Differences Between Order and Molecularity

Order of a Reaction	Molecularity of a Reaction
1. It is the **sum of powers** of the concentration terms in the rate law expression.	1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction.
2. It is an **experimentally** determined value.	2. It is a **theoretical** concept.
3. It can have **fractional** value.	3. It is always a **whole number.**
4. It can assume **zero value.**	4. It **can not have zero value.**
5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration.	5. Molecularity is **invariant** for a chemical equation.

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

$$A + B \longrightarrow \text{products}$$

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.**

Examples of Pseudo-order Reactions

(1) **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.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{(excess)}}{H_2O} \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

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

$$\begin{aligned} \text{rate} &= k\,[CH_3COOH]\,[H_2O] \\ &= k'\,[CH_3COOH] \end{aligned}$$

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

(2) **Hydrolysis of sucrose.** Sucrose upon hydrolysis in the presence of a dilute mineral acid gives glucose and fructose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{(excess)}}{H_2O} \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

If a large excess of water is present, $[H_2O]$ is practically constant and the rate law may be written as

$$\text{rate} = k\,[C_{12}H_{22}O_{11}]\,[H_2O]$$
$$= k\,[C_{12}H_{22}O_{11}]$$

The reaction though of second-order is experimentally found to be first-order. Thus it is a pseudo-first-order reaction.

ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type

	A	$\longrightarrow$	Products
Initial conc.	a		0
Final conc.	$a - x$		x

$$\text{Rate of reaction} = \frac{-\,d[A]}{dt} = k_0\,[A]^\circ$$

or
$$\frac{dx}{dt} = \frac{-d\;(a-x)}{dt} = k_0\,(a-x)^\circ = k_0$$

On integrating we get

$$k_0 = \frac{x}{t} \quad \text{or} \quad x = k_0 t$$

where k_0 is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the **rate constant is equal to the rate of reaction at all concentrations.**

FIRST ORDER REACTIONS

Let us consider a first order reaction

$$\text{A} \longrightarrow \text{products}$$

Suppose that at the beginning of the reaction ($t = 0$), the concentration of A is a moles litre^{-1}. If after time t, x moles of A have changed, the concentration of A is $a - x$. We know that for a first order reaction, the rate of reaction, dx/dt, is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k\,(a-x)$$

or
$$\frac{dx}{a-x} = k\,dt \qquad \text{...(1)}$$

Integration of the expression (1) gives

$$\int \frac{dx}{a-x} = \int k\,dt$$

or
$$-\,1\text{n}\,(a-x) = kt + \text{I} \qquad \text{...(2)}$$

where I is the constant of integration. The constant k may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$\text{I} = -\,1\text{n}\,a$$

Substituting for I in equation (2)

$$1\text{n}\,\frac{a}{a-x} = kt \qquad \text{...(3)}$$

or
$$k = \frac{1}{t}\,1\text{n}\,\frac{a}{a-x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad \text{...(4)}$$

The value of k can be found by substituting the values of a and $(a - x)$ determined experimentally at time interval t during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

Examples of First order Reactions

Some common reactions which follow first order kinetics are listed below :

(1) **Decomposition of N_2O_5 in CCl_4 solution.** Nitrogen pentoxide in carbon tetrachloride solution decomposes to form oxygen gas,

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$$

The reaction is carried in an apparatus shown in Fig. 20.4. The progress of the reaction is monitored by measuring the volume of oxygen evolved from time to time.

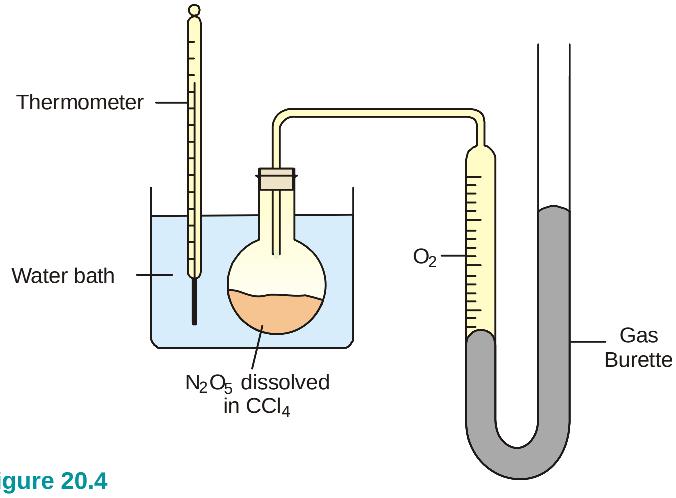

Figure 20.4
An apparatus for monitoring the volume of O_2 evolved in the decomposition of N_2O_5 dissolved in carbon tetrachloride.

If V_t be the volume of O_2 at any time t and V_∞ the final volume of oxygen when the reaction is completed, the V_∞ is a measure of the initial concentration of N_2O_5 and $(V_\infty - V_t)$ is a measure of undecomposed N_2O_5 $(a - x)$ remaining at time t. Thus,

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

On substituting values of V_∞, $(V_\infty - V_t)$ at different time intervals, t, the value of k is found to be constant. Thus it is a reaction of the first order.

SOLVED PROBLEM. From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48°C, show that the reaction is of the first order

t (mts)	10	15	20	∞
Vol of O_2 evolved	6.30	8.95	11.40	34.75

SOLUTION

For a first order reaction the integrated rate equation is

$$\frac{1}{t}\log\frac{V_\infty}{V_\infty - V_t} = k$$

In this example, $V_\infty = 34.75$

t	$V_\infty - Vt$	$\frac{1}{t}\log\frac{V_\infty}{V_\infty - V_t}$	=	k
10	28.45	$\frac{1}{10}\log\frac{34.75}{28.45}$	=	0.00868
15	25.80	$\frac{1}{15}\log\frac{34.75}{25.80}$	=	0.00862
20	23.35	$\frac{1}{20}\log\frac{34.75}{23.35}$	=	0.00863

Since the value of k is fairly constant, it is a **first order reaction**.

(2) **Decomposition of H_2O_2 in aqueous solution.** The decomposition of H_2O_2 in the presence of Pt as catalyst is a first order reaction.

$$H_2O_2 \xrightarrow{\text{Pt}} H_2O + O$$

The progress of the reaction is followed by titrating equal volumes of the reaction mixture against standard $KMnO_4$ solution at different time intervals.

SOLVED PROBLEM. A solution of H_2O_2 when titrated against $KMnO_4$ solution at different time intervals gave the following results :

t (minutes)	0	10	20
Vol $KMnO_4$ used for 10 ml H_2SO_4	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of H_2O_2 is a first order reaction.

SOLUTION

The integrated rate equation for first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

Since volume of $KMnO_4$ used in the titration is measure of concentration of H_2O_2 in solution,

$a = 23.8$ ml

$(a-x) = 14.7$ when $t = 10$ mts

$(a-x) = 9.1$ when $t = 20$ mts

Substituting these values in the rate equation above, we have

$$k = \frac{2.303}{10}\log\frac{23.8}{14.7}$$

$$= 0.2303\,(\log 23.8 - \log 14.7)$$

$$= 0.2303\,(1.3766 - 1.1673)$$
$$= 0.04820$$

and
$$k = \frac{2.303}{20} \log \frac{23.8}{9.1}$$
$$= 0.10165\,(\log 23.8 - \log 9.1)$$
$$= 0.10165\,(1.3766 - 0.9595) = 0.04810$$

Since the value of k is almost constant, the decomposition of H_2O_2 is a **first order reaction**.

(3) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate or methyl acetate in the presence of a mineral acid as catalyst, is a first order reaction.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{acetic acid}}{CH_3COOH} + C_2H_5OH$$

For studying the kinetics of the reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say N/2 HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore as the reaction proceeds, the volume of alkali required for titration goes on increasing.

SOLVED PROBLEM. The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

SOLUTION

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from t_0 to t_∞ gives the initial concentration of ester. Thus,

$a = 47.15 - 24.36 = 22.79$ ml

$(a - x)$ after 4500 sec $= 47.15 - 29.32 = 17.83$ ml

$(a - x)$ after 7140 sec $= 47.15 - 31.72 = 15.43$ ml

Substituting values in the rate equation above, we have

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455$$

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546$$

Since the values of k in the two experiments are fairly constant, the reaction is of the first order.

(4) **Inversion of Cane sugar (sucrose).** The inversion of cane sugar or sucrose catalyzed with dil HCl,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different time intervals. The optical rotation goes on changing since D-glucose rotates the plane of polarised light to the right and D-fructose to the left. **The change in rotation is proportional to the amount of sugar decomposed.**

Let the final rotation be r_∞, the initial rotation r_0 while the rotation at any time t is r_t

The initial concentration, a is ∞ $(r_0 - r_\infty)$.

The concentration at time t, $(a - x)$ is $\propto$ $(r_t - r_\infty)$

Substituting in the first order rate equation,

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

we have

$$k = \frac{2.303}{t} \log_{10} \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

If the experimental values of t $(r_0 - r_\infty)$ and $(r_t - r_\infty)$ are substituted in the above equation, a constant value of k is obtained.

SOLVED PROBLEM. The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below.

time (min)	0	7.18	18	27.1	∞
rotation (degree)	+24.09	+21.4	+17.7	+15	–10.74

Show that inversion of sucrose is a first order reaction.

SOLUTION

The available data is substituted in the first order rate equation for different time intervals.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$r_0 - r_\infty = 24.09 - (-10.74) = 34.83$ for all time intervals. Thus, the value of rate constant can be found.

time (t)	$r_t = r_\infty$	$k = \frac{1}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$
7.18	32.14	$k = \frac{1}{7.18} \log \frac{34.83}{32.14} = 0.0047$
18	28.44	$k = \frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$
27.1	25.74	$k = \frac{1}{27.1} \log \frac{34.83}{25.74} = 0.0048$

Since the value of k comes out to be constant, the inversion of sucrose is a **first order reaction**.

SECOND ORDER REACTIONS

Let us take a second order reaction of the type

$$2A \longrightarrow \text{products}$$

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,

$$\frac{dx}{dt} = k\,(a - x)^2 \qquad \text{...(1)}$$