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Module-1

Theory of Volumetric and Gravimetric Analysis

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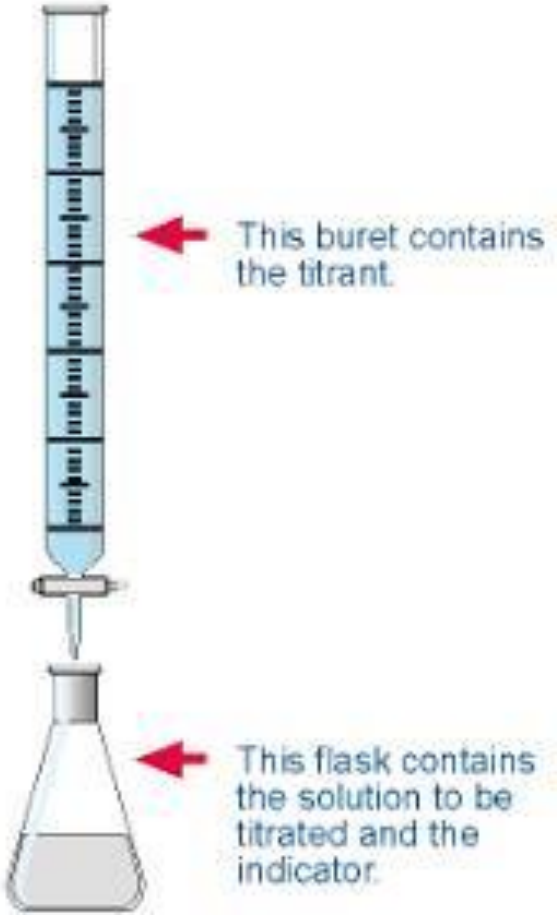
Objective



Acid-Base Titrations in Non-aqueous Solvents

Basic Background of Acid and Bases

There are three well-known theories that may be used to explain neutralization reactions in any solvent system

Arrhenius Concept: Acid is a substance that dissociates in water to form ~~H^+~~ and base is a substance that dissociate in water to form OH^- ions. NOT APPLICABLE in non-aqueous

Lewis Theory:

According to this theory, a base is an electron donor and an acid is an electron acceptor. Neutralization reactions take place because of a molecule of more → stable electronic configuration results from the sharing of one or more pairs of → electrons.

Example: $2H^+ + 2e^-$ H_2

(Acid)

$2AlCl_4^-$ $2AlCl_3 + Cl_2 + 2e^-$

(Base)

Bronsted Theory

According to this theory an acid is a proton donor and base is the proton acceptor; thus,

$$\underset{\text{acid}}{A} \rightleftharpoons \underset{\text{base}}{B} + \underset{\text{proton}}{H^+}$$

or using a familiar acid

$$\underset{\text{acid}}{HCl} \rightleftharpoons \underset{\text{base}}{Cl^-} + \underset{\text{proton}}{H^+}$$

It is apparent that when an acid loses a proton it becomes a base. Conversely, a base accepting a proton becomes an acid.

An acid or a base may be an ion or an electrically neutral molecule—for example:

$$\underset{\text{acid}}{H_2O} \rightleftharpoons H^+ + \underset{\text{base}}{^-OH}$$

Water acts both as an acid and a base and the equilibrium may be represented as

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{^-OH}$$

Acid base titration in non aqueous

Non aqueous titration refers to a type of titration in which the analyte
substance is dissolved in a solvent which does not contain water.

Non Aqueous Titration Theory

The need for non aqueous titration arises because water can behave as a weak base and a weak acid as well, and can hence compete in proton acceptance or proton donation with other weak acids and bases dissolved in it.

The procedure of non aqueous titration is very useful because:

- it satisfies two different requirements, namely – suitable titration of very weak acids or bases

- along with providing a solvent with an ability to dissolve organic compounds. An example of a reaction in which water is not a suitable

solvent is the reaction given by:

$$R\text{-}NH_2 + H^+ \rightleftharpoons R\text{-}NH_3^+$$

which is competed with in an aqueous solvent by the reaction given by:

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

This type of competition provided by water towards weak bases or
weak acids makes it difficult to detect the end point of the titration.

Therefore, these substances which have very sharp end points when
titrated in aqueous solutions due to their weakly basic or weakly acidic nature generally need to be titrated in non aqueous solvents.

Many reactions which occur in non aqueous titration procedures can be explained via the Bronsted-Lowry Theory and its definition of acids and bases. Basically, acids can be thought of as proton donors, whereas bases can be thought of as proton acceptors.

It can also be noted that potentially acidic substances can behave as acids only when a base (to which a proton can be donated) is present. The converse of this statement also holds true, i.e. potentially basic substances can behave as bases only when an acid (from which a

proton can be accepted) is present.

Non-aqueous acid-base titrations

Limitation of aqueous acid-base titrations

Titration in water solutions is limited by factors:

- It is impossible to titrate for a mix of acids or the bases
- It is impossible to titrate for a mix of strong and weak acids (bases)
- It is impossible to titrate separately for a mix of acids (bases) with near constants of dissociation
- It is impossible to define substances which are insoluble in water.

Non-aqueous titrations have the following advantages

- Organic acids and bases that are insoluble in water are soluble in non-aqueous solvent.
- A non-aqueous solvent may help two are more acids in mixture. The individual acid can give separate end point in different solvent.
- Enlargement of solubility range: many substances that are not soluble in water can be easily titrated in water-free media (e.g. fats and oils)
- Enlargement of application range: weak bases and acids can be easily titrated
- Non-aqueous solvents are useful for the titration of very weak acids or

bases that cannot be titrated in water.

- Non aqueous titrations are simple and accurate.

Selection of solvents

(1) Solubility of analyte

(2) Nature of the analyte

(3) Reactivity of the analyte

Classification of Non aqueous solvents

They are following types:-

1. **Aprotic Solvent**
2. **Protogenic Solvent**
3. **Protophillic Solvent**
4. **Amphiprotic Solvent**

Aprotic Solvent

Aprotic solvent are most important solvent in this titration.

- This solvent are chemically inert.
- Neither acidic nor basic (inert solvent).
- They have low dielectric constant and do not react with either acid or base and therefore do not favour ionization.

The most important examples of aprotic solvent are

- Chloroform
- Benzene
- Dioxan
- Ethyl acetate

Protogenic Solvent

Protogenic solvent are acidic in nature and they can
donate the proton.

Used to dissolved basic analyte.

They have high dielectric constant and ionised

Examples of Protogenic solvent are:

Glacial acetic acid, formic acid, propanoic acid

Protophilic Solvent

- Protophillic solvent are basic in nature.
- Which possess a high affinity for proton.
- Used to dissolved acidic analytes.

Examples:- Amines and ketone. Pyridine, ethylenediamine, DMF

Amphiprotic Solvent

- Amphiprotic solvent are those solvent they work as a both mean protogenic or protophillic.

- It means Amphiprotic solvent are acidic and basic in nature.

- And they are accept the proton and donate the proton.

For examples:-

Alcohols and weak organic acids

Major solvents used in non aqueous titration

(1) Glacial acetic acid

(2) Acetonitrile (CH_3CN)

(3) Alcohols

(4) Dioxane

(5) DMF

Levelling Effect:

The acidity of the weak acids can be enhanced using basic solvents because the basic solvent has higher affinity to take up protons from acid.

So, acetic acid behaves as a strong acid in ammonia solution. Also the basicity of the weak bases can be enhanced in the presence of acidic solvent. This is called the levelling effect of the solvent.

NON AQUEOUS INDICATORS

- The ionised form and unionised form or different resonant form of indicators generally apply equally for non-aqueous titration, but the colour change at the end point vary from titration to titration, as they depend on the nature of the titrant.

- The end point may be determined either by

potentiometric

titration or by colour change of the indicator.

DETERMINING END POINT

A. Potentiometric titration

B. Indicator method

A. Potentiometric titration :

- potentiometric method for the detection of the equivalence point
- The end point is determined by using indictor electrode(glass electrode) and reference electrode(saturated calomel electrode)

Detection of End point

Visual indicator are formed to the most suitable for the detection of
end point in non-aqueous titration.

- The important indicator used for non-aqueous titration are follow:-

1. Crystal voilet:-

- **It is considered as the most common indicators in the titration of the bases.**

- It is used as 0.5% solution in glacial acetic acid, it gives voilet
  colour in basic medium and yellowish green in acidic medium.

- It is most widely use for the titration of pyridine with prechloride

acid.

2. Oracet Blue B Indicator:- It is prepared o.5% glacial acetic acid. It gives blue colour in basic medium while pink colour in acidic medium.

3. Quinaldine Red: it is employed as indicator in the determination of the drug substance in dimethylformamide (DMF). It is used as 0.1% w/v solution in ethanol. The colour change is from purple red to pale green.

4. Thymol Blue: it is used as 0.2% w/v solution in methanol. The colour change is from yellow to blue. Used as an

indicator for the
titration of substances acting as acids in DMF.

Indicator method:

Indictor	Color changes		
	Basic	Neutral	Acidic
Crystal violet (0.5 per cent in glacial acetic acid)	violet	blue-green	yellowish-green
α-Naphtholbenzein (0.2 per cent in glacial acetic acid)	blue or blue-green	orange	dark-green
Oracet Blue B (0.5 per cent in glacial acetic acid)	blue	purple	pink
Quinaldine Red (0.1 per cent in methanol)	magenta	-------	almost colour less
Thymol Blue	**yellow**		**blue**

Selection of Solvent for NAT

- **Acetic acid**: used for titration of weak bases, Nitrogen containing compounds
- **Acetonitrile / with ACOH**: Metal ethanoates
- **Alcohols (IPA, nBA)** : Soaps and salts of organic acids.
- **DMF**: Benzoic acid, amides etc

Titrant for NAT

- **Perchloric acid in acetic acid**
  - Amines, amine salts, amino acids, salts of acids
- **Potassium Methoxide in Toluene-Methanol**
- **Quan ammonium hydroxide in Acetonitrilepyridine**
  - Acids, enols, imides & sulphonamides

Assay by non aqueous titration

Acidimetry in non aqueous titration—

It can be further divided in to two types, namely ;

1. Titration of primary , secondary, tertiary amines.
2. Titration of halogen acid salts of bases.

Alkalimetry in non aqueous titration-

Titration of acidic substances

Non Aqueous Titration of weak Bases

Solvents used in the titration of weak bases:

- Neutral solvents :

Ex: - alcohol, chloroform, benzene, chlorobenzene

- Acidic solvents:

Ex:-formic acid, glacial acetic acid, propionic acids

Titrant used in the titration of weak bases:

Ex:-Perchloric acid

Indicators used in the titration of weak bases

Ex:-oracat blue, crystal violet, 1-naphtholbenzein (weak bases)

Non Aqueous Titration of weak Acid

Many weakly acidic substances (alcohol or aprotic solvent)can be titrated in an appropriate non aqueous solvents with a sharp end point .

Ex:-acidic halides, acids,amino acids, enols (barbiturates, xanthines), phenols, pyrroles, sulphonamides etc,.

1) Solvents used in the titration of weak acids:

Ex:-Ethylenediamine, n-butylamine, morpholine

2) Titrant used in the titration of weak acids:

Ex:-sodium methoxide, lithium methoxide, potasium methoxide , tetrabutyl ammonium hydroxide etc.

Disadvantage

- Temperature ,moisture, CO_2 should be control.
- Solvents are expensive.
- Volatile solvents can pollute environment
- Indicator must be prepare in non aqueous medium.