

Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Agenda for the remaining course sessions

- 4th December 2024: Optional Self-Learning of Chapter 7
(no lecture & no exercise session)
- 11th December 2024: Applications of Kinetics & Dynamics
(lecture & exercise session)
NB: Tell your tutors what you would like to discuss next week!
- 18th December 2024: Q & A, exam contents, exercises
(first announcements by Sascha, then extended exercise session
for you, as promised 😊)

Recap from last session

RRK Theory of Unimolecular Reactions

- assumes $k_2 \rightarrow k(E)$ and $A^*(E, E + dE)$
- assumes for activated molecules to...

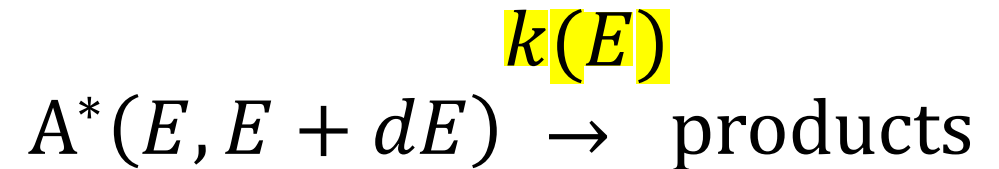
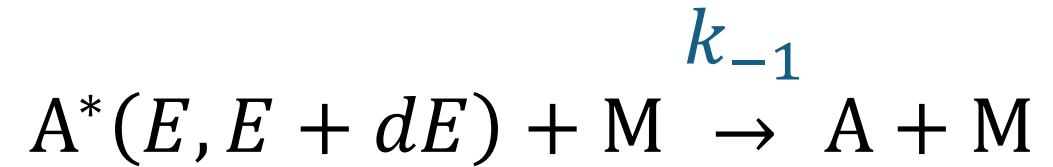
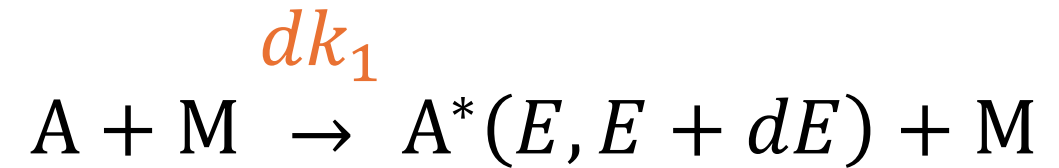
(1) form microcanonical ensemble

(2) dissociate with frequency ν once reaching $E_0 + E'$ in the critical mode

(3) continue to form a microcanonical ensemble because

(3a) *ergodic hypothesis*, i.e., energy can freely redistribute between all vibrational modes

(3b) *fast IVR* (intramolecular vibrational energy redistribution), i.e., faster than reaction



RRK theory again assumes equilibrium (so that we can use statistical TD) & classical oscillators (no QM)

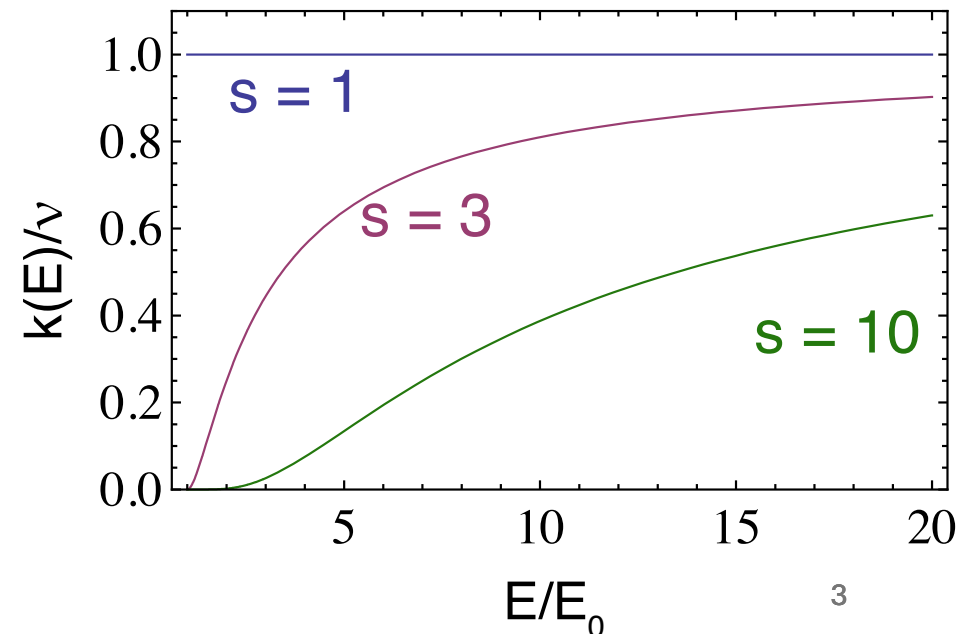
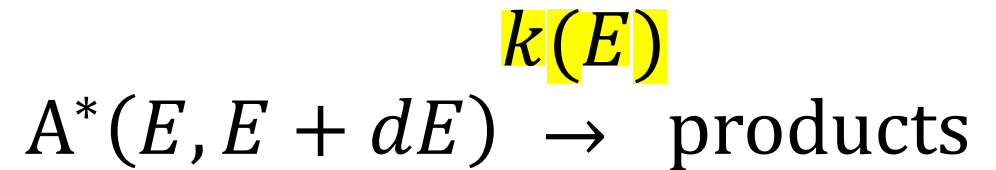
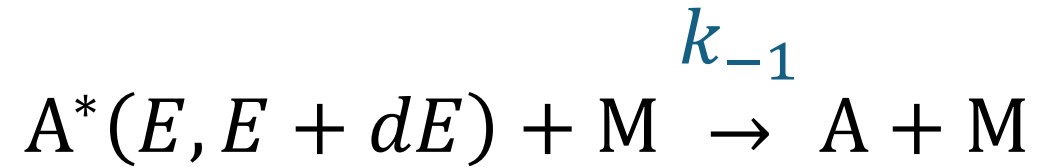
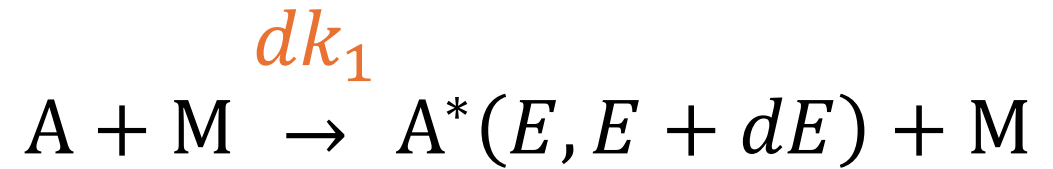
Recap from last session

RRK Theory of Unimolecular Reactions

$$k(E) = \nu \cdot P(E, E_s \geq E_0)$$

$$k(E) = \nu \cdot \frac{N(E, E_s \geq E_0)}{N(E)}$$

$$k(E) = \nu \cdot \left(\frac{E - E_0}{E} \right)^{s-1}$$



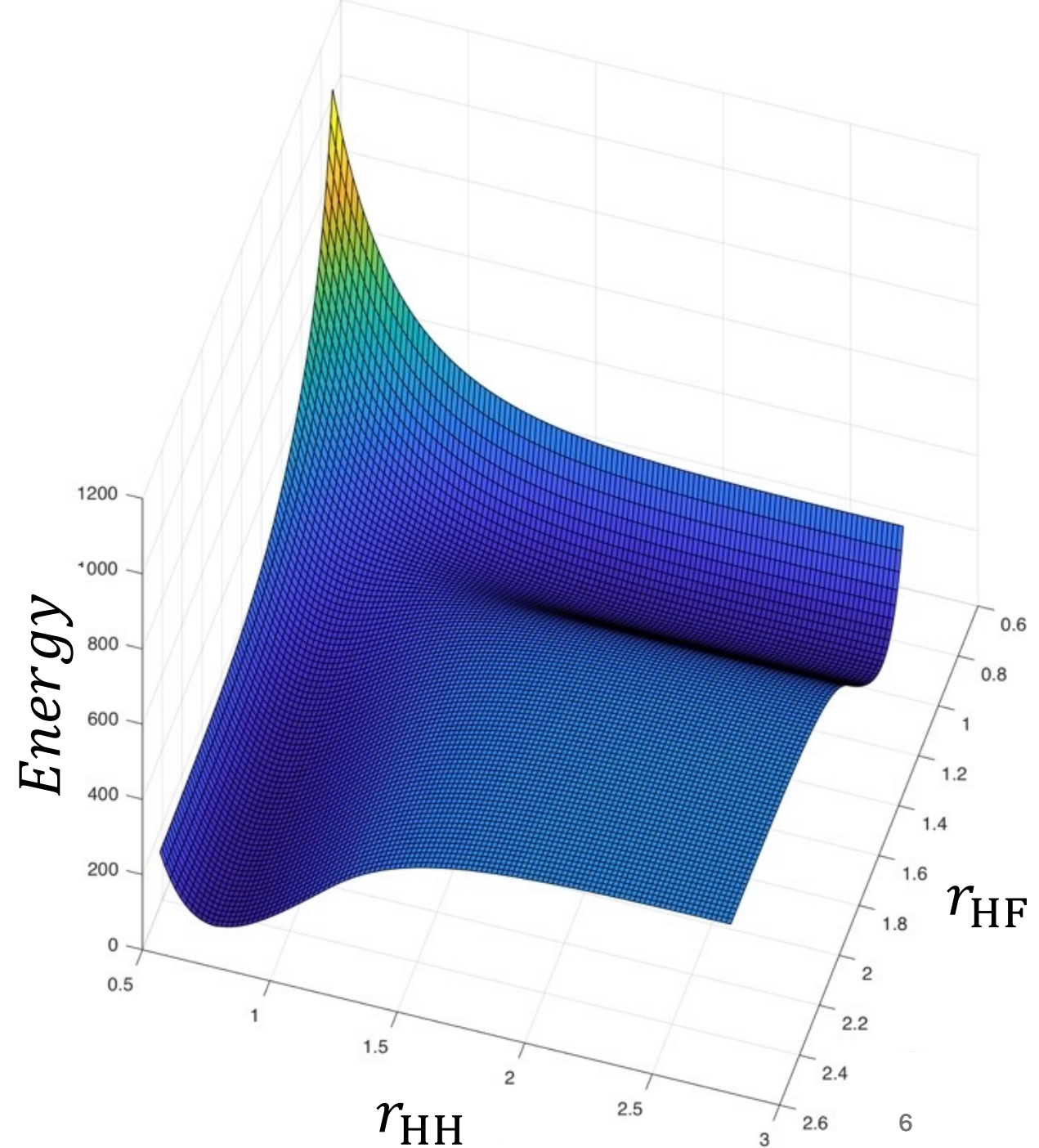
Chapter 8

Transition State Theory

8.1 Motion on the potential energy surface

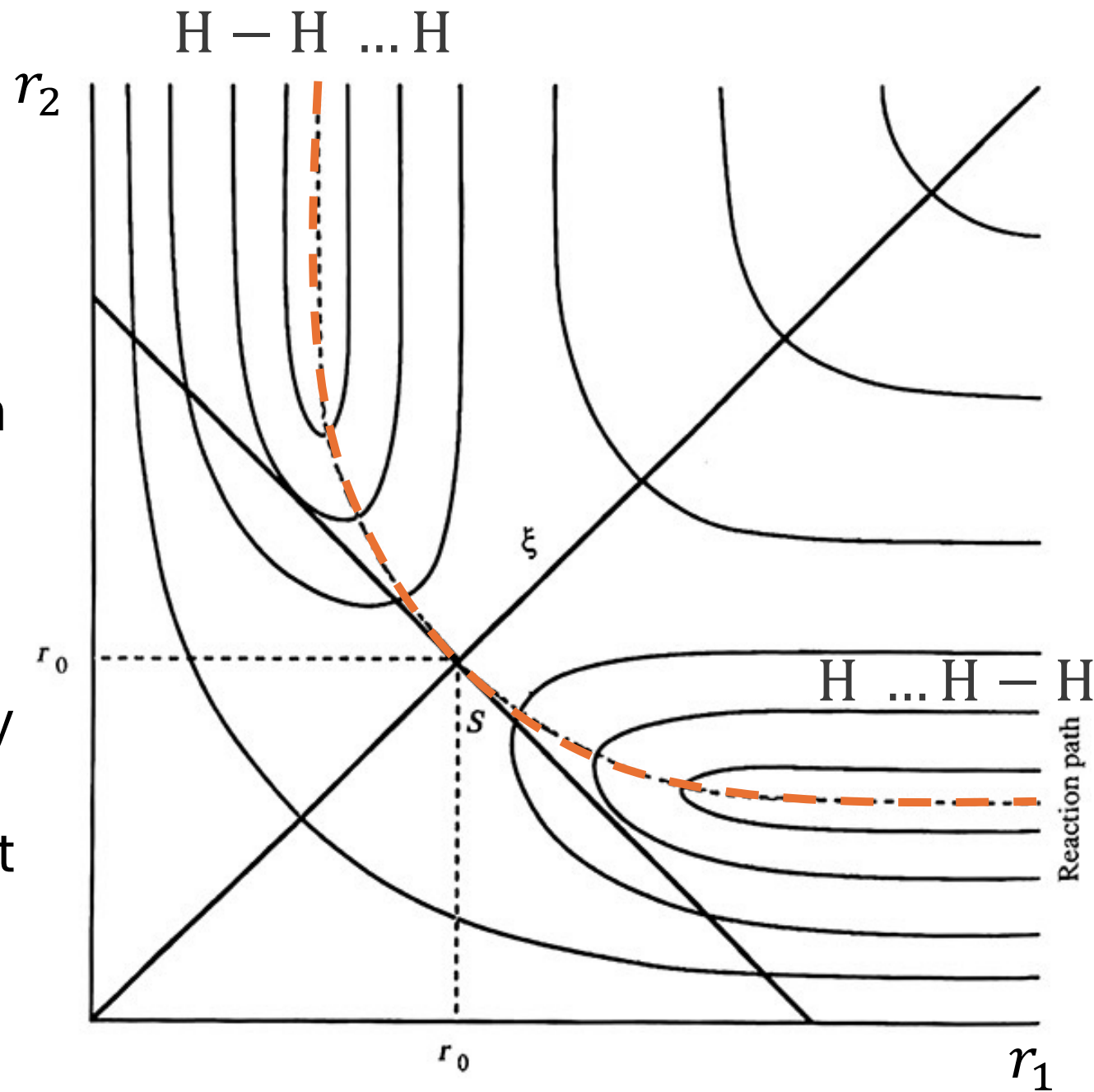
- Transition state theory (TST) assumes that transition state (TS) is in thermal equilibrium with reactants
 - can apply statistical thermodynamics to get thermal rate const.
- careful, if in experiment we do not form a statistical ensemble
- use Born-Oppenheimer approximation to separate electronic from nuclear motion:
- nuclei move in a potential created by electron cloud, which instantaneously rearranges when nuclei change positions

- Potential energy surface of reaction
$$\text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H}$$
- $3N - 6 = 3$ vibrational degrees of freedom
- To display surface, we restrict nuclei to linear collision geometry
- reduces plot to 2 coordinates: HH distance and HF distance
- Let's look at an even simpler reaction



- Contour plot of reaction

$$\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$$
- degenerate reaction, linear geometry
- Thus, surface is symmetric with respect to diagonal
- Dashed curved line: *minimum energy path*
- Saddle point of potential energy surface lying on minimum energy path: **transition state** at $r_1 = r_2 = r_0$
- If analyzing normal modes at saddle point, we find...



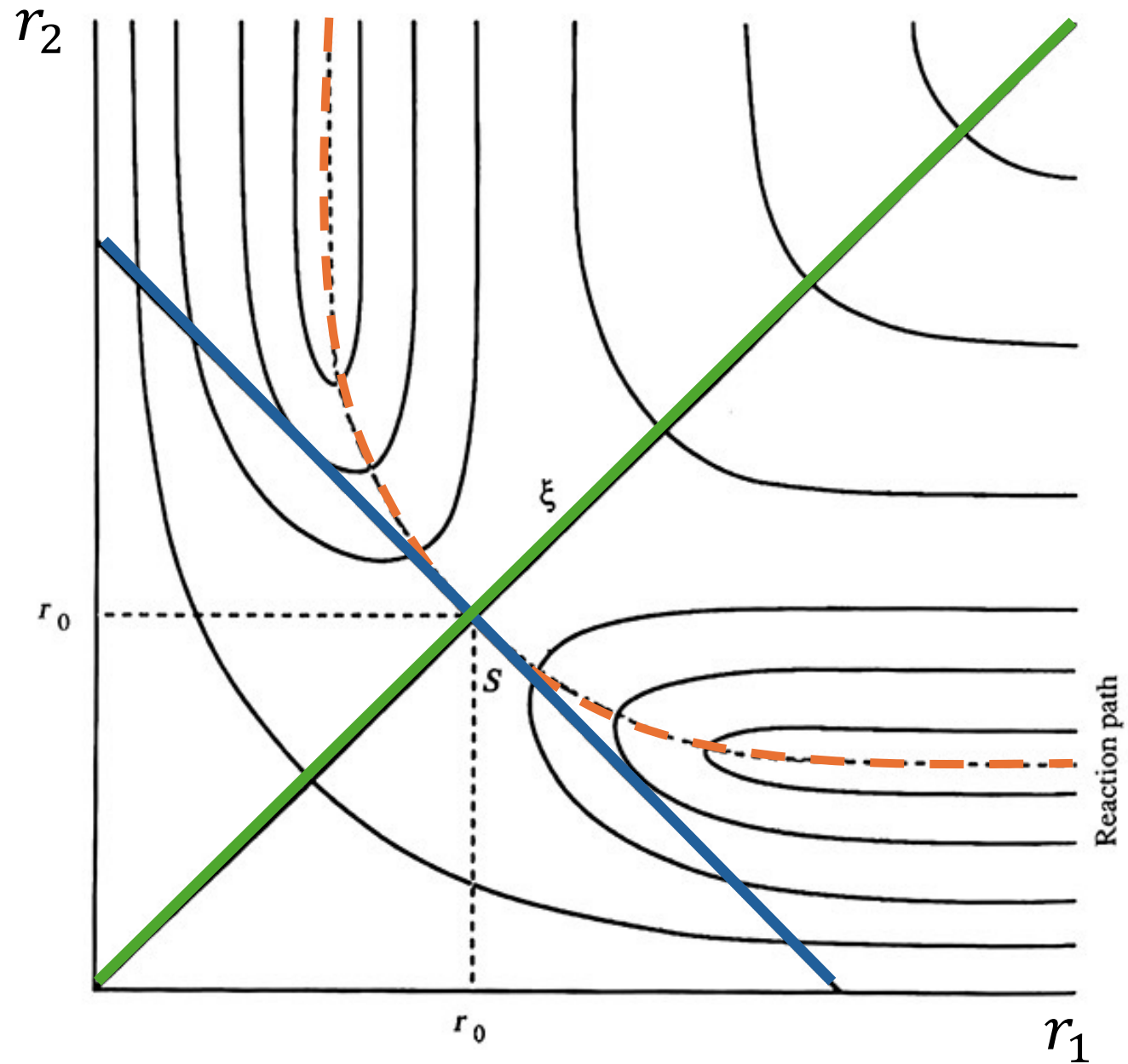
- One normal mode s corresponding to motion *along* minimum energy path:

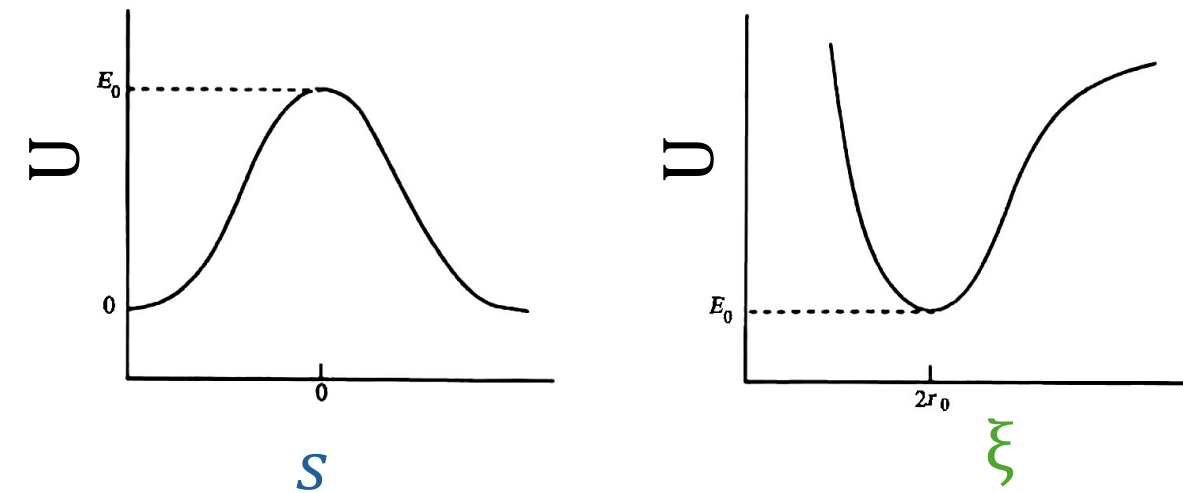
$$s = r_1 - r_2$$

- One normal mode ξ corresponding to motion *orthogonal* to minimum energy path:

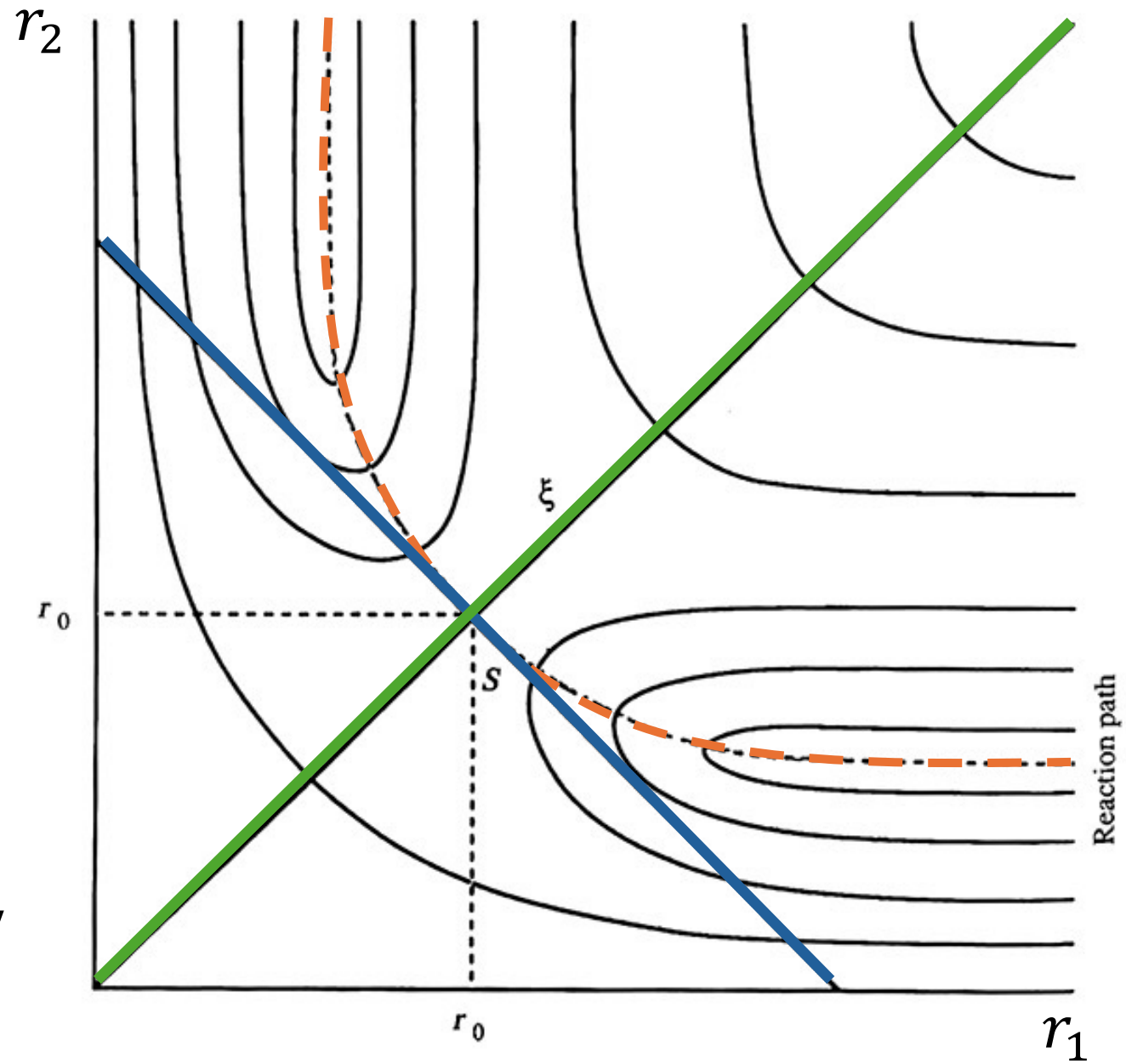
$$\xi = r_1 + r_2$$

- The potential U along those lines looks as follows

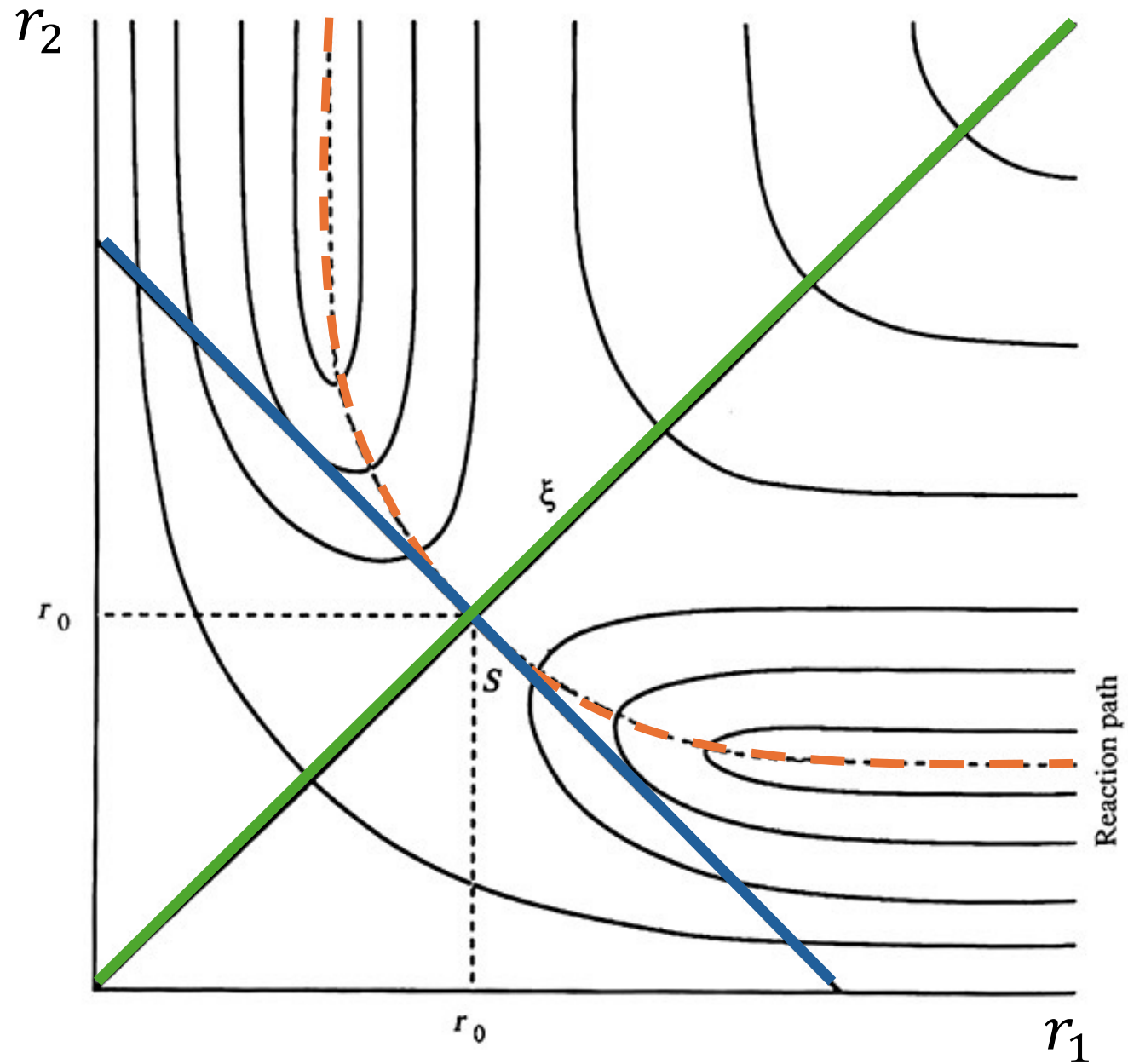




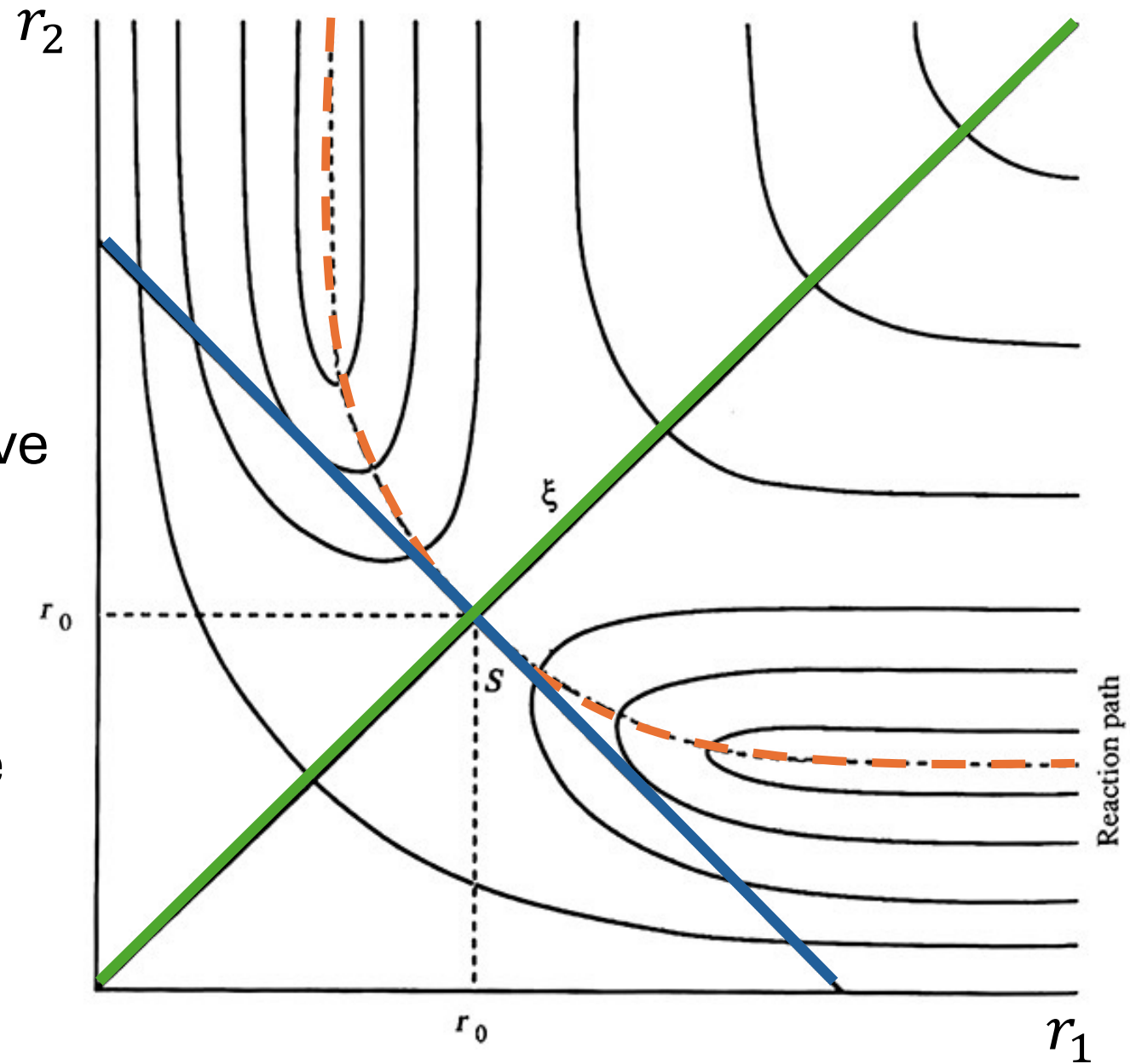
- At the TS, minimum energy path mode has *maximum*, while orthogonal path shows *minimum*
- ***In general: the transition state is a saddle point, which is a maximum along the reaction coordinate (the minimum energy path) and a minimum along all other normal modes***



- Note: all the normal modes in the system will have *real* eigenfrequency values, except for the normal mode *s* along the minimum energy path
- $3N - 7$ modes: real frequency
- mode *s*: *imaginary* frequency
- Why?
- Eigenfrequency of harmonic oscillator:
 - $\omega = \sqrt{\frac{k}{\mu}}$ with $k = \frac{d^2U}{dx^2}$
 - for all modes but one, we are at a minimum, so 2nd derivative is positive, and so k and ω are positive



- Eigenfrequency of harmonic oscillator:
 - $\omega = \sqrt{\frac{k}{\mu}}$ with $k = \frac{d^2U}{dx^2}$
 - for all modes but one, we are at a minimum, so 2nd derivative is positive, and so k and ω are positive
 - BUT: for mode along minimum energy path, 2nd derivative is negative (as it's a maximum)
- spring constant appears negative
- squareroot of sth. negative
- imaginary frequency



8.2 Postulates and Derivation

- Transition state theory (TST), developed by Eyring, Evans and Polanyi, makes 2 basic assumptions:

1) Born-Oppenheimer approximation holds (electronic and nuclear motion separable)

- only way to even model system as potential energy surface
- nuclei move within potential of electron cloud

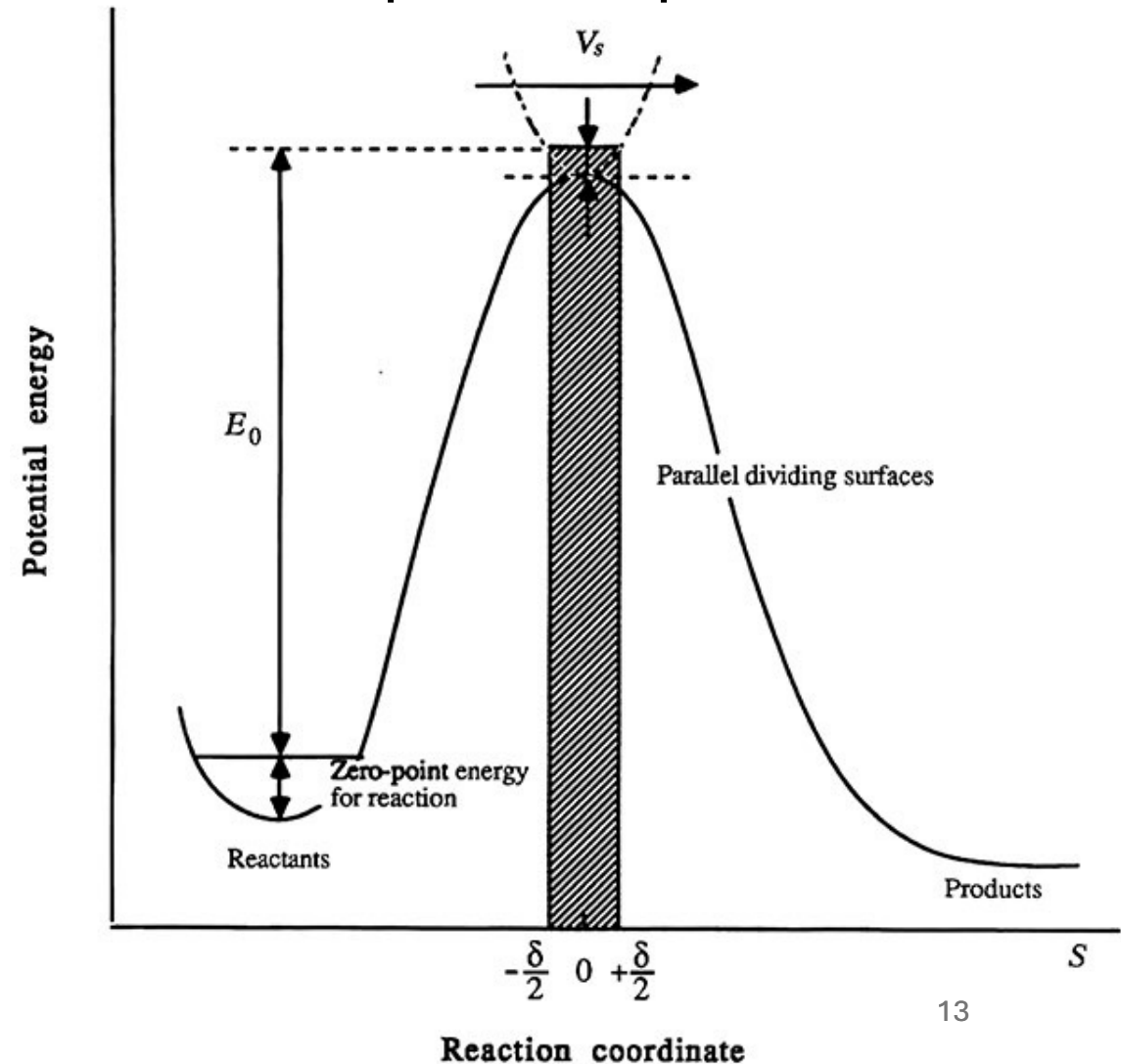
2) Reactant molecules distributed among energy states following a Boltzmann distribution

- again assuming equilibrium to use statistical thermodynamics for thermal distribution

- TST assumes elementary reaction proceeds through a transition state:

$$A + B \rightarrow X^\ddagger \rightarrow \text{products}$$
- TS $X^\ddagger$ is not an isolated intermediate, but a saddle point on potential energy surface
- Note that both reactants and TS have zero-point energy, relevant for E_0
- We consider everything between the *two dividing surfaces* a TS, so from

$$s = -\frac{\delta}{2} \text{ to } s = \frac{\delta}{2}$$
- TST makes 3 specific assumptions



TST makes 3 specific assumptions:

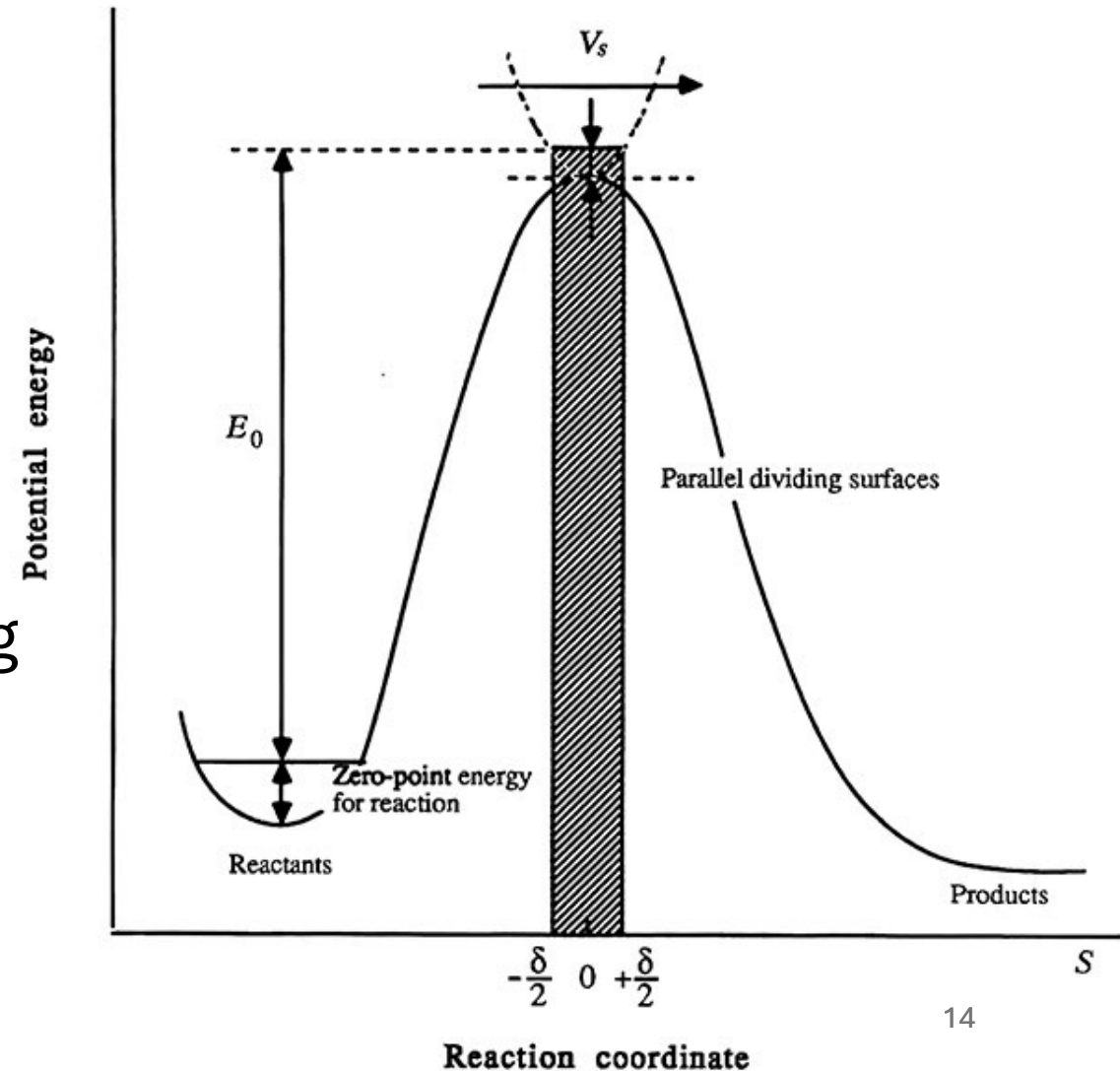
A) no re-crossing

- reactants that have crossed the transition state $X^\ddagger$ in the direction of products cannot turn around and reform reactants
- vice versa for products
- TS is “point of no return”

B) quasi-equilibrium

- transition states are distributed among their states acc. to Boltzmann distr., even if no equilibrium between reactants and products

C) classical motion along rctn. coord.

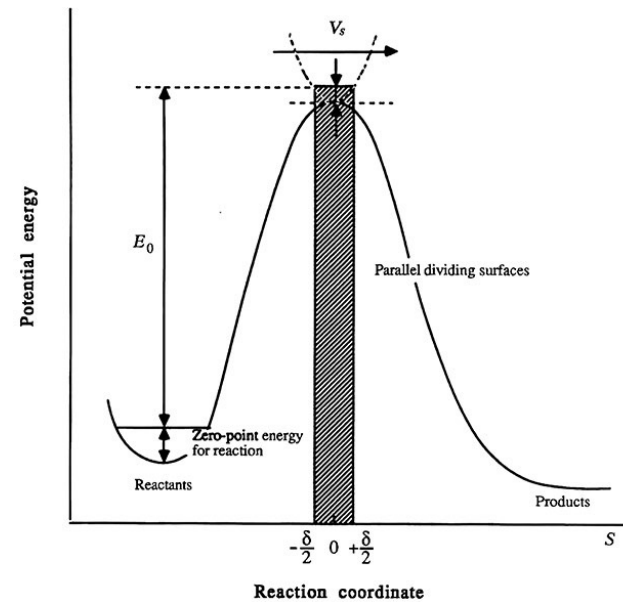


- If reactants & products in equilibrium, we have both transition states, moving forward and backward
- according to no recrossing assumption **A)** we can split them up into concentrations $N_f^\ddagger$ and $N_b^\ddagger$
- at equilibrium: $N_f^\ddagger = N_b^\ddagger$ must hold
- thus the total concentration of TS is $N^\ddagger = N_f^\ddagger + N_b^\ddagger = 2N_f^\ddagger$
- Using quasi-equilibrium assumption **B)** we can write

$$N^\ddagger = K^\ddagger [A][B]$$

- $K^\ddagger$ is equilibrium const. for the formation of the transition state

- for the forward-moving TS we find: $N_f^\ddagger = \frac{N^\ddagger}{2} = \frac{1}{2} K^\ddagger [A][B]$

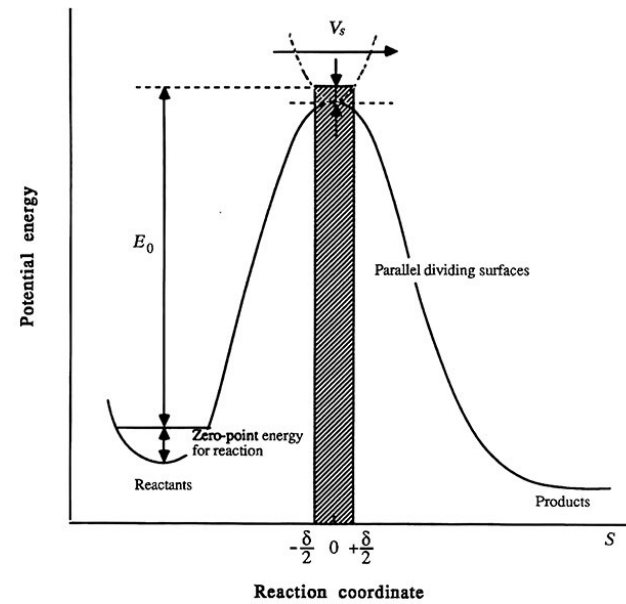


$$N_f^\ddagger = \frac{N^\ddagger}{2} = \frac{1}{2} K^\ddagger [A][B]$$

- because of equilibrium assumption, we can use statistical thermodynamics to derive $K^\ddagger$
- for a gas-phase reaction we remember (Chapter 7):

$$K^\ddagger = \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- E_0 : reaction energy at 0 K, corresponds to difference in zero-point energies between reactants & the transition state (see sketch)
- partition functions of reactants: Q_A and Q_B
- partition function of transition state: $Q_{tot}^\ddagger$
- derived from molecular partition functions q_i through: $Q_i = \frac{q_i}{N_A V} \left[\frac{\text{mol}}{L} \right]$



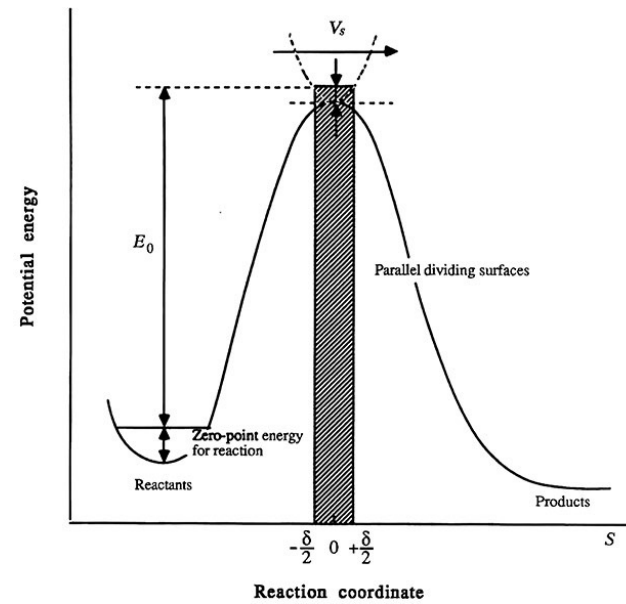
$$N_f^\ddagger = \frac{N^\ddagger}{2} = \frac{1}{2} K^\ddagger [A][B]$$

$$K^\ddagger = \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- The *rate* of the reaction to form products is: $R = k^\ddagger N_f^\ddagger$
- $k^\ddagger$ describes the *rate constant* of forward-moving TS to form products
- for the overall reaction rate constant of A & B to form products, we divide the overall rate R by the reactant concentrations:

$$k_{TST} = k^\ddagger \frac{N_f^\ddagger}{[A][B]} = \frac{1}{2} k^\ddagger K^\ddagger$$

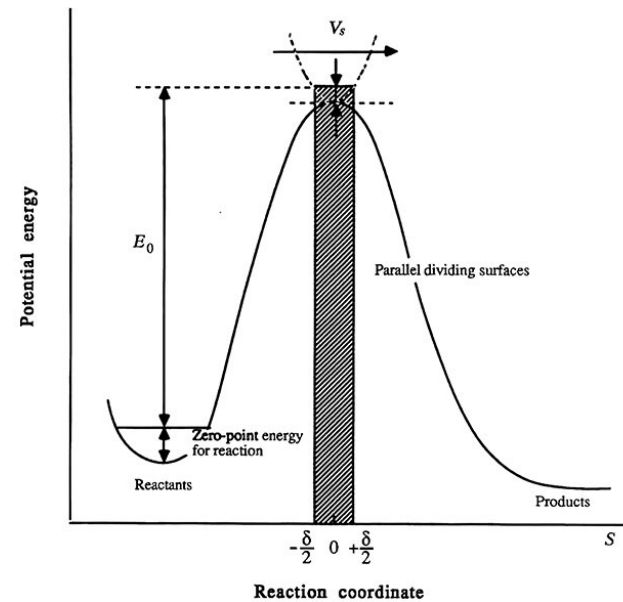
$$\text{because } \frac{N_f^\ddagger}{[A][B]} = \frac{1}{2} K^\ddagger$$



$$K^\ddagger = \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

$$k_{TST} = k^\ddagger \frac{N_f^\ddagger}{[A][B]} = \frac{1}{2} k^\ddagger K^\ddagger$$

- now we only have to figure out $k^\ddagger$ and are done
- let's use assumption **C**), *i.e.*, being able to treat the motion along the reaction coordinate as *classical* (not QM), separated from the other coordinates
- Neglect quantum tunneling & quantum reflections
- What is the average time spent in the transition state acc. to sketch?

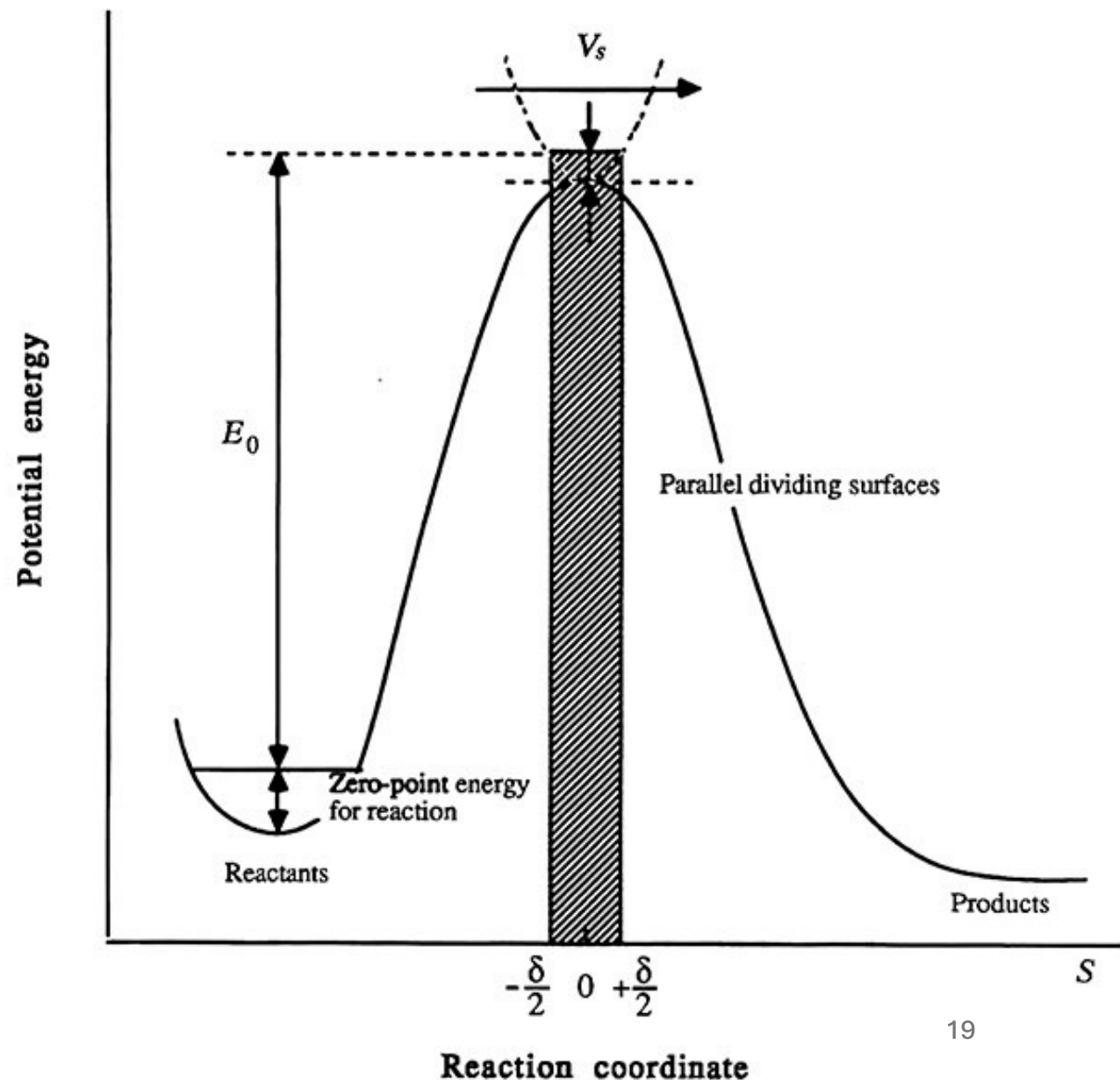


- What is the average time spent in the transition state acc. to sketch?
- Average time δt for TS to traverse the dividing surfaces is:

$$\delta t = \frac{\delta}{\langle v_s \rangle}$$

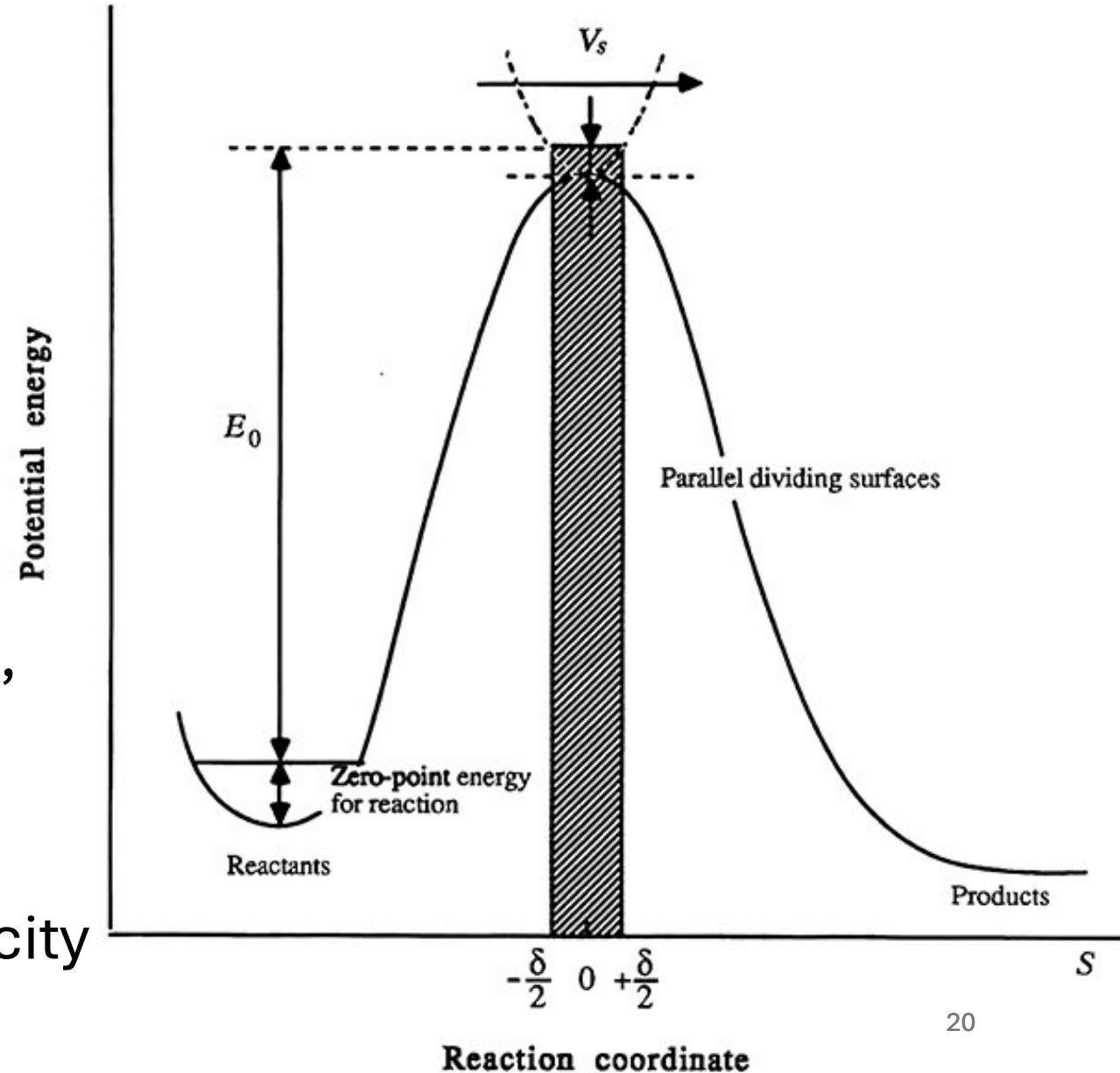
- $\langle v_s \rangle$ is the average velocity in the reaction coordinate s
- If we treat this classically and in pre-equilibrium, it results from Boltzmann distribution:

$$\langle v_s \rangle = \frac{\int_0^\infty v_s e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s}{\int_0^\infty e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s} = \sqrt{\frac{2k_B T}{\pi \mu_s}}$$



$$\langle v_s \rangle = \frac{\int_0^\infty v_s e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s}{\int_0^\infty e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s} = \sqrt{\frac{2k_B T}{\pi \mu_s}}$$

- motion just like a 1D ideal gas:
- dividing integrated Boltzmann population by partition function
- Note that sufficiently close to the potential surface maximum (at TS), the potential is seen as flat
 → we pretend the particle sees *no* potential at all $\cong$ 1D ideal gas velocity



$$\langle v_s \rangle = \frac{\int_0^\infty v_s e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s}{\int_0^\infty e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s} = \sqrt{\frac{2k_B T}{\pi \mu_s}}$$

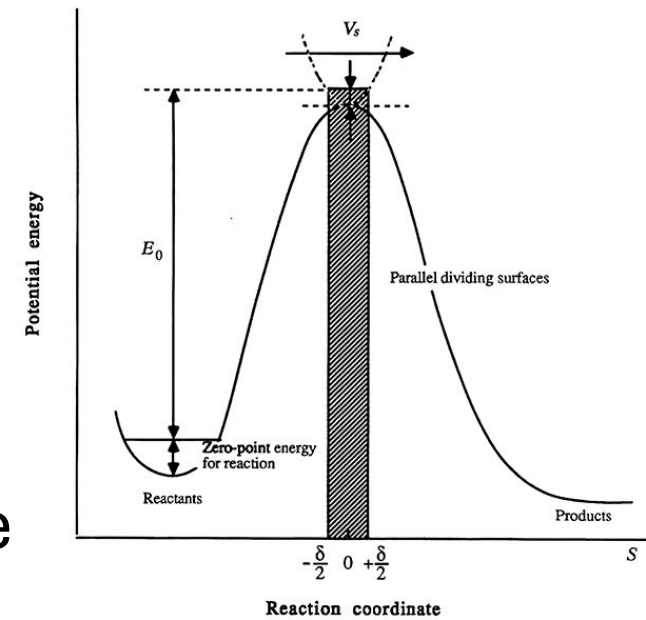
- The average time in the transition state δt is the inverse of the frequency with which the reaction proceeds, so

$$k^\ddagger = \frac{1}{\delta t} = \frac{\langle v_s \rangle}{\delta} = \frac{1}{\delta} \sqrt{\frac{2k_B T}{\pi \mu_s}}$$

- So the overall TST rate constant for the reaction is:

$$k_{TST} = \frac{1}{2} k^\ddagger K^\ddagger = \frac{1}{2\delta} \sqrt{\frac{2k_B T}{\pi \mu_s}} \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- two annoying aspects in this expression: $Q_{tot}^\ddagger$ needs to account for one special mode vs. the rest, and the δ is also not yet properly defined...



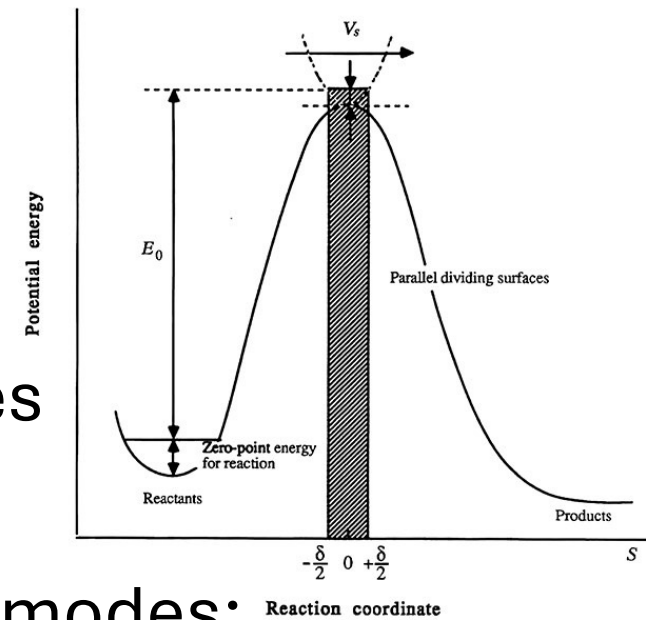
$$k_{TST} = \frac{1}{2} k^\ddagger K^\ddagger = \frac{1}{2\delta} \sqrt{\frac{2k_B T}{\pi\mu_s}} \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- Since we assume we can isolate the translational motion along reaction coordinate from all other degrees of freedom, total energy must be sum of translational energy of reaction coordinate + vibr. energy in all other modes:

$$Q_{tot}^\ddagger = Q_s Q^\ddagger$$

- so, the total partition function is the product of that of the translation along s (Q_s) and that of the remaining modes ($Q^\ddagger$)
- What is the partition function of the reaction coordinate?
- just that of a free particle translation with mass μ_s in a 1D box of length δ :

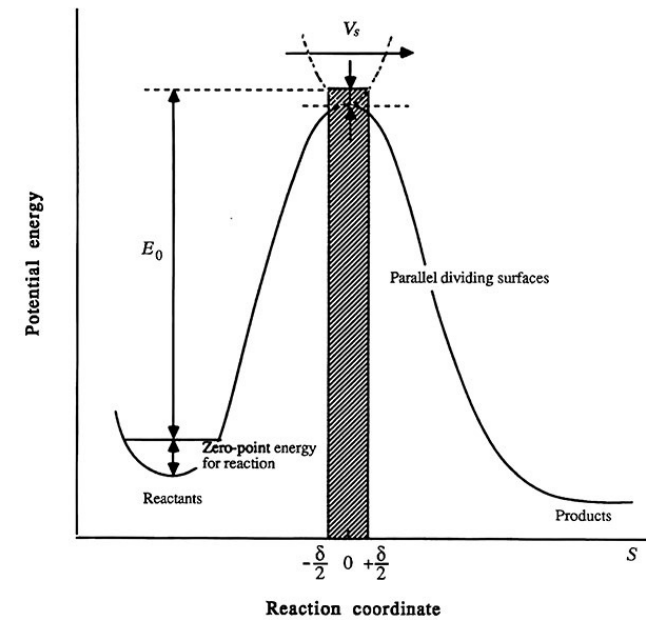
$$Q_s = \frac{\delta}{h} \sqrt{2\pi\mu_s k_B T}$$



$$k_{TST} = \frac{1}{2} k^\ddagger K^\ddagger = \frac{1}{2\delta} \sqrt{\frac{2k_B T}{\pi\mu_s}} \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

$$Q_{tot}^\ddagger = Q_s Q^\ddagger$$

$$Q_s = \frac{\delta}{h} \sqrt{2\pi\mu_s k_B T}$$



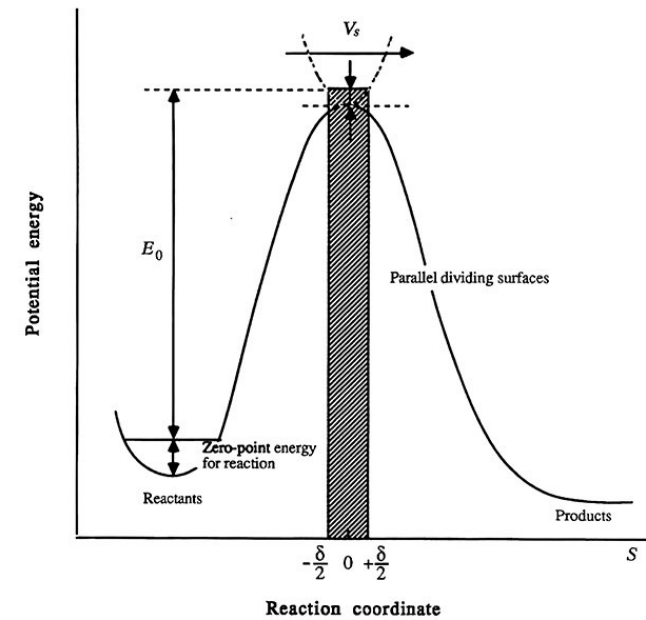
- inserting this result in the above yields

$$k_{TST} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- Note: no more δ or reduced mass in equation! ☺
- need to know: E_0 and partition functions of reactants and of TS (and for those need rotational constants and eigenfrequencies of oscillators); for TS values typically relying on quantum chemical calculations

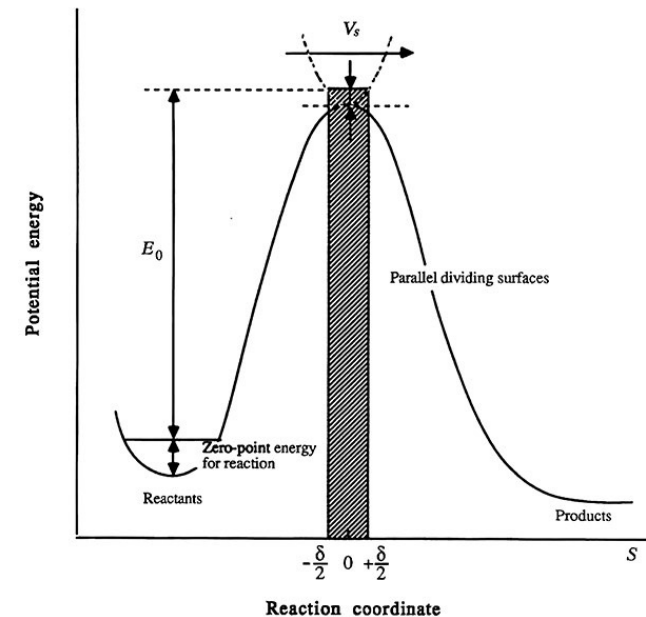
$$k_{TST} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

- the prefactor $\frac{k_B T}{h}$ is called *frequency factor*
- ca. $6.25 \cdot 10^{12} \text{ s}^{-1}$ at 300 K
- approx. timescale of a slow vibration, but lower than timescale of molecular collisions



Shortcomings of TST:

- Classical treatment of motion along reaction coordinate is wrong; should be quantum-mechanical
 - QM dictates the TS cannot be described as definite configuration of nuclei moving at one specific velocity
 - Uncertainty principle demands TS is delocalized in space
 - TS cannot have infinitesimally short lifetime at a finite energy uncertainty
- Potential along reaction coordinate is *not* flat
 - *not* a free translation, as reaction path leads over a barrier, so quantum tunneling & reflections can occur
 - reaction path may be curved, so cannot be decoupled from other vibrations; partition function factoring wrong



8.3 Thermodynamic formulation

- TST rate constant can be reformulated in thermodynamic terms
- convenient, as we don't need to know partition functions
- can also try to fit kinetic data to extract thermodynamic properties
- We know that:

$$k_{TST} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}} = \frac{k_B T}{h} K^\ddagger$$

- $K^\ddagger$, the equilibrium const. for formation of TS from reactants, is connected to the *molar standard Gibbs free energy* through:

$$\Delta G^{\ddagger o} = -RT \ln K^\ddagger$$

molar standard Gibbs free energy: $\Delta G^{\ddagger o} = -RT \ln K^{\ddagger}$

- substituting this yields

$$k_{TST} = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger o}}{RT}}$$

- which we can relate to the enthalpy and entropy of activation:

$$k_{TST} = \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger o}}{R}} e^{-\frac{\Delta H^{\ddagger o}}{RT}}$$

- Comparing the Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$ and its activation energy $E_a = RT^2 \frac{d \ln k}{dT}$, we can formulate for the TST rate const.:

$$RT^2 \frac{d \ln k_{TST}}{dT} = RT + RT^2 \frac{d \ln K^{\ddagger}}{dT}$$

$$RT^2 \frac{d \ln k_{TST}}{dT} = RT + RT^2 \frac{d \ln K^\ddagger}{dT}$$

- the *Gibbs-Helmholtz Equation* states: $\frac{d \ln K^\ddagger}{dT} = \frac{\Delta E^{\ddagger o}}{RT^2}$

- so that $E_a = RT + \Delta E^{\ddagger o}$

- for the activation enthalpy at constant pressure follows:

$$\Delta H^{\ddagger o} = \Delta E^{\ddagger o} + p\Delta V^{\ddagger o} = E_a - RT + p\Delta V^{\ddagger o}$$

- substituting this into our TST rate constant yields:

$$k_{TST} = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^{\ddagger o}}{R}\right)} e^{-\frac{p\Delta V^{\ddagger o}}{RT}} e^{-\frac{E_a}{RT}}$$

$$k_{TST} = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^\ddagger_0}{R}\right)} e^{-\frac{p\Delta V^\ddagger_0}{RT}} e^{-\frac{E_a}{RT}}$$

- we can keep on using thermodynamic relationships and, for example, find for the Arrhenius factor for an ideal gas:

$$A = \frac{k_B T}{h} e^{\left(1 - \Delta n^\ddagger + \frac{\Delta S^\ddagger_0}{R}\right)}$$

- where $\Delta n^\ddagger$ is the change of the particle number in the TS, e.g., $\Delta n^\ddagger = -1$ for a bimolecular reaction
- *We see that we can predict prefactors and other kinetic properties of reactions from thermodynamic (often tabulated) values ☺*

Next week:

Optional Statistical Thermodynamics Revision

- 4th December 2024: Optional Self-Learning of Chapter 7
(no lecture & no exercise session)