## DETERMINE THE ORDER OF REACTION

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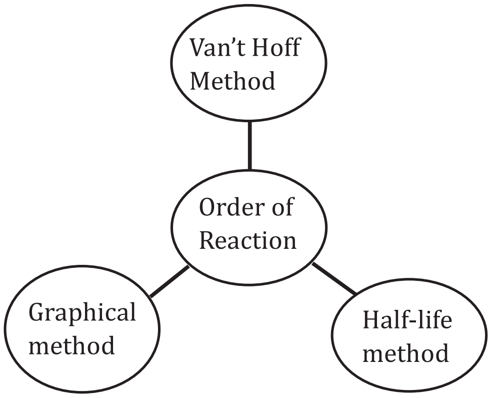


### Initial Rate Method

In this method initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant

$$R = k[A]^x[B]^y[C]^z$$

if [B] & [C] = Constant then for two different initial concentrations of A we have

$$R_{0_1} = k[A_0]_1^a \quad \text{And} \quad R_{0_2} = k[A_0]_2^a$$

$$\frac{R_{0_1}}{R_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^n$$

### Graphical Method

This technique is applicable when there is a sole reactant involved. If the graph of the natural logarithm of [A] against time (t) forms a linear relationship, the reaction adheres to a first-order mechanism. When the plot of the reciprocal of [A] against time is a straight line, the reaction conforms to second order. If the graph of the reciprocal of the square of [A] yields a straight line, the reaction corresponds to third order. In general, for a reaction of nth order, the graph of the reciprocal of [A] raised to the power of (n-1) against time must exhibit a linear trend. Here, [A] denotes the concentration of the reactant at any given time during the reaction, excluding t = 0. The expression [A] = (a-x) is used, where 'a' represents the initial concentration and 'x' signifies the extent of the reaction at time 't'.

### Half Life Method

This method is used only when the rate law involved by only one concentration term.

$$t_{(1/2)} \infty a^{1-n}$$

$$t_{(1/2)} = k' \, 1/a^{n-1}$$

$$\log t_{(1/2)} = \log k' + (1-n)a$$

Plotting $\log(t_{\frac{1}{2}})$ against log(a) results in a linear graph with a slope of (1-n), where 'n' represents the order of the reaction. The determination of the slope allows us to ascertain the reaction order, with 'n' being the obtained value.

If half-life at different concentrations is given then

$$(t_{1/2})_1 \alpha \frac{1}{a_1^{n-1}}$$

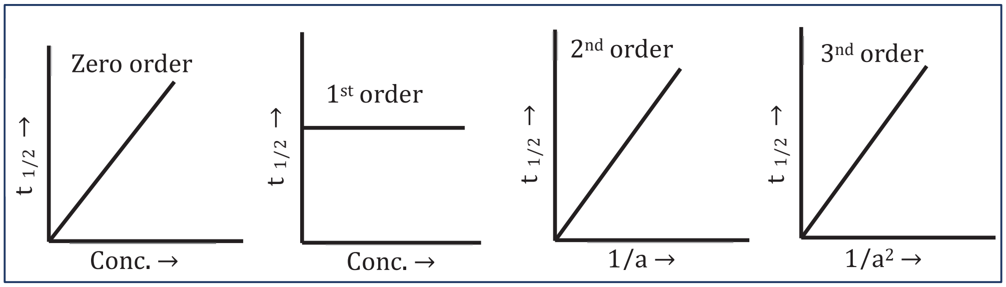
$$(t_{1/2})_2 \alpha \frac{1}{a_2^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = (\frac{a_2}{a_1})^{n-1}$$

Taking logarithm and rearranging

$$n = 1 + \frac{\log (t_{1/2}) - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$

Plots of half-lives concentration ($t_{1/2} \infty a^{1-a}$):



This relation can be used to determine order of reaction 'n'

## Van't Hoff Differential Method

The rate of a reaction is known to change according to the nth power of the concentration of the reactant, with 'n' representing the reaction order.

Thus, for two different initial concentrations $C_1$ and $C_2$, equations can be written in the form

$$\log\left(\frac{dC_1}{dt}\right) = \log k + n \log C_1 \qquad ....(i)$$

and

$$\log\left(\frac{dC_2}{dt}\right) = \log k + n \log C_2 \qquad ....(ii)$$

Taking logarithms,

Subtracting Eq. (ii) from (i),

$$\log (\frac{dC_1}{dt}) - \log (\frac{dC_2}{dt}) = n(\log C_1 - \log C_2)$$

or

$$n = [\log (-(dC_1)/dt)-\log((dC_2)/dt)] \div [\log C_1 - \log C_2] \qquad .... (iii)$$

$-dc_1/dt$ and $-dc_2/dt$ are determined from concentration vs. time graphs and the value of 'n' can be determined.

## Half-life of Order of Reactions

The half-life of a chemical reaction is the duration it takes for the concentration of a specific reactant to decrease to 50% of its initial concentration, signifying the time for the reactant concentration to reach half of its starting value. Represented by the symbol '$t_{1/2}$', it is commonly measured in seconds.

## Half-Life Formula

It's crucial to emphasize that the formula for the half-life of a reaction changes depending on the reaction order.

In the case of a zero-order reaction, the mathematical expression that can be utilized to calculate the half-life is: $t_{1/2} = [R]_0/2k$

For a first-order reaction, the half-life is given by: $t_{1/2} = 0.693/k$
For a second-order reaction, the formula for the half-life of the reaction is: $1/k[R]_0$
Were,
$t_{1/2}$ is the half-life of the reaction (unit: seconds)
$[R_0]$ is the initial reactant concentration (unit: mol. $L^{-1}$ or M)
k is the rate constant of the reaction (unit: $M^{(1-n)}s^{-1}$ where 'n' is the reaction order)

## Derivation of Half-Life Formula for Zero-Order Reactions

In a zero-order reaction, the rate constant is expressed in units of mol. $L^{-1}.s^{-1}$. The formula for the rate constant in a zero-order reaction is:

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

Substituting $t = t_{1/2}$, at which point $[R] = [R]_0/2$ (at the half-life of a reaction, reactant concentration is half of the initial concentration).

$$k = \frac{[R]_0 - [R]_0/2}{t_{1/2}}$$

Rearranging the equation, the expression for the half-life of a zero-order reaction is found to be:

$$t_{1/2} = \frac{[R]_0}{2k}$$

Derivation of Half-Life Formula for First-Order Reactions
For a first-order reaction, the rate constant can be mathematically expressed as follows:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

From the definition of reaction half-life, at $t = t_{1/2}$, $[R] = [R]_0/2$. Substituting these values in the expression for the first-order rate constant, the following equation is obtained:

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R_0]}{[R]_0/2}$$

Rearranging the expression to find the value of $t_{1/2}$:

$$t_{1/2} = \frac{2.303}{k} \log (2) = \frac{0.693}{k}$$

Thus, the half-life of a first-order reaction is given by 0.693/k.

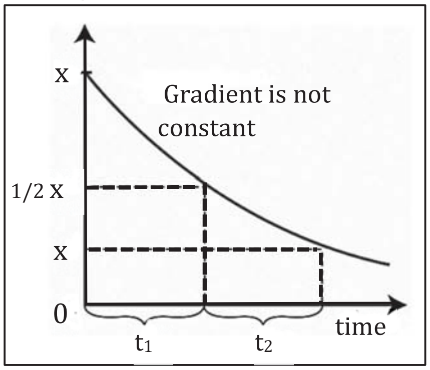
## Pseudo First Order Reaction

A Pseudo first-order reaction is characterized as a second-order or bimolecular reaction manipulated to exhibit behavior akin to a first-order reaction. This phenomenon occurs when one reactant is abundantly present or is maintained at a consistent concentration relative to the other substance. In this segment, we will explore pseudo-first-order reactions and their corresponding rate equations. Initially, we'll delve into reactions that exhibit characteristics of second-order reactions but, upon closer examination, can be approximated as first-order reactions.
For example, a second-order of the reaction is given by the equation,

$$A + B \text{—->} C + D$$

This reaction relies on the concentrations of both A and B, but one of the components is significantly abundant, causing its concentration to remain nearly constant throughout the reaction progression. Therefore, if component B is present in substantial excess with a much higher concentration than that of A, the reaction is classified as a pseudo-first-order reaction concerning A. Conversely, if component A is in substantial excess with a much higher concentration than that of B, the reaction is regarded as pseudo-first order with respect to B.

Graphing Pseudo-First Order Reactions



## Example of First-Order Reaction

To illustrate the concept more comprehensively, let's examine an example. Take the hydrolysis of ethyl acetate as a case study. During this hydrolysis, the concentration of ethyl acetate is 0.02 mol/L, while the quantity of water is substantial at 20 mol/L, given the extensive use of water in the hydrolysis process. Let's assume the hydrolysis process reaches completion in a time period denoted as 't.'

The reaction can be represented as

$$CH_3COOC_2H5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

(ethyl acetate) (Water) (Acetic acid) (ethyl alcohol)

| Components | $CH_3COOC_2H_5$ | $H_2O$ | $CH_3COOH$ | $C_2H_5OH$ |
|---|---|---|---|---|
| Concentration t = 0 | 0.02 | 20 | 0 | 0 |
| Concentration t | 0 | 19.8 | 0.02 | 0.02 |

For the above-mentioned reaction, the rate equation can be given as,

$$\text{Rate} = k\,[CH_3COOC_2H_5]\,[H_2O]$$

In this scenario, the concentration of water is notably elevated, leading to minimal fluctuations throughout the reaction. Consequently, it can be asserted that the reaction rate remains unaffected by variations in the concentration of $H_2O$. Putting the term for change of concentration of water in the above reaction to being zero we can write the effective rate equation as,

$$\text{Rate} = k\,[CH_3COOC_2H_5]$$

Here, the term kt takes into account the value of the constant concentration of water.

Where, $K = K'\,[H_2O]$

We see that the reaction behaves as a first-order reaction. Such reactions are termed pseudo-first-order reactions.

Another example of pseudo-first-order reaction is the inversion of cane sugar, given by the following reaction,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

(Cane sugar) (Water) (Glucose) (Fructose)

The rate equation can be given as,

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$