Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 5

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MOLECULARITY OF A REACTION

Chemical Reaction can be Classified into two types:

- Elementary Reactions- a simple reaction which occurs in a single step
- Complex Reactions – which occurs in two or more steps

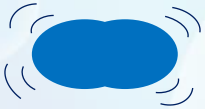
Molecularity of an Elementary Reaction

the number of reactant molecules involved in a reaction.

So the molecularity of an elementary reaction is 1,2,3, etc., according as one, two or three reactant molecules are participating in the reaction and called unimolecular, bimolecular and termolecular respectively .

- unimolecular reactions: (molecularity = 1)

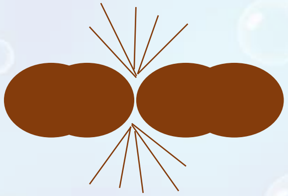
$$A \longrightarrow \text{Product}$$



Examples are: $Br_2 \longrightarrow 2Br$

ii. Malic acid $\longrightarrow$ Fumaric Acid

MOLECULARITY OF AN ELEMENTARY REACTION



- ❖ Bimolecular reactions : (molecular = 2)

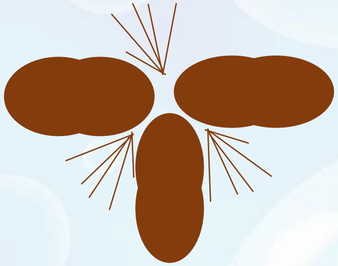
  A + B → Products

  A + A → Products

Examples are :

i. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

ii. $2HI \rightarrow H_2 + I_2$



- ❖ Termolecular reactions : (molecularity = 3)

  A + B + C → Products

Examples are : $2NO + O_2 \rightarrow 2NO_2$

$2NO + Cl_2 \rightarrow 2NOCl$

Why High Molecularity Reactions are 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.

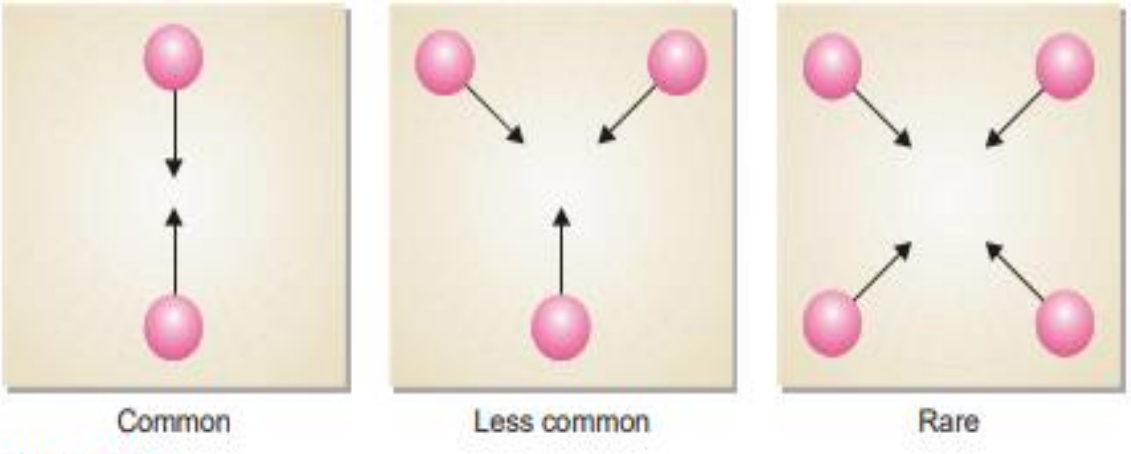
The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules.

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.

Why High Molecularity Reactions are Rare ?

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.



Common

Less common

Rare

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

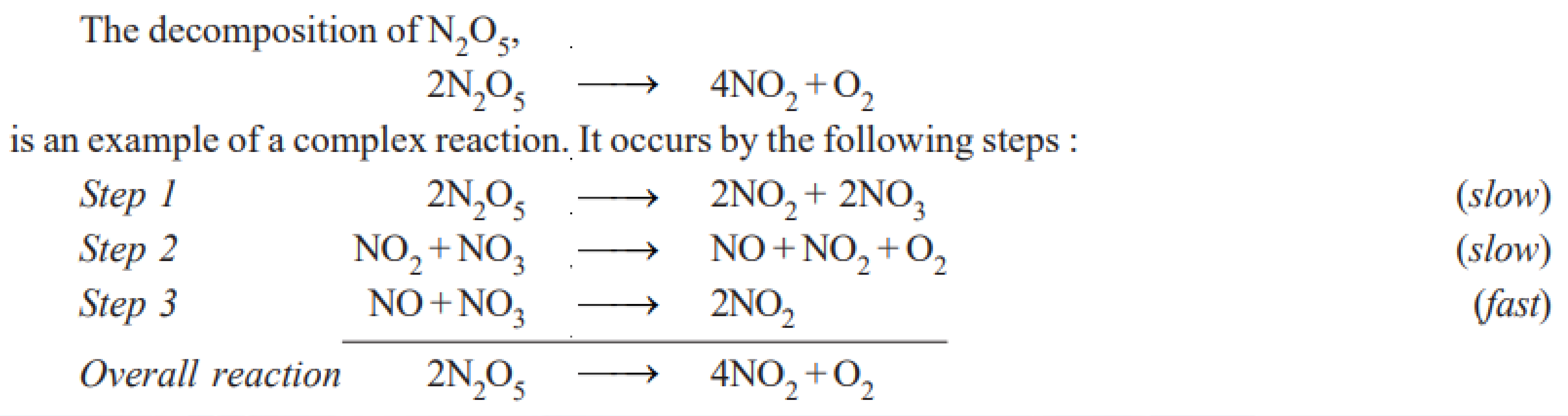
MOLECULARITY OF AN COMPLEX REACTION

Most chemical reactions are complex reactions which occurs in a series of steps. Each step is an elementary reaction.

The stepwise sequence of elementary reactions that convert reactants 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 :

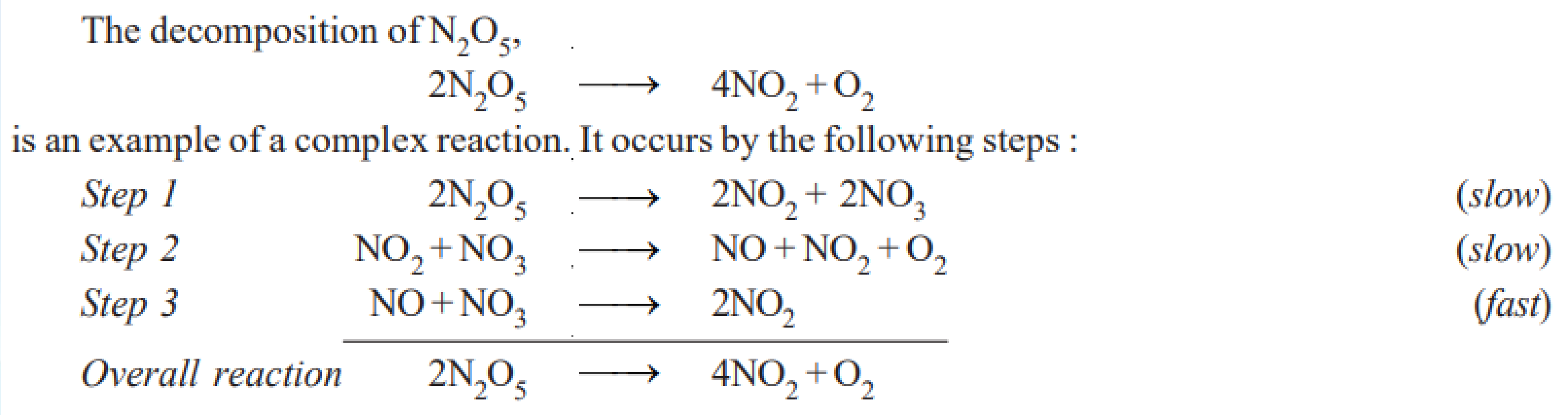
Step 1 $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (*slow*)

Step 2 $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (*slow*)

Step 3 $NO + NO_3 \longrightarrow 2NO_2$ (*fast*)

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

MOLECULARITY OF AN COMPLEX REACTION



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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.

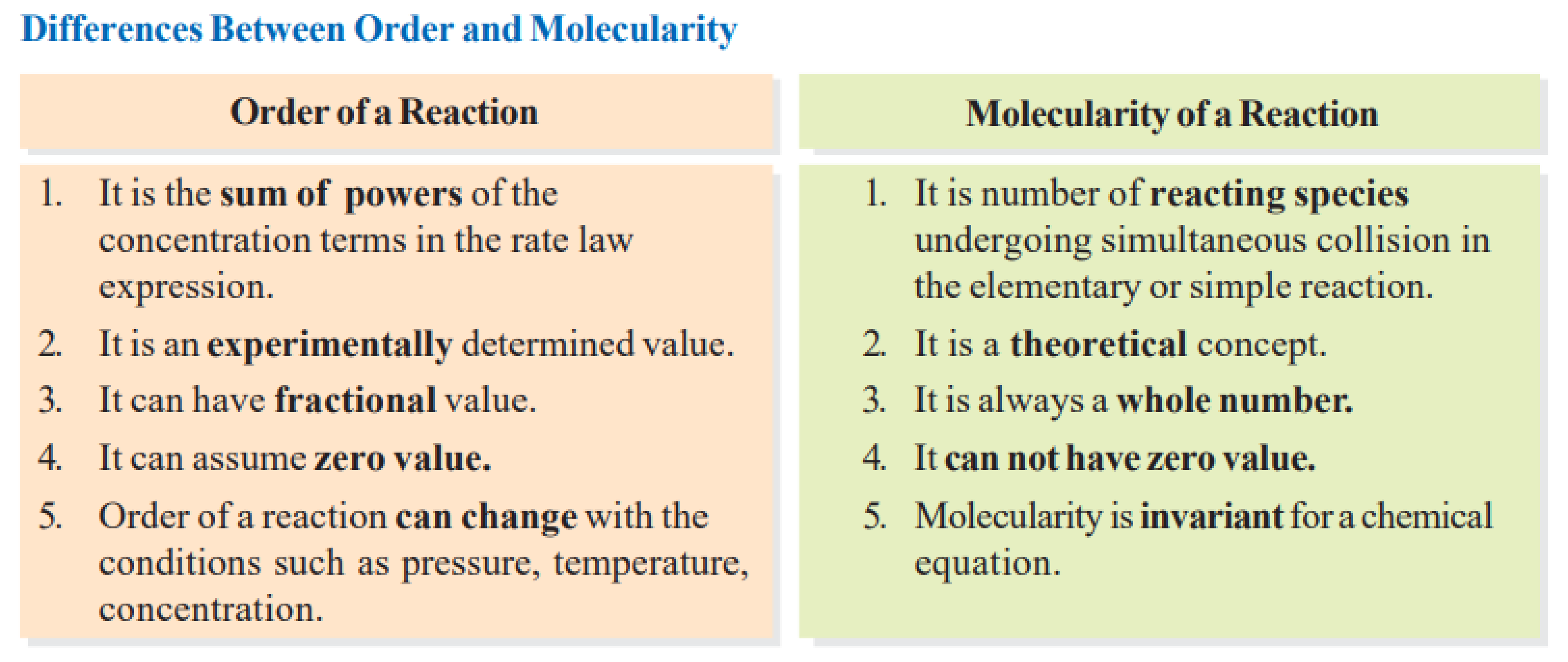
At best could be thought of as : the number of molecules or atoms taking part in the rate-determining step.

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 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.



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 first-order reaction

a second-order or ***bimolecular reaction*** that is made to behave like a first-order reaction.

This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.

Let us consider a reaction

$$A + B \rightarrow \text{Products}$$

where component B is in large excess. Since it is an elementary rection , its rate law can be written as

$$\text{rate} = K\,[A][B]$$

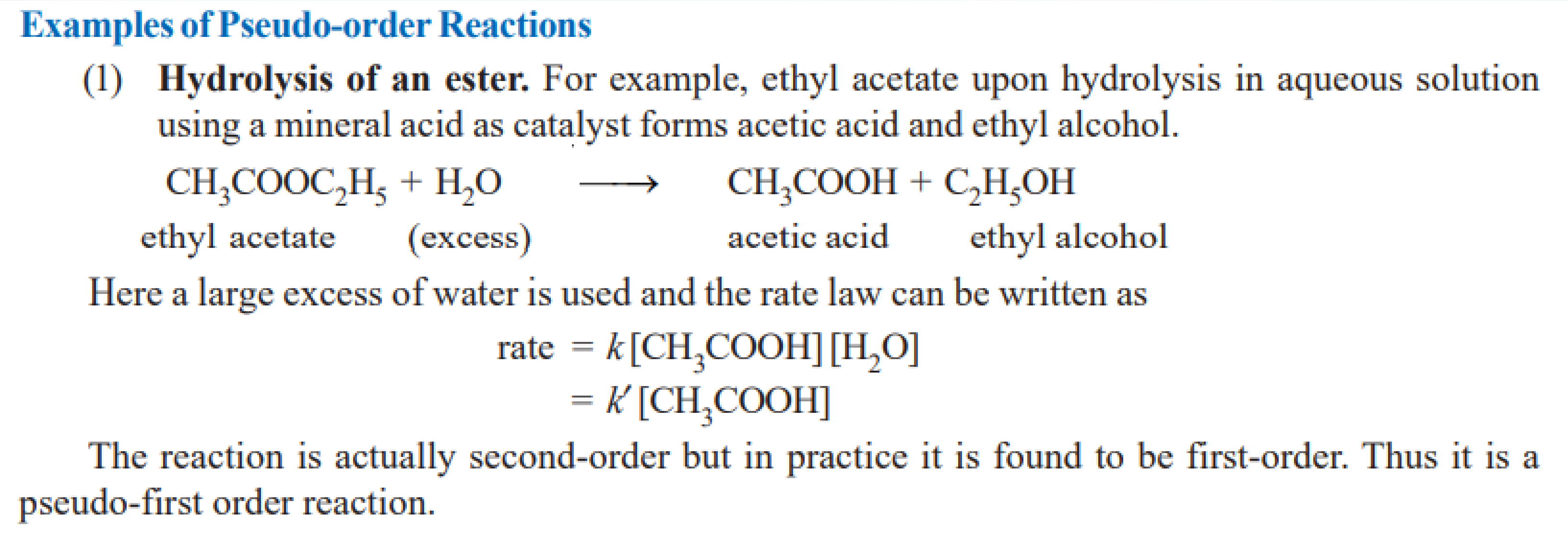
As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

$$\text{rate} = k'\,[A] \qquad \text{where,} \quad k' = k[B]$$

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

Pseudo first-order reaction



Examples of Pseudo-order Reactions

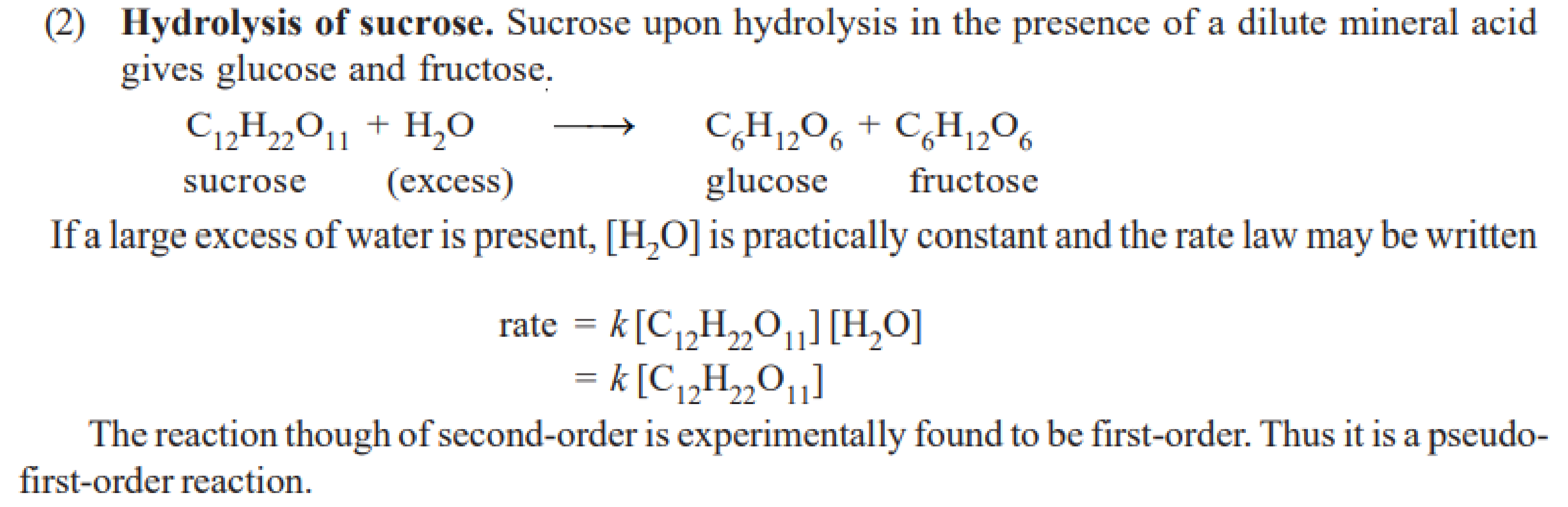
(1) **Hydrolysis of an ester.** For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

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

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

$$\begin{aligned}\text{rate} &= k[C_{12}H_{22}O_{11}][H_2O] \\ &= k[C_{12}H_{22}O_{11}]\end{aligned}$$

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

Temperature Dependance of Rate Constants

With very few exceptions, reaction rates increase with increasing temperature.

For example, the time required to hard-boil an egg in water is much shorter if the "reaction" is carried out at 100°C (about 10 min) than at 80°C (about 30 min).

Conversely, an effective way to preserve foods is to store them at subzero temperatures, thereby slowing the rate of bacterial decay.

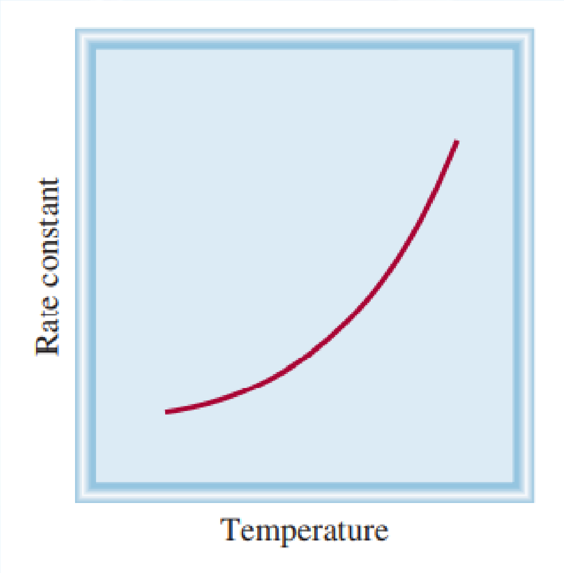


Figure 13.15 Dependence of rate constant on temperature. The rate constants of most reactions increase with increasing temperature.

In order to explain this behavior, we must ask how reactions get started in the first place.

COLLISION THEORY OF REACTION RATES

A chemical reaction takes place only by collisions between the reacting molecules. the rate of a reaction to be directly proportional to the number of molecular collisions per second, or to the frequency of molecular collisions:

$$\text{rate} \propto \frac{\text{number of collisions}}{\text{s}}$$

But not all collisions are effective. Only a small fraction of the collisions produce a reaction.

The two main conditions for a collision between the reacting molecules to be productive are :

(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction.

(2) The reacting molecules must collide with proper orientation.

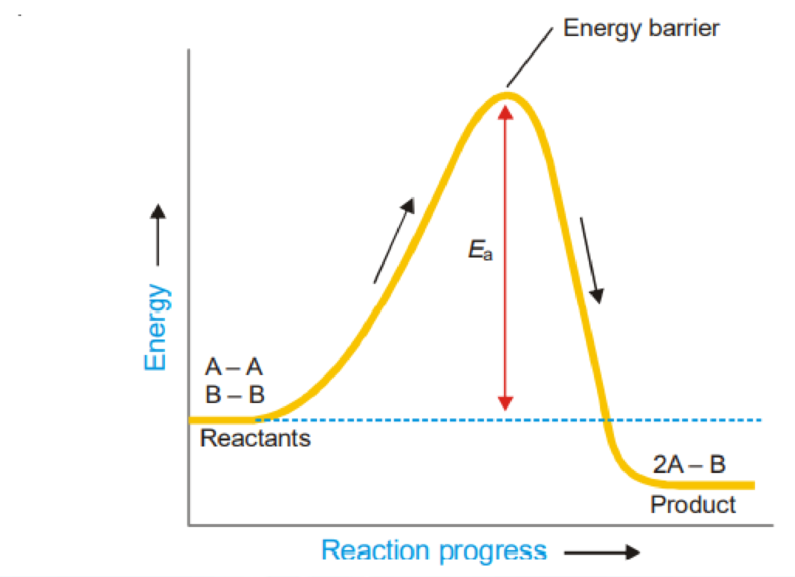
(1) The molecules must collide with sufficient kinetic energy

Let us consider a reaction

$$A-A + B-B \longrightarrow 2A-B$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision

the activation energy, E_a that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules that collide with a kinetic energy greater than E_a, are able to get over the barrier and react. The molecules colliding with kinetic energies less that E_a fail to surmount the barrier. The collisions between them are unproductive and the molecules simply bounce off one another.



■ **Figure 20.9**

The energy of the colliding molecules as the reaction $A_2 + B_2 \rightarrow 2AB$ proceeds. The activation energy E_a provides the energy barrier.

(2) The molecules must collide with correct orientation

The reactant molecules must collide with favourable orientation (relative position).

The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds. (Fig. 20.10)

From the above discussion it is clear that : Only the molecules colliding with kinetic energy greater that E_a and with correct orientation can cause reaction

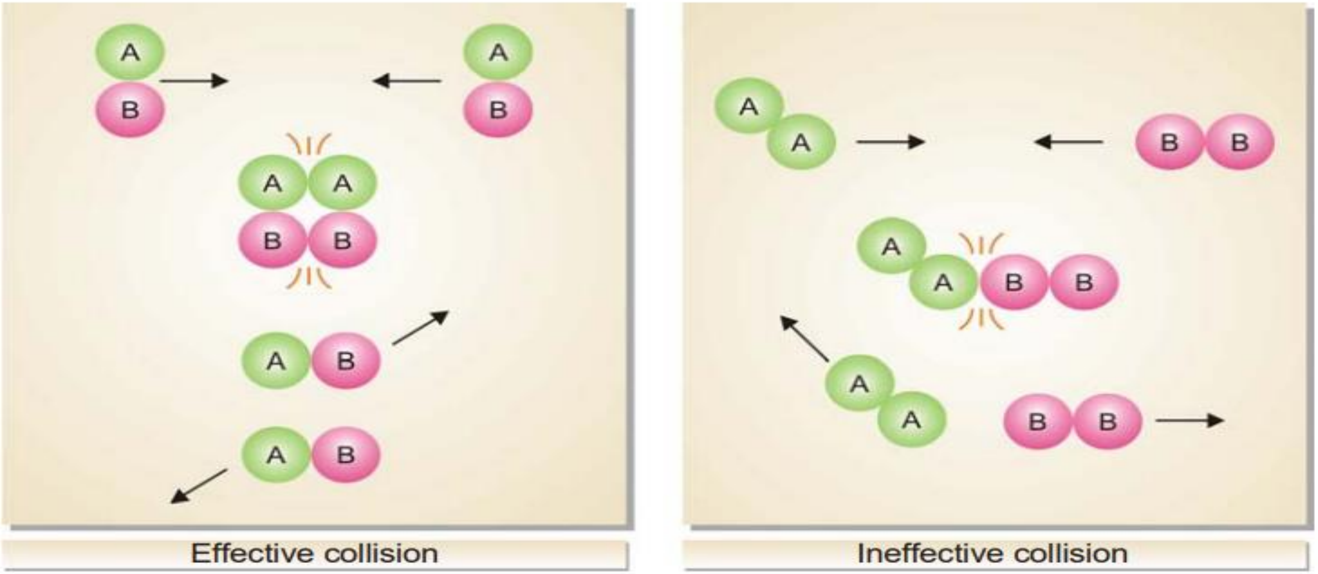


Figure 20.10
Orientations of reacting molecules A_2 and B_2 which lead to an effective and ineffective collision.

Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

(1) The theory applies to simple gaseous reactions only. It is also valid for solutions in which the reacting species exist as simple molecules

(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.

(3) There is no method for determining the steric effect (p) for a reaction whose rate constant has not been determined experimentally.

(4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

(5) The collision theory is silent on the cleavage and formation of bonds involved in the reaction. The various drawbacks in the simple collision theory do not appear in the modern transition-state theory