to the slope of a straight line drawn tangent to the curve at that time. For example, in Fig. 20.2 the instantaneous rate at 10 seconds is found to be 0.0022 mol l^{-1} s^{-1}.

RATE LAWS

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions it is shown that : **the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.**

Thus for a substance A undergoing reaction,

rate $\qquad \text{rate} \propto [A]^n$

or $\qquad \text{rate} = k\,[A]^n \qquad$ ...(1)

For a reaction

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

the reaction rate with respect to *A* or *B* is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(2)$$

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations.

An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

The power (exponent) of concentration *n* or *m* in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant *k* is called the **rate constant** for the reaction.

Examples of rate law :

	REACTIONS	RATE LAW
(1)	$2N_2O_5 \longrightarrow 4\,NO_2 + O_2$	rate = $k\,[N_2O_5]$
(2)	$H_2 + I_2 \longrightarrow 2HI$	rate = $k\,[H_2]\,[I_2]$
(3)	$2NO_2 \longrightarrow 2NO + O_2$	rate = $k\,[NO_2]^2$
(4)	$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	rate = $k\,[H_2]\,[NO]^2$

In these rate laws where the quotient or concentration is not shown, it is understood to be 1. That is $[H_2]^1 = [H_2]$.

It is apparent that the rate law for a reaction must be determined by experiment. It cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action. However, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation. **But usually the powers of concentration in the rate law are different from coefficients.** Thus for the reaction (4) above, the rate is found to be proportional to $[H_2]$ although the quotient of H_2 in the equation is 2. For NO the rate is proportional to $[NO]^2$ and power '2' corresponds to the coefficient.

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

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(1)$$

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	REACTION ORDER
rate = $k\,[N_2O_5]$	1
rate = $k\,[H_2]\,[I_2]$	$1 + 1 = 2$
rate = $k\,[NO_2]^2$	2
rate = $k\,[[H_2]\,[NO]^2$	$1 + 2 = 3$
rate = $k\,[CHCl_3]\,[Cl_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

Reactions may be classified according to the order. If in the rate law (1) above

$m + n = 1$, it is **first order reaction**

$m + n = 2$, it is **second order reaction**

$m + n = 3$, it is **third order reaction**

ZERO ORDER REACTION

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $[A]^0 = 1$.

A zero order reaction is one whose rate is independent of concentration. For example, the rate law for the reaction

$$NO_2 + CO \longrightarrow NO + CO_2$$

at 200° C is

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

Here the rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is **zeroth order** with respect to CO. The reaction is second order with respect to $[NO_2]$. The overall reaction order is $2 + 0 = 2$.

MOLECULARITY OF A REACTION

Chemical reactions may be classed into two types :

(*a*) Elementary reactions

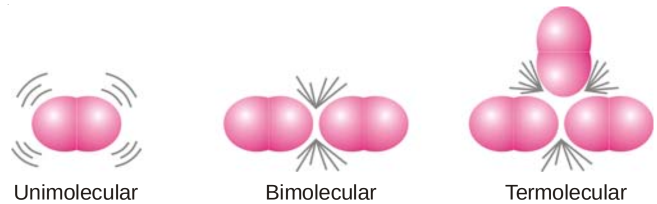
(*b*) Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

A **complex reaction** is that which occurs in two or more steps.

Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as : **the number of reactant molecules involved in a reaction.**



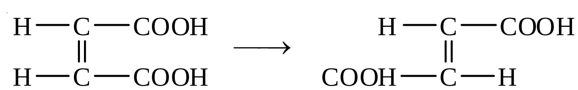
Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called **unimolecular, bimolecular and termolecular** respectively. Thus we have :

(*a*) **Unimolecular reactions :** (molecularity = 1)

$$A \longrightarrow \text{product}$$

Examples are : (*i*) $Br_2 \longrightarrow 2Br$

(*ii*)



maleic acid → fumaric acid

(*b*) **Bimolecular reactions :** (molecularity = 2)

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

Examples are :

(*i*) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$
Ethyl acetate → acetic acid + ethyl alcohol

(*ii*) $2HI \longrightarrow H_2 + I_2$

(*c*) **Termolecular reactions** : (molecularity = 3)

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

Examples are :

$$2NO + O_2 \longrightarrow 2NO_2$$
$$2NO + Cl_2 \longrightarrow 2NOCl$$

Why High Molecularity Reactions are Rare ?

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are very rare. The rarity of reactions with high molecularity can be explained on the basis of the kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules. Thus the possibility of three molecules colliding together is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closed and collide with one another at the same time. The possibility of their doing so is much less than even in the case of termolecular reaction. Hence the reactions involving many molecules proceed through a series of steps, each involving two or three or less number of molecules. Such a reaction is called a complex reaction and the slowest step determines the overall rate of the reactions.

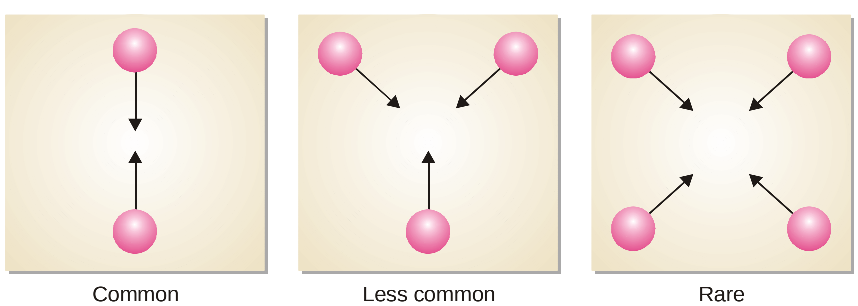


Figure 20.3
Chances of simultaneous collision between reacting molecules decrease as the molecularity increases.

Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the **mechanism of the reaction.** In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the **rate-determining step** of the reaction.

The decomposition of N_2O_5,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is an example of a complex reaction. It occurs by the following steps :

Step 1	$2N_2O_5$	$\longrightarrow$	$2NO_2 + 2NO_3$	(*slow*)
Step 2	$NO_2 + NO_3$	$\longrightarrow$	$NO + NO_2 + O_2$	(*slow*)
Step 3	$NO + NO_3$	$\longrightarrow$	$2NO_2$	(*fast*)
Overall reaction	$2N_2O_5$	$\longrightarrow$	$4NO_2 + O_2$	

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as : **the number of molecules or atoms taking part in the rate-determining step.**

Thus step 2 in the above mechanism is rate-determining and has molecularity '2' which could be considered as the molecularity of the decomposition reaction of N_2O_5.

MOLECULARITY *VERSUS* ORDER OF REACTION

The term molecularity is often confused with order of a reaction.

The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the **molecularity of reaction.**

The sum of the powers to which the concentrations are raised in the rate law is known as the **order of reaction.**

Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.

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

$$\text{rate} \propto [A][A][B]$$

or $$\text{rate} = k[A]^2[B]$$ (*rate law*)

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is 2 + 1 = 3. The sum of powers in the rate law is 2 + 1 and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal.**

TABLE 20.1. MOLECULARITY AND ORDER FOR ELEMENTARY REACTIONS.

Reactions	Molecularity	Rate law	Order
$A \longrightarrow$ products	1	rate = $k[A]$	1
$A + A \longrightarrow$ products	2	rate = $k[A]^2$	2
$A + B \longrightarrow$ products	2	rate = $k[A][B]$	2
$A + 2B \longrightarrow$ products	3	rate = $k[A][B]^2$	3
$A + B + C \longrightarrow$ products	3	rate = $k[A][B][C]$	3