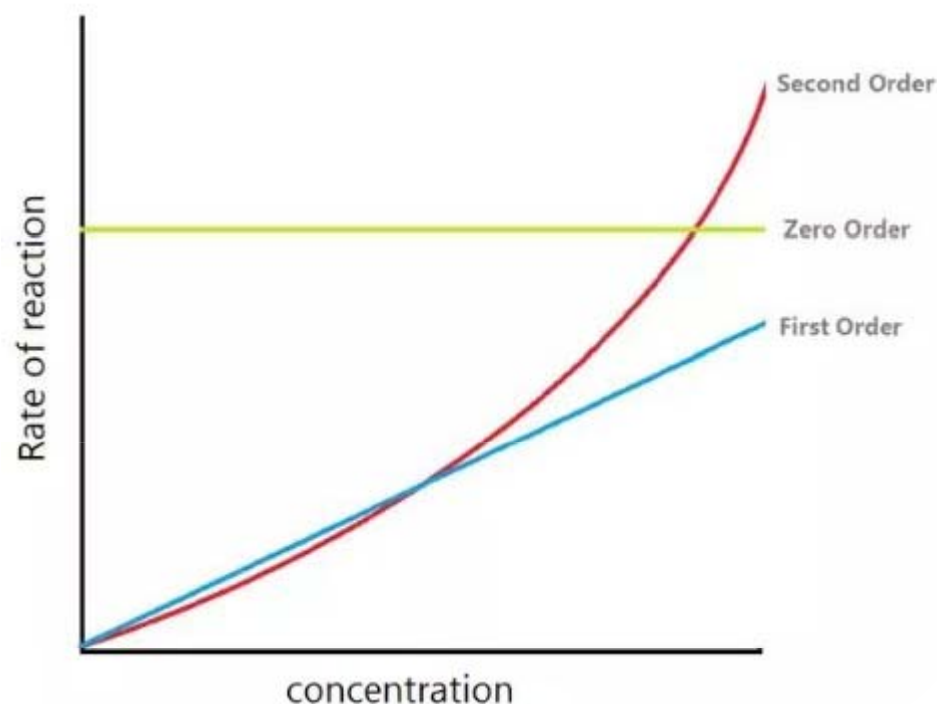


Methods for the determination of the order of a reaction

Part 1: Integrated rate equations



By-

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ORDER OF A REACTION

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k [A]^m [B]^n \quad \dots(1)$$

The order of such a reaction is $(m + n)$.

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n. The overall order of reaction $(m + n)$ may range from 1 to 3 and can be fractional.

Examples of reaction order :

RATE LAW

$$\text{rate} = k [N_2O_5]$$

$$\text{rate} = k [H_2] [I_2]$$

$$\text{rate} = k [NO_2]^2$$

$$\text{rate} = k [H_2] [NO]^2$$

$$\text{rate} = k [CHCl_3] [Cl_2]^{1/2}$$

REACTION ORDER

$$1$$

$$1 + 1 = 2$$

$$2$$

$$1 + 2 = 3$$

$$1 + 1/2 = 3/2$$

PSEUDO-ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. The experimental order which is not the actual one is referred to as the pseudo-order. Since for elementary reactions molecularity and order are identical, pseudo-order reactions may also be called pseudo molecular reactions.

Let us consider a reaction



in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can be written as

$$\text{rate} = k [A] [B]$$

As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

$$\text{rate} = k' [A]$$

where the new rate constant $k' = k [B]$. Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a pseudo-first order.

Example of Pseudo-order Reactions:

Hydrolysis of an ester.

For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.



ethyl acetate (excess) acetic acid ethyl alcohol

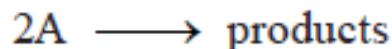
Here a large excess of water is used and the rate law can be written as

$$\begin{aligned}\text{rate} &= k [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}] \\ &= k' [\text{CH}_3\text{COOC}_2\text{H}_5]\end{aligned}$$

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.

SECOND ORDER REACTIONS

Let us take a second order reaction of the type



Suppose the initial concentration of A is a moles litre⁻¹. If after time t , x moles of A have reacted, the concentration of A is $(a - x)$. We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots(1)$$

where k is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a-x)^2} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{a-x} = kt + I \quad \dots(3)$$

where I is integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \quad \dots(4)$$

Substituting for I in equation (3)

$$\begin{aligned} \frac{1}{a-x} &= kt + \frac{1}{a} \\ kt &= \frac{1}{a-x} - \frac{1}{a} \end{aligned}$$

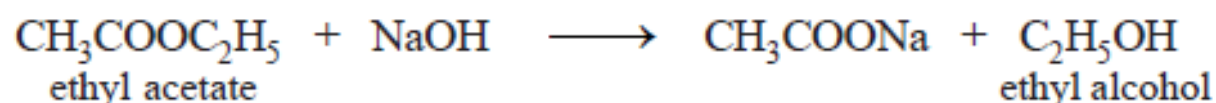
Thus

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

This is the integrated rate equation for a second order reaction.

Examples of Second order Reaction

Hydrolysis of an Ester by NaOH. This is typical second order reaction.



INTEGRATED RATE EQUATION WHEN REACTANT ARE DIFFERENT



where the initial concentration of A is $a \text{ mol dm}^{-3}$ and that of B is $b \text{ mol dm}^{-3}$. After time t , $x \text{ mol dm}^{-3}$ of A and $x \text{ mol dm}^{-3}$ of B react to form $x \text{ mol dm}^{-3}$ of the product. Thus, the reactant concentrations at time t are $(a - x)$ and $(b - x)$, respectively. The differential rate expression for the second-order reaction is, evidently,

$$r = -d[A]/dt = -d[B]/dt = d[P]/dt = k_2[A][B]$$

$$\text{This can be written as } r = dx/dt = k_2(a - x)(b - x) \quad \dots(13)$$

where k_2 is the second-order rate constant. Separating the variables, we have

$$dx/(a - x)(b - x) = k_2 dt \quad \dots(14)$$

Resolving into partial fractions (assuming that $a > b$), we have

$$\frac{1}{(a - x)(b - x)} = \frac{1}{a - b} \left[\frac{1}{b - x} - \frac{1}{a - x} \right] \quad \dots(15)$$

Using this result, we can integrate Eq. 14 as follows :

$$\int \frac{dx}{(a - x)(b - x)} = \frac{1}{a - b} \left[\int \frac{dx}{b - x} - \int \frac{dx}{a - x} \right] = k_2 \int dt \quad \dots(16)$$

We have taken the factor $1/(a - b)$ outside the integral sign because this quantity is a constant.

Carrying out the integration, we have

$$\frac{1}{a - b} \left[-\ln(b - x) - \{-\ln(a - x)\} \right] = k_2 t + C$$

$$\text{or} \quad \frac{1}{a - b} \ln \left[\frac{a - x}{b - x} \right] = k_2 t + C \quad \dots(17)$$

where C is the constant of integration. To determine C , we recall that at $t=0$, $x=0$. Hence, from Eq. 17,

$$C = \frac{1}{a-b} \ln \left(\frac{a}{b} \right) \quad \dots(18)$$

Substituting this value of C in Eq. 17, we have

$$\frac{1}{a-b} \ln \left(\frac{a-x}{b-x} \right) = k_2 t + \frac{1}{a-b} \ln \left(\frac{a}{b} \right)$$

Rearranging and solving for k_2 , we get

$$k_2 = \frac{1}{(a-b)t} \left[\ln \left(\frac{a-x}{b-x} \right) - \ln \left(\frac{a}{b} \right) \right] = \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)} \quad \dots(19)$$

Eq. 19 is the required integrated expression for the rate constant of a second-order reaction. Here we have assumed that $a > b$. If we had assumed that $b > a$, then the reader can easily verify that

$$k_2 = \frac{1}{(b-a)t} \ln \frac{a(b-x)}{b(a-x)} \quad \dots(20)$$

It can be easily seen that neither Eq. 19 nor Eq. 20 is applicable when the concentrations of both the reactants are the same, *i.e.*, when $a=b$.

If we write Eq. 19 in the form

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = k_2 t \quad \dots(21)$$

we see that it is the equation of a straight line passing through the origin (*viz.*, $y=mx$), where

$$y \equiv \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} ; \quad m \equiv k_2 ; \quad x \equiv t$$

The plot of the left-hand side of Eq. 21 versus t gives a straight line (Fig. 5) whose slope is equal to the rate constant, k_2 .

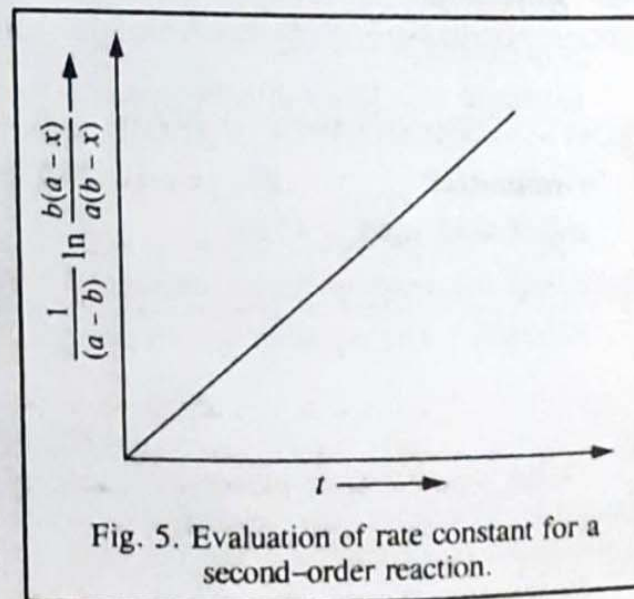


Fig. 5. Evaluation of rate constant for a second-order reaction.

$$\begin{aligned}
\frac{1}{(a-x)(b-x)} &= \frac{a-b}{(a-b)\{(a-x)(b-x)\}} \\
&= \frac{a-b-x+x}{(a-b)\{(a-x)(b-x)\}} \\
&= \frac{(a-x)-(b-x)}{(a-b)\{(a-x)(b-x)\}} \\
&= \frac{1}{(a-b)} \left\{ \frac{(a-x)-(b-x)}{(a-x)(b-x)} \right\} \\
&= \frac{1}{(a-b)} \left\{ \frac{1}{(b-x)} - \frac{1}{(a-x)} \right\}
\end{aligned}$$

Example 26. Derive an expression for the half-life of an n th-order reaction where $n \geq 2$.

Solution : An n th-order reaction may be represented as

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

The differential rate equation is

$$- d[A]/dt = k_n[A]^n \quad \dots (i)$$

where k_n is the n th-order rate constant.

Separating the variables and integrating, we obtain

$$\int -\frac{d[A]}{[A]^n} = k_n \int dt \quad \dots (ii)$$

or
$$t = \frac{1}{k_n(n-1)[A]^{n-1}} + C \quad \dots (iii)$$

where C is the constant of integration which we have to determine.

Let $[A] = a$ and $[A]_0 = a_0$, the initial concentration. Then, Eq. (iii) can be written as

$$t = \frac{1}{k_n(n-1)a^{n-1}} + C \quad \dots (iv)$$

At $t=0$, $a=a_0$, so that
$$C = \frac{1}{k_n(n-1)a_0^{n-1}} \quad \dots (v)$$

Substituting for C in Eq. (iv), we get

$$t = \frac{1}{k_n(n-1)} \left[\frac{1}{a^{n-1}} - \frac{1}{a_0^{n-1}} \right] \quad \dots (vi)$$

When $t=t_{1/2}$, $a=a_0/2$ so that from Eq. (vi),

$$t_{1/2} = \frac{1}{k_n(n-1)} \left[\frac{1}{(a_0/2)^{n-1}} - \frac{1}{a_0^{n-1}} \right] \quad \dots (vii)$$

or
$$t_{1/2} = \frac{2^{n-1} - 1}{k_n(n-1)a_0^{n-1}} \quad \dots (viii)$$

which is the desired expression. This expression shows that for an n th-order reaction, $t_{1/2} \propto (1/a_0)^{n-1}$ where $n \geq 2$.

