DIAZOTIZATION TITRATION

BY

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Introduction

- The diazotization titration is nothing but the conversion of the primary aromatic amine to a diazonium compound.
- This process was first discovered in 1853 and was applied to the synthetic dye industry.
- The reaction mechanism was first proposed by Peter Griessin.
- In this method, the primary aromatic amine is reacted with the sodium nitrite in acidic medium to form a diazonium salt.
- This method is first used in the determination of dyes.

Principle:

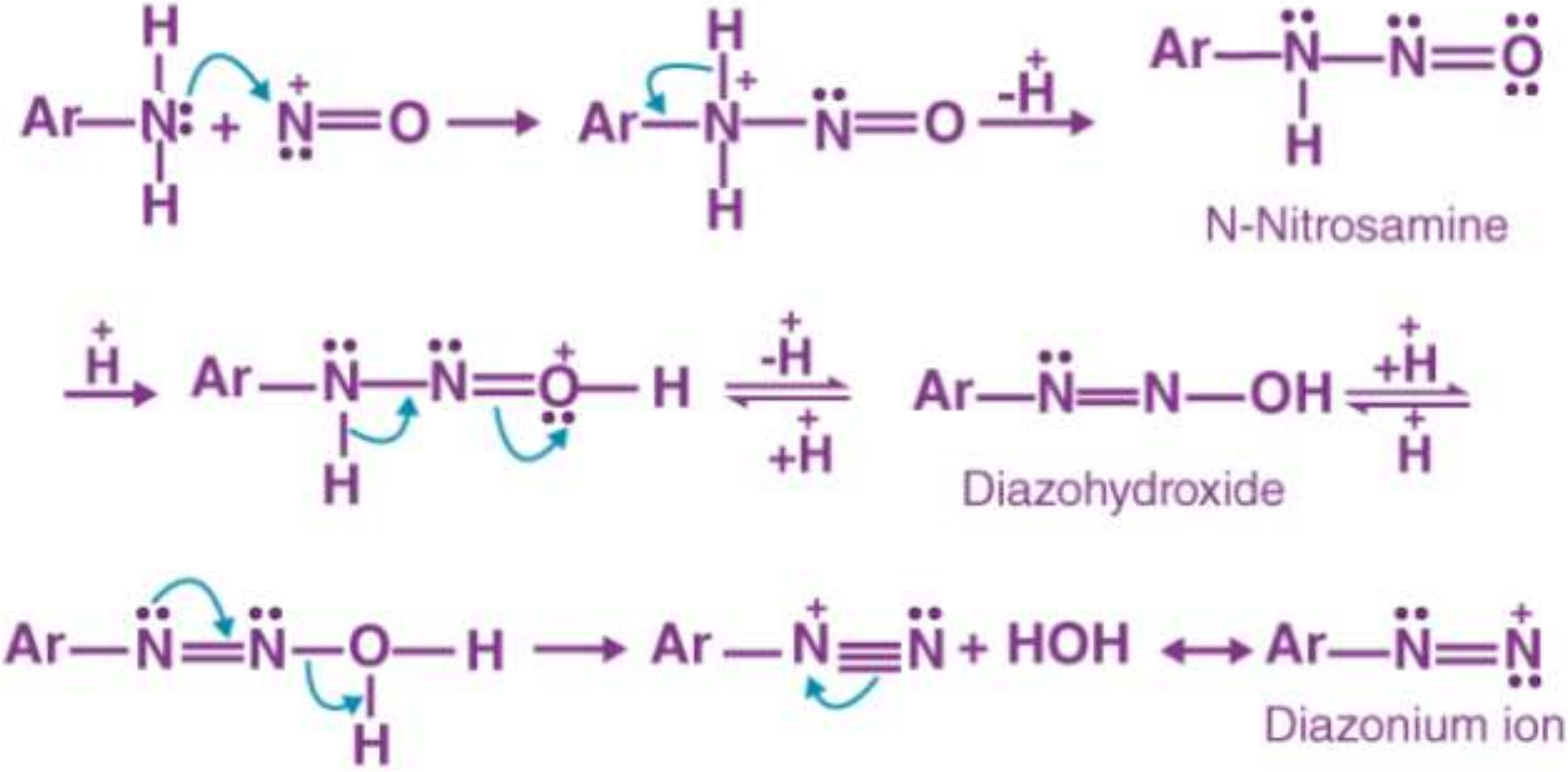
- The principle involved in this method is that the primary aromatic amine present in the sample reacts with the sodium nitrite in the presence of acid such as hydrochloric acid to obtain a diazonium salt.

$$R - NH_2 + NaNO_2 + HCl \rightarrow R - N^+ \equiv N - Cl^- + NaCl + H_2O$$

- A solution of amine is added to an acid solution at 0-5°C accompanied by the addition of sodium nitrite. A reaction between the amine and nitrous acid results in the formation of nitrosamine, followed by tautomerization, which results in the water being lost. In diazonium, positive charges are displaced at ortho and para positions to stabilize the ions.

$$C_6H_5NH_2 + NaNO_2 + HCl \longrightarrow C_6H_5N = NCl + NaCl + H_2O$$

Mechanism of Diazotization:



Theory

- The reaction between sodium nitrite and hydrochloric acid produces sodium chloride and nitrous acid.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

- As a result of the reaction between the nitrous acid and the aromatic amine, the diazonium salt is obtained.
- In addition to nitrous acid, ammonium sulfate solution is added to remove excess nitrous acid.

$$R - NH_2 + HNO \longrightarrow R - N = NH + H_2O$$

- Starch iodide paper produces a blue color when it comes into contact with the endpoint.
- To prepare this solution, mix starch mucilage with potassium iodide and soak the filtered paper in it.

$$KI + HCl \rightarrow HI + KCl$$

$$2HI + 2HONO \rightarrow I_2 + 2NO + 2H_2O \text{ (excess)}$$

$$I_2 + \text{Solution of paste of starch} \rightarrow \text{blue colour (endpoint)}$$

Types of Diazotization Titrations:

- Based on the diazotization titration, it can be of three primary methods:

1. Direct Method: This method involves treating the given amino group with an acid solution to yield the diazonium salts of diazonium compounds. This solution will be kept in the ice water to maintain the temperature between 0-5 °C. Now, titrate it with sodium nitrate and wait for the endpoint.
2. Indirect Method: The application of the indirect method of titration is for insoluble diazonium salts. In this method, we shall have to add the excess nitrous acid to the titration solution sample. As it is an insoluble diazonium salt, we have to titrate it against some other titrant.
3. Other Methods: The other method involves the conversion into diazo oxides rather than the diazo compounds, as they tend to be more stable.

Factors Affecting Diazotization Titrations:

- Some of the factors that will affect the diazotization titration are as follows:

1. pH of $NaNO_2$
2. the concentration of the acid that we will use for the titration
3. the temperature of the reaction
4. Time duration of the reaction
5. Efficiency (fast or slow) of attached diazotized groups.

Conditions required for Diazotization Titrations:

- Some of the basic conditions that are necessary to maintain for the diazotization titration to proceed are as follows:

1. Maintaining the **Temperature** of the Reaction: All reactions require their appropriate temperature to take place. Increasing or decreasing this optimum temperature can greatly affect the reaction rate and stop the reaction. Similarly, the diazonium compounds formed after the reactions easily decompose at higher temperatures. Therefore, it is necessary to maintain the optimum temperature (i.e. between 0 to 5°C) to get the best result without errors. Moreover, at optimum temperature, more stable diazo compounds are formed.

2. Rate of Titration: The rate of reaction varies with different compounds. Similarly, the rate of reaction of amino compounds with HONO will differ. Based on this, amino compounds are classified into two main groups:

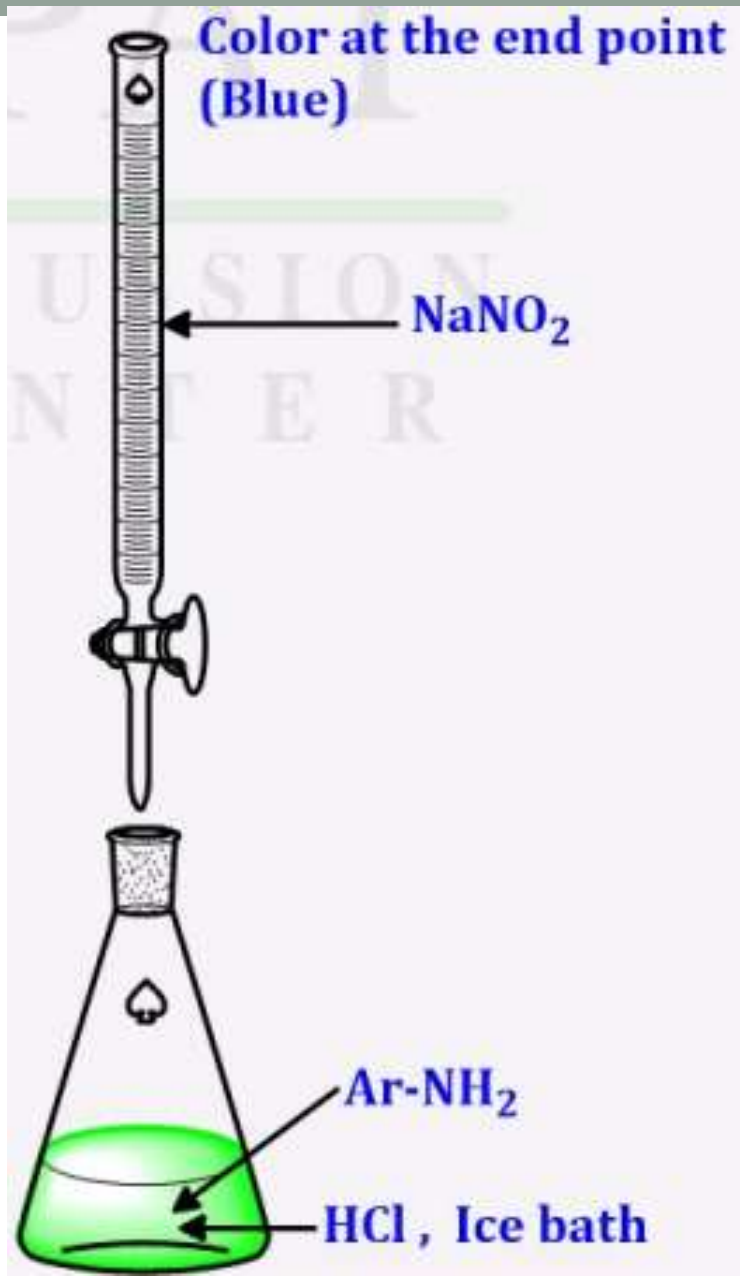
a) **Fast diazotisable:** Compounds with only amino groups or sometimes –CH3 or hydroxyl groups come under fast diazotisable compounds. e.g. aminophenol and aniline

b) **Slow diazotisable:** Compounds containing nitrous oxide groups, carboxylic groups, sulpha groups etc. come under the category of slow diazotisable compounds. e.g. sulphanilic acid, anthranilic acid etc.

Procedure:

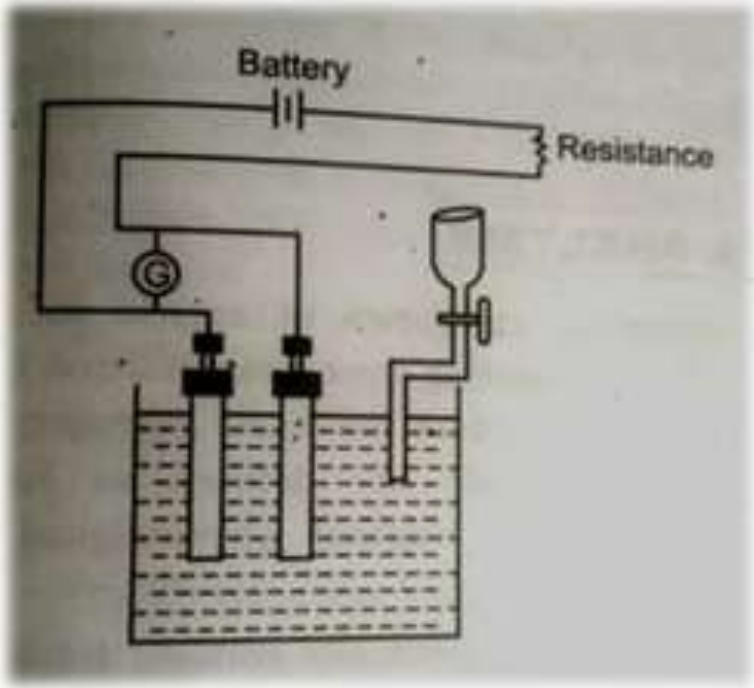
Standard Solution:

- 2.5 gm of the sample is accurately weighed and transferred into a 250 ml standard flask. To this, 50 ml of concentrated hydrochloric acid and 5 gm potassium bromide are added. Final volume is made up with distilled water.
- From this standard solution appropriate volume (50 ml) is pipetted out into a stoppered conical flask and the temperature is maintained at **0-5°C**. Then the solution is titrated with the **N/10 NaNO2** solution until the **starch iodide paper** turns into **blue colour.**



Potentiometric Titration :

- Alternatively, the titration can be performed using Potentiometry also.



- Apparatus consists of a beaker (200 ml) capacity with two similar platinum electrode having 0.5 to 1.0 sq.cm surface area & placed 1.5 cm apart fitted with magnetic stirrer.
- 1.5 volt dry cell battery
- variable potentiometer with sensitive galvanometer.
- Surface of electrode cleaned by immersing boiling nitric acid with small amount of ferric chloride followed by washing with water.

Procedure:

- About 0.5 gm of sample is weighed accurately and transferred into a 250 ml beaker. The contents are dissolved using **10 ml HCI** and **7.5 ml of water.**
- A pair of bright platinum electrodes are inserted into the solution and connected through a sensitive galvanometer. A potential drop between 30-50 mμ across the electrodes is produced using a suitable potentiometer.
- Titration is slowly carried out with N/10 $NaNO_2$ with continuous stirring until **a permanent deflection** of the galvanometer is observed at the end point.
- Liberation of excess of nitrous acid at the **end point depolarizes** the **electrode,** current flows and full deflection in galvanometer needle is observed.
- This is known as the dead stop end point. The electrode must be clean otherwise the end point is sluggish.
- Cleaning the electrodes in boiling nitric acid containing a little ferric chloride for about 30 sec and then washing with water will solve the problem of sluggish endpoint.
- The blank determination is carried out and the volume is subtracted front the sample titration volume to give the exact volume required to react with the amine.

Advantages & Disadvantages:

Advantages:

- Selective for all types of sulphonamides
- Sensitive
- Reproducible

Disadvantages:

- Useful for very less variety of sample.
- Relatively slow as compared to other methods.
- Temperature condition are essential to maintain for the reaction.
- End point detection is very difficult.
- Color produce is not stable.
- Lack of specificity.

Applications

1. Sulphonamides are determined using this method: Weigh a sample of 1 mg of sulphonamide accurately and dissolve it in 4ml of concentrated HCl and 10ml of distilled water. The 0.1 M Solution of Sodium Nitrite solution is then titrated with this solution after cooling to 15 °C. After one drop of the solution has been streaked on the starch iodide paper, until the blue color appears, you know you have reached the endpoint. Based on the following equation, the percentage content of the sulpha drug is determined:

- This formula requires

$$\text{Percentage of sulpha drug} = \frac{V \times M \times EW}{W \times 10}$$

V - the volume of the titrant consumed;

M - the molarity of the titrant;

EW- the weight of equivalent drug;

W- the weight of the sample.

- **Applied to the determination of chlorpheniramine.**
- **This is used to determine the amount of dopamine in a sample.**
- **Procaine is determined with this substance.**
- **Amphetamine is determined by using this reaction.**
- **Procaine is determined by using this test.**
- **For determining ephedrine.**
- **This test is used in determining how much P-amino benzoic acid (vitamin B4) is present in food.**

Thank You....