



Miss Preeti Verma
Assistant Professor
Faculty of Pharmaceutical Sciences,
Rama University,
Kanpur, U.P.

UNIT-II

Acid Base Titration

Titration is a method of analysis that will allow you to determine the precise endpoint of a reaction and therefore the precise quantity of reactant in the titration flask. The chemical reaction involved in acid-base titration is known as neutralisation reaction.

Theory of Indicator

An acid-base indicator is a weak acid or a weak base.

Examples of indicators used in acid base reactions

- Litmus
- Phenolphthalein
- Methyl orange

thymol blue, methyl yellow, methyl orange, bromphenol blue, bromcresol green, methyl red, bromthymol blue, phenol red, neutral red, phenolphthalein, thymolphthalein, alizarin yellow, tropeolin O, nitramine, and trinitrobenzoic acid.

Indicators	pH range	Color for weak acid	Color for conjugated base
Methyl orange	4-6	Orange	Yellow
Bromophenol blue	6-7	Yellow	Blue
Thymol blue	8-9	Yellow	Blue
Phenolphthalein	9-10	Colourless	Pink
Alizarin yellow	10-12	Yellow	Red

Table: 1 pH range and colour of indicators

An indicator is a substance which is used to determine the end point in a titration. In acid base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below

Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

Table: 2 Colour change and the pH range of some common indicators

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

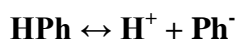
Ostwald's theory:

According to this theory, the colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form. The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H⁺ ions while it is fairly ionised in alkalise. Similarly if the indicator is a weak base, its ionisation is large in acids and low in alkalises due to common OH⁻ ions.

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh.

It ionises in solution to a small extent as:



Colourless Pink Applying law of mass action,

$$K = \frac{[\text{H}^+][\text{Ph}^-]}{[\text{HPh}]}$$

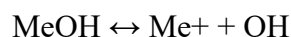
The un-dissociated molecules of phenolphthalein are colourless while Ph⁻ ions are pink in colour. In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H⁺ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH⁻ ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph⁻ ions increases in solution and they impart pink colour to the solution.

Let us derive Handerson equation for an indicator



Methyl orange:

It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me⁺ and OH⁻ ions.



Yellow Red

Applying law of mass action,

$$K = \frac{[\text{Me}^+][\text{OH}^-]}{[\text{MeOH}]}$$

In presence of an acid, OH⁻ ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me⁺ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH⁻ ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, i.e., yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH⁻ ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

Indicators	pK_{ind}	pH
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Methylorange	3.7	3.1-4.4
Phenolphthaline	9.3	8.3-10.0

Table: 3 Titration of weak acid with strong base.

Titration curve

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.

Titration curve of a strong acid with a strong base

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

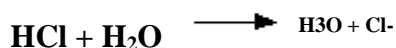


Diagram of solution transformation prior to titration

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 of H_3O^+ 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 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. $\text{pH} = 7$.

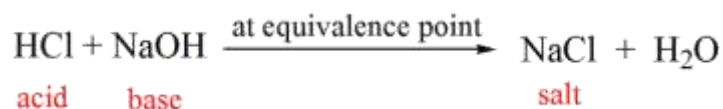


Diagram of solution transformation at equivalence point

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).

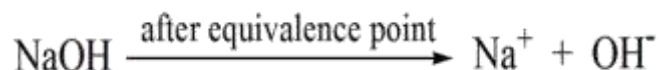


Diagram of solution transformation after equivalence point

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.

Titration curve of a weak acid with a strong base

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



Diagram of solution transformation as titration begins

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

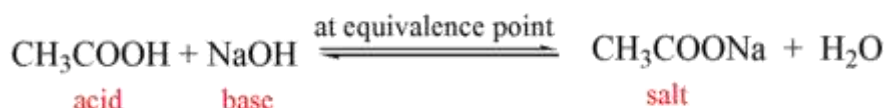


Diagram of solution transformation at equivalence point

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 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 H_2O to produce hydroxide ions (OH^-) thus increasing the pH to ~ 9 at the equivalence point.

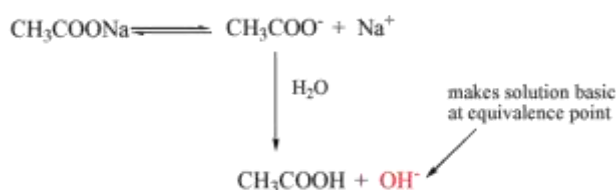


Diagram of CH₃COO⁻ reacting with H₂O to produce hydroxide ions (OH⁻)

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

3) Titration of a strong acid with a weak base

Suppose our analyte is hydrochloric acid HCl (strong acid) and the titrant is ammonia NH₃ (weak base). If we start plotting the pH of the analyte against the volume of NH₃ 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 NH₃ added yet, so the pH of the analyte is low (it predominantly contains H₃O⁺ from dissociation of HCl).



Diagram of solution transformation prior to titration

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



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 OH^- 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.

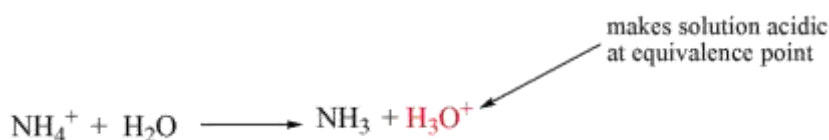


Diagram of NH_4^+ reacting with H_2O to produce hydronium ions

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

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.

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.

Non aqueous titration

Non aqueous titration is the titration of substances dissolved in solvents other than water. It is the most common titrimetric procedure used in pharmacopoeial assays and serves a double purpose: it is suitable for the titration of very weak acids and very weak bases, and it provides a solvent in which organic compounds are soluble.

The most commonly used procedure is the titration of organic bases with perchloric acid in anhydrous acetic acid. These assays sometimes take some perfecting in terms of being able to judge the endpoint precisely.

The Karl Fischer titration for water content is another nonaqueous titration, usually done in methanol or sometimes in ethanol. Since water is the analyte in this method, it cannot also be used as the solvent.

Need of Non aqueous titrations

- Often times we need to perform an acid-base titration in non- aqueous solvent due to:
- The analyte is too weak acid or a base to be titrated in H_2O
- Reactants or products are insoluble in H_2O
- Reactants or products react with H_2O
- Titration in H_2O doesn't allow a sharp end point but in a nonaqueous solvent with a stronger base than OH^- it is possible to get a sharp end point

Bronsted Lowry; a general definition applicable to both aqueous and non-aqueous systems

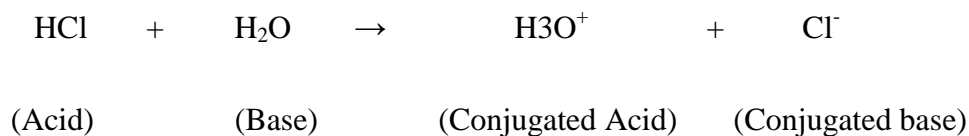
Acids: proton donors

Bases: proton acceptors

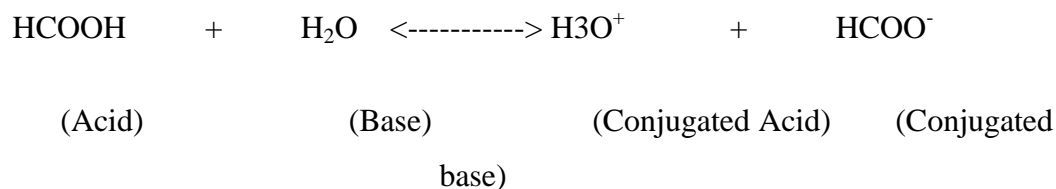
Lewis theory: Acids: electron pair acceptors

Bases: electron pair donors

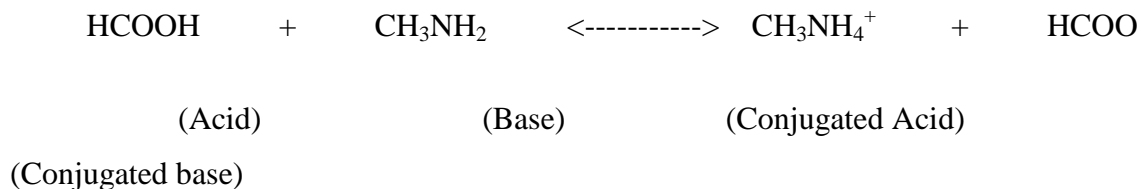
Strong acids in water:



Weak acids in water:



Weak acids in non-aqueous solvents:



It follows from these definitions that an acid may be either:

- * an electrically neutral molecule, e.g. HCl, or
- * a positively charged cation, e.g. C₆H₅NH₃⁺, or
- * a negatively charged anion, e.g. HSO₄⁻. A base may be either:
 - * an electrically neutral molecule, e.g. C₆H₅NH₂, or an anion, e.g. Cl⁻.
- * Substances which are potentially acidic can function as acids only in the presence of a base to which they can donate a proton. Conversely basic properties do not become apparent unless an acid also is present.
- * The apparent strength of an acid or base is determined by the extent of its reaction with a solvent.

- * In aqueous solution all strong acids appear equally strong because they react with the solvent to undergo almost complete conversion to hydronium ion (H_3O^+) and the acid anion.
- * In a weakly protophilic solvent such as acetic acid, the extent of formation of the acetonium ion ($\text{CH}_3\text{COOH}_2^+$) due to the addition of a proton provides a more sensitive differentiation of the strength of acids and shows that the order of decreasing strength for acids is perchloric, hydrobromic, sulfuric, hydrochloric, and nitric.
- * Acetic acid reacts incompletely with water to form hydronium ion and is, therefore, a weak acid.
- * In contrast, it dissolves in a base such as ethylenediamine, and reacts so completely with the solvent that it behaves as a strong acid. This so-called levelling effect.

Levelling effect or solvent levelling

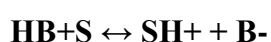
- * Levelling effect or solvent: leveling refers to the effect of solvent on the properties of acids and bases.
- * The strength of a strong acid is limited ("leveled") by the basicity of the solvent. Similarly the strength of a strong base is leveled by the acidity of the solvent.
- * When a strong acid is dissolved in water, it reacts with it to form hydronium ion (H_3O^+). [2] An example of this would be the following reaction, where "HA" is the strong acid:
- * $\text{HA} + \text{H}_2\text{O} \rightarrow \text{A}^- + \text{H}_3\text{O}^+$
- * Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+ . Therefore, no acid stronger than H_3O^+ exists in H_2O .
- * Similarly, when ammonia is the solvent, the strongest acid is ammonium (NH_4^+), thus HCl and a super acid exert the same acidifying effect.
- * The same argument applies to bases. In water, OH^- is the strongest base. Thus, even though sodium amide (NaNH_2) is an exceptional base (pK_a of $\text{NH}_3 \sim 33$), in water it is only as good as sodium hydroxide.
- * On the other hand, NaNH_2 is a far more basic reagent in ammonia than is NaOH .

Solvents used in non aqueous titration

- * Solvent which are used in non aqueous titration are called non aqueous solvent.
- * They are following types:-

1. Aprotic Solvent
2. Protogenic Solvent
3. Protophilic Solvent
4. Amphiprotic Solvent

- * **Aprotic solvents** are neutral, chemically inert substances such as benzene and chloroform. They have a low dielectric constant, do not react with either acids or bases and therefore do not favor ionization. The fact that picric acid gives a colorless solution in benzene which becomes yellow on adding aniline shows that picric acid is not dissociated in benzene solution and also that in the presence of the base aniline it functions as an acid, the development of yellow color being due to formation of the picrate ion. Carbon tetrachloride and toluene come in this group; they possess low dielectric constants, do not cause ionization in solutes and do not undergo reactions with acids and bases. Aprotic solvents are frequently used to dilute reaction mixture
- * **Protogenic solvents** are acidic substances, e.g. sulfuric acid. They exert a leveling effect on bases. Anhydrous acids such as hydrogen fluoride and sulphuric acid fall in this category, because of their strength and ability to donate protons, they enhance the strength of weak bases. Ex:- sulphuric acid, formic acid, propanoic acid, acetic anhydride etc. They have high dielectric constant and ionised because of their strength and ability to donate protons.
- * **Protophilic solvents** are the substances that possess a high affinity for protons. The over all reaction can be represented as:



The equilibrium in this reversible reaction will be generally influenced by the nature of the acid and the solvent. Weak acids are normally used in the presence of strongly protophilic solvents as their acidic strengths are then enhanced and then become comparable to these of strong acids; this is known as the levelling effect.

- * **Amphiprotic solvents** have both protophilic and protogenic properties. Examples are acetic acid and the alcohols. They are dissociated to a slight extent. The dissociation of acetic acid, which is frequently used as a solvent for titration of basic substances, is shown in the equation below:



Here the acetic acid is functioning as an acid. If a very strong acid such as perchloric acid is dissolved in acetic acid, the latter can function as a base and combine with protons donated by the perchloric acid to form protonated acetic acid, an onium ion:



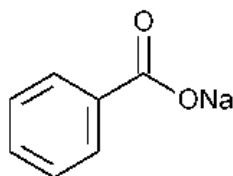
Since the $\text{CH}_3\text{COOH}_2^+$ ion readily donates its proton to a base, a solution of perchloric acid in glacial acetic acid functions as a strongly acidic solution.

Titriments used in non aqueous titration

- **Acidic titriments:**
 - Perchloric acid
 - p- Toluenesulfonic acid,
 - 2,4-Dinitrobenzenesulfonic acid

- **Basic titriments**
 - Tetrabutylammonium hydroxide
 - Sodium acetate
 - Potassium methoxide
 - Sodium aminoethoxide

ESTIMATION OF SODIUM BENZOATE

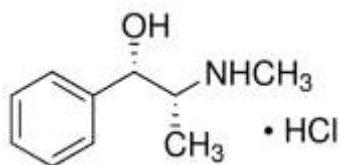


Molecular Formula : $\text{C}_7\text{H}_5\text{NaO}_2$ Mol. Wt. 144.1 Sodium Benzoate contains not less than 99.0 per cent and not more than 100.5 per cent of $\text{C}_7\text{H}_5\text{NaO}_2$ calculated on the dried basis.

Description: A white, crystalline or granular powder or flakes; odourless or with a faint odour; hygroscopic.

Preparation of 0.1N solution of HClO₄ and its standardization: Dissolve 8.5 ml of 72% HClO₄ in about 900 ml glacial acetic acid with constant stirring, add about 30 ml acetic anhydride and make up the volume (1000 ml) with glacial acetic acid and keep the mixture for 24 hour. Acetic anhydride absorbed all the water from HClO₄ and glacial acetic acid and renders the solution virtually anhydrous. HClO₄ must be well diluted with glacial acetic acid before adding acetic anhydride because reaction between HClO₄ and acetic anhydride is explosive. Unit II: Non-Aqueous Titration Standardisation of HClO₄: To 500 mg of potassium acid phthalate add 25 ml of glacial acetic acid and add few drops of 5% w/v crystal violet in glacial acetic acid as indicator. This solution is titrated with 0.1 HClO₄. The colour changes from blue to blue green. 1 ml of 0.1N HCl Assay Procedure: Weigh accurately about 0.25 g of Sodium Benzoate, dissolve in 20 ml of anhydrous glacial acetic acid, warming to 50° if necessary, cool. Titrate with 0.1 M perchloric acid, using 0.05 ml of 1 naphtholbenzein solution as indicator. Carry out a blank titration. Equivalent factor or I.P factor : 1 ml of 0.1 M perchloric acid is equivalent to 0.01441 g .

ESTIMATION OF EPHEDRINE HYDROCHLORIDE



Molecular Formula: C₁₀H₁₅NO, HCl Mol. Wt. 201.7 Ephedrine Hydrochloride contains not less than 99.0 per cent and not more than 101.0 per cent of C HCl calculated on the dried basis. Description: Colourless crystals or a white, crystalline powder; odourless. It is affected by light.

Preparation of 0.1N solution of HClO₄ and its standardization 900 ml glacial acetic acid with constant stirring, add about 30 m (1000 ml) with glacial acetic acid and keep the mixture for 24 hour. Acetic anhydride absorbed all the water from HClO₄ and glacial acetic acid and renders the solution virtually anhydrous. HClO₄ must be well dilut with glacial acetic acid before adding acetic anhydride because reaction between HClO₄ and acetic anhydride is explosive. Standardisation of HClO₄: To 500 mg of potassium acid phthalate add 25 ml of glacial acetic acid and add few drops of 5% w/v crystal violet in glacial acetic acid as indicator. This solution is titrated with 0.1 HClO₄. The colour changes from blue to blue green. 1 ml of 0.1N HClO₄ = 0.020414 gms of potassium acid Phthalate. To 500 mg of

potassium acid phthalate add 25 ml of glacial acetic acid and add few drops of 5% w/v crystal violet in glacial acetic acid as indicator. This solution is titrated with 0.1 HClO₄. The colour changes from blue to blue green. 1 ml of 0.1N HClO₄ = 0.020414 gms of potassium acid Phthalate. Weigh accurately about 0.25 g of Sodium Benzoate, dissolve in 20 ml of anhydrous glacial acetic acid, warming to 50° if necessary, cool. Titrate with 0.1 M perchloric acid, using 0.05 ml of 1 naphtholbenzein solution as indicator. Carry out a blank titration. or I.P factor : 1 ml of 0.1 M perchloric acid is equivalent to 0.01441 g.