Methods for Determination of Order of a reaction

(1) **Substitution method in integrated rate equation:** (Hit and Trial method)

(i) The method can be used with various sets of a, x, and t with integrated rate equations.

(ii) The value of k is determined and checked for all sets of a, x and t.

(iii) If the value of k is constant, the used equation gives the order of reaction.

(iv) If all the reactants are at the same molar concentration, the kinetic equations are :

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$ (*For first order reactions*)

$$k = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{a-x}\right]$$ (*For second order reactions*)

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$ (*For third order reactions*)

(2) **Half life method :** This method is employed only when the rate law involved only one concentration term.

$t_{1/2} \propto a^{1-n}$; $t_{1/2} = ka^{1-n}$; $\log t_{1/2} = \log k + (1-n) \log a$, a plotted graph of $\log t_{1/2}$ *vs log a* gives a straight line with slope $(1-n)$, determining the slope we can find the order n. If half life at different concentration is given then.

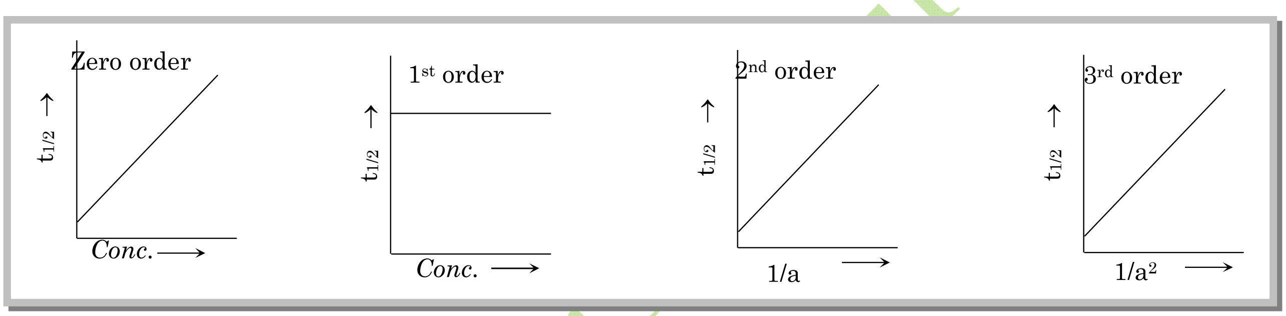
$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}};\ (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)\ [\log_{10} a_2 - \log_{10} a_1]$$

$$\boxed{n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}};$$

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

Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)



(3) **Graphical method :** A graphical method based on the respective rate laws, can also be used.

(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

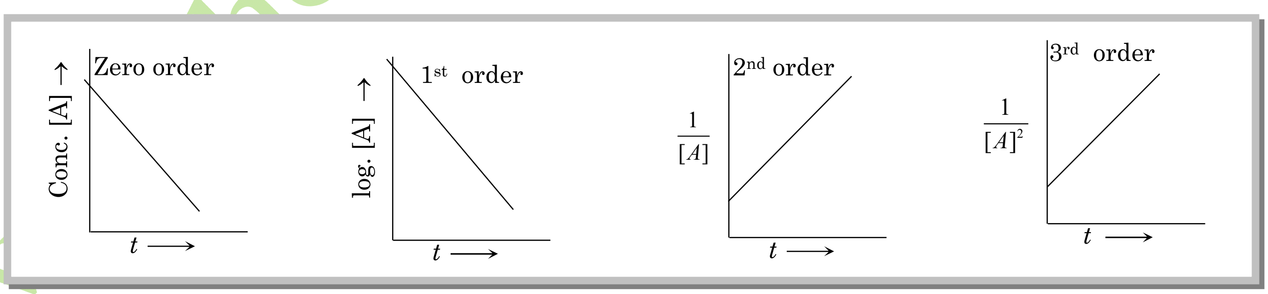
(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

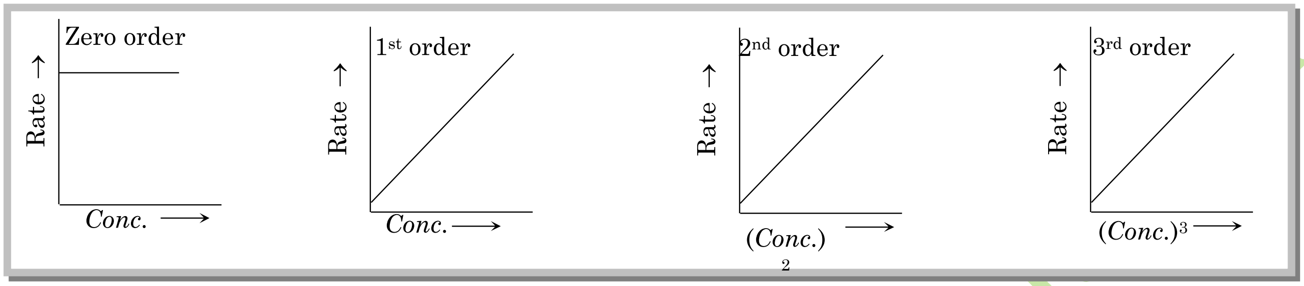
Graphical determination of order of the reaction

Order	Equation	Straight line plot		Slope	Intercept on *Y*-axis
		Y- axis	X-axis		
Zero	$x = k_0 t$	x	t	k_0	0
First	$\log_{10}(a-x) = \frac{-k_1 t}{2.303} + \log_{10} a$	$\log_{10}(a-x)$	t	$\frac{-k}{2.303}$	$\log_{10} a$
Second	$(a-x)^{-1} = k_2 t + a^{-1}$	$(a-x)^{-1}$	t	k_2	a^{-1}
n^{th}	$(a-x)^{1-n} = (n-1)k_n t + a^{1-n}$	$(a-x)^{1-n}$	t	$(n-1)k_n$	a^{1-n}

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = k(conc.)^n]



(4) **Van't Haff differential Method :** The rate of reaction varies as the n^{th} power of the concentration Where n is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form, $\frac{-dC_1}{dt} = kC_1^n$ and $\frac{-dC_2}{dt} = kC_2^n$

Taking logarithms, $\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n \log_{10} C_1$ .....(i)

and $\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n \log_{10} C_2$ .....(ii)

Subtracting equation (ii) from (i),

$$\boxed{n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2}} \quad .....(iii)$$

$\frac{-dC_1}{dt}$ and $\frac{-dC_2}{dt}$ are determined from concentration Vs time graphs and the value of 'n' can be determined.

(5) **Ostwald's isolation method** (Initial rate method) **:** This method can be used irrespective of the number of reactants involved *e.g.,* consider the reaction, $n_1A + n_2B + n_3C \rightarrow \text{Products}$.

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (*A*, *B*, *C*). Now the concentration of one of the reactants is changed (say that of *A*) taking the concentrations of other reactants (*B* and *C*) same as before. The initial rate of the reaction is determined again. This gives the rate expression with respect to *A* and hence the order with respect to *A*. The experiment is repeated by changing the concentrations of *B* and taking the same concentrations of *A* and *C* and finally changing the concentration of *C* and taking the same concentration of *A* and *B*. These will give rate expressions with respect to *B* and *C* and hence the orders with respect to *B* and *C* respectively. Combining the different rate expressions, the overall rate expression and hence the overall order can be obtained.

Suppose it is observed as follows:

(i) Keeping the concentrations of *B* and *C* constant, if concentration of *A* is doubled, the rate of reaction becomes four times. This means that, Rate $\propto [A]^2$ *i.e.,* order with respect to *A* is 2

(ii) Keeping the concentrations of *A* and *C* constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto$ $[B]$ *i.e.,* order with respect to *B* is 1

(iii) Keeping the concentrations of *A* and *B* constant, if concentration of *C* is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of *C* *i.e.,* order with respect to *C* is zero. Hence the overall rate law expression will be, Rate = $k[A]^2\,[B]\,[C]^0$

∴ Overall order of reaction = 2 + 1 + 0 = 3.

Examples based on Rate law, Rate constant and Order of reaction

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Example 1 : For a reaction, activation energy $(E_a) = 0$ and rate constant $(k) = 3.2\times10^{6}s^{-1}$ at 300*K*. What is the value of the rate constant at 310*K*.

(a) $3.2\times10^{-12}s^{-1}$ (b) $3.2\times10^{6}s^{-1}$ (c) $6.4\times10^{12}s^{-1}$ (d) $6.4\times10^{6}s^{-1}$

Solution (b) : When $E_a = 0$, the rate constant is independent of temperature so that rate constant $(k) = 3.2\times10^{6}\ sec^{-1}$.

Example 2 : 87.5% of a radioactive substance disintegrates in 40 minutes. What is the half life of the substance

(a) 13.58 min (b) 135.8 min (c) 1358 min (d)None of these

Solution(a) : Determination of *k* by substituting the respective values.

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40}\log\frac{a}{a-0.875a} = \frac{2.303}{40}\log\frac{a}{0.125a} = \frac{2.303}{40}\log 8$$

$= 0.051\ \ min^{-1}$

$$\therefore\ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.051} = 13.58\ \ min$$

Example 3 : The half-life period of a first order reaction is 100 sec. The rate constant of the reaction is

(a) $6.93\times10^{-3}\,\text{sec}^{-1}$ (b) $6.93\times10^{-4}\,\text{sec}^{-1}$

(c) $0.693\ \text{sec}^{-1}$ (d) $69.3\,\text{sec}^{-1}$

Solution (a) : $k=\frac{0.693}{t_{1/2}}=\frac{0.693}{100\ \text{sec}}=6.93\times10^{-3}\,\text{sec}^{-1}$

Example 4 : The rate constant of a first order reaction is 3×10^{-6} per second. If the initial concentration is 0.10*mol*, the initial rate of reaction is

(a) $3\times10^{-5}\text{mol}\ \text{s}^{-1}$ (b) $3\times10^{-6}\text{mol}\ \text{s}^{-1}$

(c) $3\times10^{-8}\text{mol}\ \text{s}^{-1}$ (d) $3\times10^{-7}\text{mol}\ \text{s}^{-1}$

Solution (d) : Given that, rate constant for first order reaction (k) = 3×10^{-6} per sec and initial concentration (a) = 0.10 *mol* we know that initial rate of reaction = $k(a)=3\times10^{-6}\times0.10=3\times10^{-7}\text{mol}\ \text{sec}^{-1}$

Example 5 : In a first order reaction the concentration of reactant decreases from $800\text{mol}/\text{dm}^3$ to $50\text{mol}/\text{dm}^3$ in $2\times10^2\,\text{sec}$. The rate constant of reaction in sec^{-1} is

(a) 2×10^4 (b) 3.45×10^{-5} (c) 1.386×10^{-2} (d) 2×10^{-4}

Solution (c) : $k=\frac{2.303}{t}\ \log_{10}\frac{a}{(a-x)}$;

$t=2\times10^2\,\text{sec}, a=800\text{mol}/\text{dm}^3,\ (a-x)=50\text{mol}/\text{dm}^3$

$$k=\frac{2.303}{2\times10^2}\log_{10}\frac{800}{50}=1.386\times10^{-2}\,\text{sec}^{-1}$$

Example 6 : The rate of a gaseous reaction is halved when the volume of the vessel is doubled. The order of reaction is

(a) 0 (b) 1 (c) 2 (d) 3

Solution (b) : (i) $R = k\ a^n$ (ii) $\frac{R}{2} = k\left(\frac{a}{2}\right)^n$

Dividing (i) by (ii), $2 = 2^n$. Hence $n = 1$.

Example 7 : The first order rate constant for the decomposition of N_2O_5 is $6.2\times10^{-4}\,sec^{-1}$. The half-life period for this decomposition in seconds is

(a) 1117.7 (b) 111.7 (c) 223.4 (d) 160.9

Solution (a) : $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2\times10^{-4}} = 1117.7\,sec$

Example 9 : A substance $'A'$ decomposes by a first order reaction initially with $(a) = 2.00mol$ and after $200\,min$, $(a-x) = 0.15mol$. For this reaction what is the value of k

(a) $1.29\times10^{-2}\,min^{-1}$ (b) $2.29\times10^{-2}\,min^{-1}$

(c) $3.29\times10^{-2}\,min^{-1}$ (d) $4.40\times10^{-2}\,min^{-1}$

Solution (a) : Given $[a] = 2.00mol$, $t = 200minute$ and $(a-x) = 0.15mol$

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} = \frac{2.303}{200}\log_{10}\frac{2.00}{0.15} = 1.29\times10^{-2}\,min^{-1}$$

Example 10 : The half-life for the reaction, $N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$ in 24 hrs. at 30^oC. Starting with $10g$ of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 *hours*

(a) 1.25g (b) 0.63g (c) 1.77g (d) 0.5g

Solution (b) : $k = \frac{0.693}{t_{1/2}} = \frac{0.69}{24} = \frac{2.303}{96}\log_{10}\frac{1}{(a-x)}$

Or $\log\frac{10}{(a-x)} = 1.2036$ or

$1 - \log(a-x) = 1.2036$ Or $\log(a-x) = -0.2036$; $(a-x) = 0.6258g$

Example 11 : Thermal decomposition of a compound is of the first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose

(a) 399 min (b) 2.99 min (c) 39.9 min (d) 3.99 min

Solution (a) : Half life of reaction =120 min

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.77\times10^{-3}\ \text{min}^{-1}$$

Applying first order reaction equation, $t = \frac{2.303}{k}\log_{10}\frac{a}{(a-x)}$; If $a = 100,\ x = 90$ or $(a-x) = 10$

$$\text{So, } t = \frac{2.303}{5.77\times10^{-3}}.\log_{10}10 = \frac{2.303}{5.77\times10^{-3}} = 399\,\text{min}$$

Example 12 : For a reaction $A+2B \rightarrow C+D$, the following data were obtained

Expt. Initial concentration (*moles litre*$^{-1}$)			**Initial Rate of formation of *D* (*moles litre*$^{-1}$ *min*$^{-1}$)**
S. No.	**[*A*]**	**[*B*]**	
1.	0.1	0.1	6.0×10^{-3}
2.	0.3	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.4×10^{-2}

The correct rate law expression will be

(a) Rate $= k[A]\ [B]$ (b) Rate $= k[A]\ [B]^2$

(c) Rate $= k[A]^2[B]^2$ (d) Rate $= k[A]^2[B]$

Solution (b) : From 1 and 4, keeping [*B*] constant, [*A*] is made 4 times, rate also becomes 4 times. Hence rate $\propto [A]$. From 2 and 3 keeping [*A*] constant, [*B*] is doubled, rate becomes 4 times. Hence rate $\propto [B]^2$. Overall rate law will be : rate = $k[A][B]^2$.

Example 13 : The rate of elementary reaction, $A \rightarrow B$, increases by a 100 when the concentration of *A* is increased ten folds. The order of the reaction with respect to *A* is

(a) 1 (b) 10 (c) 2 (d) 100

Solution (c) : $R = k[A]^n$; Also, $100R = k[10A]^n$; $\frac{1}{100} = \left[\frac{1}{10}\right]^n$; $\therefore n = 2$

Molecularity of Reaction

"*It is the sum of the number of molecules of reactants involved in the balanced equation*".

Or

"*It is the minimum number of reacting particles* (*Molecules, atoms or ions*) *that collide in a rate determining step to form product or products*".

- Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. Slowest step is the rate-determining step. This was proposed by ***Van't Hoff.***

Example : $NH_4NO_2 \rightarrow N_2 + 2H_2O$ *(Unimolecular)*

$NO + O_3 \rightarrow NO_2 + O_2$ *(Bimolecular)*

$2NO + O_2 \rightarrow 2NO_2$ *(Trimolecular)*

- Molecularity of a reaction can't be Zero, *negative* or fractional.
- Molecularity of a reaction is derived from the mechanism of the given reaction.
- Molecularity can not be greater than three because more than three molecules may not mutually collide with each other.

$$A_2 \;+\; \frac{3}{2}B_2 \;\rightarrow\; A_2B_3$$

Mechanism

Step I : $2A \rightarrow A_2$ *(Bimolecular)*

Step II : $A_2 \;+\; \frac{1}{2}B_2 \;\rightarrow\; A_2B$ *(Trimolecular)*

Step III : $A_2B \;+\; B_2 \;\rightarrow\; A_2B_3$ *(Bimolecular)*

Example **:** *Decomposition of* H_2O_2

$2H_2O_2 \rightarrow 2H_2O + O_2$ (*Overall reaction Mechanism*)

$H_2O_2 \rightarrow H_2O + O$ (*Slow*)

$H_2O_2 + O \rightarrow H_2O + O_2$ (*Fast*)

Rate = $K[H_2O_2]$; The reaction is unimolecular

(1) **Pseudo Unimolecular Reaction :** Reaction whose actual order is different from that expected using rate law expression are called ***pseudo-order reaction.*** For example, $RCl + H_2O \rightarrow ROH + HCl$

Expected rate law : Rate $= k[RCl][H_2O]$; Expected order $= 1 + 1 = 2$

Actual rate law : Rate $= k[RCl]$; Actual order $=1$

Because of water is taken in excess amount; therefore, its concentration may be taken constant. The reaction is therefore, pseudo first order. Similarly the acid catalysed hydrolysis of ester, viz.,

$$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$$

(follow first order kinetic) : Rate = k[RCOOR′]

Those reactions which may have order of reaction as one while molecularity of reaction 2 or more than two are as follows :

Examples **:**

(i) $2N_2O_5 \rightarrow 4NO_2 + O_2$; Order = 1; molecularity = 2

(ii) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$;

$r = k[CH_3COOC_2H_5]$ Order =1 , Molecularity = 2

(iii) inversion of cane sugar :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose glucose fructose

Order = 1, Molecularity = 2

(iv) $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$

Order = 1, Molecularity = 2

(v) $2H_2O_2 \xrightarrow{Pt,} 2H_2O + O_2$

Order = 1, Molecularity = 2

Difference between Molecularity and Order of reaction

Molecularity	**Order of Reaction**
It is the number of molecules of reactants terms taking part in elementary step of a reaction.	It is sum of the power of the concentration terms of reactants in the rate law expression.
Molcularity is a theoretical value	Order of a reaction is an experimental value
Molecularity can neither be zero nor fractional.	Order of a reaction can be zero, fractional for integer.
Moleculaity has whole number values only i.e., 1, 2, 3, etc.	Order of a reaction may have negative value.
It is assigned for each step of mechanism separately.	It is assigned for overall reaction.
It is independent of pressure and temperature.	It depends upon pressure and temperature.