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

Physical Chemistry

Lecture 7

Scholar year 2023-2024

First semester

Reaction Velocity

Transition State Theory (TST)

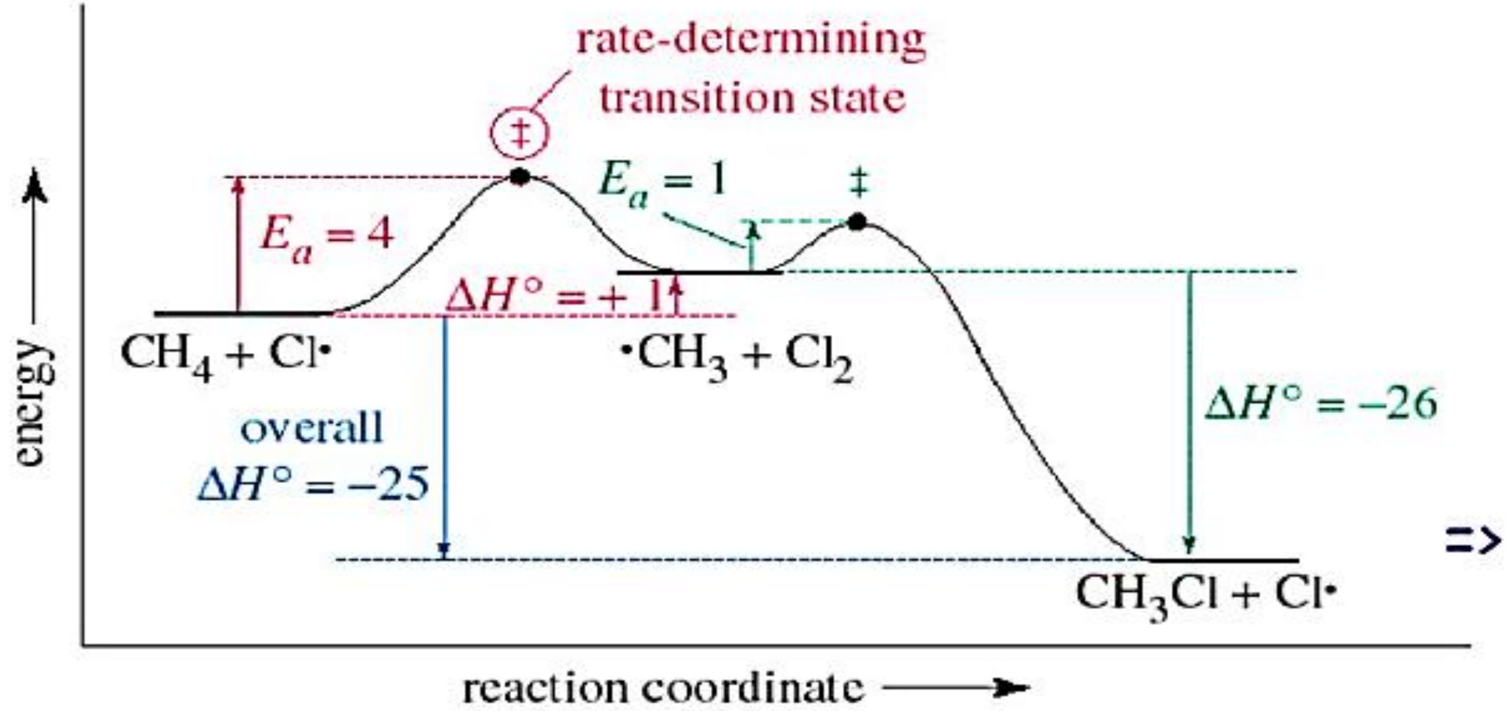
Mechanism of the reaction

By

Dr. Assel Amer Hadi

Energy Diagram for a Two-Step Reaction

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



=>

Rate-Determining Step

- Reaction intermediates are stable as long as they don't collide with another molecule or atom, but they are very reactive.

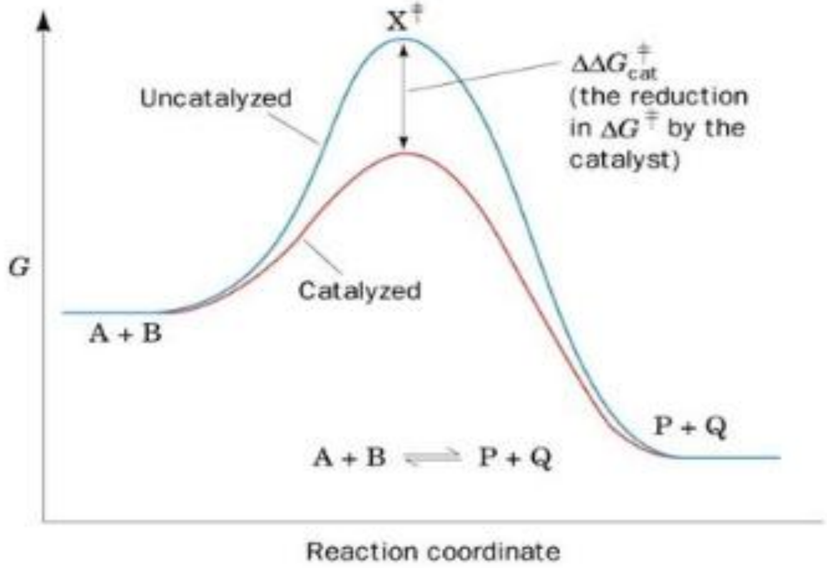
Trapping agents are used to determine intermediate

Transition states are at energy maxima.

The reaction step with highest *E*a will be the slowest,

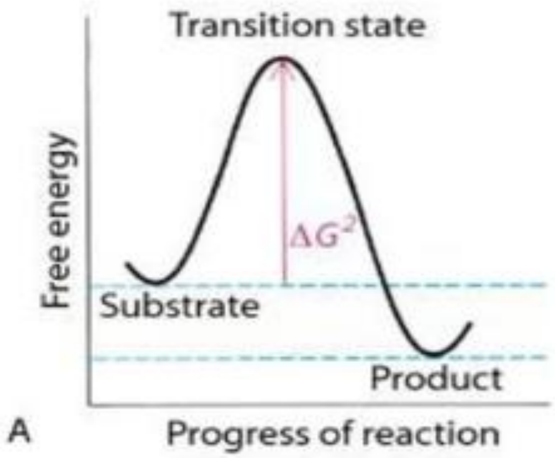
therefore rate-determining for the entire reaction.

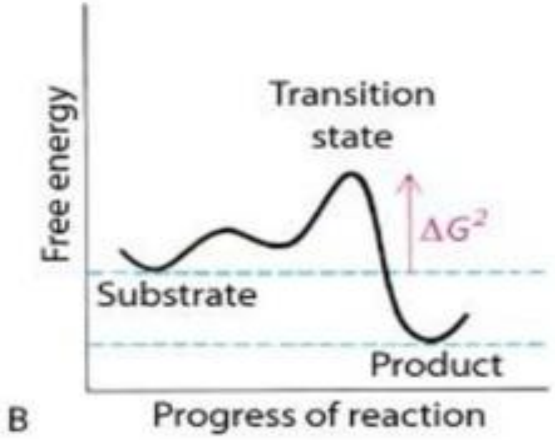
Reaction Coordinate Diagram



The course of a reaction can be illustrated by means of a reaction coordinate diagram. The **Transition State** is the point of highest energy along the minimum energy trajectory (i.e., the reaction coordinate) of a reaction. The **Energy of Activation** is defined as the energy required to attain the Transition State.

Transition State and Reaction Velocity





$$[S^{+}] = [S]\, e^{-\Delta G^{+}/RT}$$

$$V = \frac{kT}{h}[S^{+}] = \frac{kT}{h}[S]\, e^{-\Delta G^{+}/RT}$$

$\Delta G_{final} - \Delta G_{initial}$ = constant

$\Delta G_{activation}$ has changed

"Activated complex" or "transition state" theory:

$$B + C \Leftrightarrow BC^{\ddagger} \Leftrightarrow D + E$$

$BC^{\ddagger}$ is the activated complex or transition state

maximum energy barrier

$$\text{rate} = \left(\frac{\text{k}T}{h}\right)\left[BC^{\ddagger}\right]$$

$$K^{\ddagger} = \frac{\left[\text{BC}^{\ddagger}\right]}{[\text{B}][\text{C}]} = e^{\left(-\frac{\Delta G^{\ddagger}}{RT}\right)} = e^{\left(-\frac{\Delta H^{\ddagger}}{RT}+\frac{\Delta S^{\ddagger}}{R}\right)}$$

$$\text{rate} = \left(\frac{\text{k}T}{h}\right)K^{\pm}[\text{B}][\text{C}] = k[\text{B}][\text{C}]$$

k = Boltzmann constant

h = Plank's constant

$$\boxed{k = \left(\frac{\text{k}T}{h}\right)e^{\Delta S^{\ddagger}/R}\cdot e^{-\Delta H^{\ddagger}/RT}}$$

E_a = potential energy of activation, $\Delta H^{\ddagger}$ is the total:

$$\Delta H^{\ddagger} = E_a - RT$$

Thermodynamic approach

- Suppose that the activated complex AB‡ is in equilibrium with the reactants with an equilibrium constant designated K‡ and decomposes to products with rate constant $\mathbf{k}^{\ddagger}$

$$A + B \underset{}{\overset{K^{\ddagger}}{\rightleftharpoons}} \text{activated complex } AB^{\ddagger} \xrightarrow{\mathbf{k}^{\ddagger}} \text{products}$$

where $K^{\ddagger} = \dfrac{[AB^{\mp}]}{[A][B]}$

- Therefore rate of formation of products = $\mathbf{k}^{\ddagger}[AB^{\ddagger}] = \mathbf{k}^{\ddagger} K^{\ddagger}[A][B]$
- Compare this expression to the rate law: rate of formation of products = $k_r [A][B]$
- Hence the rate constant $k_r = \mathbf{k}^{\ddagger} K^{\ddagger}$
- The Gibbs energy for the process is given by $\Delta^{\ddagger} G = -RT\ln(K^{\ddagger})$ and so $K^{\ddagger} = \exp(-\Delta^{\ddagger} G/RT)$
- Hence rate constant $k_r = \mathbf{k}^{\ddagger} \exp(-(\Delta^{\ddagger} H - T\Delta^{\ddagger} S)/RT)$.
- Hence $k_r = \mathbf{k}^{\ddagger} \exp(\Delta^{\ddagger} S/R) \exp(-\Delta^{\ddagger} H/RT)$
- This expression has the same form as the Arrhenius expression.
  - The activation energy E_a relates to $\Delta^{\ddagger} H$
  - Pre-exponential factor $A = \mathbf{k}^{\ddagger} \exp(\Delta^{\ddagger} S/R)$

Statistical thermodynamic approach

- The activated complex can form products if it passes though the transition state $AB^{\ddagger}$
- The **equilibrium constant** $K^{\ddagger}$ can be derived from statistical mechanics
  - q is the **partition function** for each species
  - ΔE_0 (kJ mol^{-1})is the difference in internal energy between A, B and $AB^{\ddagger}$ at T=0

$$K^{\ddagger} = \frac{q_{AB\mp}}{q_A q_B} \exp(-\frac{\Delta E_0}{RT})$$

- Suppose that a very loose vibration-like motion of the activated complex $AB^{\ddagger}$ with frequency ν along the reaction coordinate tips it through the transition state.
  - The **reaction rate** is depends on the **frequency** of that motion. Rate = $\nu\,[AB^{\ddagger}]$
- It can be shown that the **rate constant** k_r is given by the **Eyring equation**
  - the contribution from the critical vibrational motion has been resolved out from quantities $K^{\ddagger}$ and $q_{AB\ddagger}$
  - ν cancels out from the equation
  - k = **Boltzmann constant** h =

$$k_r = \frac{kT}{h} \overline{K}^{\ddagger}$$

$$\text{Hence } k_r = \frac{kT}{h} \frac{\overline{q_{AB\mp}}}{q_A q_B} \exp(\frac{-\Delta E_0}{RT})$$

Statistical thermodynamic approach

continued

- Can determine partition functions q_A and q_B from spectroscopic measurements but transition state has only a transient existence (picoseconds) and so cannot be studied by normal techniques (into the area of femtochemistry)
- Need to postulate a structure for the activated complex and determine a theoretical value for $q^{‡}$.
  - Complete calculations are only possible for simple cases, e.g., $H + H_2 \rightarrow H_2 + H$
  - In more complex cases may use mixture of calculated and experimental parameters
- **Potential energy surface:** 3-D plot of the energy of all possible arrangements of the atoms in an activated complex. Defines the easiest route (the col between regions of high energy) and hence the exact position of the transition state.
- For the simplest case of the reaction of two structureless particles (e.g., atoms) with no vibrational energy reacting to form a simple diatomic cluster the expression for k_r derived from statistical thermodynamics resembles that derived from collision theory

Example of a potential energy surface

- Hydrogen atom exchange reaction $H_A + H_B—H_C \rightarrow H_A—H_B + H_C$
- Atoms constrained to be in a straight line (collinear) $H_A \cdot\cdot H_B \cdot\cdot H_C$
- Path C goes up along the valley and over the col (pass or saddle point) <u>between</u> 2 regions (mountains) of higher energy and descends down along the other valley.
- Paths A and B go over much more difficult routes through regions of high energy
- Can investigate this type of reaction by collision of molecular/ atomic beams with defined energy state.
  - Determine which energy states (translational and vibrational) lead

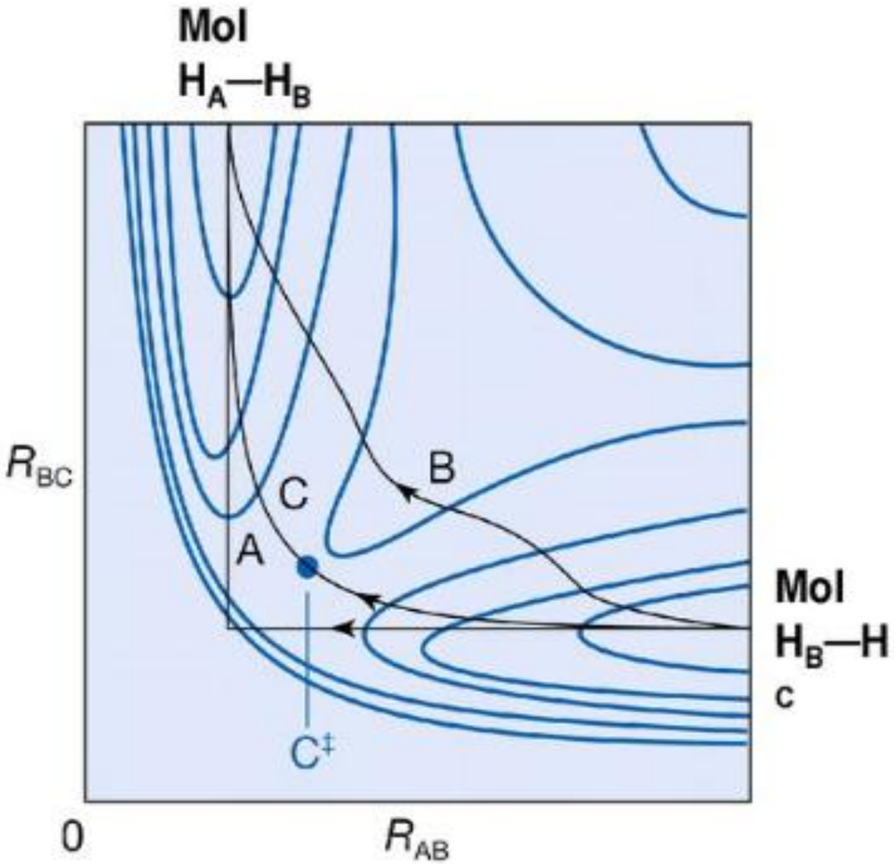


Diagram :www.oup.co.uk/powerpoint/bt/atkins

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


Thank you