

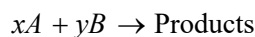
## Order of Reaction.

"The order of reaction is defined as the number of atoms or molecules whose concentration change during the chemical reaction."

*Or*

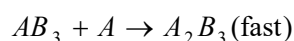
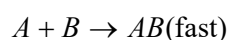
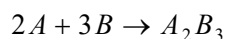
"The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction."

**Order of reaction = Sum of exponents of the concentration terms in rate law**



By the rate law,  $\text{Rate} = [\text{A}]^x [\text{B}]^y$ , then the overall order of reaction.  $n = x + y$ , where x and y are the orders with respect to individual reactants.

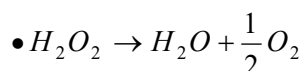
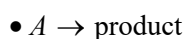
If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.



(Here, the overall order of reaction is equal to two.) An order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.

(1) **First order reaction:** When the rate of reaction depends only on the one concentration term of reactant.

Examples:

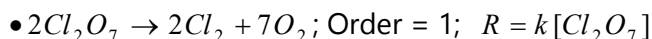
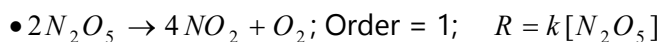
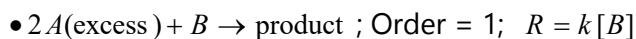


- All radioactive reactions are first order reaction.
- Rate of growth of population if there is no change in the birth rate or death rate.
- Rate of growth of bacterial culture until the nutrients are exhausted.

**Exception:**  $H_2O, H^+, OH^-$  and excess quantities are not considered in the determining process of order.

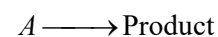
Examples: •  $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ ; Order = 1;

$$R = k[CH_3COOC_2H_5]$$



$$R = k[(CH_3)_3C-Cl]$$

(i) **Velocity constant for first order reaction** : Let us take the reaction



Initially  $t = 0$

$a$

0

After time  $t = t$

$(a - x)$   $x$

Here, ' $a$ ' be the concentration of A at the starting and  $(a - x)$  is the concentration of A after time  $t$  i.e.,  $x$  part has been changed in to products. So, the rate of reaction after time  $t$  is equal to

$$\frac{dx}{dt} \propto (a - x) \text{ or } \frac{dx}{dt} = k(a - x) \text{ or } \frac{dx}{(a - x)} = k \cdot dt \quad \dots(i)$$

integrated rate constant is,

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

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

(ii) **Half life period of the first order reaction** : when  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ , then eq. (ii)

becomes

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{\left(a - \frac{a}{2}\right)}; \quad t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{a/2}$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} 2 \quad (\because \log 2 = 0.3010); \quad \therefore t_{1/2} = \frac{2.303}{k} \times 0.3010$$

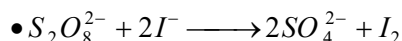
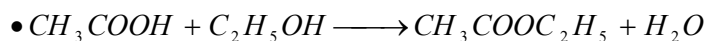
$$t_{1/2} = \frac{0.693}{k}$$

Half life period for first order reaction is independent from the concentration of reactant.

Time for completion of  $n^{\text{th}}$  fraction, 
$$t_{1/n} = \frac{2.303}{K} \log \frac{1}{\left(1 - \frac{1}{n}\right)}$$

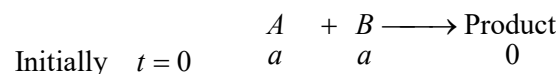
(iii) **Unit of rate constant of first order reaction** :  $k = (\text{sec})^{-1}$

(2) **Second order reaction**: Reaction whose rate is determined by change of two concentration terms is said to be a second order reaction. For example,



(i) **Calculation of rate constant**:  $2A \longrightarrow \text{product}$  or  $A + B \longrightarrow \text{product}$

When concentration of  $A$  and  $B$  are same.

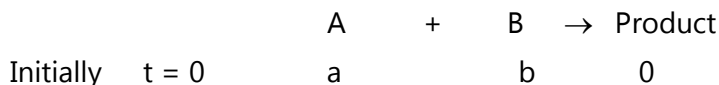


After time  $t = t$   $(a - x)$   $(a - x)$   $x$

$$\frac{dx}{dt} = k[A][B] = k[a - x][a - x]$$

$$\frac{dx}{dt} = k[a - x]^2; \text{ Integrated equation is } \boxed{k = \frac{1}{t} \cdot \frac{x}{a(a - x)}}; \quad \boxed{t = \frac{1}{k} \cdot \frac{x}{a(a - x)}}$$

When concentration of  $A$  and  $B$  are taken different



After time  $t = t$   $(a - x)$   $(b - x)$   $x$

$$\frac{dx}{dt} = k[a - x].[b - x], \text{ Integrated equation is,}$$

$$\boxed{k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}}; \quad \boxed{t = \frac{2.303}{k(a - b)} \log \frac{b(a - x)}{a(b - x)}}$$

(ii) **Half-life period of the second order reaction:** When  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ ;

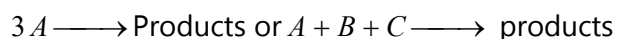
$$t_{1/2} = \frac{1}{k} \left( \frac{\frac{a}{2}}{a \times (a - \frac{a}{2})} \right) = \frac{1}{ka}$$

Half-life of second order reaction depends upon the concentration of the reactants.

$$t_{1/2} \propto \frac{1}{a}$$

(iii) **Unit of rate constant:**  $k = \text{mol}^{1-\Delta n} \text{ lit}^{\Delta n-1} \text{ sec}^{-1}$ ;  $\Delta n = 2$ ,  $k = \text{mol}^{-1} \text{ lit. sec}^{-1}$  (Where  $\Delta n$  = order of reaction)

(3) **Third order reaction:** A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

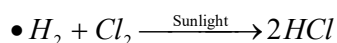


(i) **Calculation of rate constant:**  $\frac{dx}{dt} = k(a-x)^3$ , integrated equation is  $k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$

(ii) **Half-life period of the third order reaction:** Half-life period =  $\frac{3}{2a^2k}$ ;  $t_{1/2} \propto \frac{1}{a^2}$ ; Thus, half-life is inversely proportional to the square of initial concentration.

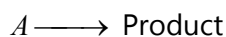
(iii) **Unit of rate constant:**  $k = \left( \frac{\text{mol}}{\text{litre}} \right)^{-2} \text{ time}^{-1}$  or  $k = \text{litre}^2 \text{ mol}^{-2} \text{ time}^{-1}$

(4) **Zero order reaction:** Reaction whose rate is not affected by concentration or in which the concentration of reactant do not change with time are said to be of zero order reaction. For example,



- Dissociation of  $HI$  on gold surface.
- Reaction between acetone and bromine.
- The formation of gas at the surface of tungsten due to adsorption.

(i) **Calculation of Rate Constant:** Let us take the reaction



Initially  $t = 0$        $a$        $0$

$$\frac{dx}{dt} = k[A]^0, \quad \frac{dx}{dt} = k; \quad dx = k \cdot dt$$

Integrated rate equation,  $\boxed{k = \frac{x}{t}}$ ; the rate of reaction is independent of the concentration of the reacting substance.

(ii) **Half-life period of zero order reaction:** When  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ ;  $t_{1/2} = \frac{a}{2k}$  or  $\boxed{t_{1/2} \propto a}$ ; the half-life period is directly proportional to the initial concentration of the reactants.

(iii) **Unit of Rate constant:**  $k = \frac{\text{mole}}{\text{lit. sec.}}$ ; Unit of rate of reaction = Unit of rate constant.

**Note:** In general, the units of rate constant for the reaction of  $n^{\text{th}}$  order are:

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

$$\frac{\text{mol L}^{-1}}{\text{s}} = k(\text{mol L}^{-1})^n \text{ or } k = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$$

**Units of rate constants for gaseous reactions:** In case of gaseous reactions, the concentrations are expressed in terms of pressure in the units of atmosphere. Therefore, the rate has the units of atm per second. Thus, the unit of different rate constants would be:

(i) Zero order reaction :  $\text{atm s}^{-1}$

(ii) First order reaction :  $\text{s}^{-1}$

(iii) Second order reaction:  $\text{atm}^{-1} \text{s}^{-1}$

(iv) Third order reaction:  $\text{atm}^{-2} \text{s}^{-1}$

In general, for the gaseous reaction of  $n^{\text{th}}$  order, the units of rate constant are  $(\text{atm})^{1-n}\text{s}^{-1}$

Modified expressions for rate constants of some common reactions of first order

Reaction	Expression for rate constant
$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$ <p>Here <math>V_t</math> = volume of <math>O_2</math> after time <math>t</math> and <math>V_\infty</math> = volume of <math>O_2</math> after infinite time.</p>
$NH_4NO_2(aq) \longrightarrow 2H_2O + N_2$	Same as above, here $V_t$ and $V_\infty$ are volumes of $N_2$ at time $t$ and at infinite time respectively.
$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$	$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$ <p>Here <math>V_0</math> and <math>V_t</math> are the volumes of <math>KMnO_4</math> solution used for titration of same volume of reaction mixture at zero time (initially) and after time <math>t</math>.</p>
$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$ <p>Here <math>V_0</math>, <math>V_t</math> and <math>V_\infty</math> are the volumes of <math>NaOH</math> solution used for titration of same volume of reaction mixture after time, 0, <math>t</math> and infinite time respectively.</p>
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{d\text{-Sucrose}}{C_6H_{12}O_6} + \underset{l\text{-Fructose}}{C_6H_{12}O_6}$ <p>(After the reaction is complete the equimolar mixture of glucose and fructose obtained is laevorotatory)</p>	$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$ <p>Here, <math>r_0</math>, <math>r_t</math> and <math>r_\infty</math> are the polarimetric readings after time 0, <math>t</math> and infinity respectively.</p>

Examples of reactions having different orders

Examples	Rate Law	Order
<i>First order reaction</i>		
$2H_2O_2 \longrightarrow 2H_2O + O_2$	$r = k [H_2O_2]$	1
$C_2H_5Cl \longrightarrow C_2H_4 + HCl$	$r = k [C_2H_5Cl]$	1

$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$r = k [N_2O_5]$	1
$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	$r = k [SO_2Cl_2]$	1
$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$	$r = k [\text{ester}][H_2O]^0$	1
$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$	$r = k [\text{sugar}][H_2O]^0$	1
All radioactive decay	$r = k [\text{radioactive species}]$	1
<i>Second order reactions</i>		
$NO + O_3 \longrightarrow NO_2 + O_2$	$r = k [NO][O_3]$	2
$2NO_2 \longrightarrow 2NO + O_2$	$r = k [NO_2]^2$	2
$H_2 + I_2 \longrightarrow 2HI$	$r = k [H_2][I_2]$	2
$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$	$r = k [CH_3CO_2C_2H_5][OH^-]$	2
$C_2H_4 + H_2 \longrightarrow C_2H_6$	$r = k [C_2H_4][H_2]$	2
$2N_2O \longrightarrow 2N_2 + O_2$	$r = k [N_2O]^2$	2
$2CH_3CHO \longrightarrow 2CH_4 + 2CO$	$r = k [CH_3CHO]^2$	2
<b>Third order reactions</b>		
$2NO + O_2 \longrightarrow 2NO_2$	$r = k [NO]^2[O_2]$	3
$2NO + Br_2 \longrightarrow 2NOBr$	$r = k [NO]^2[Br_2]$	3
$2NO + Cl_2 \longrightarrow 2NOCl$	$r = k [NO]^2[Cl_2]$	3
$Fe^{2+} + 2I^- \longrightarrow FeI_2$	$r = k [Fe^{2+}][I^-]^2$	3
<b>Zero order reactions</b>		
$H_2 + Cl_2 \longrightarrow 2HCl$ (over water)	$r = k [H_2]^0[Cl_2]^0$	0
$2NH_3 \xrightarrow{Pt} N_2 + 3H_2$	$r = k [NH_3]^0$	0
<b>Fractional order reactions</b>		
Para $H_2 \longrightarrow$ ortho $H_2$	$r = k [\text{para } H_2]^{1.5}$	1.5
$CO + Cl_2 \longrightarrow COCl_2$	$r = k [CO]^2[Cl_2]^{1/2}$	2.5
$COCl_2 \longrightarrow CO + Cl_2$	$r = k [COCl_2]^{3/2}$	1.5
$CH_3CHO \longrightarrow CH_4 + CO$	$r = k [CH_3CHO]^{3/2}$	1.5
<b>Negative order reaction</b>		
$2O_3 \longrightarrow 3O_2$	$r = k [O_3]^2[O_2]^{-1}$	-1 with respect to $O_2$ . Overall order = 1