Ministry of Higher Education and Scientific Research
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# Physical Chemistry

## Lecture 5

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*First semester*

## Transition State Theory (TST)

By

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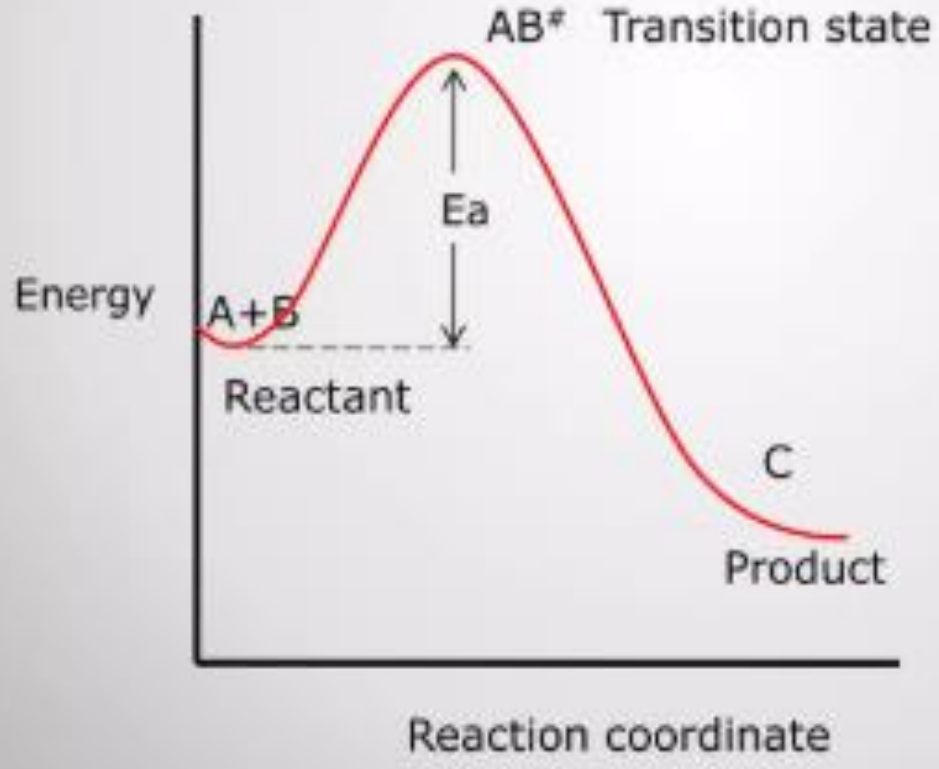
# Transition state theory

According to this theory, the reactant molecules is first transformed into intermediate transition state. The transition state is formed by loose association or bonding of reactant molecules. The activated complex is unstable and breaks into the products at a definite rate.



The theory suggests that there are three major factors that determine whether a reaction will occur :

- The concentration of the activated complex.
- The rate at which the activated complex breaks apart.
- whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Consider a reaction

$$A+B \rightarrow C$$

The rate law is given by, Rate = k[A][B] ---------- (1)

Where k is rate constant. According to activated state model Transition state $AB^{\#}$ is formed

$$A+B \overset{K^{\#}}{\rightleftharpoons} [AB]^{\#} \xrightarrow{k^{\#}} C$$

$$\text{Rate} = k^{\#}[AB]^{\#}$$

$k^{\#}$ is the rate constant of activated complex

$$K^{\#} = [AB]^{\#}/[A][B]$$

Rate of the reaction depends on the two factors 1)concentration activated complex and 2) Frequency of vibration of activated complex that converts activated complex to products. Hence

$$\text{Rate} = \nu[AB^{\#}]$$

$$\text{Rate} = \nu[A][B]K^{\#}$$

where, $\nu = k_bT/h$

$K_b$ = Boltzman constant

h = planck's constant

Therefore ,

$$\text{Rate} = K^{\#}[A][B]\cdot k_bT/h \quad \text{----------} \quad (2)$$

Comparing equation (1) and (2)

$$k[A][B] = K^{\#}[A][B] \cdot k_b T/h$$

$$k = k_b T/h \cdot K^{\#}$$

# Difference between transition state theory and collision theory :

| Collision theory | Transition state theory |
| --- | --- |
| Describes the collision of gas molecules in gas phase with sufficient kinetic energy. | Explains reaction rates by assuming the formation of intermediate compound that are transition state |
| States chemical reaction occur due to collision between reactants | States that chemical reaction occur by going through transition state. |
| The collision theory used to predict the rates of chemical reactions particularly for gases | TST can be used to determine the reaction rates of elementary reactions. |

# Advantages of transition state theory

- Provides a complete description of the nature of the reaction including
  - the changes in structure and the distribution of energy through the transition state
  - the origin of the pre-exponential factor A with units $t^{-1}$ that derive from frequency or velocity
  - the meaning of the activation energy $E_a$
- Rather complex fundamental theory can be expressed in an easily understood pictorial diagram of the transition state - plot of energy vs the reaction coordinate
- The pre-exponential factor A can be derived *a priori* from statistical mechanics in simple cases
- The steric factor P can be understood as related to the change in order of the system and hence the entropy change at the transition state
- Can be applied to reactions in gases or liquids
- Allows for the influence of other properties of the system on the transition state (e.g., solvent effects).

Disadvantage

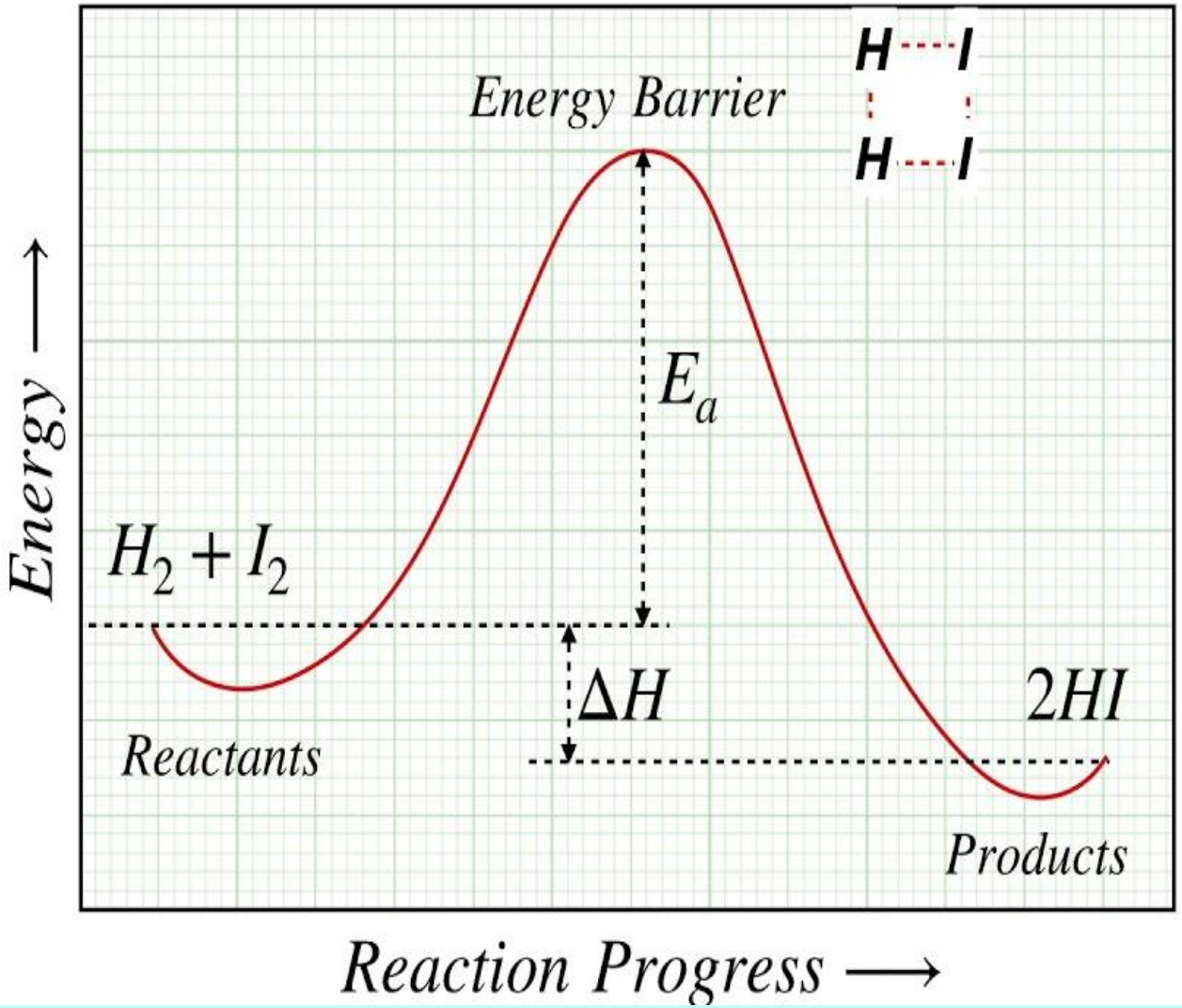
- Not easy to estimate fundamental properties of the transition state except for very simple reactions
  - theoretical estimates of A and $E_a$ may be 'in the right ball-park' but still need experimental values

Arrhenius Theory → $K \propto e^{-E_a/RT}$.

Collision Theory → $K \propto T^{1/2} e^{-E_a/RT}$

Transition State Theory → $K \propto T e^{-E_a/RT}$

# Transition State Theory OR Absolute Reaction Rate Theory




$E_a$ = Energy of Activation

$\Delta H$ = Heat of Reaction

Thank you