Ministry of Higher Education and Scientific Research
AL-Mustaqbal University College of Science
Department of Biochemistry

Physical Chemistry

Lecture 7

Scholar year 2025-2026

First semester

Transition State Theory (TST)

Mechanism of the reaction

By

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Introduction

•In 1930 while studying on Quantum Mechanics the two scientists namely EYRING and POLANYI gave this theory.

•**Transition state theory** (TST) explains the reaction rates of elementary chemical reactions.

•The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes.

•**TST** is used primarily to understand qualitatively how chemical reactions take place.

•It has been successful in calculating the standard enthalpy of activation (**Δ‡H°**), the standard entropy of activation (**Δ‡S°**), and the standard Gibbs energy of activation (**Δ‡G°**) for a particular reaction if its rate constant has been experimentally determined.

•**TST** is also referred to as "activated-complex theory," "absolute-rate theory," and "theory of absolute reaction rates."

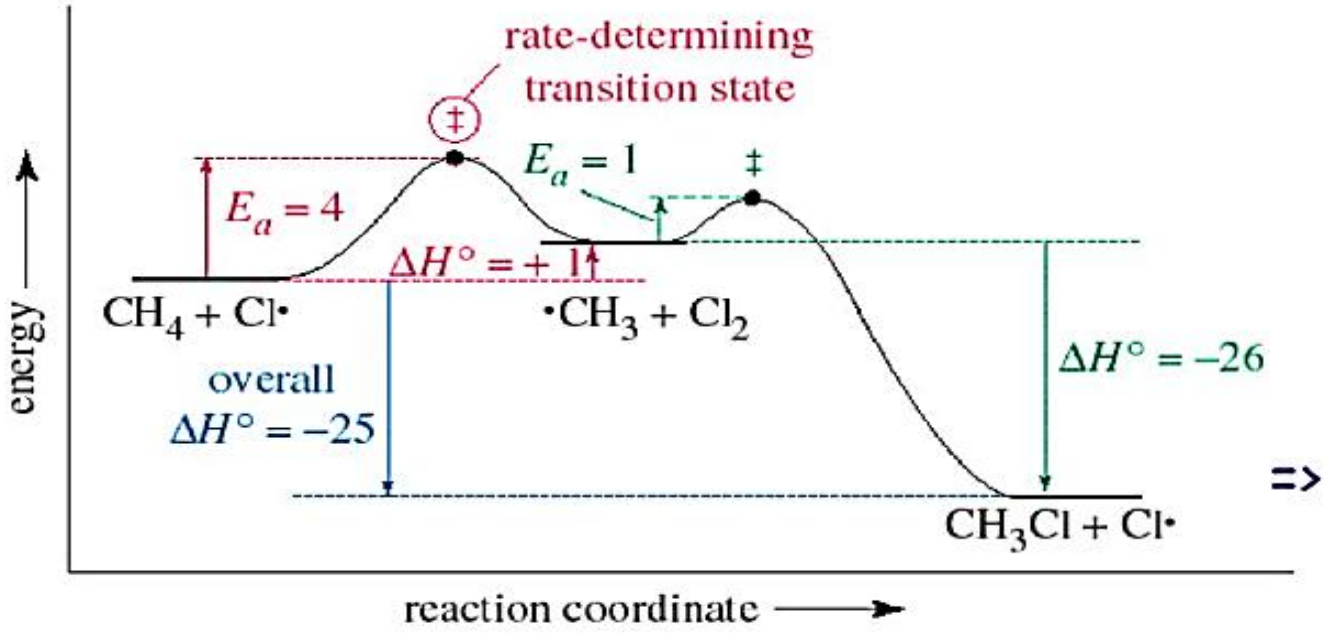
•Before the development of **TST**, the Arrhenius rate law was widely used to determine energies for the reaction barrier.

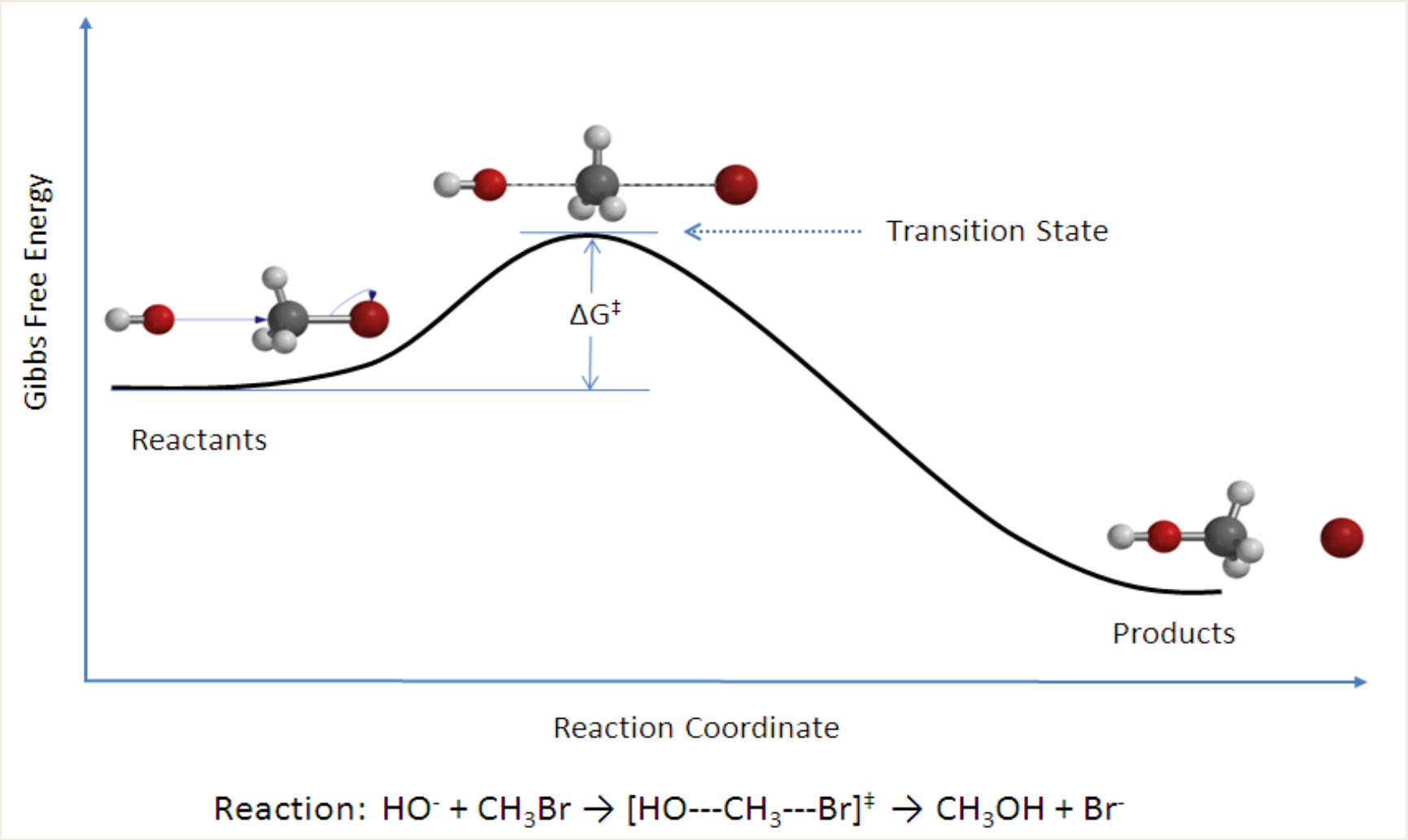
•An intermediate stage lies between the reactants and the products is **transition state.**

•The transitional species with partial bonds is **activated complex.**

Energy Diagram for a Two-Step Reaction

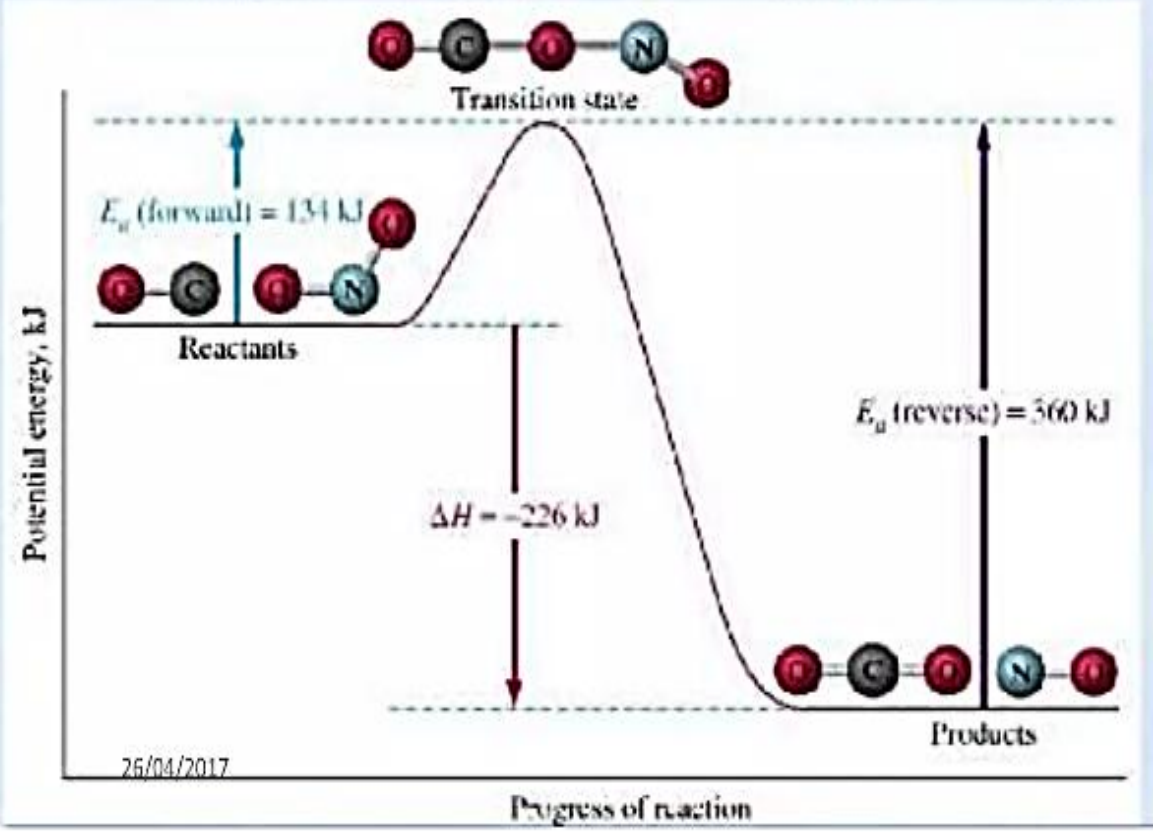
- Reactants → transition state → intermediate
- Intermediate → transition state → product





Reaction: $HO^- + CH_3Br \rightarrow [HO{-}{-}{-}CH_3{-}{-}{-}Br]^{\ddagger} \rightarrow CH_3OH + Br^-$

$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ ΔH = -ve



CO + NO_2

↓

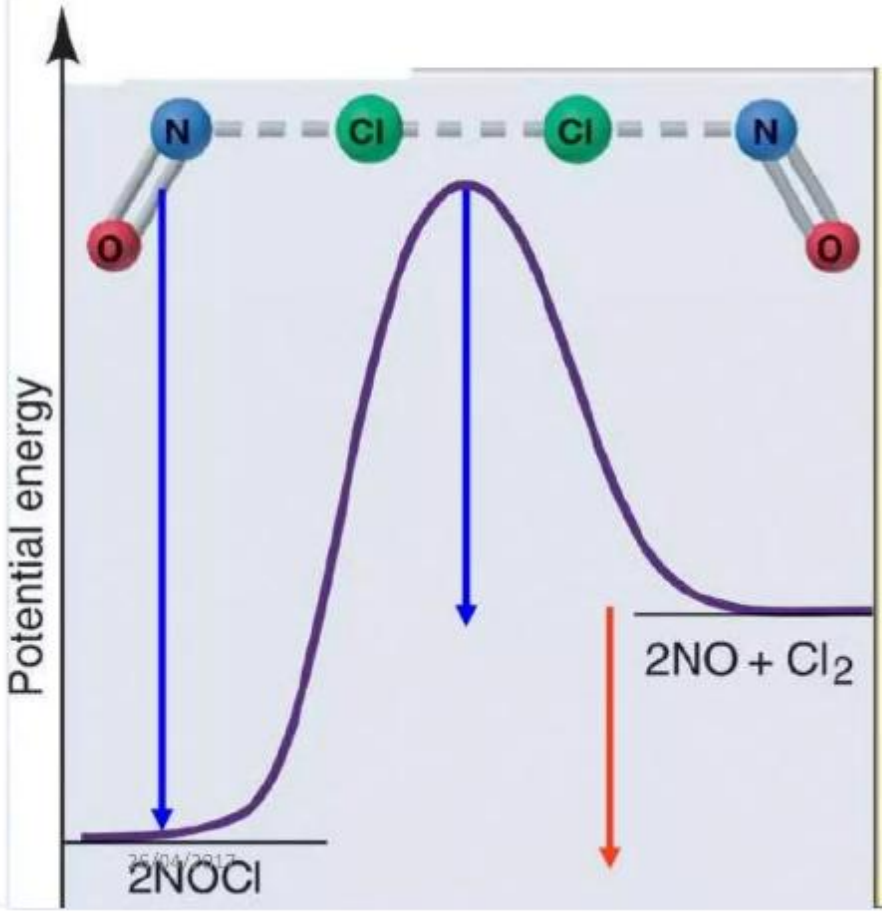
[CO---O---NO]

Activated complex

↓

CO_2 + NO

$2NOCl \rightarrow 2NO + Cl2 \qquad \Delta H = +ve$



NO-Cl + Cl-NO

↓

[NO---Cl---Cl---NO]

Activated complex

↓

$2NO + Cl_2$

Thermodynamics:

$$A = \frac{k_B T}{h}\left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right) e^{\Delta S^*/R_g}$$

$$E = \Delta H^*$$

These two relations are the predictions of the activated-complex theory for the frequency factor and

Characteristics of an Activated Complex

1- Very **unstable**
2- It has a short half-life
3- Its **potential energy** is greater than reactants or products
4- In an **activated complex**, the bonds in the reactant molecules are in the process of breaking while the new bonds in the product molecules are starting to form.
5- The activated complex and the reactants are in **chemical equilibrium**
6- It **decomposes** to form products or reactants.

Is a transition state stable?

•All chemical reactions must go through the **transition state** to form a product from a substrate molecule.
It has more free energy in comparison to the substrate or product; thus, it is the least **stable state**.

What is the transition state of an enzyme?

•The **enzyme's** ability to make the reaction faster depends on the fact that it stabilizes the **transition state**.
•The **transition state's** energy or, in terms of a reaction, the activation energy is the minimum energy that is needed to break certain bonds of the reactants so as to turn them into products.

TST postulates three major factors that determine whether or not a reaction will occur.

These factors are:

1•The **concentration** of the activated complex.
2• The rate at which the activated complex breaks apart.
3• The mechanism by which the activated complex breaks apart; it can either be converted into products, or it can "**revert**" back to reactants.

Difference Between Collision Theory and CTST

A- **Collision theory** is only for reaction involving gaseous reactants ….. while **transition state theory** can be applied to reactions taking place in solution as well as in the gas phase.

B- In the **collision theory** reaction occurs when two molecules collide, but only if the collision is sufficiently vigorous.

C- **Transition state theory** is used to explain in detail what happens when reactant molecules come together in a collision.

APPLICATION

- Application of **TST** is important in terms of deriving an extended form of rate equation, which can be used to understand even most complicated or **complex reactions** in qualitative way.

❖The Comparison of Collision and Activated Complex Theory

After studying the collision as well as the transition state theories in detail, it is time to highlight the key points of similarities and differences between the two. A comparative analysis of both theories is quite beneficial as far as the practicality is concerned.

The comparison between the collision theory and transition state theory.

Collision Theory	Activated Complex Theory
1. According to the collision theory, the chemical reactions occur when the reactant molecules collide with a sufficient amount of kinetic energy.	1. According to the transition state theory, the primary cause of the reaction is actually the formation of an activated complex or the transition state, which in turn, converts to the final product.
2. It is based upon the kinetic theory of gases.	2. It is derived from the fundamentals of thermodynamics.
3. This theory considers the activation energy as the minimum energy required to make the collision effective.	3. This theory assumes the activation energy as the difference between the energy of the reacting molecules and the energy of the activated complex.
4. This theory tells nothing about the entropy of activation.	4. The transition state theory enables us to measure the entropy of activation.
5. Collision theory is applicable to simple chemical reactions and large deviations with experimental results are observed as the complexity increases.	5. This theory provided reasonable predictions even for the complex reactions.
6. The incorporation of the correction factor in modified collision theory was arbitrary.	6. The incorporation of correction factor was justified in terms of entropy of activation i.e. ΔS^*.
7. This theory tells nothing about the mechanism involved.	7. The formation of the activated complex is very much correlated with the actual mechanism going on.

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Transition State Theory or **Activated Complex Theory**

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Thank
you