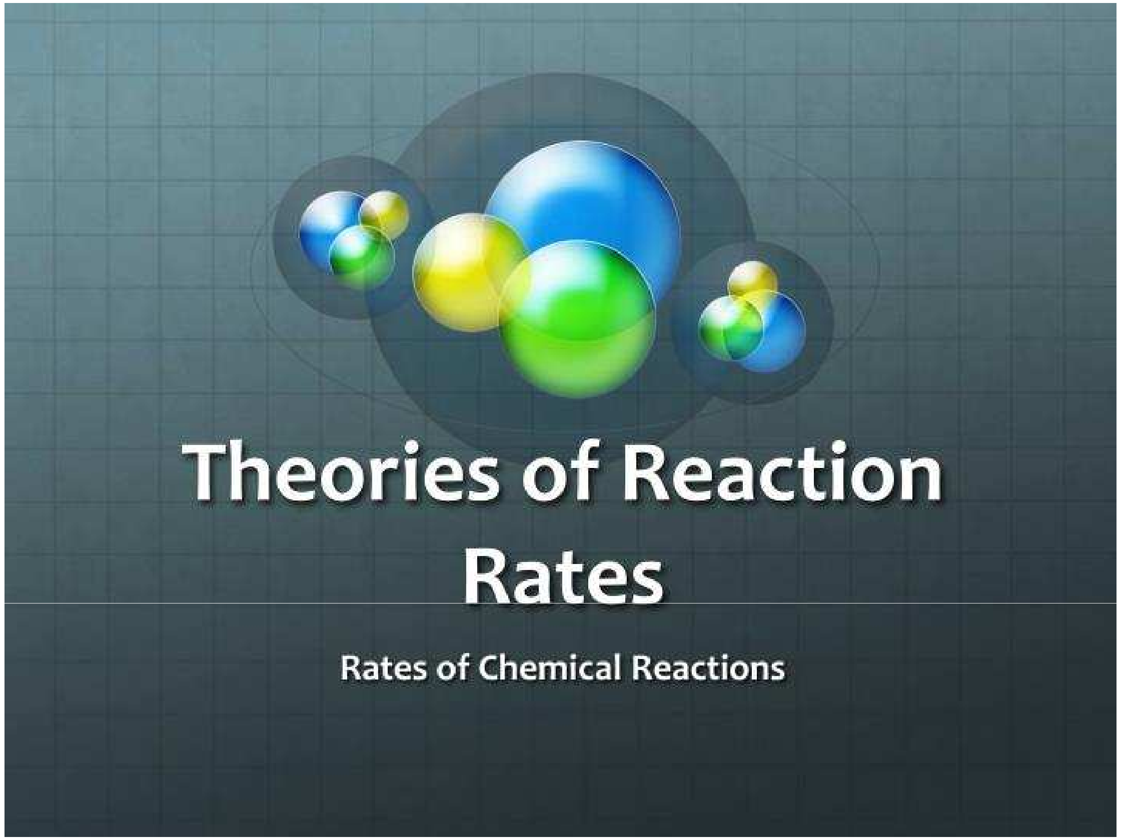

Theories of Reaction Rates

Rates of Chemical Reactions

PART-I

By-

Dr. Sudhir Kumar Gupta

Department of Chemistry, HBTU Kanpur
(PhD-IIT Roorkee)

The Nobel Prize in Chemistry 1901: ***Jacobus Henricus van 't Hoff***
"in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions"

The Nobel Prize in Chemistry 1908: ***Ernest Rutherford***
"for his investigations into the disintegration of the elements, and the chemistry of radioactive substances"

The Nobel Prize in Chemistry 1909: ***Wilhelm Ostwald***
"in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction"

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The Nobel Prize in Chemistry 1992: ***Rudolph A. Marcus***
"for his contributions to the theory of electron transfer reactions in chemical systems“.

The Nobel Prize in Chemistry 1995: ***Paul J. Crutzen, Mario J. Molina*** *and* ***F. Sherwood Rowland***
"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone“.

The Nobel Prize in Chemistry 1999: ***Ahmed H. Zewail***
"for his studies of the transition states of chemical reactions using femtosecond spectroscopy”.

The Nobel Prize in Chemistry 2007: ***Gerhard Ertl***
"for his studies of chemical processes on solid surfaces“.

The Nobel Prize in Chemistry 2015: ***Tomas Lindahl, Paul Modrich and Aziz Sancar***
"for mechanistic studies of DNA repair“.

How does a reaction progress: *Theories proposed*

1) ***Collison Theory***
2) ***Transition State Theory or Activated Complex Theory***
3) ***Lindeman's Theory of Unimolecular Reaction***

1) *Collison Theory:*

This theory was proposed independently by ***Max Trautz*** in ***1916*** and ***William Lewis*** in ***1918***.

The reaction constant, k is determined by several factors.

$$k = Z f p$$

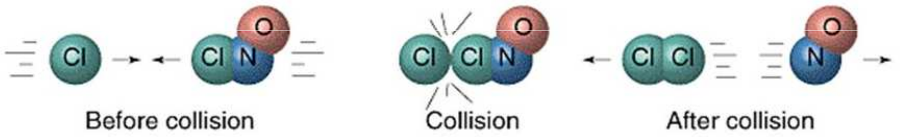
Z: collision frequency

p, the fraction with proper orientation

f, fraction of collision having sufficient energy for reaction

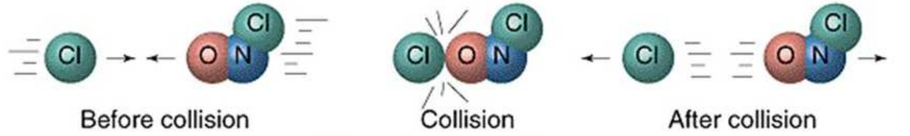
where E_a is the activation energy,.

$$f \infty e^{-Ea/RT} \text{ or } \exp(-E_a / R\,T)$$



Cl
Cl
N
O
Before collision
Cl
Cl
N
O
Collision
Cl
Cl
N
O
After collision

(a) Effective collision



Cl
O
N
Cl
Before collision
Cl
O
N
Cl
Collision
Cl
O
N
Cl
After collision

(b) Ineffective collision

- A successful collision between molecules requires the correct geometry to break bonds and form products

$$\boxed{k = A\, e^{-Ea/RT}}$$

where, 'R' is the gas constant, 'T' is the temperature in Kelvin and 'A' is constant called ***Arrhenius constant*** *and the equation is called as the* ***Arrhenius equation*** *.*

COLLISION THEORY OF REACTION RATES

According to this theory, **a chemical reaction takes place only by collisions between the reacting molecules.** 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.

Now let us have a closer look at these two postulates of the collision theory.

(1) The molecules must collide with sufficient kinetic energy

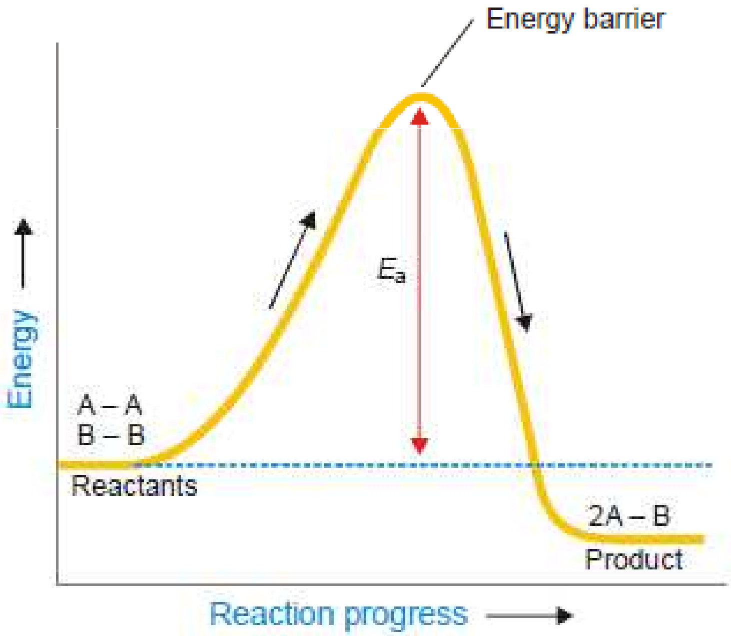


Figure 20.9

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)

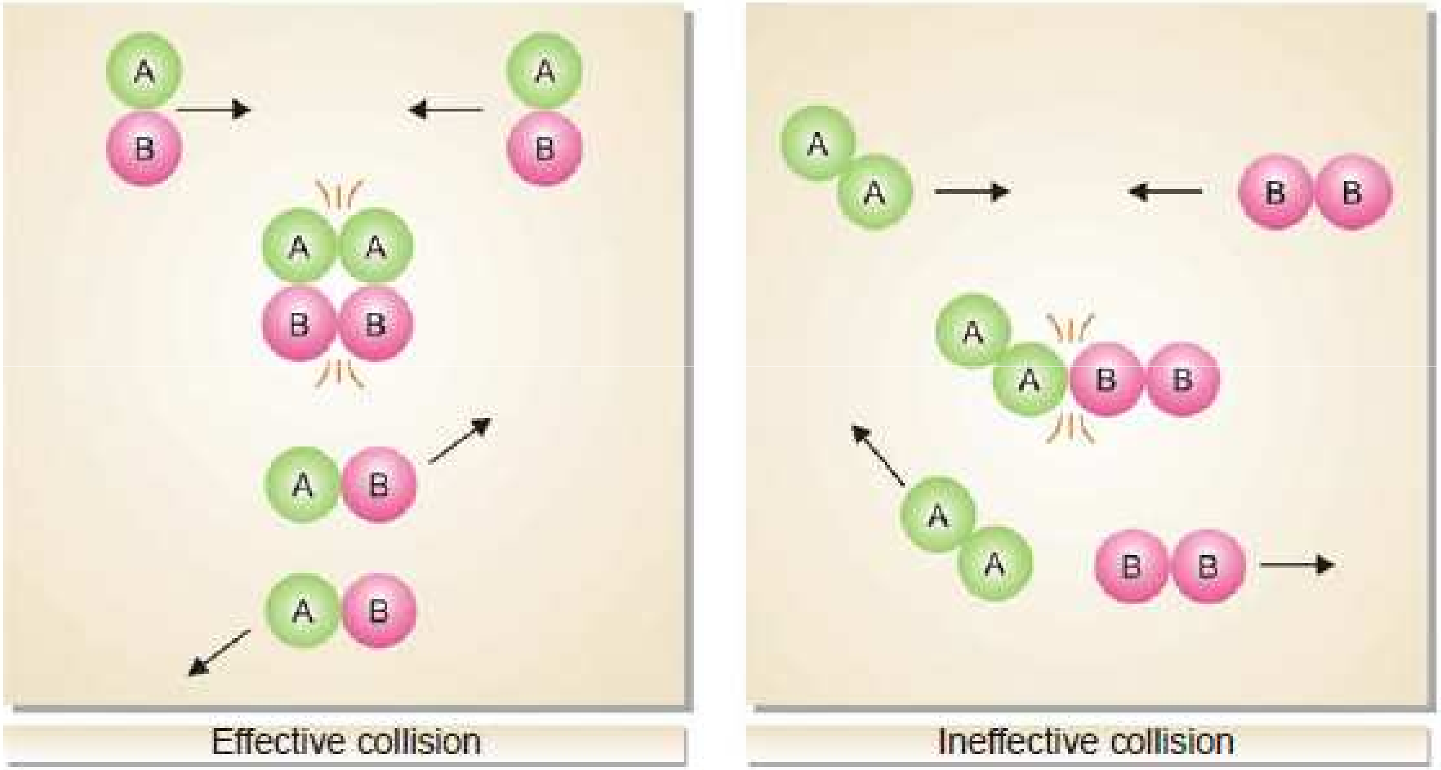

A
B
A
B
A
A
B
B
A
B
A
B
Effective collision
A
A
B
B
A
A
B
B
A
A
B
B
Ineffective collision

Figure 20.10

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

The Arrhenius Equation

1903 Nobel Prize "in recognition of the extraordinary services rendered by Arrhenius to the advancement of chemistry by his electrolytic theory of dissociation".

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$\log k = \frac{-E_a}{2.303\,RT} + \log A$$

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Arrhenius equation is valuable because it can be used to calculate the activation energy, E_a, if the value of the rate constant is known.

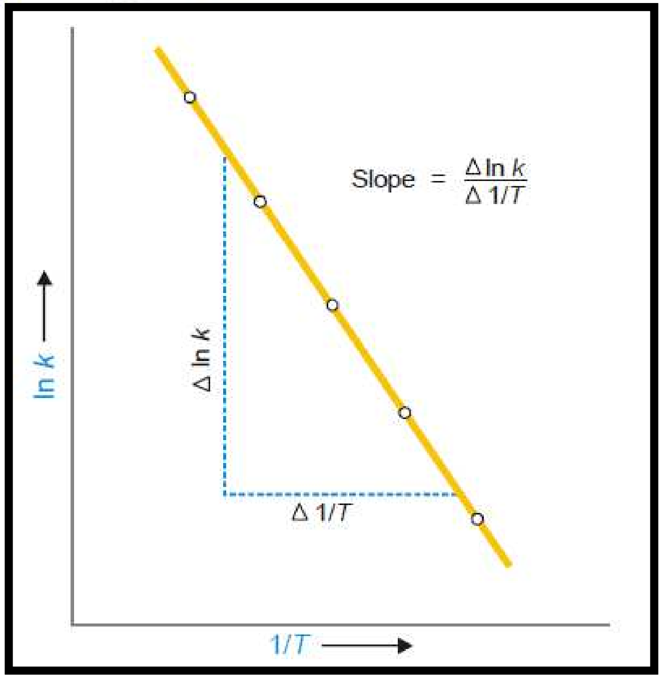


Fig.- The plot of ln *K versus 1/T* gives a straight line. The slope of the line, Δ *ln k/* Δ*1/T* gives E_a using Arrhenius equation.

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.

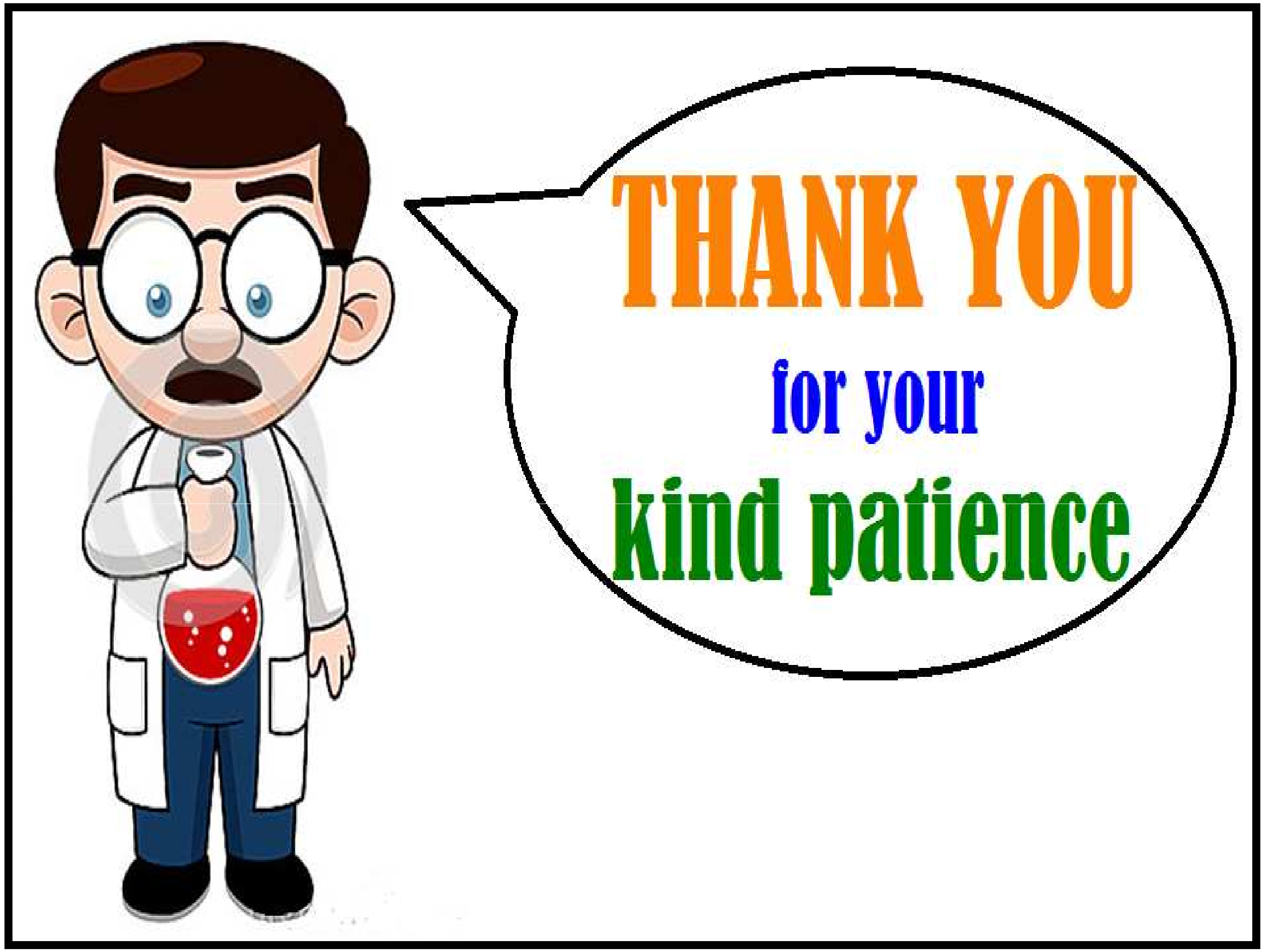
(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. **For reactions involving complex molecules, the experimental rate constants are quite different from the calculated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


THANK YOU
for your
kind patience