

Chemical dynamics

CHEM674

Transition State Theory
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University of Delaware
2020

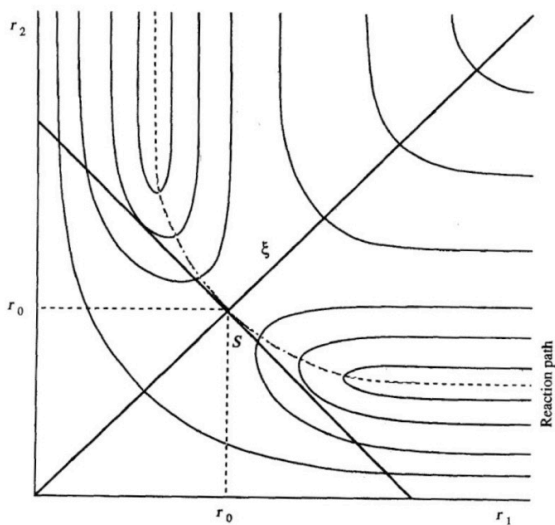
Outline

- From macroscopic observables to a microscopic description of chemical reactions (reading Steinfeld et al. Chapter 6 & 7)
 - Potential energy surfaces
 - Long-range potentials
 - Empirical potentials
 - Molecular bonding potentials
 - Internal coordinates and Normal Modes of vibration
 - Ab Initio calculation of potential energy surfaces
 - Analytic potential energy functions
 - Reaction path and introduction to transition state theory
 - Potential energy surfaces of electronically excited molecules

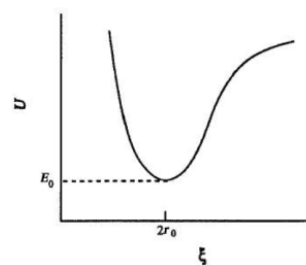
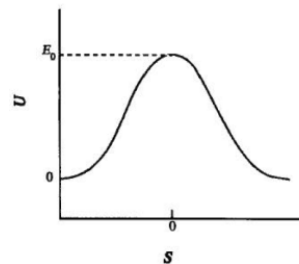
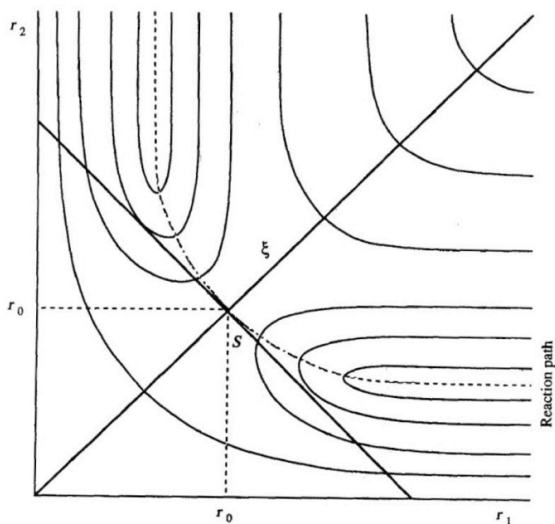
Outline

- Statistical approach to reaction dynamics transition state theory
 - Motion on the potential surface
 - Basic postulates and derivation of transition state theory
 - Dynamical derivation of transition state theory
 - Quantum mechanical effects in transition state theory
 - Thermodynamic formulation of transition state theory
- Application of transition state theory
 - Evaluating partition functions by statistical mechanics
 - Electronic partition function
 - Translational partition function
 - Vibrational partition function
 - Rotational partition function
 - Symmetry and statistical factors
 - Collision between atoms

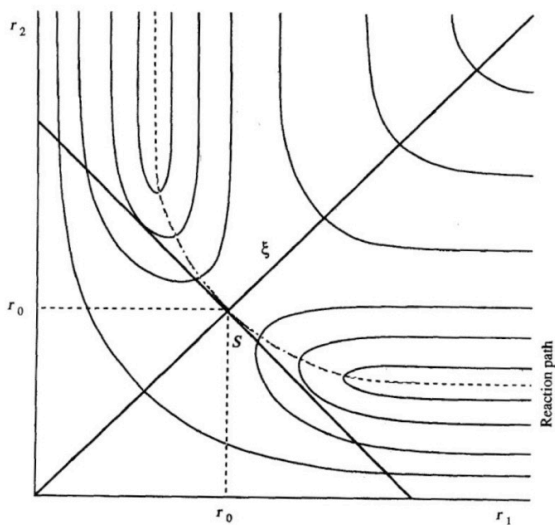
Motion on the potential surface



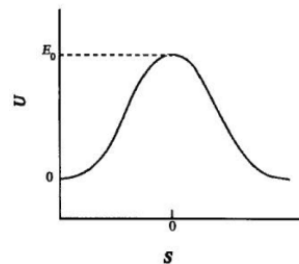
Motion on the potential surface



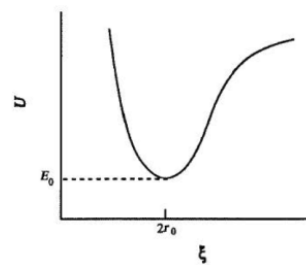
Motion on the potential surface



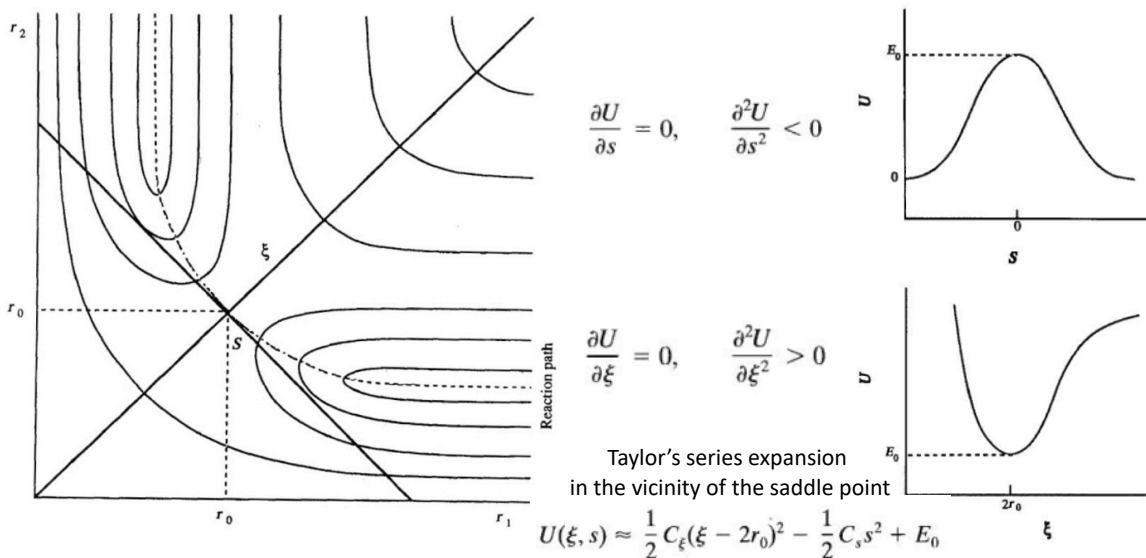
$$\frac{\partial U}{\partial s} = 0, \quad \frac{\partial^2 U}{\partial s^2} < 0$$



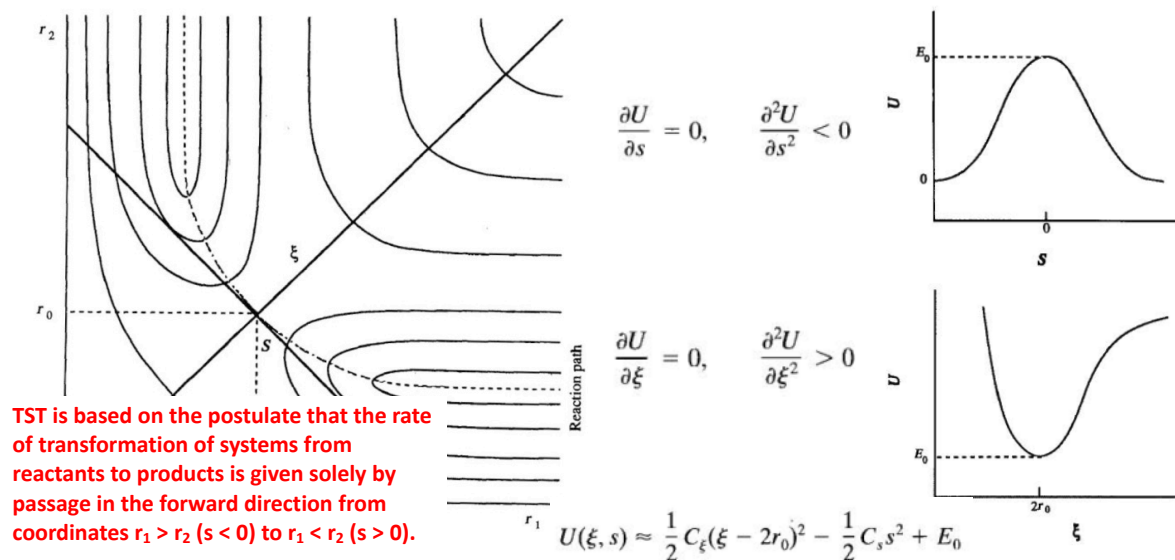
$$\frac{\partial U}{\partial \xi} = 0, \quad \frac{\partial^2 U}{\partial \xi^2} > 0$$



Motion on the potential surface



Motion on the potential surface



Derivation of transition state theory

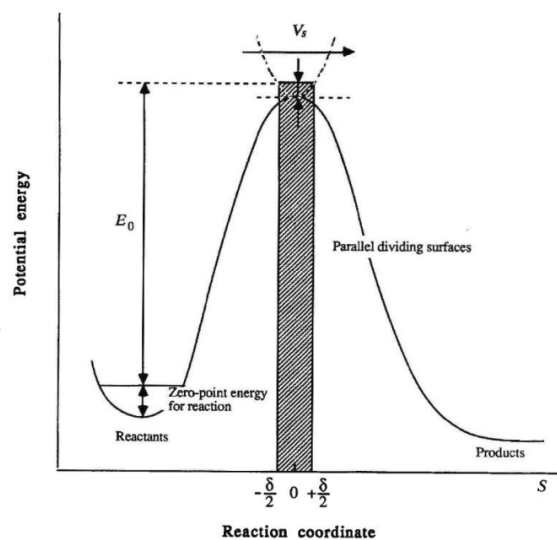
Eyring, Evans, and Polanyi introduced it in 1935
Based essentially on classical mechanics

Two basic assumptions:

- 1) Separation of electronic and nuclear motions (equivalent to Born-Oppenheimer approximation)
- 2) Maxwell-Boltzmann distribution of molecules among their states

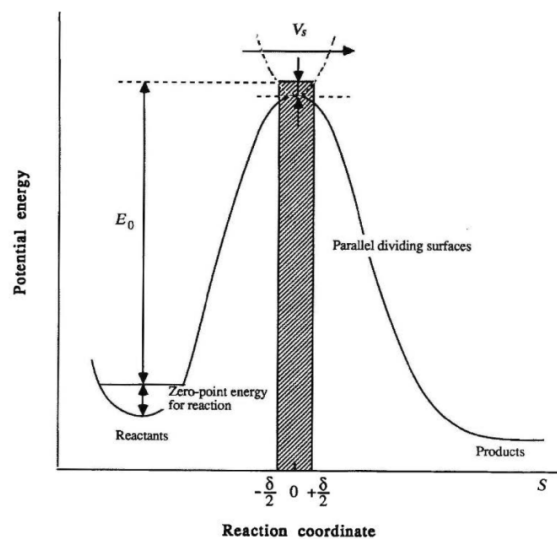
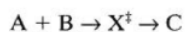
Additional assumptions:

- 1) Molecular systems that cross the transition state in the direction of the products cannot turn back and reform the reactants
- 2) In the transition state, motion along the reaction coordinate may be separated from other motions and treated classically
- 3) Even in the absence of equilibrium, the transition states that are becoming products are distributed according to Maxwell-Boltzmann



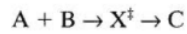
Derivation of transition state theory

Suppose the bimolecular reaction :



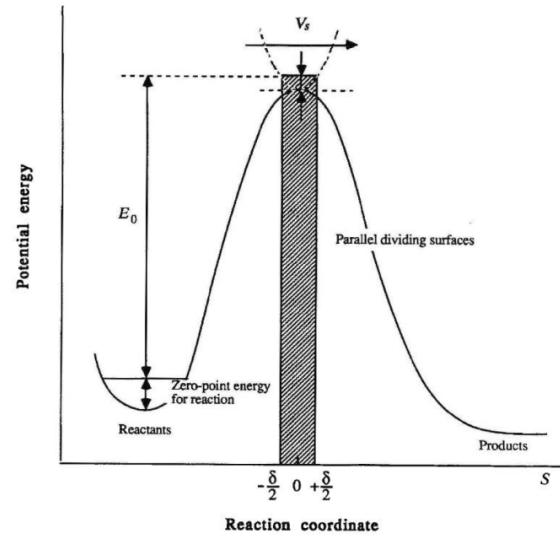
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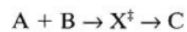
At equilibrium :

$$N_f^\ddagger + N_b^\ddagger = N^\ddagger = K^\ddagger[A][B]$$



Derivation of transition state theory

Suppose the bimolecular reaction :



At equilibrium :

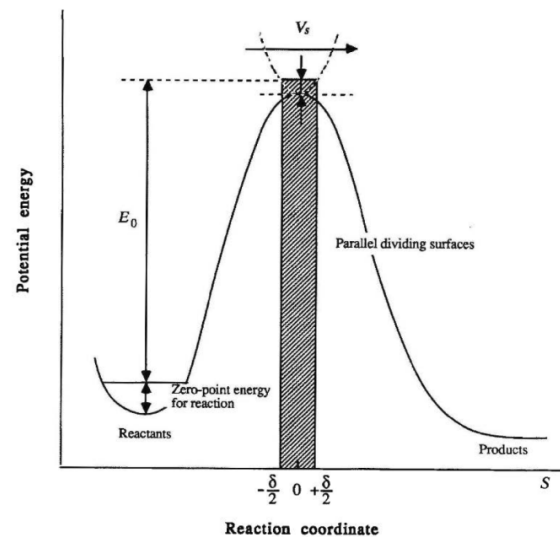
$$N_f^\ddagger + N_b^\ddagger = N^\ddagger = K^\ddagger[A][B]$$

We move the system out of equilibrium by doing,

$$N_b^\ddagger = 0$$

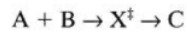
Therefore (since backward reaction should not change):

$$N_f^\ddagger = K^\ddagger[A][B]/2$$



Derivation of transition state theory

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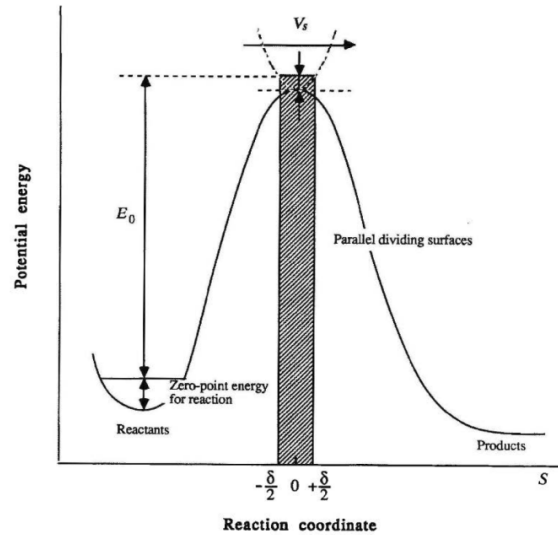
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Therefore :

$$N_f^\ddagger = K^\ddagger[A][B]/2$$

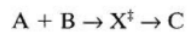
The average velocity at which transition states pass over the barrier to products, we derive :

$$\frac{dN}{dt} (\text{reactants} \rightarrow \text{products}) = \frac{\delta N^\ddagger}{\delta t}$$



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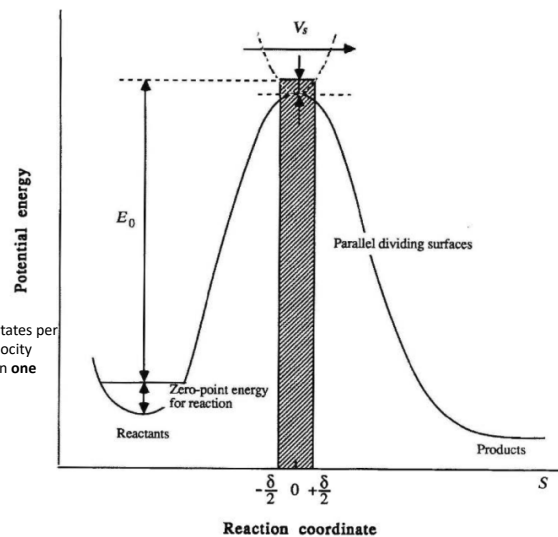
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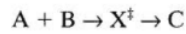
$$\frac{dN}{dt} (\text{reactants} \rightarrow \text{products}) = \frac{\delta N^\ddagger}{\delta t}$$

Number of transition states per unit volume having velocity between v and $v + dv$ in one direction.



Derivation of transition state theory

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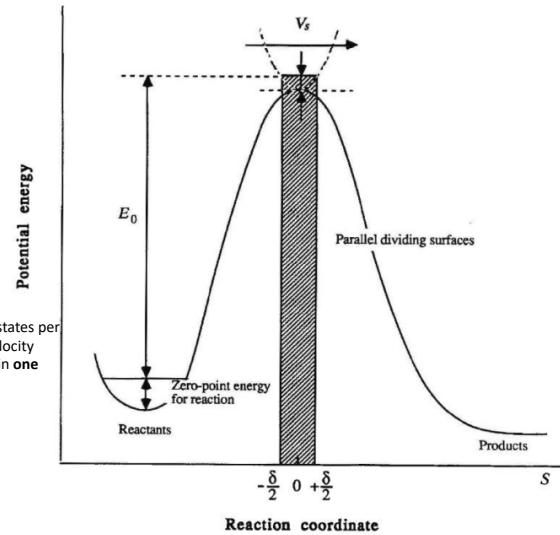
The average velocity at which transition states pass over the barrier to products, we derive :

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Average time
to cross the barrier

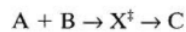
$$\delta t = \frac{\delta}{\bar{v}_s}$$

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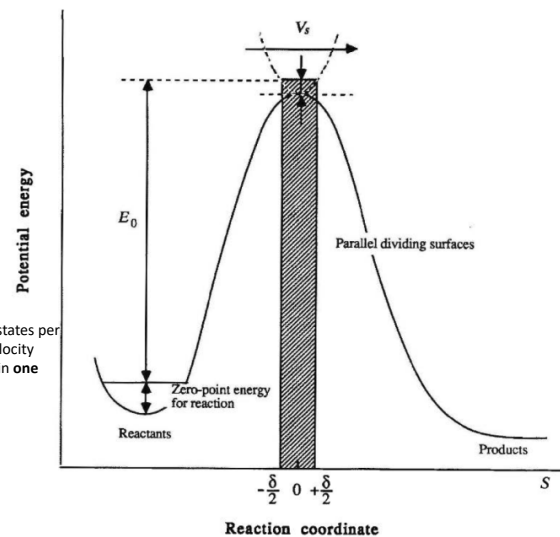
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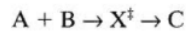
$$\delta t = \frac{\delta}{\bar{v}_s} \quad \longrightarrow \quad \frac{dN}{dt} = \delta N^\ddagger \frac{\bar{v}_s}{\delta}$$

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Derivation of transition state theory

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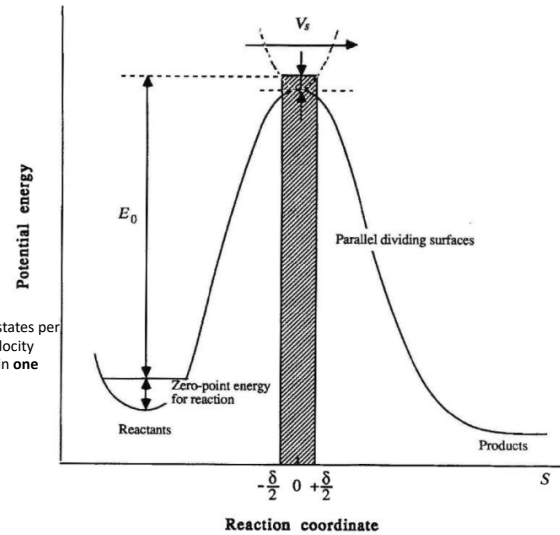
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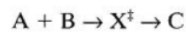
$$\delta t = \frac{\delta}{\bar{v}_s} \Rightarrow \frac{dN}{dt} = \delta N^\ddagger \frac{\bar{v}_s}{\delta}$$

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Derivation of transition state theory

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$$N_f^\ddagger + N_b^\ddagger = N^\ddagger = K^\ddagger[A][B]$$

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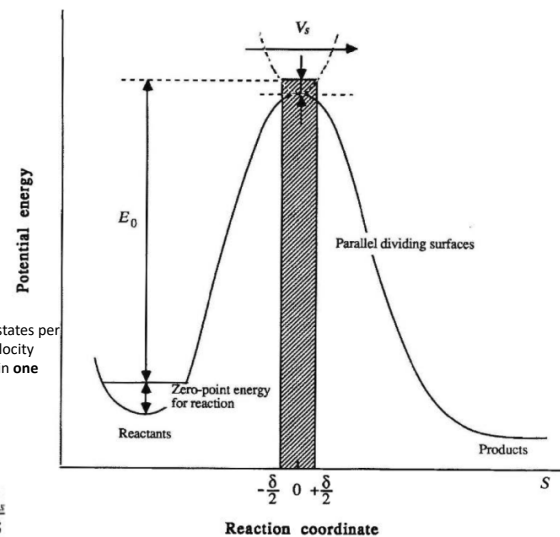
$$N_f^\ddagger = K^\ddagger[A][B]/2 \Rightarrow \delta N^\ddagger = \frac{N^\ddagger}{2}$$

The average velocity at which transition states pass over the barrier to products, we derive :

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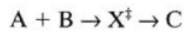
$$\delta t = \frac{\delta}{\bar{v}_s} \Rightarrow \frac{dN}{dt} = \delta N^\ddagger \frac{\bar{v}_s}{\delta} \Rightarrow \frac{dN}{dt} = \frac{N^\ddagger}{2} \frac{\bar{v}_s}{\delta}$$

Number of transition states per unit volume having velocity between v and $v + dv$ in one direction.



Derivation of transition state theory

Suppose the bimolecular reaction :



At equilibrium :

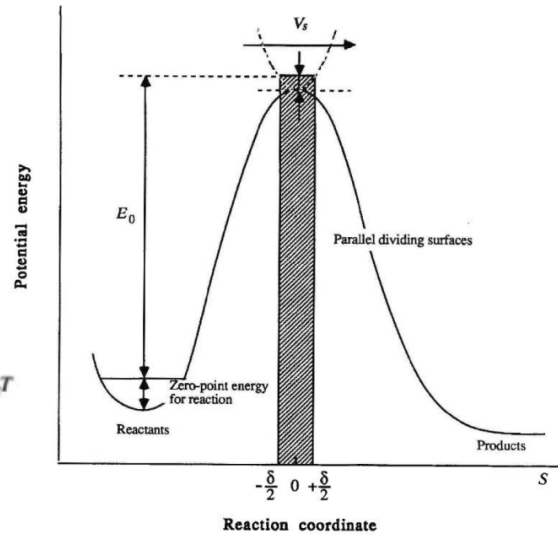
$$N_f^\ddagger + N_b^\ddagger = N^\ddagger = K^\ddagger[A][B]$$

$$\frac{dN}{dt} = \delta N^\ddagger \frac{\bar{v}_s}{\delta} \quad \Rightarrow \quad \frac{dN}{dt} = \frac{N^\ddagger}{2} \frac{\bar{v}_s}{\delta}$$

$$\bar{v}_s = \frac{\int_0^\infty v_s e^{(-\mu_s v_s^2/2k_B T)} dv_s}{\int_0^\infty e^{(-\mu_s v_s^2/2k_B T)} dv_s} = \left(\frac{2k_B T}{\pi \mu_s}\right)^{1/2} \quad \Rightarrow \quad \frac{dN}{dt} = \frac{N^\ddagger}{2} \left(\frac{2k_B T}{\pi \mu_s}\right)^{1/2} \frac{1}{\delta}$$

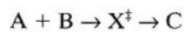
$$K^\ddagger = \frac{N^\ddagger}{[A][B]} \quad \Rightarrow \quad K^\ddagger = \frac{N^\ddagger}{[A][B]} = \frac{Q_{\text{tot}}^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

$$\frac{dN}{dt} = \left(\frac{2k_B T}{\pi \mu_s}\right)^{1/2} \frac{1}{2\delta} \frac{Q_{\text{tot}}^\ddagger}{Q_A Q_B} e^{-E_0/k_B T} [A][B]$$



Derivation of transition state theory

Suppose the bimolecular reaction :



At equilibrium :

$$N_f^\ddagger + N_b^\ddagger = N^\ddagger = K^\ddagger[A][B]$$

$$\frac{dN}{dt} = \left(\frac{2k_B T}{\pi \mu_s}\right)^{1/2} \frac{1}{2\delta} \frac{Q_{\text{tot}}^\ddagger}{Q_A Q_B} e^{-E_0/k_B T} [A][B]$$

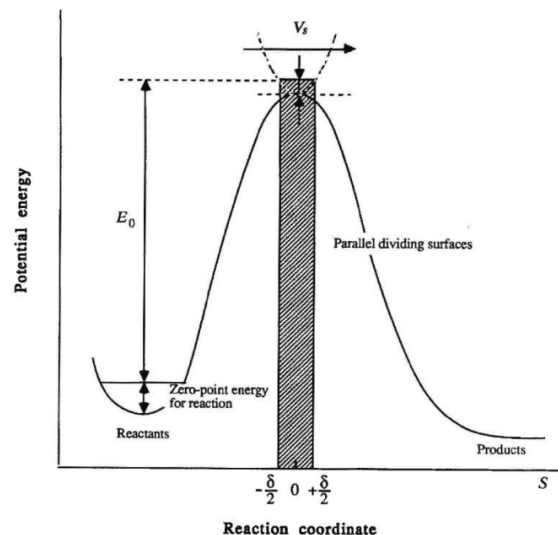
Translational

All other 3N-1
degrees of freedom

$$Q_{\text{tot}}^\ddagger = Q_s Q^\ddagger \quad Q_s = (2\pi \mu_s k_B T)^{1/2} \delta / h$$

$$\frac{dN}{dt} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T} [A][B] \quad \frac{dN}{dt} = k [A][B]$$

$$k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$



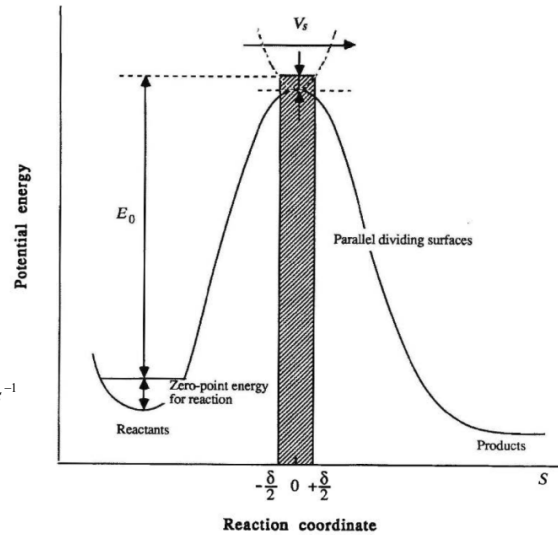
Derivation of transition state theory

$$k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

Remember the TPD pre-exponential factor for the 1st order process?

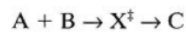
$$f = \frac{k_b T}{h}$$

$$k = f \frac{q^{\ddagger S}}{q^{\text{Reactants}}} \approx f = \frac{k_b T}{h} = \frac{1.3806505 \times 10^{-23} \frac{\text{J}}{\text{K}} \times 298.15 \text{K}}{6.6260693 \times 10^{-34} \text{J s}} = 6.212 \times 10^{12} \text{s}^{-1}$$



Derivation of transition state theory

Suppose the bimolecular reaction :



At equilibrium :

$$k = k_{\text{abs}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

$$k = \frac{k_B T}{h} K_c^\ddagger$$

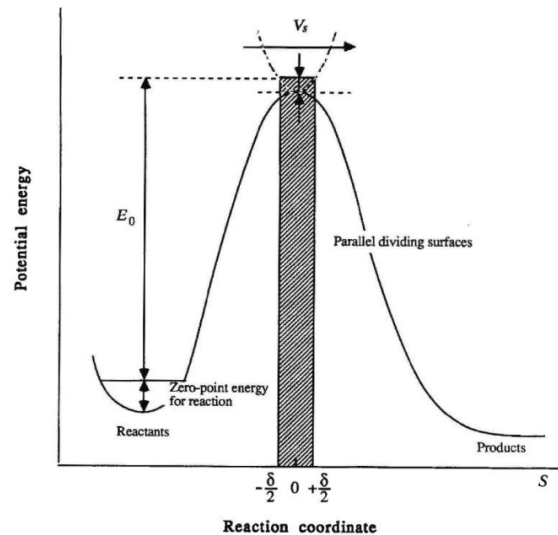
$$K_c^\ddagger = \frac{Q^\ddagger}{Q_A Q_B} e^{-E_0/k_B T}$$

$$\Delta G^\ddagger = -RT \ln K_c^\ddagger$$

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$



Transition state theory

- Molecular systems that have crossed the transition state in the direction of products cannot turn around and reform reactants.
- In the transition state, motion along the reaction coordinate may be separated from the other motions and treated classically as a translation.
- Even in the absence of an equilibrium between reactant and product molecules, the transition state that are becoming products are distributed among their states according to the Maxwell-Boltzmann laws.

Transition state theory: Some Issues

- Uses classical mechanics to evaluate partition functions and canonical averages. Does not describe tunneling (important for light species, such as H and D)
- Simplifies motion on the potential surface to 1D along reaction coordinate, the actual motion may include a normal component
- Uses harmonic potentials, which may be an issue at high temperatures
- Experimental evidence suggests that there may be multiple crossings of the TS, meaning that the forward motion is not representative of half of the TS
- If recrossing of the TS does occur, then the local equilibrium is not maintained
- There may be non-Boltzmann distributions (can be selective energy consumption by the reactants and specific energy release by the products), however, that may be fine if relaxation of reactants and products is rapid compared with the reaction rate
- Solvent effects often lead to significant deviations from the TS theory (diffusion limit)