

# Lecture 11

## Chemical reaction

### Rate Theories

### Transition State Theory

# Transition state theory(TST)

- The transition-state theory **or** the theory of absolute reaction rates
- Work of Scientist Eyring
- It relates the rates of chemical complex reactions to the thermodynamic properties
- It assumes that the transformation of reactants into products does not occur directly
- It assumes reacting molecules must go through a transition state before they turn into resulting substances which called [**active state** ]in which an unstable active complex is formed called  
the[ **transitional active complex** ]

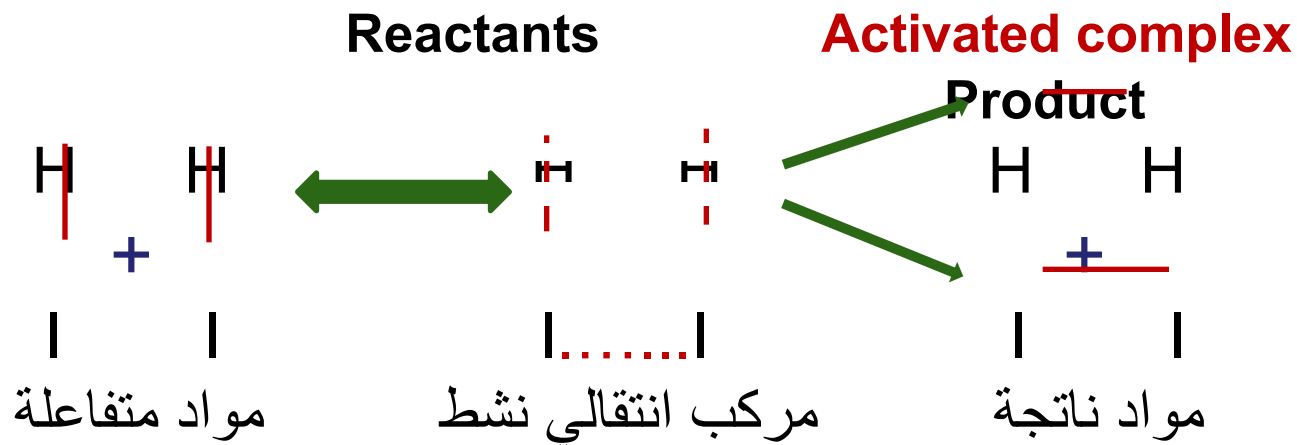
According to Transition State Theory,

- The transitional active complex exist in an intermediate state known as the transition state in which molecules exist in state between reactants and products
- The species that forms during the transition state is in a higher-energy species known as the **activated complex**.
- These complexes will be in **equilibrium** with the reactants

## In these theory

-The active complex as a regular molecule that does not differ from other molecules except disintegrates quickly to give the result

-A complex or transitional compound is formed as a result of breaking the bonds between the molecules of the reactants and forming bonds between the molecules of the products



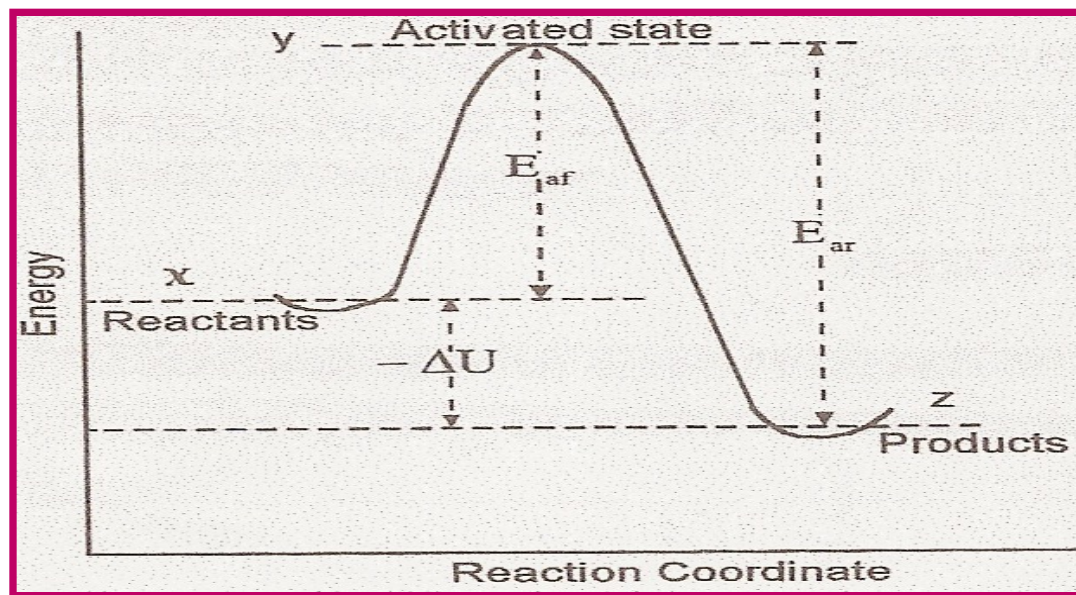
## Hypotheses of the Transition-state theory

1)- In order for any chemical reaction to take place, it is necessary that the reactants, possessing sufficient energy must approach one another to form the activated complex. These complexes will be in equilibrium with the reactants



The rate of the reaction is equal to the rate of decomposition of the activated complexes

2-The activation energy of a reaction is defined as the additional energy which the reacting molecules should acquire before forming the intermediate activated complex for the reaction. This is shown in the Figure.



**The difference of energy when reactants are converted into products**

3-The reaction rate in the transition state theory depends on two factors:

1)-The concentration of the activated complex.

2)-The rate at which the activated complex breaks apart.

The mechanism by which the activated complex breaks apart; it can either be converted into products, or it can “revert” back to reactants.

To illustrate this, we assume that we have a simple two-molecular gaseous reaction that occurs between the molecules of the two reactants A and B



**C\*** active compound or the transition state compound that reactants A, B pass through before giving the final products





The equilibrium constant for this step:

$$K^* = \frac{C^*}{a b} \quad (1)$$

$a, b, c^*$  the concentrations of the reactants and the active complex at time  $t$ , concentration of the active complex

$$C^* = K^* a b \quad (2)$$

The rate of the reaction is directly proportional to the concentration  $C^*$

$$\frac{dx}{dt} = m c^* \quad (3)$$

$m =$  rate constant, from second order rate constant  $K$

$$\frac{dx}{dt} = K a b \quad (4)$$

From equation (3) ,(4)

$$k_{ab} = m c^*$$

$$K = m (c^* / a b ) \longrightarrow m K^* = K' \quad (5)$$

The constant  $m$  can be understood as equal to the vibration frequency of the bond

The frequency of vibration can be calculated using the Planck relation

$$\Delta E = h \nu = RT/N$$

$$\nu = RT/Nh = m \quad (6)$$

From equation (5) ,(6)  $m=V$

$$K = (RT/Nh) \cdot K^* \quad (7)$$

When:

$$R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad , \quad N = 6.03 \times 10^{23} \text{ mol}^{-1}$$

$$T = 300 \text{ K}^\circ \quad , \quad h = 6.6 \times 10^{-34} \text{ J} \cdot \text{S}$$

Substitution in equation (6)

$$V = RT/Nh = m \quad (6)$$

$$= (8.314 \times 300) / (6.03 \times 10^{23} \times 6.6 \times 10^{-34})$$

$$V = 6.3 \times 10^{12} \text{ S}^{-1}$$

It is equal to the frequency of vibration

From the laws of thermodynamics, it is possible to calculate the value of the equilibrium constant  $K^*$  in terms of the free energy of activation as follows  $\Delta G^*$

$$K^* = e^{\frac{-\Delta G^*}{RT}}$$

$$K = (RT/Nh) \cdot K^*$$

$$K = (RT/Nh) \cdot e^{\frac{-\Delta G^*}{RT}}$$

## Rate constant in Collision theory

$$K = P Z_0 e^{-\frac{E_a}{RT}}$$

## Rate constant in transition state theory

$$K = \left(\frac{RT}{Nh}\right) \cdot e^{-\frac{\Delta G^*}{RT}}$$

Through the two theories ,we find that **the activation energy** is the influential factor in determining the rate of the reaction

Thank you