Lecture 10
Chemical reaction
Rate Theories
Collision Theory

In This Lecture we will go over The Following Topic

- Chemical Reaction Rate Theories

- Definition of Collision Theory

- Hypotheses of the Collision Theory-

- Advantages and disadvantages of collision - theory

Studying the kinetic of Chemical Reaction enable us to calculate the rate of any chemical reaction from the particles properties of the reactants as mass – Diameter –moment of inertia-vibration frequency of the particles

For that we will focus on two theories

First: Collision theory
Second: transition state theory

First: Collision Theory

-According to the collision theory, molecules must collide to react and the rate of a chemical reaction is proportional to the number of reacting molecules i.e.

$$Rate \propto Number\ of\ colliding\ molecules\ per\ litre/second$$

- It based on the kinetic theory of gases
- Can be applied to two molecular reactions

Hypotheses of the Collision Theory:

1)- Molecules must collide to react.

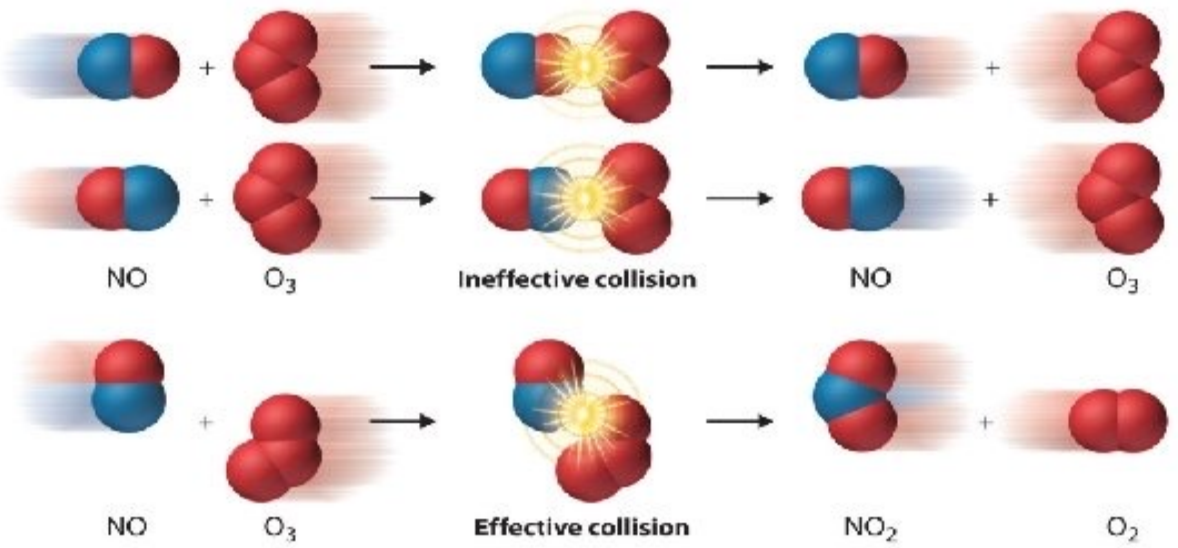
2)- The collisions between all molecules do not lead to chemical reaction but fruitful collisions are those that lead to the occurrence of a chemical reaction, The collision is fruitful if two important conditions are met:

Hypotheses of the Collision Theory:

a)-The collisions between such molecules which possess energy of activation lead to the chemical reaction. So, if the energy of the colliding molecules is less than activation energy, no reaction occurs. If the energy of the colliding molecules is equal to or greater than activation energy, reaction occurs

b)-The particles are in an appropriate position at the time of collision OR molecules must also be correctly oriented if they will react

Collision Theory



Hypotheses of the Collision Theory:

3)- the activated part of collision particles that have the same energy or more than activation energy of reaction known as poltiz man F agent

$$F = N_2 / N1 = e^{-\frac{Ea}{RT}}$$

F= total number of molecules /The number of activated molecules

Solved Examples:

Calculate the value of the fraction or fraction of molcules activated at temperature 25 C° and activation energy 80 Kj/mol

Solution:

R = 8.314 J . K^{-1} .mol $^{-1}$, E_a = 80000 J mol $^{-1}$

T = 25 + 273=298 °K , F=?

Use equation

$$F = e^{-\frac{Ea}{RT}} = e^{-14}$$

4)- The increase in temperature lead to the increase in the fraction of this activated particles which increase the reaction rate ,this fraction between 0 and 1 which is apply for the very big and very small of activation energy respectively

5)- It is instructive to relate the rates of reactions in the gas phase with the frequencies of collisions between the reactant molecules per second per cm^3

- **Z** The collision number, Z, may be thus defined as "the number of collisions per second when there is only one reactant molecule per ml of the gas.

$$\text{Rate} = Z\, e^{-\frac{Ea}{RT}} \longrightarrow (2)$$

-If we have a two molecular interaction as between gass A and B

$$A + B \longrightarrow AB$$

-The reaction rate can be calculated as fallow :

$$\text{Rate} = dn/dt = Z_{AB}\, e^{-\frac{Ea}{RT}} \longrightarrow \quad (3)$$

where

n the number of products molecules formed per cc

Z_{AB} the collision number of bimolecular collisions per second per cc

E the activation energy. The number of collisions of molecule A with that of B per second per cc in a bimolecular mixture will be given as

- From Second-order rate constant

$$dn/dt = K . N_A . N_B \longrightarrow (4)$$

- Where N_A, N_B the number of molecules formed per unit volume of reactant A,B respectively

- By comparing equation(3) with (4) we get the reaction rate constant value

$$K . N_A . N_B = Z_{AB}\, e^{-\frac{Ea}{RT}} \longrightarrow (5)$$

$$K = (Z_{AB} / N_A . N_B)\, e^{-\frac{Ea}{RT}}$$

$$K = Z_o\, e^{-\frac{Ea}{RT}} \longrightarrow (6)$$

Z_o collision constant

-By comparing equation(3) with Arrhenius equation

$$K = A_o e^{-\frac{Ea}{RT}}$$

- Where replace the frequency coefficient A_o

with collision constant Z_o

Advantages of collision theory

1)- Provides a pictorial model of how a chemical reaction occurs

2)- it was able to successfully explain the rates of the speed of some chemical reactions, but there are many reaction whose rates are less than 10^5 or more than the calculated values, which indicates that there is a possibility of a spatial distribution, so it is necessary to introduce a factor **P** to the reaction rate equation(6)

$$K = P Z_o e^{-\frac{Ea}{RT}} \longrightarrow (7)$$

where **P** is the probability factor and is equal to the ratio between the observed K value and the K computed from the collision theory

disadvantages of the collision theory

- The values of **P** could not be correlated to the characteristics of reacting molecules.

- Sometimes, abnormally high rates of reaction are observed which could not be explained by this theory.

Thank you