Determination of Order of Reaction

The order of a reaction cannot generally be determined from the balanced chemical equation because the stoichiometric coefficients do not necessarily represent the dependence of the reaction rate on the concentration of the reactants. Instead, the order of a reaction is determined experimentally by studying how the reaction rate varies with the concentration of one or more reactants under controlled conditions. Several experimental methods have been developed for this purpose, each based on a different mathematical or graphical approach. The choice of method depends on the nature of the reaction and the experimental data available.

The commonly used methods for determining the order of a reaction are:

- Differential Method (Van't Hoff Method)
- Method of Integration (Integrated Rate Equation Method)
- Half-Life Method
- Isolation Method (Ostwald's Method)

Each of these methods provides a reliable means of determining the order of a reaction by analysing the relationship between reaction rate, reactant concentration, and time. These methods are discussed in detail in the following sections.

Differential Method (Van't Hoff Method)

The **Differential Method**, also known as the **Van't Hoff Method**, is one of the earliest experimental methods used to determine the order of a chemical reaction. This method is based on the direct measurement of the instantaneous rate of reaction at different reactant concentrations. By comparing how the reaction rate changes with concentration, the order of the reaction can be calculated mathematically.

Consider a reaction

$$A \longrightarrow \text{Products}$$

whose rate law is

$$\text{Rate} = k[A]^n$$

where k is the rate constant and n is the order of the reaction.

Suppose two experiments are performed with different initial concentrations.

For the first experiment,

$$R_1 = k[A_1]^n$$

For the second experiment,

$$R_2 = k[A_2]^n$$

Dividing the two equations,

$$\frac{R_2}{R_1} = \left(\frac{A_2}{A_1}\right)^n$$

Taking logarithms on both sides,

$$\log\left(\frac{R_2}{R_1}\right) = n \log\left(\frac{A_2}{A_1}\right)$$

Therefore, the order of the reaction is

$$\boxed{n = \frac{\log(R_2/R_1)}{\log(A_2/A_1)}}$$

Procedure

1. Measure the initial concentration of the reactant.
2. Determine the initial rate of reaction.
3. Repeat the experiment using different initial concentrations.
4. Substitute the observed values into the Van't Hoff equation.
5. Calculate the value of the order of the reaction.

Advantages

- Simple mathematical treatment.
- Suitable for reactions whose rates can be measured accurately.
- Can determine fractional as well as integral orders.

Limitations

- Accurate measurement of instantaneous reaction rates is difficult.
- Small experimental errors in rate measurement may produce large errors in the calculated order.
- Not suitable for very fast or very slow reactions.

Important Points

- The method is based on the differential rate equation.
- The reaction order is obtained experimentally.
- The balanced chemical equation is not required for determining the order.
- The method is also known as the **Van’t Hoff Differential Method**.