

Method of Integration (Integrated Rate Equation Method)

The **Method of Integration**, also known as the **Integrated Rate Equation Method**, is one of the most widely used methods for determining the order of a chemical reaction. In this method, the experimentally measured concentrations of the reactant at different time intervals are substituted into the integrated rate equations corresponding to zero-order, first-order, and second-order reactions. The equation that gives a constant value of the rate constant k throughout the reaction indicates the correct order of the reaction.

Unlike the differential method, this method does not require the measurement of instantaneous reaction rates. Instead, it uses concentration-time data obtained experimentally, making it more accurate and convenient for many reactions.

Principle

Suppose the concentration of a reactant is measured at different times during a reaction. The experimental data are tested using the integrated rate equations for different reaction orders.

Case I: Zero-Order Reaction

The integrated rate equation is

$$[A] = [A]_0 - kt$$

or

$$k = \frac{[A]_0 - [A]}{t}$$

If the calculated value of k remains constant for all observations, the reaction is a **zero-order reaction**.

Case II: First-Order Reaction

The integrated rate equation is

$$k = \frac{2.303}{t} \log \left(\frac{[A]_0}{[A]} \right)$$

If the calculated value of k is constant at different time intervals, the reaction follows **first-order kinetics**.

Case III: Second-Order Reaction

The integrated rate equation is

$$k = \frac{1}{t} \left(\frac{1}{[A]} - \frac{1}{[A]_0} \right)$$

If the calculated value of k remains constant, the reaction is a **second-order reaction**.

Graphical Method

The order of a reaction can also be determined graphically by plotting the appropriate functions of concentration against time.

Order of Reaction	Graph	Nature of Graph
Zero Order	$[A] \text{ vs } t$	Straight line with negative slope
First Order	$\ln[A] \text{ vs } t$	Straight line with negative slope
Second Order	$1/[A] \text{ vs } t$	Straight line with positive slope

Procedure

1. Measure the concentration of the reactant at different time intervals.
2. Calculate the rate constant using the integrated rate equation for zero-order, first-order, and second-order reactions separately.
3. Compare the calculated values of the rate constant.
4. The equation that produces a constant value of k represents the correct order of the reaction.

Advantages

- Simple and accurate method for determining reaction order.
- Does not require measurement of instantaneous reaction rates.
- Applicable to most homogeneous reactions.
- Provides both the reaction order and the rate constant simultaneously.

Limitations

- Requires accurate concentration-time data.
- Errors in concentration measurements affect the calculated rate constant.
- Less suitable for highly complex reactions involving multiple mechanisms.

Important Points

- The method is based on integrated rate equations.
- The correct reaction order is identified by obtaining a constant value of the rate constant.
- It is one of the most commonly used experimental methods in chemical kinetics.
- The graphical approach provides an additional confirmation of the reaction order.