

CHEMICAL KINETICS

ORDER, MOLECULARITY, Determination of order of reaction

Order of reaction

The rate of a given chemical reaction at constant temperature depends on the product of the concentration terms of the reactants. The equation representing the rate of reaction is called rate law. The sum of the powers of the concentration terms in the rate equation is called order of the reaction.

In the rate equation, $\text{rate} = k [C]^n$, the order of the reaction is 'n'.

For a general reaction, $aA + bB \rightarrow \text{products}$, if the rate equation is given as, $\text{Rate} = k [A]^x [B]^y$.

The order with respect to reactant A is 'x', with respect to reactant B is 'y' and the overall order of the reaction is $(x+y)$. Here the stoichiometric coefficients of the reactants 'a' and 'b' may or may not be equal to 'x' and 'y'.

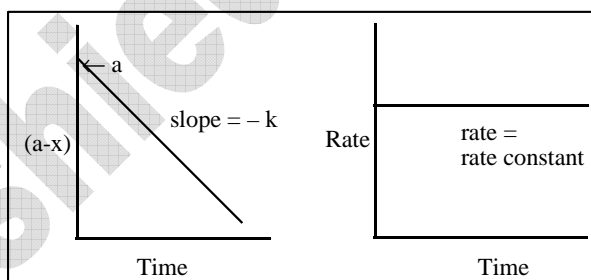
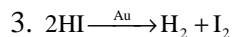
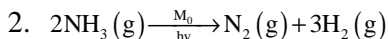
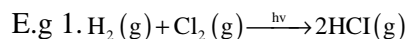
Order of the reaction may be zero, a finite number or fractional. Accordingly reactions are classified as zero, first, second, third, etc., or in general n^{th} order reaction. Integrated rate equations

Zero order: Reaction in which rate of the reaction is independent of the concentration of the reaction substances is called zero order reaction. Starting from an initial concentration of reactant is $[R]_0 = 'a'$, if 'x' is the concentration transformed in a time interval of 't', the concentration of the reactant after time 't' is $[R]_t = '(a - x)'$.

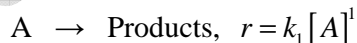
$$\text{Rate} = -\frac{dC}{dt} = \frac{d(a-x)}{dt} = k(a-x)^0 = k$$

For zero order, unit of rate constant K is $\text{mol.lit}^{-1}\text{S}^{-1}$

Half life $t_{1/2} = a/2k$



First order: Reaction in which rate of the reaction is directly proportional to the single concentration term of the reacting substance is called first order reaction



1. Rate Equation is: $\frac{dx}{dt} = k_1(a-x)$

2. Equation for rate constant: $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$

3. Units for rate constant: sec^{-1}

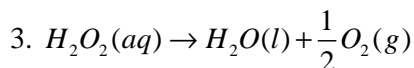
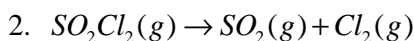
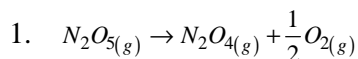
4. Half life time : $t_{1/2} = \frac{0.693}{k_1}$

5. in a first order gas phase reaction $A(g) \rightarrow B(g) + C(g)$

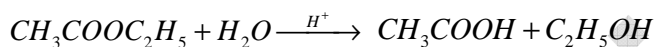
P_i be the initial pressure of A and P_t the total pressure of the reaction mixture at time 't' then

$$k = \frac{2.303}{t} \log \frac{P_i}{(2P_i - P_t)}$$

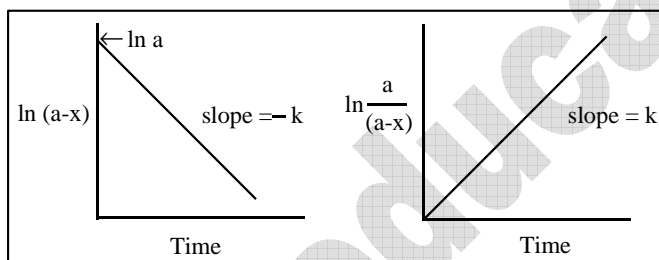
EXAMPLES:



4. Acid Hydrolysis of ester.



5. Disintegration of radioactive elements



In a First order reaction both Rate constant & half life are independent of initial concentration of reactants.

The time taken for completion of given fraction of first order reaction is always constant.

Time for completion of i. 75% of 1st order reaction = 2 $t_{1/2}$

ii 87.5% of 1st order = 3 $t_{1/2}$

iii. 90% of 1st order = 10/3 $t_{1/2}$

iv. 99% of 1st order = 20/3 $t_{1/2}$

v. 99.9% of 1st order = 10 $t_{1/2}$

SECOND ORDER REACTIONS:

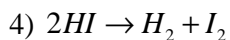
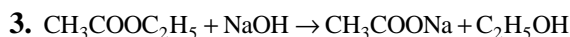
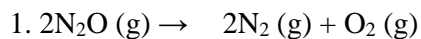


$$r = k_2 [A]^2 \text{ (or) } r = k_2 [A][B]$$

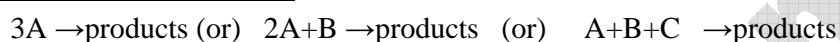
1. Units for rate constant: $\text{lit. mole}^{-1}.\text{sec}^{-1}$

2. Half life time : $t_{1/2} = \frac{1}{k_2 a}$

Examples:



THIRD ORDER REACTIONS:

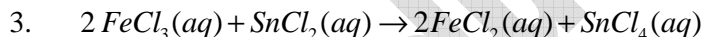
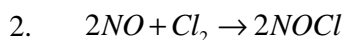
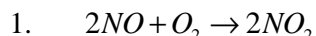


Rate, $r = K_1[\text{A}]^3$ (or) $r = K_2[\text{A}]^2[\text{B}]^1$ (or) $r = K_3[\text{A}]^1[\text{B}]^1[\text{C}]^1$

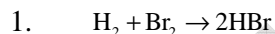
Units for rate constant: $\text{lit}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$.

Half life time : $t_{1/2} \propto \frac{1}{a^2}$

EXAMPLES:



FRACTIONAL ORDER REACTIONS:



Rate = $k[\text{H}_2][\text{Br}_2]^{1/2}$ Order = 1.5

NEGATIVE ORDER REACTIONS:

Conversion of ozone into oxygen

Rate = $K = [\text{O}_3]^2 [\text{O}_2]^{-3}$

Order with respect to oxygen is -1

PSEUDO UNIMOLECULAR REACTIONS:

The reactions with molecularity greater than or equal to 2 but order is one are called Pseudo unimolecular or Pseudo first order reactions.

E.g.: 1. Hydrolysis of ethyl acetate in acid medium

2. Inversion of cane sugar

MOLECULARITY OF THE REACTIONS:

1. The number of atoms or molecules or ions participating in the slowest step is called molecularity
2. Molecularity cannot be zero (or) fraction. It is always a whole number or integer.
3. Molecularity is obtained from reaction mechanism.
4. The sequence of the elementary steps of a chemical reaction is known as reaction mechanism.

- The slowest elementary step of the reaction is called rate determining step or rate limiting step.
- The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

Eg : 1. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, Unimolecular with order 1.

2. $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, Bimolecular with order 2.

3. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ trimolecular with order 3.

4. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$, Bimolecular with order 1.

5. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$, Bimolecular with order 2.

Molecularity may or may not be equal to order of the reaction.

Determination of order of reaction:

Starting from initial concentration 'a' if the change in concentration in time 't' is 'x' the rate equation in terms of order of the reaction 'n' is given as, Rate of reaction = $\frac{dx}{dt} = k(a-x)^n$

The order of a reaction is determined using integrated equation method, half-life method, Van't Hoff's differential method and Ostwald's isolation method.

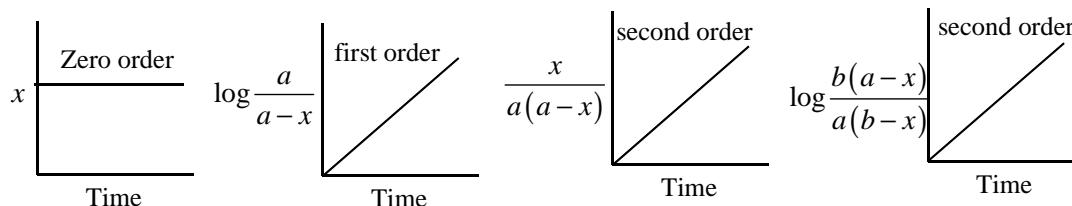
Integrated form of rate equation method:

It is also called trial and error method. The kinetic data is substituted in one of the integrated rate laws and the specific rates are calculated. If the same value of 'k' is obtained from the data of a reaction, the trail of choosing the rate law is successful and the corresponding order is obtained.

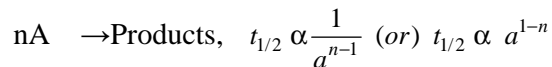
Order of reaction	Differential rate equation	Integral rate law
Zero order	- dC/dt = K	$k = \frac{x}{t}$
First order	- dC/dt = K[a-x]	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
Second order	- dC/dt = K[a-x] ²	$k = \frac{1}{t} \frac{x}{a(a-x)}$

Alternately, the order can also be ascertained graphically interpreting the results in terms of integrated rate law.

- x vs time is a straight line parallel to time axis denotes zero order.
- $\log [a/(a-x)]$ vs time is a straight line with a positive slope passing through origin denotes first order.
- $[x/a(a-x)]$ vs time is a straight line with a positive slope passing through origin denotes second order.



2. Half-time method: The time required for the initial concentration (a) of the reactant to become one-half of its value (a/2) during the progress of the reaction is called half-time ($t_{1/2}$) of the reaction. Half-time, also known as half-life is inversely proportional to $a^{(n-1)}$, where n is the order of the reaction of the type,



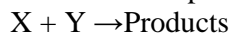
Say a given reaction is started separately with two initial concentrations 'a₁', and 'a₂'. The half - time values ($t_{1/2}$)₁ and ($t_{1/2}$)₂ are determined experimentally and the order is established from the equation.

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

3. Differential method: The rate of a reaction of order 'n' is given for two initial concentrations, C₁ and C₂ as $-\frac{dC_1}{dt} = kC_1^n$ and $-\frac{dC_2}{dt} = kC_2^n$ Hence, order of the reaction, is obtained by using Van't Hoff's equation.

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

4. Ostwald's isolation method: The isolation method is useful for the determination of order with respect to each of the reactant separately.



By applying Ostwald's method, the order n_x with respect to the reactant X and n_y with respect to reactant Y are separately determined.

For the purpose of determining orders, two experiments are conducted. In one experiment, concentration of Y is taken in large excess compared to that of X. Order, n_x is determined by varying the concentration of X in one of the three methods described above.

In the second experiment concentration of X is taken in large excess. Order, n_y is determined. The total order of the reaction is ($n_x + n_y$).

#. Concentration Vs time:

Order	X-axis	Y-axis	Nature of graph
i) Zero	time	C	Straight line with -Ve slope
ii) 1st	time	log C	Straight line with -Ve slope
iii) nth	time	1/C	Straight line not (n>1) passing through origin

#) Initial concentration Vs half life (t_{50}):

Order	X-axis	Y-axis	Nature of graph
i) Zero	C	$t_{1/2}$	Straight line passing through origin
ii) 1st	C	$t_{1/2}$	Straight line parallel to X-axis
iii) 2 nd	C	$t_{1/2}$	Straight line with -Ve slope