beaker; add 100 ml of glacial acetic acid.
- Stir until the sample is completely dissolved.
- Add crystal violet indicator, and titrate with 0.1 N perchioric acids in glacial acetic acid.
- Each ml of 0.1 N perchioric acid is equivalent to 14.41 mg of $C_7H_5NaO_2$.
- Perform a blank determination.

Calculation:

Calculate the percentage of sodium benzoate ($C_7H_5NaO_2$) in the Sample taken:

Result = [(VS VB) × N × F]/W × 100

VS = = volume of Titrant consumed by the Sample (mL)
VB = = volume of Titrant consumed by the Blank (mL)
N = = actual normality of the Titrant (mEq/mL)
F = = equivalency factor, 144.1 mg/mEq
W = = weight of the Sample (mg)

Titration Calculations: An Example

1.

The balanced equation of a titration reaction is the key calculating the unknown molarity. For example, sulfuric acid is titrated with sodium hydroxide according to this equation:

$$H_2SO_4\ (aq) + 2\ NaOH\ (aq) \rightarrow Na_2SO_4\ (aq) + 2\ H_2O\ (l)$$

A 25 mL solution of H_2SO_4 is completely neutralized by 18 mL of 1 M NaOH solution. What is the molarity/concentration of H_2SO_4 solution?

M NaOH = 1.0M VNaOH = 18 mL = 0.018 L
M H_2SO_4 = ? V H_2SO_4 = 25 mL = 0.025 L

Calculate the moles of NaOH in the standard from the titration data: molarity of the base (M_B) and the volume of the base (V_B).

In other words, mol NaOH in standard = (mol/L)(L) = M_B V_B
= (1)x(0.018) = 0.018 mol

From the equation, you know that the mole ratio of NaOH to H_2SO_4 is 2:1.
Two moles of NaOH are required to neutralize 1 mol of H_2SO_4.

mol H_2SO_4 titrated = mol NaOH in standard x (1 mol H_2SO_4 / 2 mol NaOH)
= mol NaOH in standard / 2 mol NaOH
= 0.018 / 2 = 0.009 mol of H_2SO_4

M_A represents the molarity of the acid and V_A represents the volume of the acid in liters.

M H_2SO_4 = *mol H_2SO_4 titrated/V_A* $^=$ *0.009 mol /0.025L = 0.36M*

In Short Form...

$M_AV_A = M_BV_B$ (mol acid/mol base) This is the mole ratio

$M_AV_A = M_BV_B$ (mol acid/mol base)

(mol acid/L acid)(L acid) = (mol base/L base)(L base) (mol acid/mol base)

mol acid = mol base (mol acid/mol base)

mol acid = mol acid