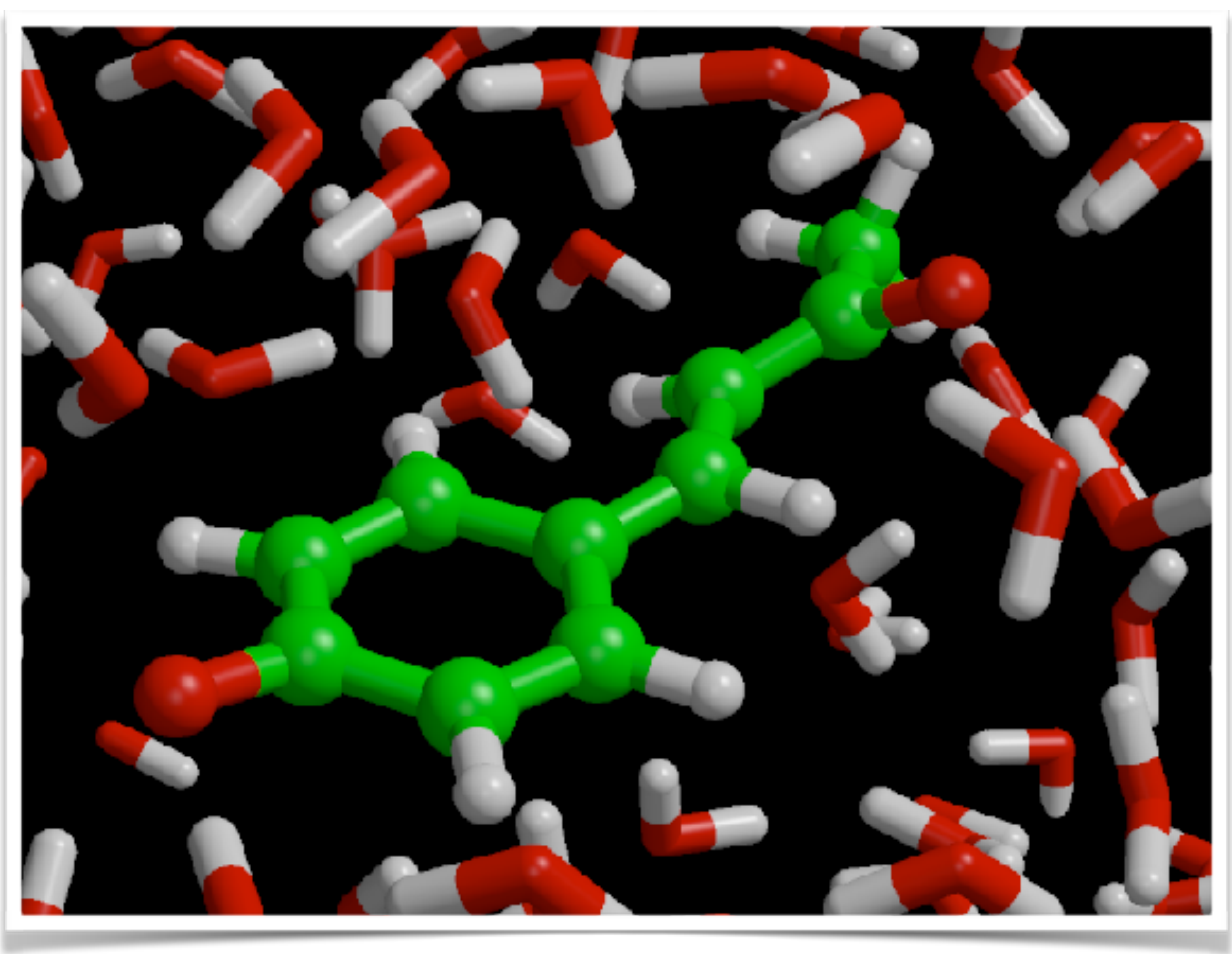
Rate Theory (overview)

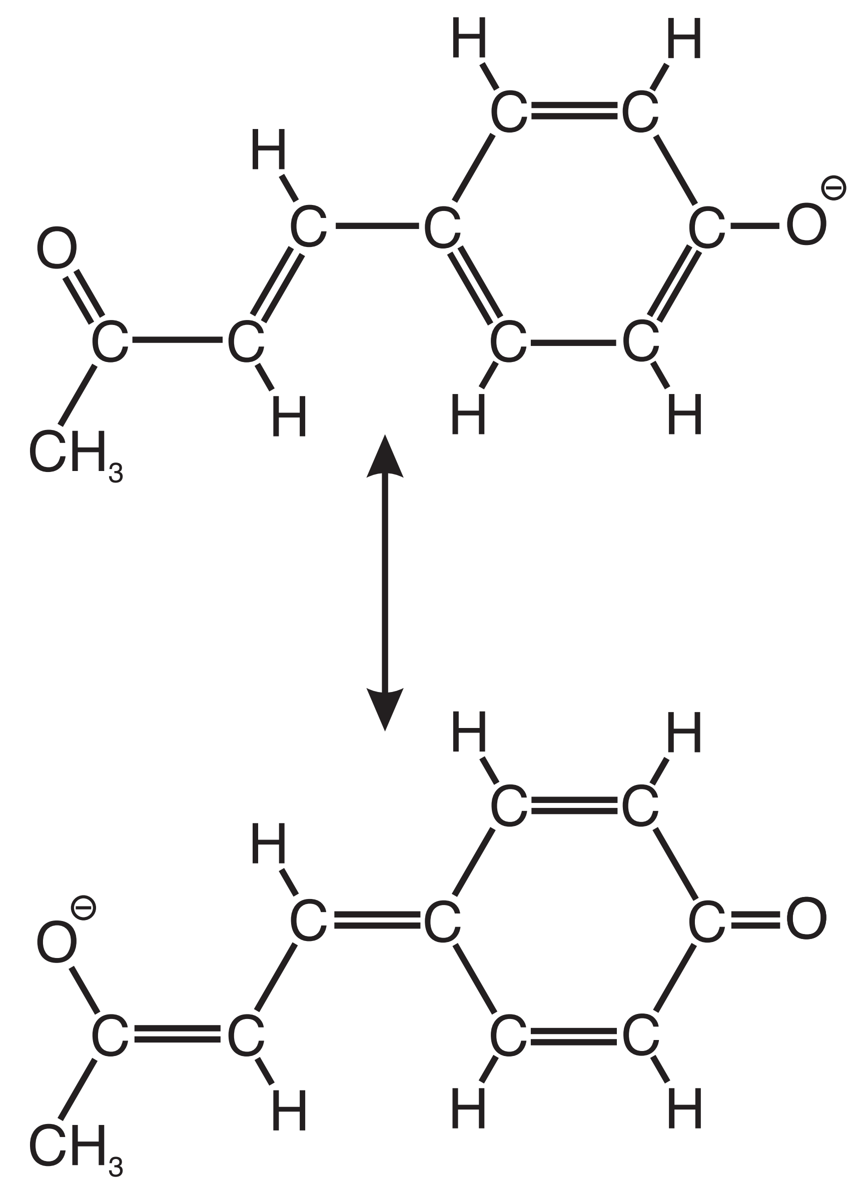
- macroscopic view (phenomenological)
  - rate of reactions
  - experiments
  - thermodynamics
    - Van 't Hoff & Arrhenius equation
- microscopic view (atomistic)
  - statistical mechanics
  - transition state theories
    - Eyring theory
  - effect of environment
    - static: potential of mean force
    - dynamic: Kramer's theory
- computing reaction rate
  - optimizating transition states
    - normal mode analysis
  - simulating barrier crossing
    - practical next week

Chromophore in water

p-hydroxybenzylidene acetone (pck)

CASSCF(6,6)/3-21G//SPCE molecular dynamics

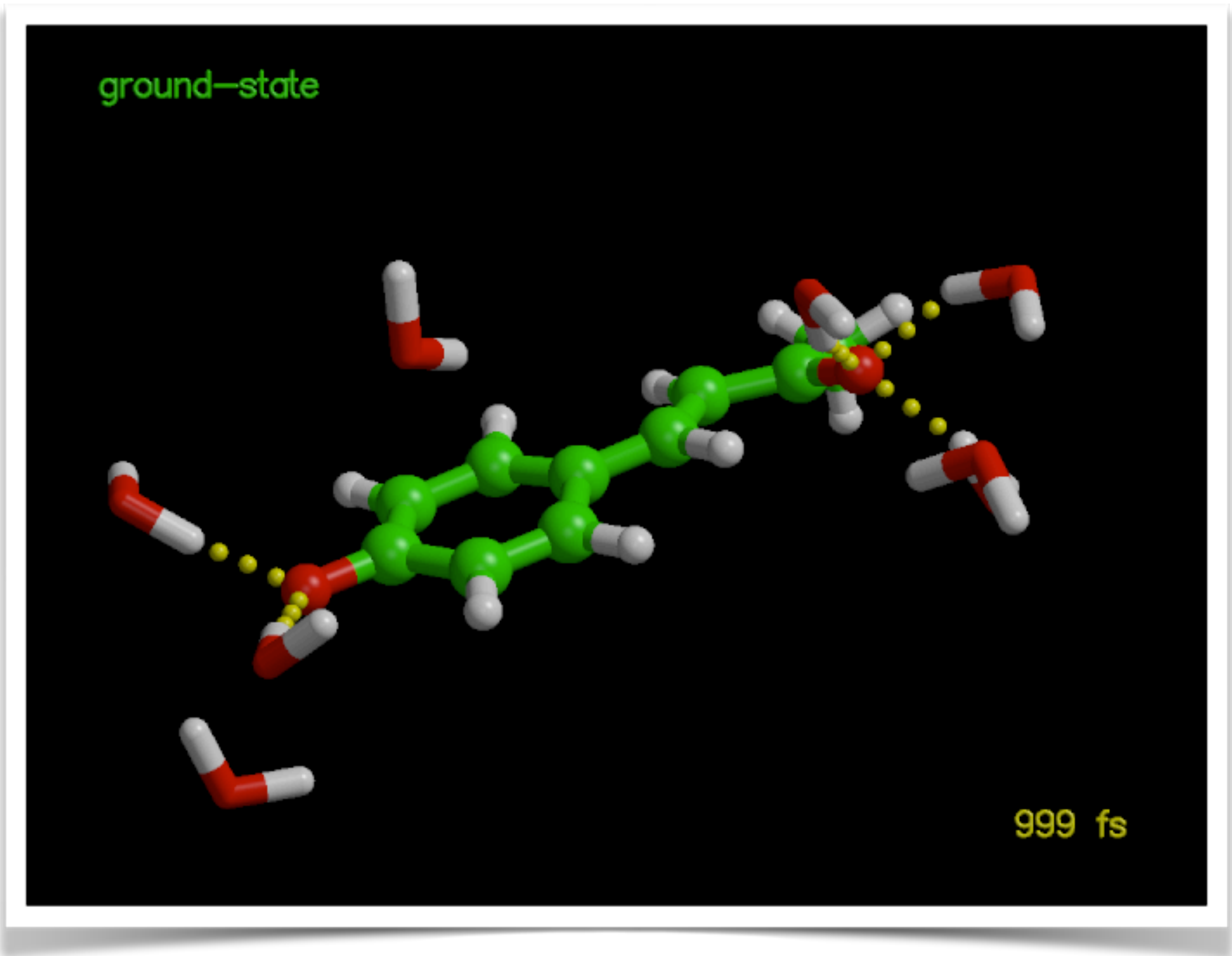




resonance structures

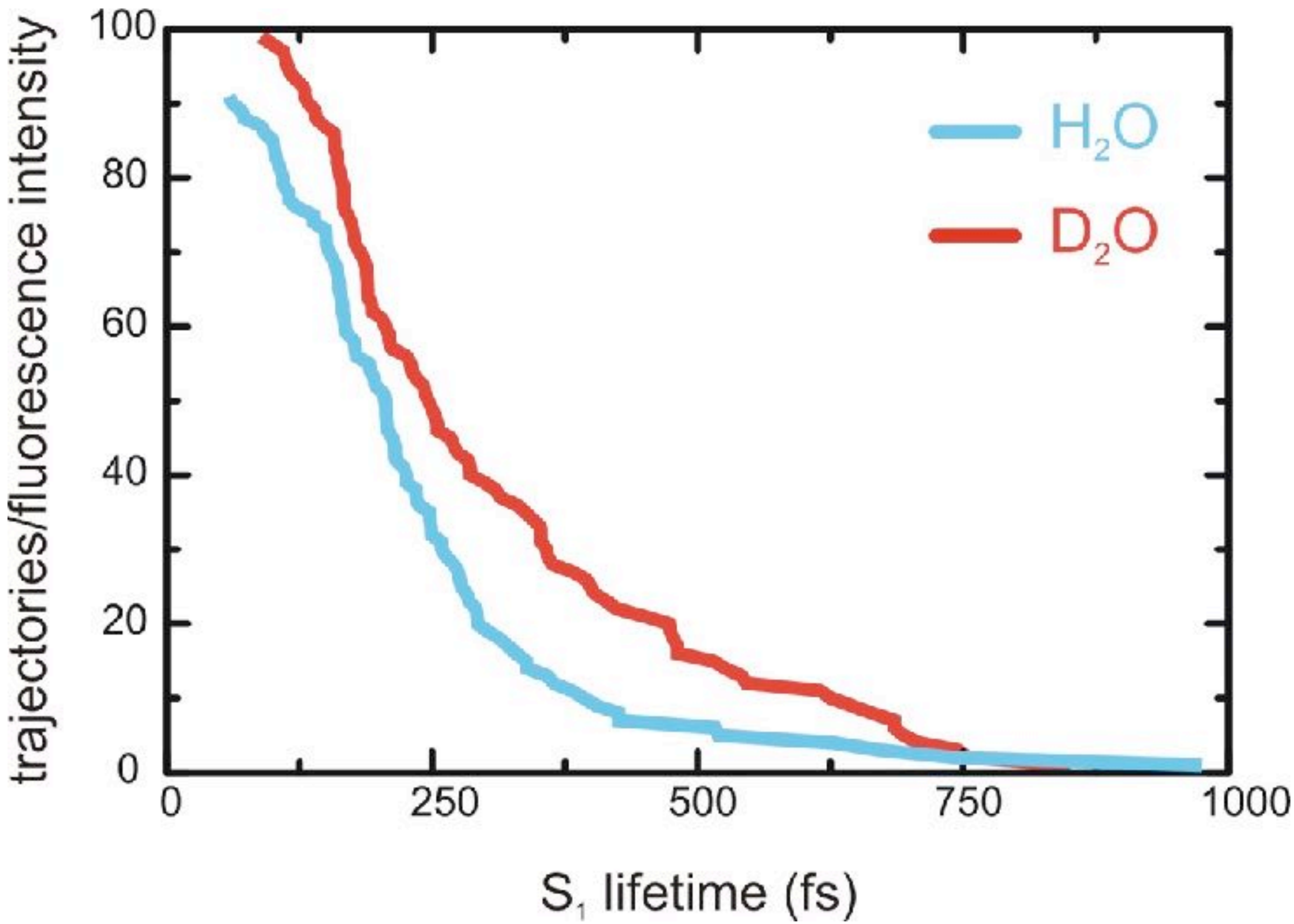
Rate of photoisomerization of double bond

uni-molecular process, initiated by photon absorption



measuring reaction rate

simulation & pump-probe fluorescence



kinetics & thermodynamics

approaching equilibrium

unimolecular process

$$A \underset{k_-}{\overset{k_+}{\rightleftarrows}} B$$

$$\frac{d[A]}{dt} = -k_+[A] + k_-[B]$$

$$\frac{d[B]}{dt} = +k_+[A] - k_-[B]$$

conservation law

$$[A] + [B] = [A]_0$$

so that

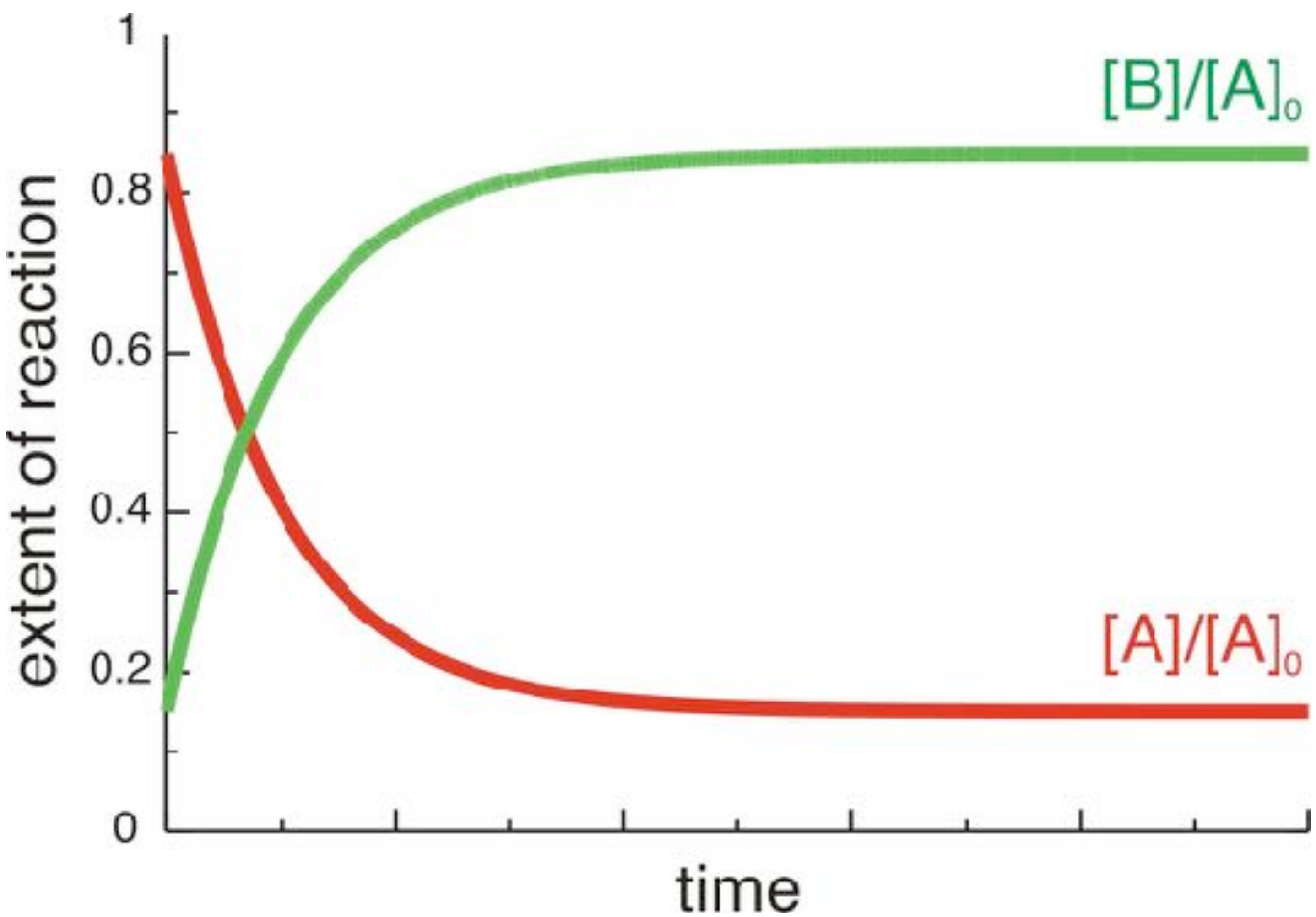
$$\frac{d[A]}{dt} = -k_+[A] + k_-\left([A]_0 - [A]\right) = -\left(k_+ + k_-\right)[A] + k_-[A]_0$$

solution of the differential equations

$$[A] = \frac{k_- + k_+ e^{-(k_- + k_-)t}}{k_+ + k_-}[A]_0$$

kinetics & thermodynamics

approaching equilibrium



eventually....

$$\lim_{t\to\infty}[A] = \frac{k_-}{k_+ + k_-}[A]_0 \qquad \lim_{t\to\infty}[B] = [A]_0 - [A]_\infty = \frac{k_+}{k_+ + k_-}[A]_0$$

equilibrium constant & reaction free energy

$$K = \frac{[B]_\infty}{[A]_\infty} = \frac{k_+}{k_-} = \exp\left[-\frac{\Delta G}{RT}\right]$$

temperature dependence of reaction rates

Gibbs-Helmholtz relation

$$G = H - TS \qquad S = \frac{H - G}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S = \frac{G - H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

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$$T\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T}$$

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temperature dependence of reaction rates

Van 't Hoff equation

equilibrium constant

$$\ln K = -\frac{\Delta G}{RT}$$

Gibbs-Helmholtz predicts effect of temperature on equilibrium constant

$$\frac{d\ln K}{dT} = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G}{T}\right)_p = \frac{\Delta H}{RT^2} \longrightarrow \frac{d\ln K}{d1/T} = -\frac{\Delta H}{R}$$

temperature dependence of reaction rates

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relation between equilibrium and rate constant

$$K = \frac{k_+}{k_-} \qquad \frac{d}{dT}\ln k_+ - \frac{d}{dT}\ln k_- = \frac{\Delta H}{RT^2}$$

temperature dependence of reaction rates

Van ‘t Hof equation

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relation between equilibrium and rate constant

$$K = \frac{k_+}{k_-} \qquad \frac{d}{dT}\ln k_+ - \frac{d}{dT}\ln k_- = \frac{\Delta H}{RT^2}$$

therefore

$$\frac{d}{d1/T}\ln k_+ = -\frac{E^\ddagger}{R} \longrightarrow \ln k_+ = \ln A - \frac{E^\ddagger}{RT}$$

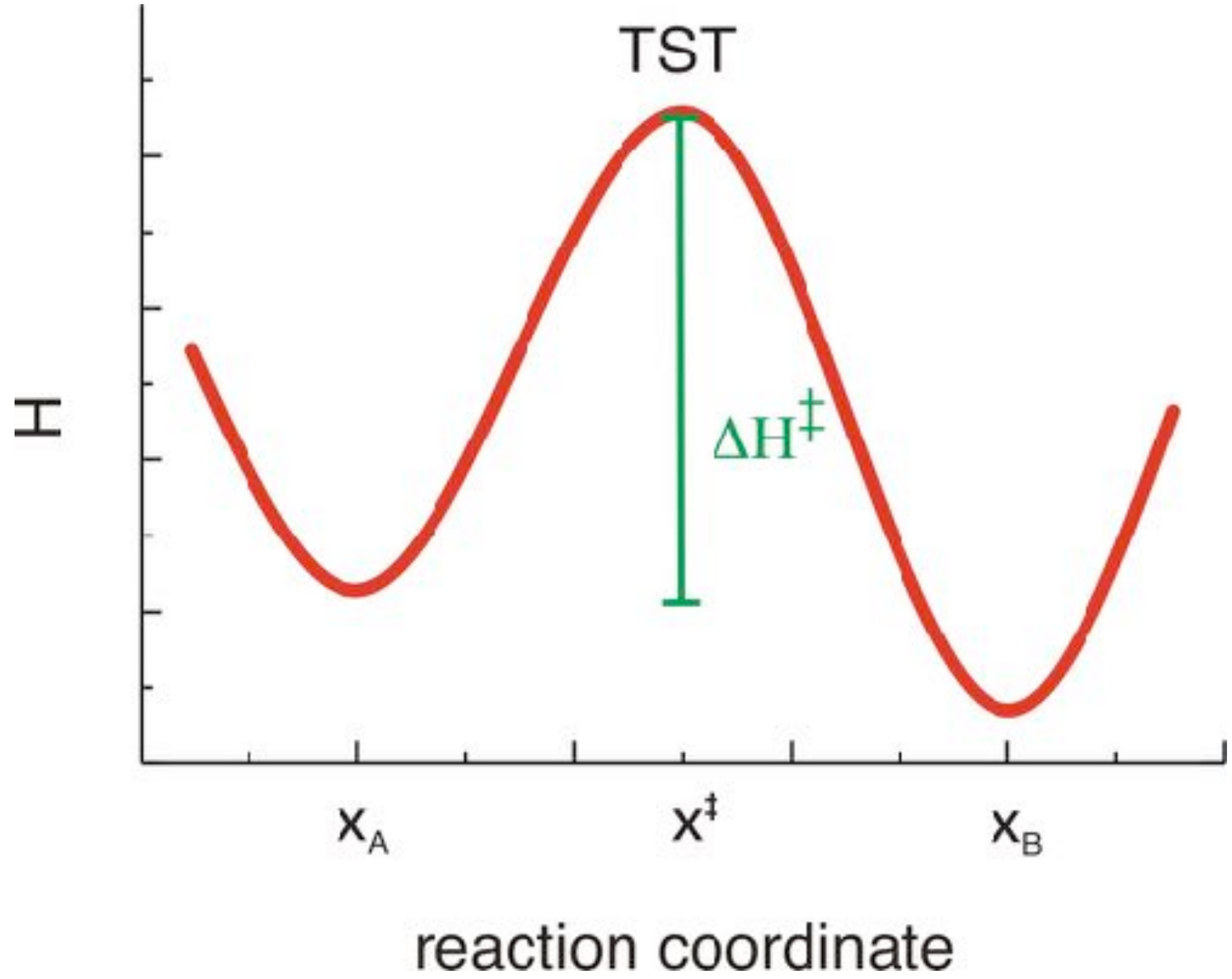
temperature dependence of reaction rates

Arrhenius equation

activated state

$$A \rightleftarrows A^{\ddagger} \rightarrow B$$

$$K^{\ddagger} = \frac{[A^{\ddagger}]}{[A]}$$



temperature dependence of reaction rates

Arrhenius equation

activated state

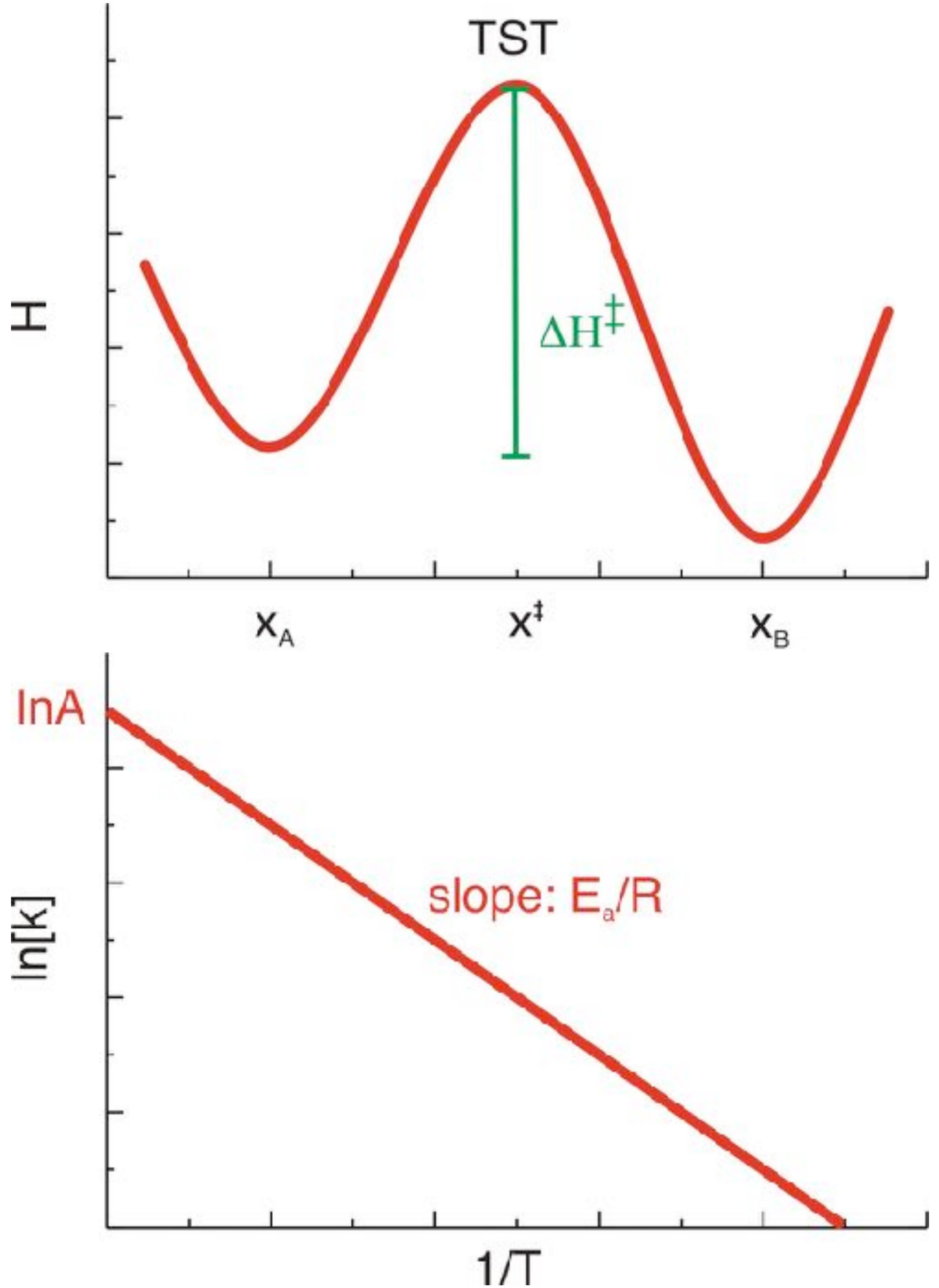
$$A \rightleftarrows A^{\ddagger} \rightarrow B$$

$$K^{\ddagger} = \frac{[A^{\ddagger}]}{[A]}$$

$$\frac{d \ln K^{\ddagger}}{d1/T} = -\frac{\Delta H^{\ddagger}}{R}$$

$$k = a \exp\left[-\frac{E_a}{RT}\right]$$

$$\ln k = \ln a - \frac{E_a}{R}\frac{1}{T}$$



microscopic picture

statistical mechanics

partition function

$$K = \frac{p_B}{p_A} = \frac{Q_B}{Q_A} = \frac{\int_B \exp[-\beta H] dp dq}{\int_A \exp[-\beta H] dp dq} \qquad \beta = \frac{1}{k_\mathrm{B} T}$$

microscopic picture

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Hamiltonian

$$H = T + V$$

$$H = \sum_i \frac{p_i^2}{2m_i} + V(q_1, q_2, .., q_n)$$

microscopic picture

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Hamiltonian

$$H = T + V$$

$$H = \sum_i \frac{p_i^2}{2m_i} + V(q_1, q_2, .., q_n)$$

integrate over momenta

$$K = \frac{\int_B \exp[-\beta V] dq}{\int_A \exp[-\beta V] dq}$$

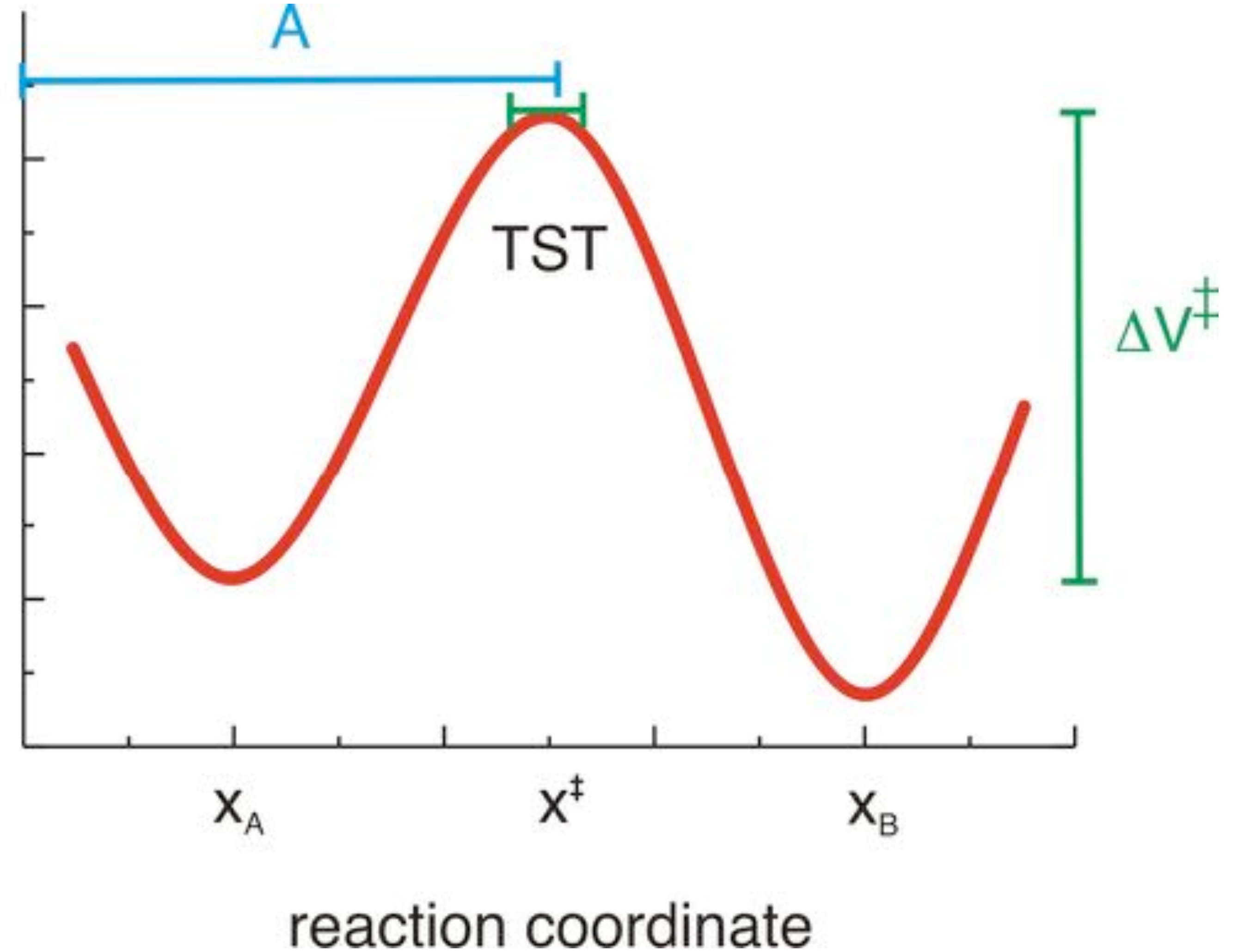
equilibrium determined solely by potential energy surface

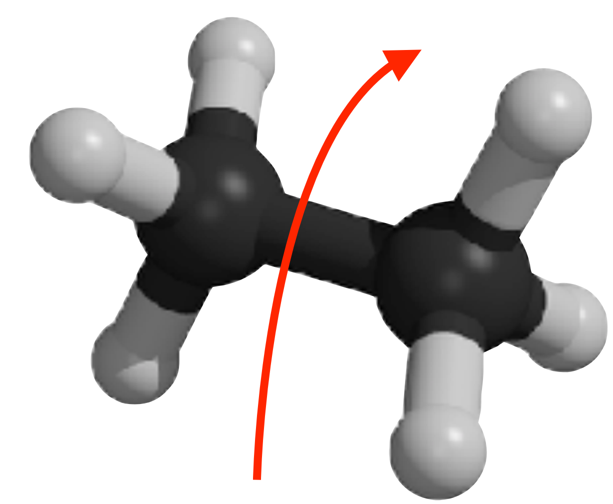
microscopic picture

compute rates from simulations

rare event

$$\tau_{\rm rxn} \gg \tau_{\rm eq} \qquad k = 1/\tau_{\rm rxn} >$$





microscopic picture

compute rates from simulations

rare event

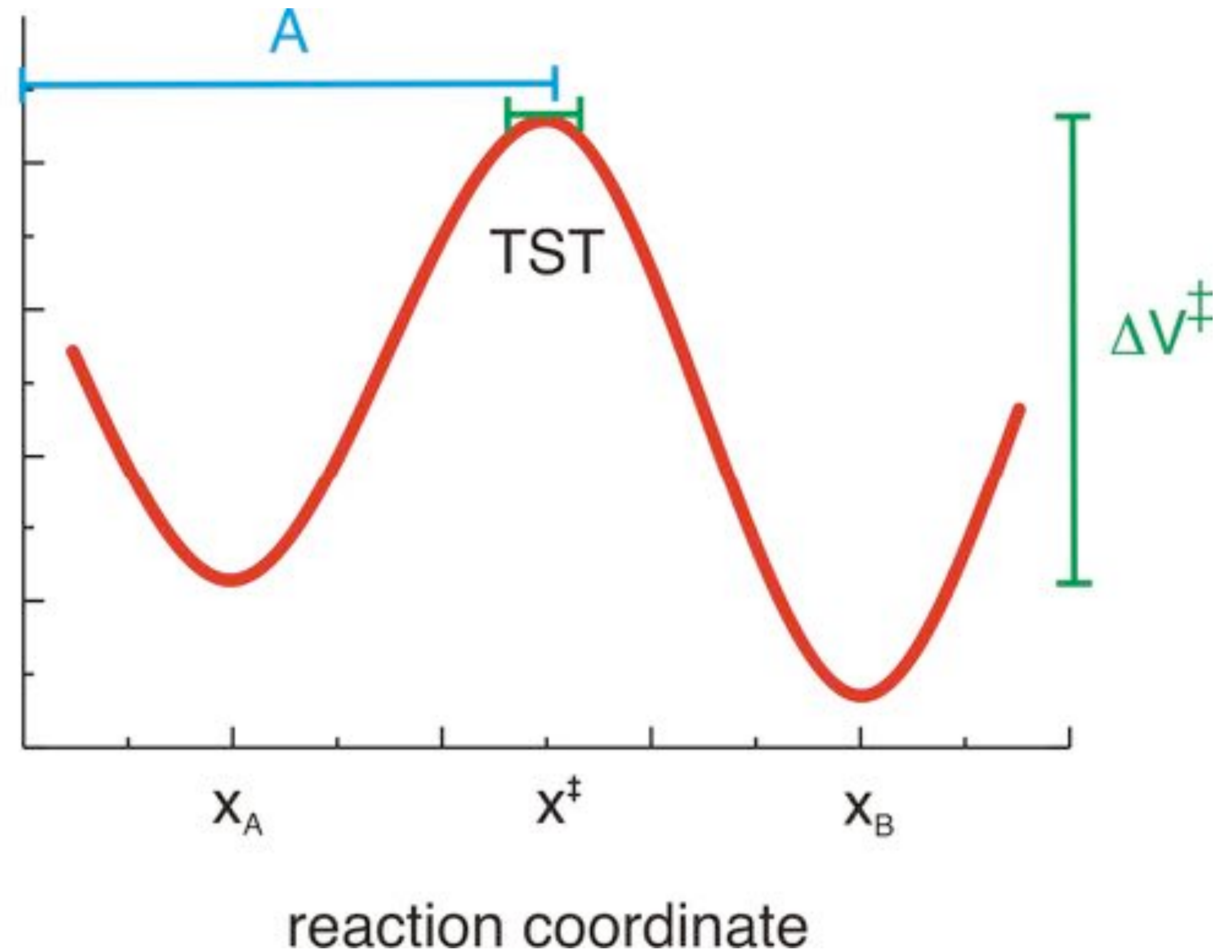
$\tau_{\rm rxn} \gg \tau_{\rm eq} \qquad k = 1/\tau_{\rm rxn} >$

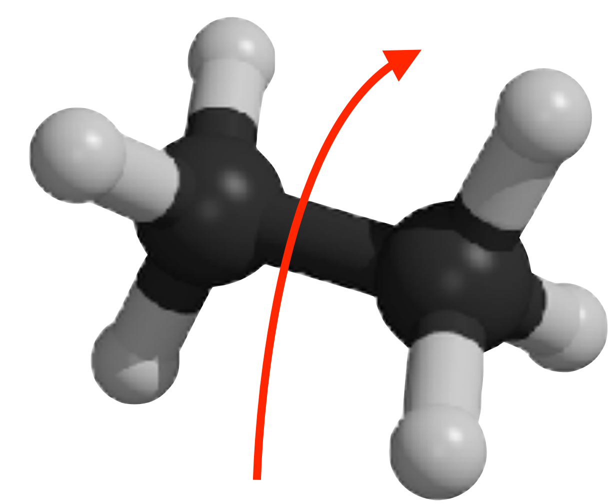
basic assumptions

initial rate

stationary conditions

$$\frac{d\rho(p,q)}{dt} = 0$$





microscopic picture

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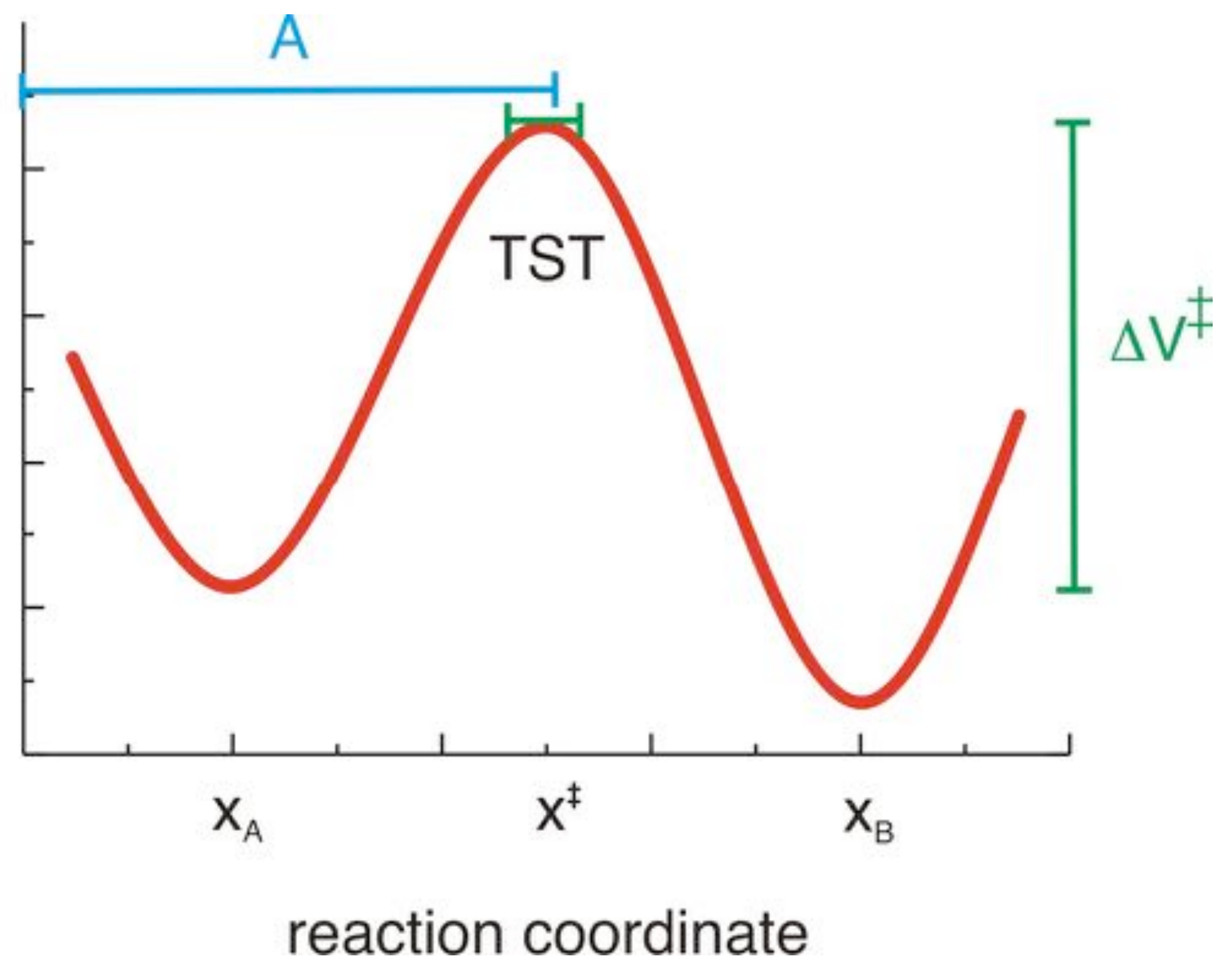
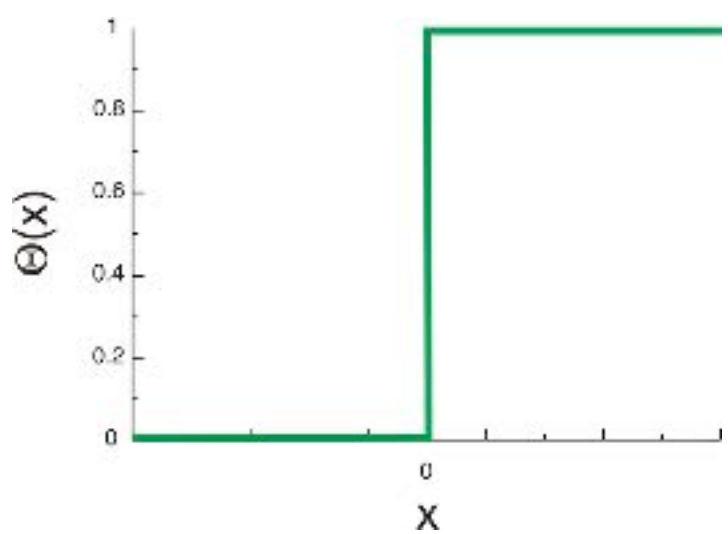
$$\frac{d\rho(p,q)}{dt} = 0$$

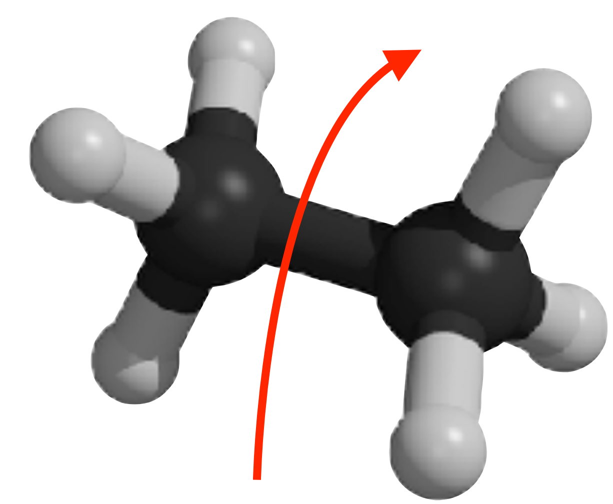
flux

$$J = kc_A$$

$$c_A = \langle \Theta(x^\ddagger - x) \rangle$$







microscopic picture

compute rates from simulations

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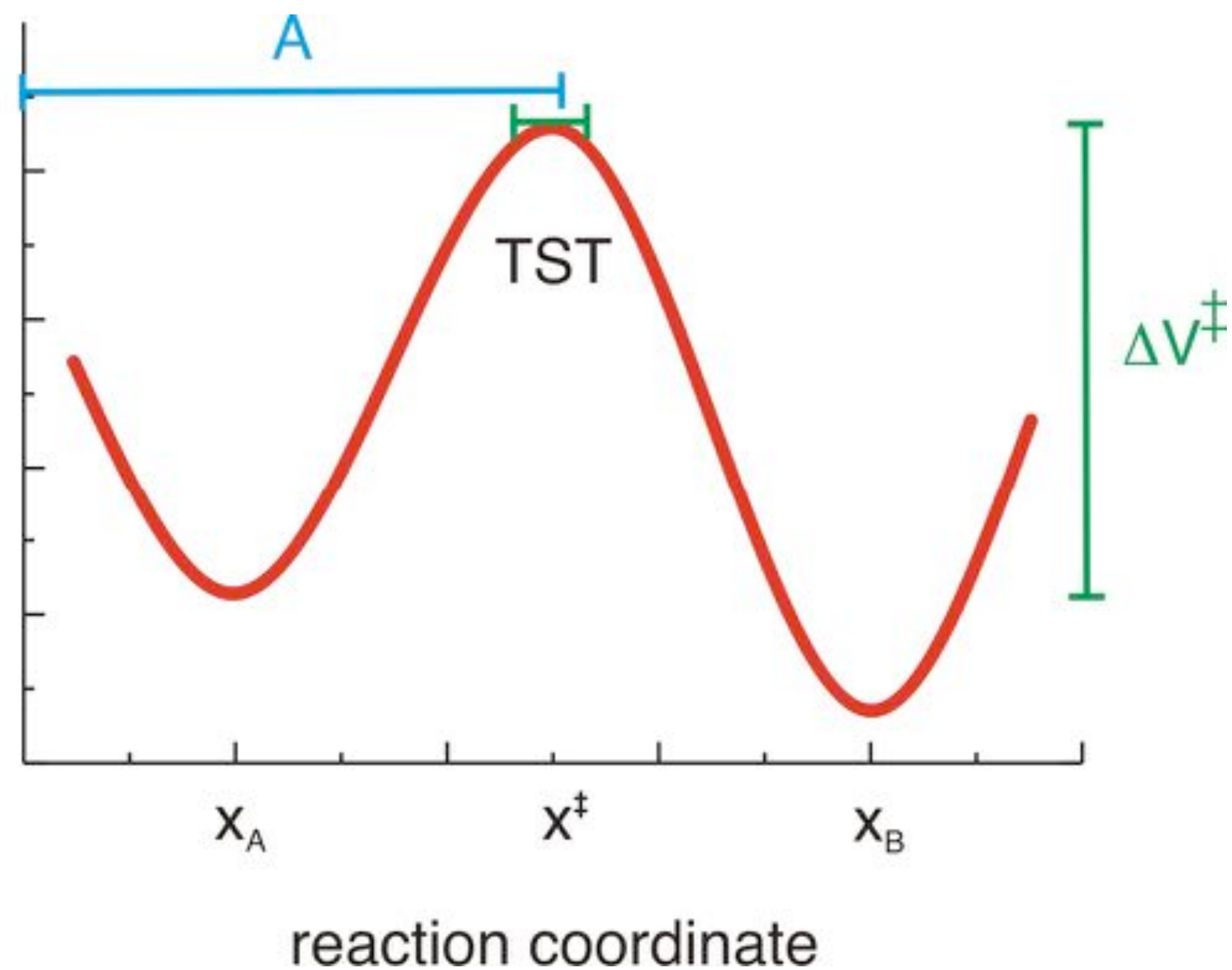

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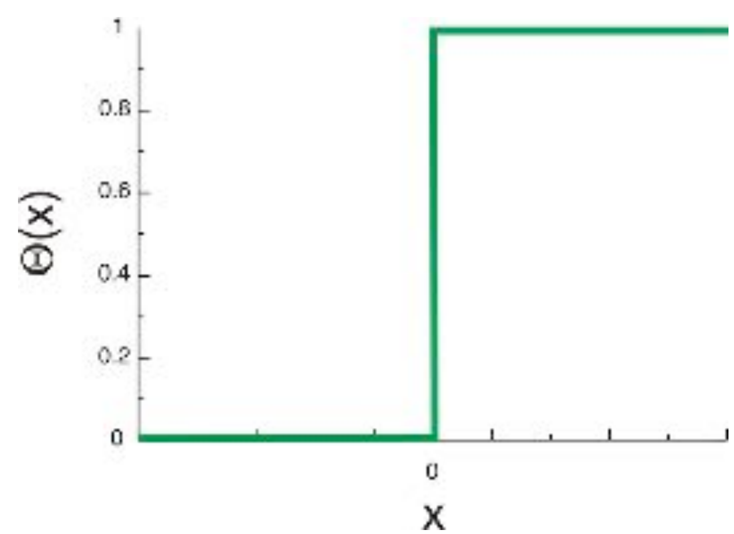
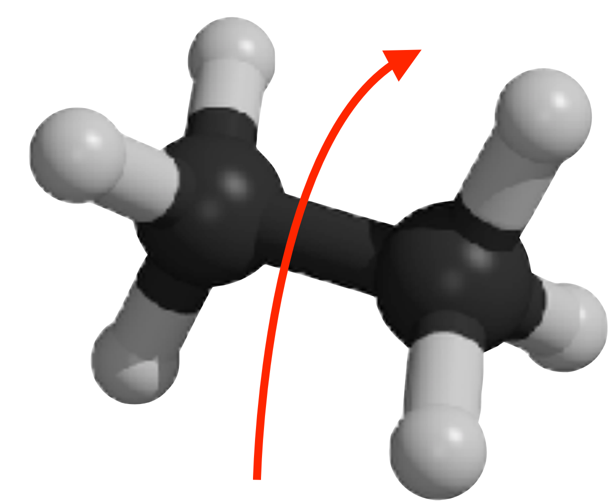




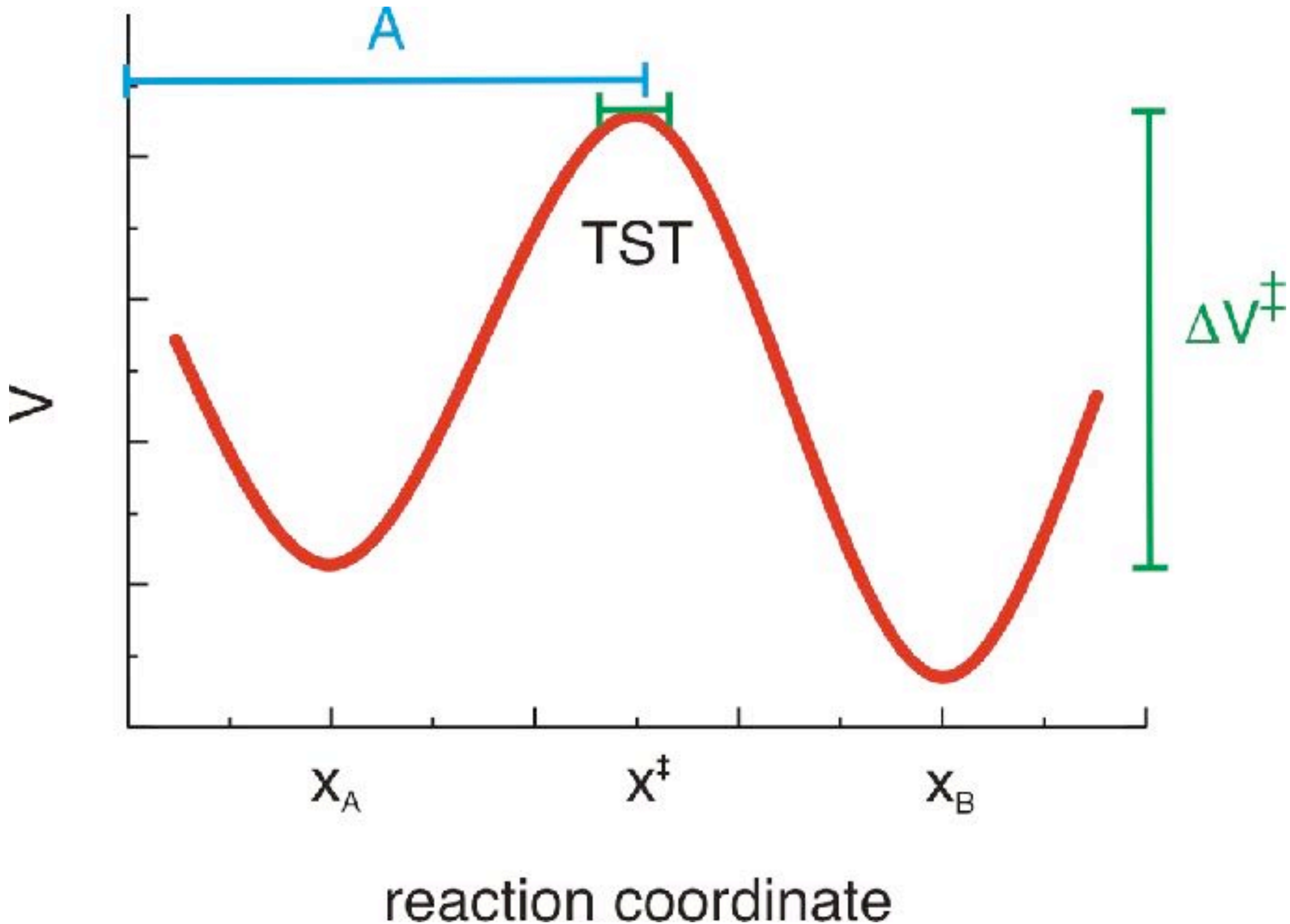
sampling problem...

$$\rho(x^{\ddagger}) = \frac{\int \exp[-\beta V(x)]\delta(x - x^{\ddagger})dx}{\int \exp[-\beta V(x)]dx}$$

Eyring theory

assumptions

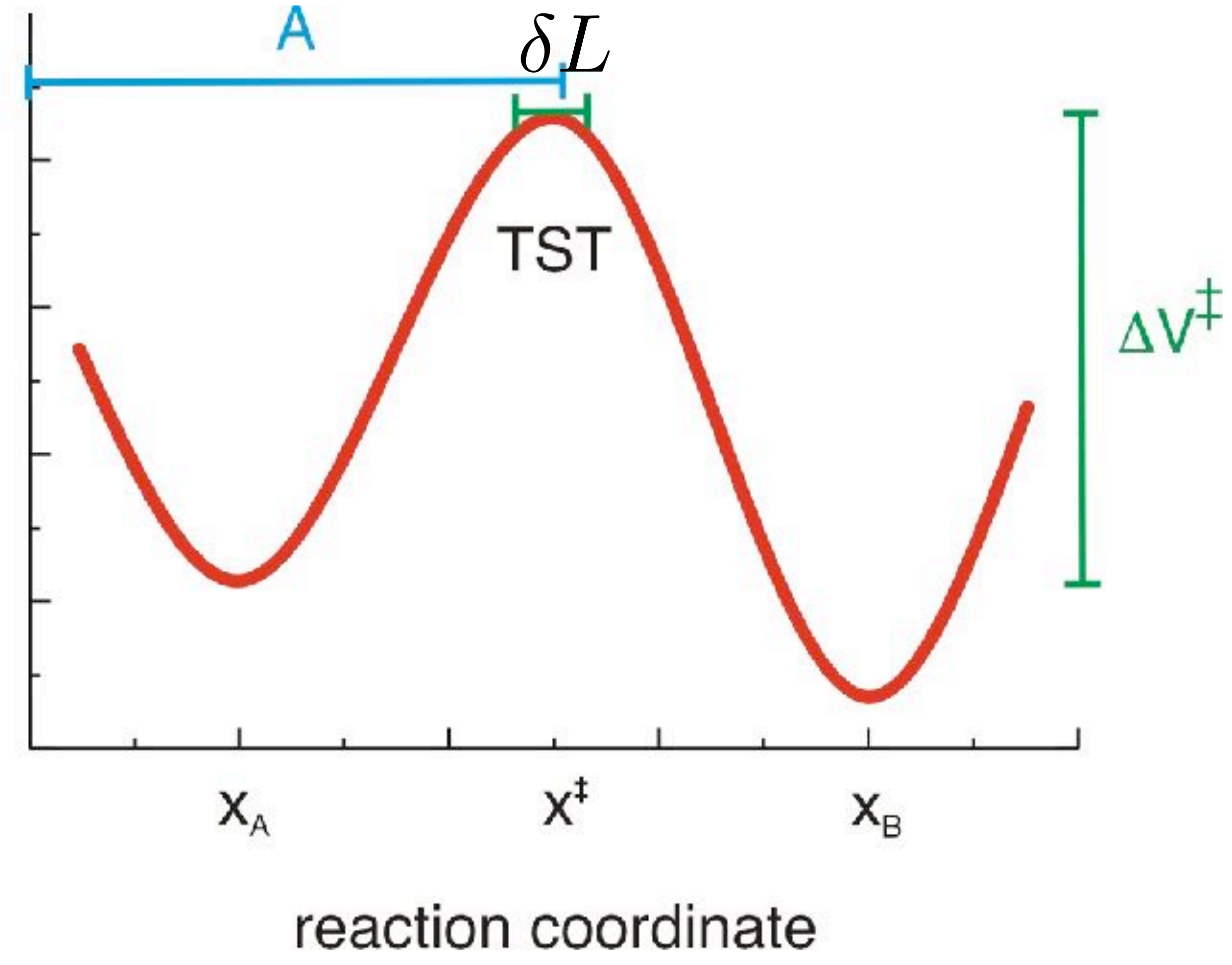
- classical dynamics
- no recrossing
- molecules at barrier in thermal equilibrium with molecules in reactant well



Eyring theory

observations

barrier is flat: $f(x^{\ddagger}) = \frac{dU}{dx}|_{x=x^{\ddagger}} = 0$ >



Eyring theory

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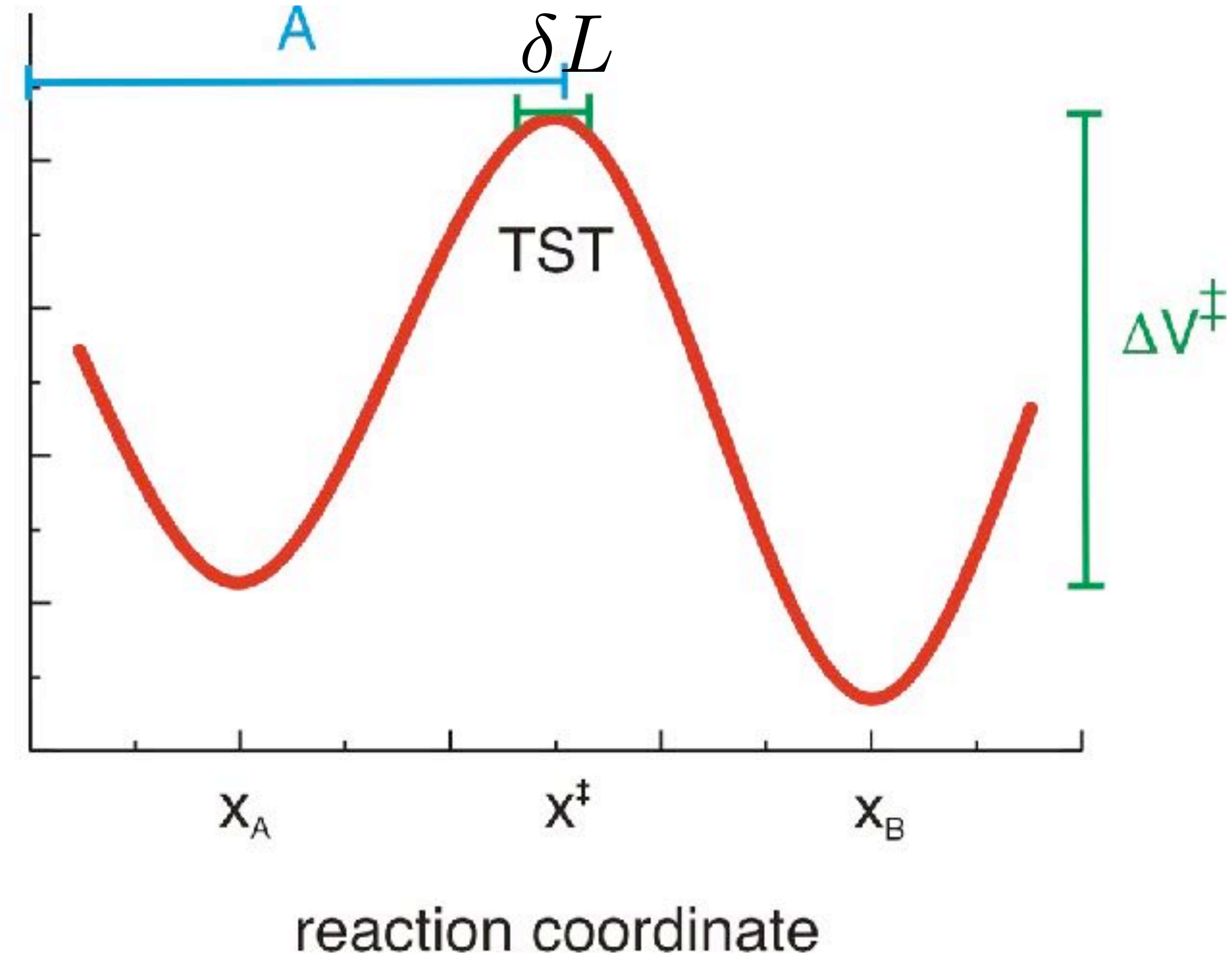
there are δN molecules in δL



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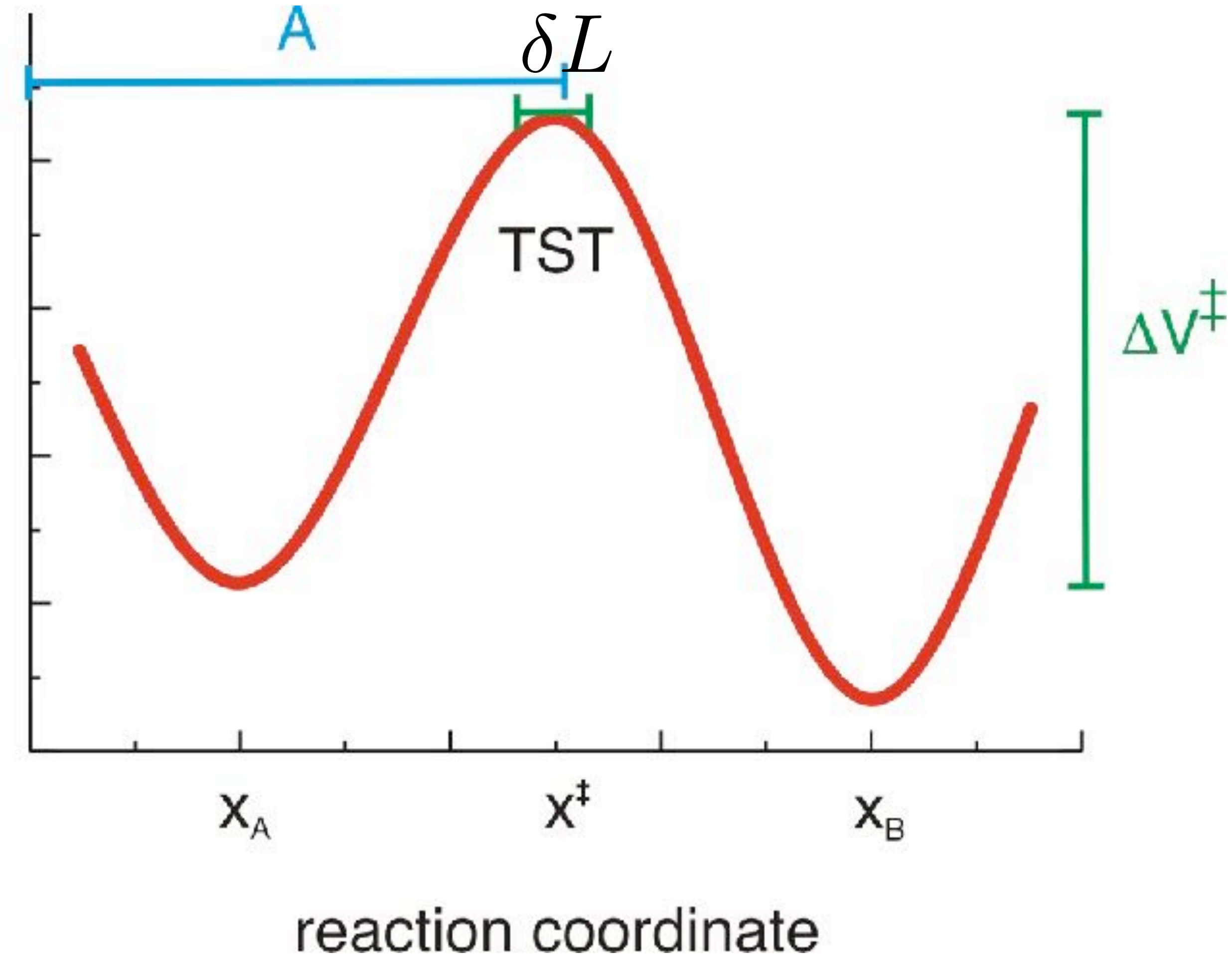
reaction if $v > \frac{\delta L}{\delta t}$



Eyring theory

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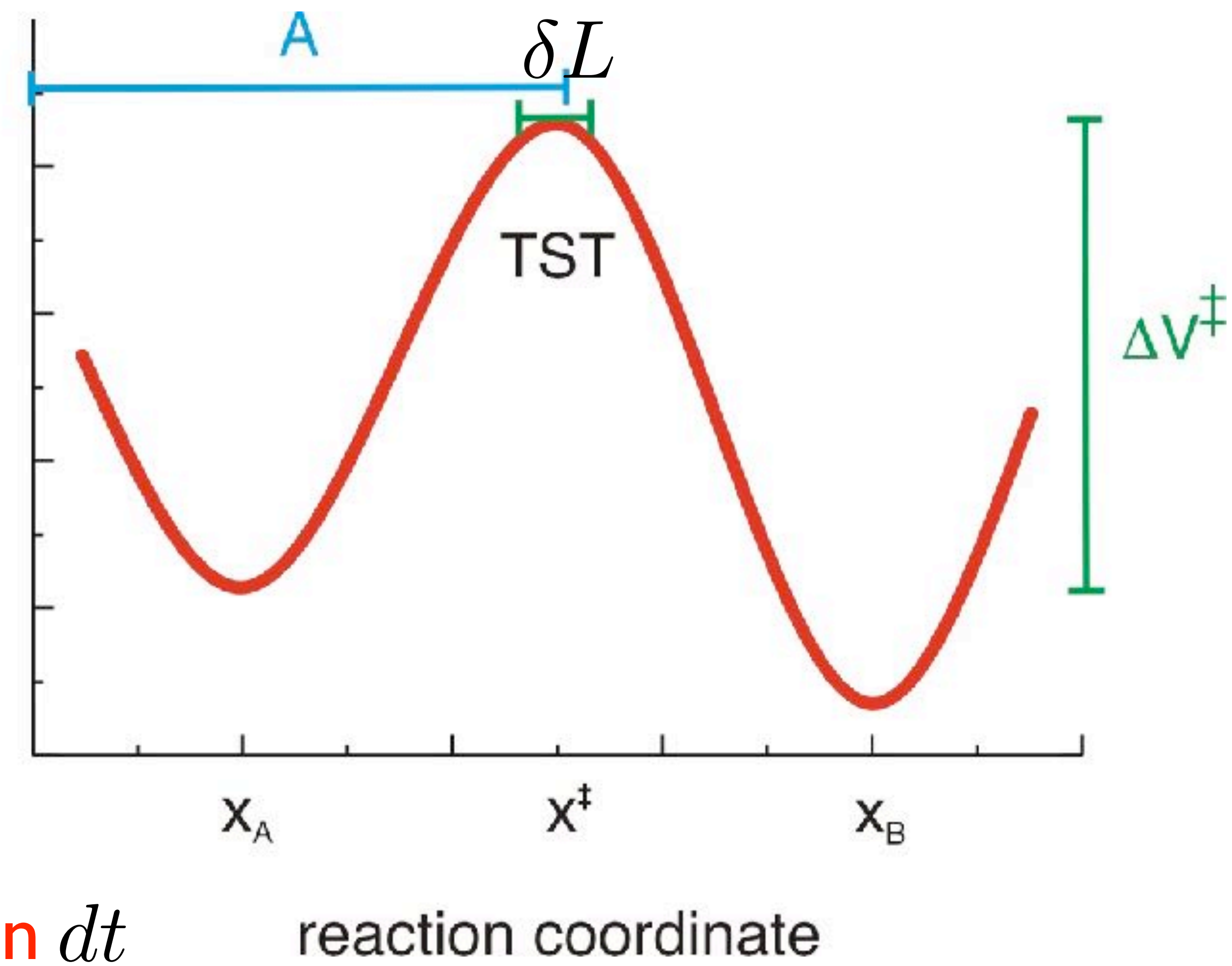
the number of molecules passing TST in dt

$$N^{\mathrm{rxn}} = \delta N \frac{v dt}{\delta L}$$



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there are δN molecules in δL

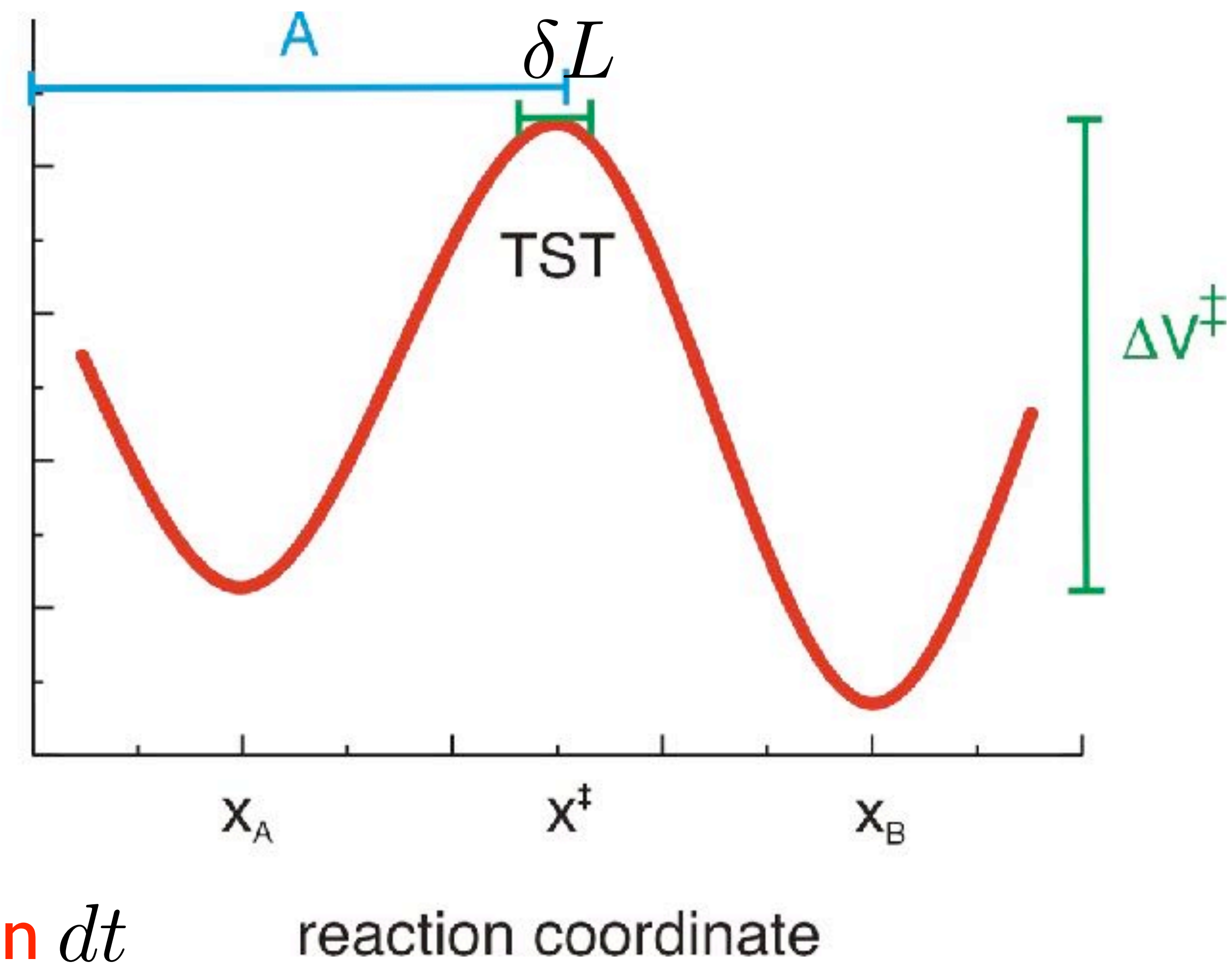
reaction if $v > \frac{\delta L}{\delta t}$

the number of molecules passing TST in dt

$$N^{\text{rxn}} = \delta N \frac{vdt}{\delta L}$$

reaction rate

$$k_+ = \frac{N^{\text{rxn}}}{Ndt} = \frac{\delta N}{N} \frac{v}{\delta L}$$



Eyring theory

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$$N^{\mathrm{rxn}} = \delta N \frac{v dt}{\delta L}$$

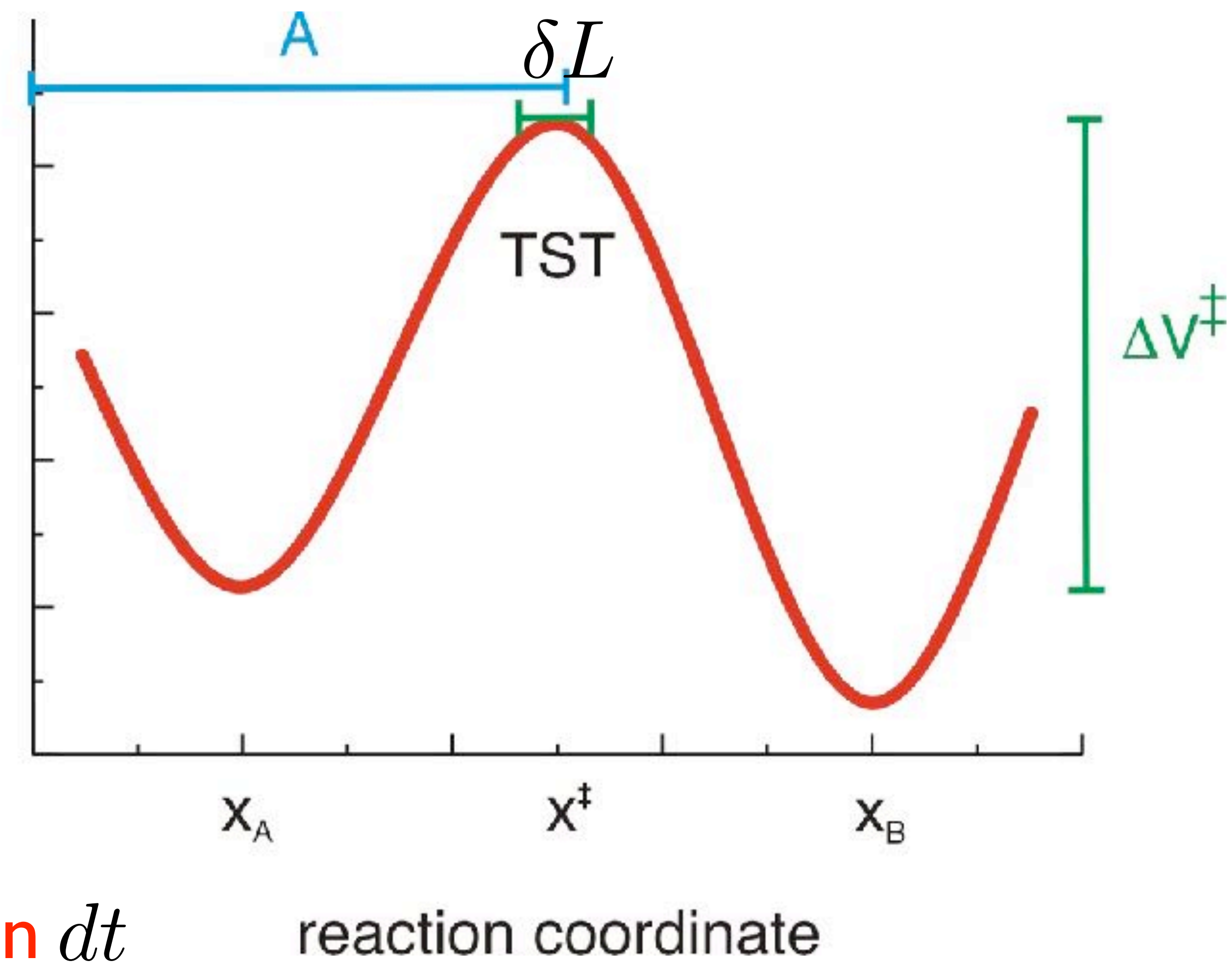
reaction rate

$$k_{+} = \frac{N^{\mathrm{rxn}}}{N dt} = \frac{\delta N}{N} \frac{v}{\delta L}$$

$$\frac{\delta N}{N} = \frac{q^{\ddagger}}{q_A}$$

partition function

$$k_{+} = \frac{q^{\ddagger}}{q_A} \frac{v}{\delta L}$$



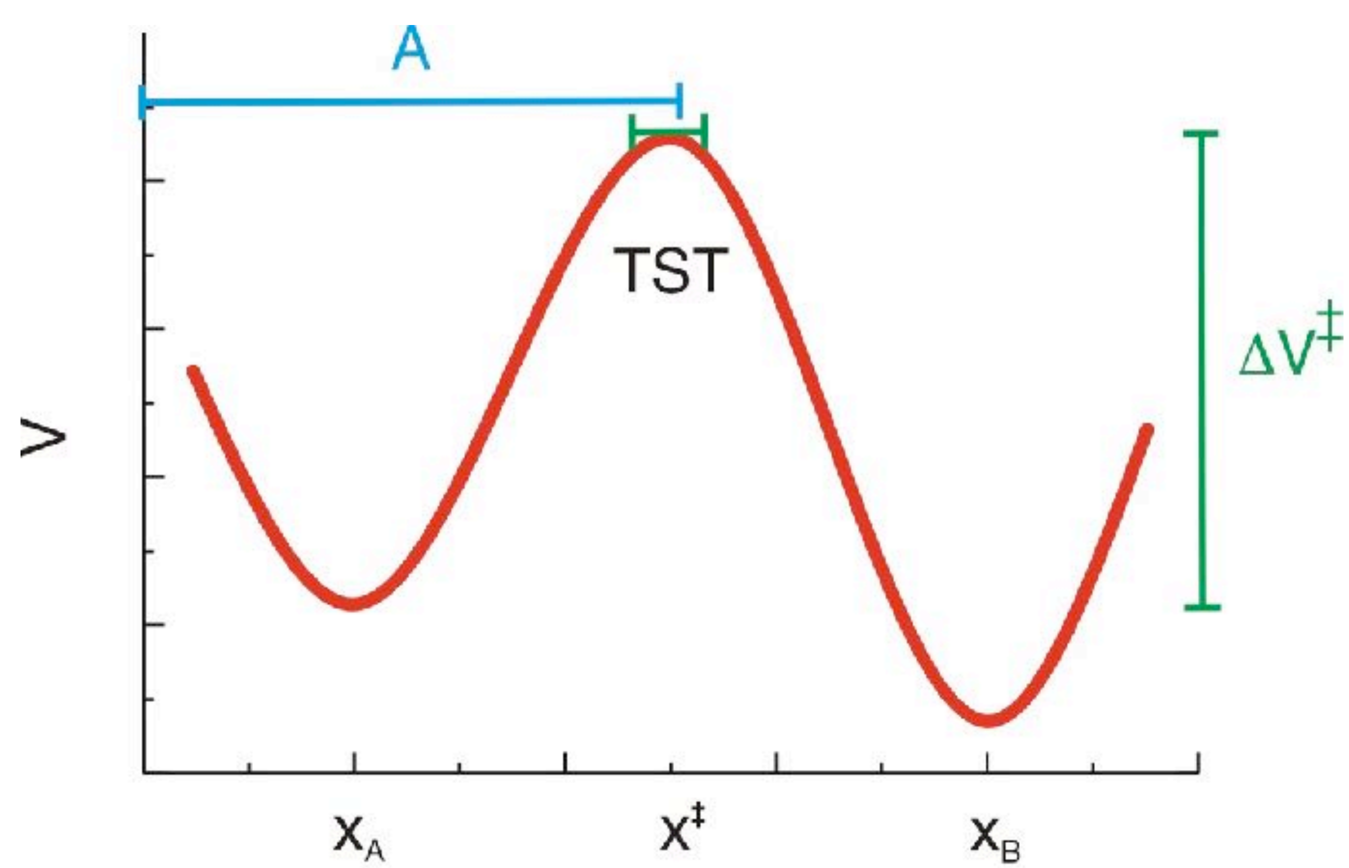
Eyring theory

partition function of TST

$$q^{\ddagger} = \frac{1}{h}\delta L \int_{-\infty}^{\infty} \exp[-\beta(\frac{p^2}{2m} + V(x^{\ddagger})]dp$$

$$q^{\ddagger} = \frac{\delta L}{h} \int_{-\infty}^{\infty} \exp[-\beta \frac{p^2}{2m}]dp \exp[-\beta V(x^{\ddagger})]$$

$$q^{\ddagger} = \frac{\delta L}{h} \sqrt{2mk_{\mathrm{B}}T\pi} \exp[-\frac{V(x^{\ddagger})}{k_{\mathrm{B}}T}]$$



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$$q^{\ddagger} = \frac{\delta L}{h} \int_{-\infty}^{\infty} \exp[-\beta\frac{p^2}{2m}]dp \exp[-\beta V(x^{\ddagger})]$$

$$q^{\ddagger} = \frac{\delta L}{h}\sqrt{2mk_{\mathrm{B}}T\pi} \exp[-\frac{V(x^{\ddagger})}{k_{\mathrm{B}}T}]$$

only positive velocities contribute

$$\langle v_+ \rangle = \frac{\int_{-\infty}^{\infty} v\Theta(v) \exp[-\beta\frac{p^2}{2m}]dp}{\int_{-\infty}^{\infty} \exp[-\beta\frac{p^2}{2m}]dp}$$

$$\langle v_+ \rangle = \frac{\frac{1}{m}\frac{1}{2}2mk_{\mathrm{B}}T}{\sqrt{2mk_{\mathrm{B}}T\pi}} = \sqrt{\frac{k_{\mathrm{B}}T}{2\pi m}}$$

Eyring theory

taking together to express rate

$$k_+ = \frac{\delta L}{h} \frac{\sqrt{2mk_\mathrm{B}T\pi}}{\delta L q_A} \sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \exp\left[-\frac{V(x^\ddagger)}{k_\mathrm{B}T}\right]$$

$$k_+ = \frac{k_\mathrm{B}T}{h q_A} \exp\left[-\frac{V(x^\ddagger)}{k_\mathrm{B}T}\right]$$

Eyring theory

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$$k_+ = \frac{k_{\mathrm{B}}T}{hq_A} \exp\left[-\frac{V(x^{\ddagger})}{k_{\mathrm{B}}T}\right]$$

partition function of A

$$q_A = \frac{1}{h} \int_{-\infty}^{x^{\ddagger}} \exp\left[-\frac{V(x)}{k_{\mathrm{B}}T}\right] dx \int_{-\infty}^{\infty} \exp\left[-\beta \frac{p^2}{2m}\right] dp$$

$$q_A = \frac{1}{h} \sqrt{2\pi m k_{\mathrm{B}}T} \int_{-\infty}^{x^{\ddagger}} \exp\left[-\frac{V(x)}{k_{\mathrm{B}}T}\right] dx$$

Eyring theory

taking together to express rate

$$k_+ = \frac{\delta L}{h} \frac{\sqrt{2mk_\mathrm{B}T\pi}}{\delta L q_A} \sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \exp\left[-\frac{V(x^\ddagger)}{k_\mathrm{B}T}\right]$$

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partition function of A

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$$q_A = \frac{1}{h} \sqrt{2\pi m k_\mathrm{B}T} \int_{-\infty}^{x^\ddagger} \exp\left[-\frac{V(x)}{k_\mathrm{B}T}\right] dx$$

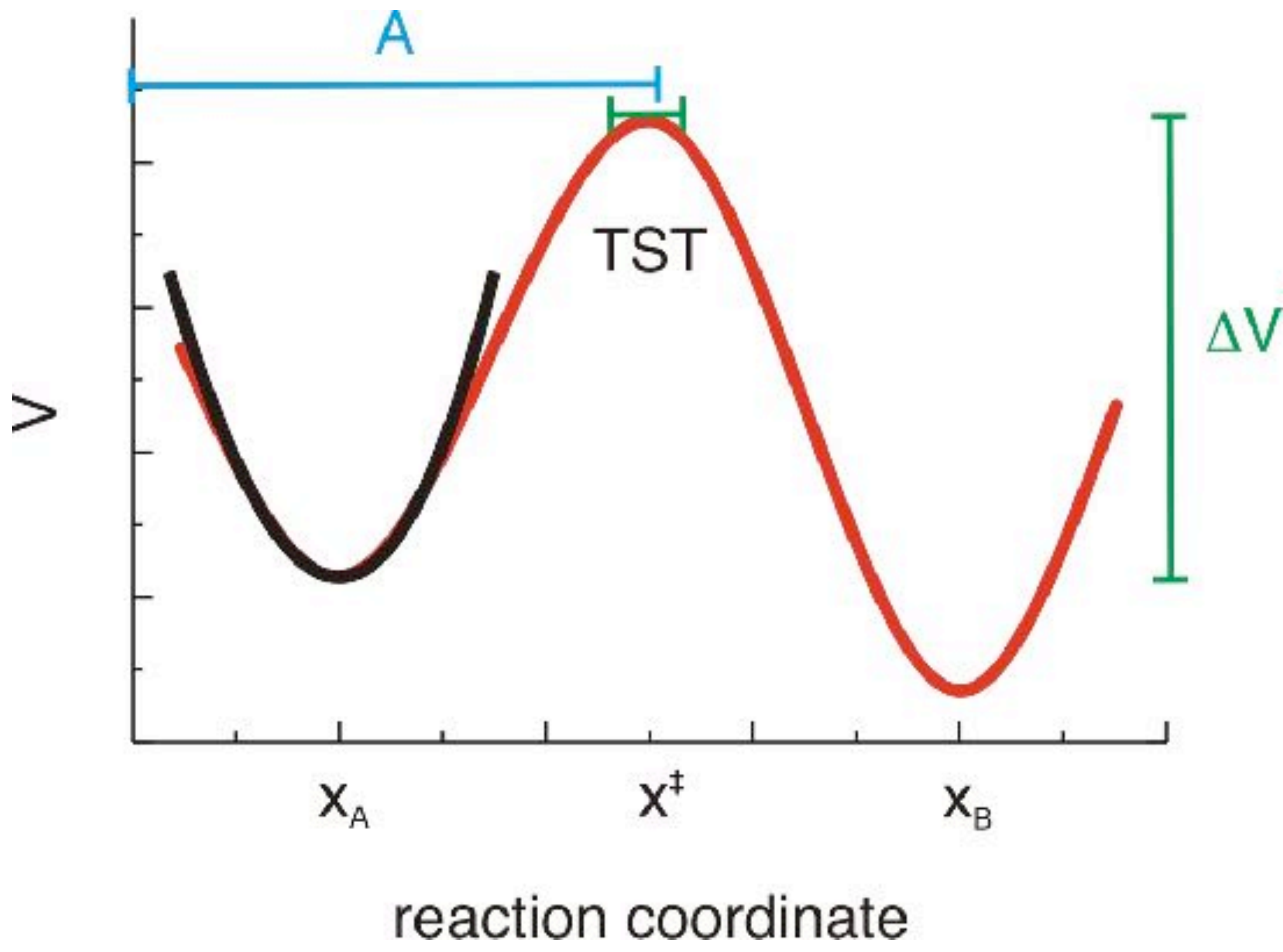
Eyring theory

harmonic approximation

$$V(x) \approx \frac{1}{2} k_f (x - x_A)^2$$

$$V(x) \approx \frac{1}{2} m\omega_A^2 (x - x_A)^2$$

$$\omega_A = \sqrt{\frac{k_f}{m}}$$



Eyring theory

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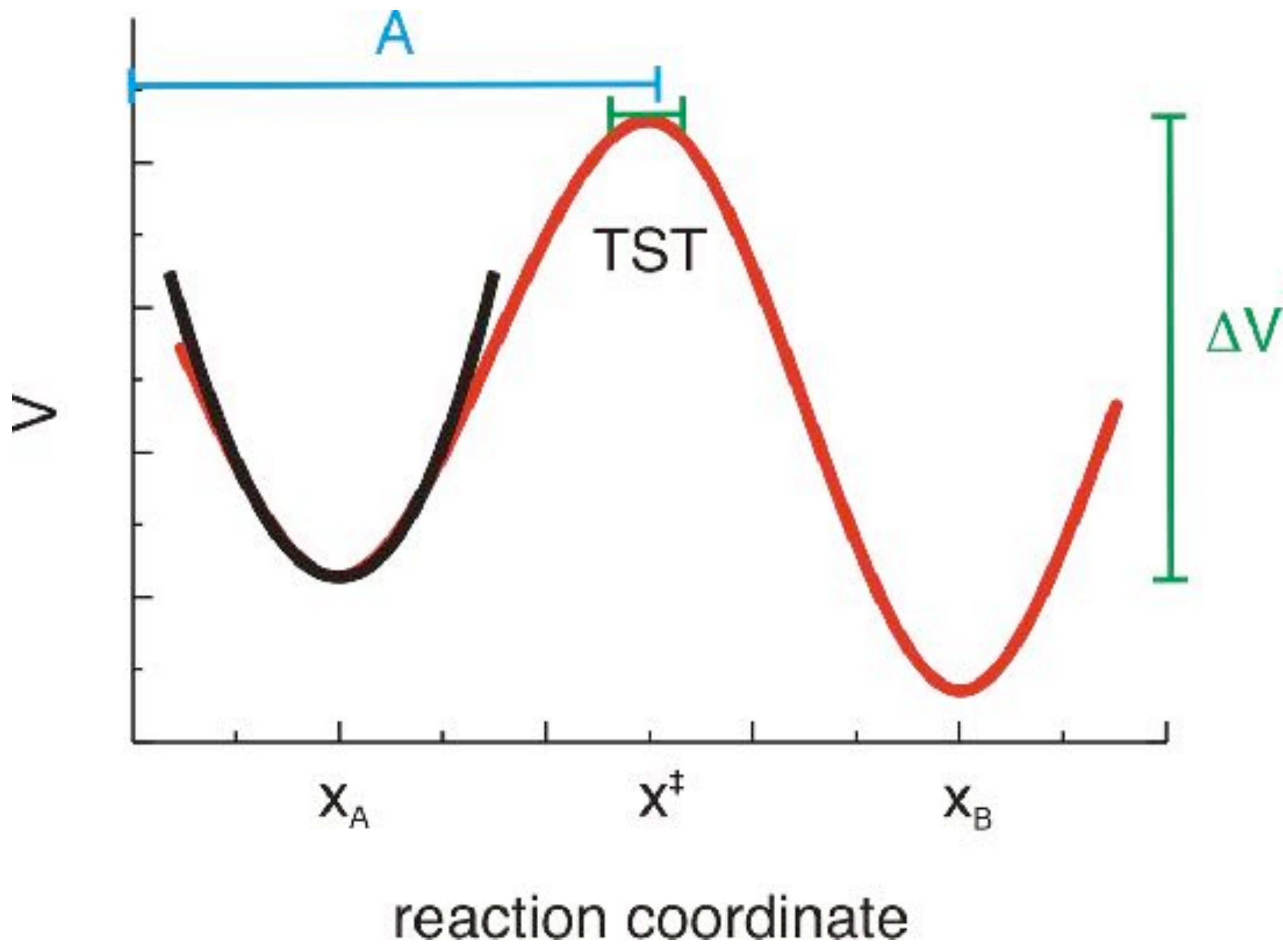


partition function

$$q_A = \frac{1}{h}\sqrt{2\pi m k_\mathrm{B} T}\sqrt{\frac{2k_\mathrm{B}T}{m\omega_A^2}}\sqrt{\pi}$$

$$q_A = \frac{1}{h} 2\pi k_\mathrm{B} T \frac{1}{\omega_A}$$

Eyring theory

harmonic approximation

$$V(x) \approx \frac{1}{2}k_f(x - x_A)^2$$

$$V(x) \approx \frac{1}{2}m\omega_A^2(x - x_A)^2$$

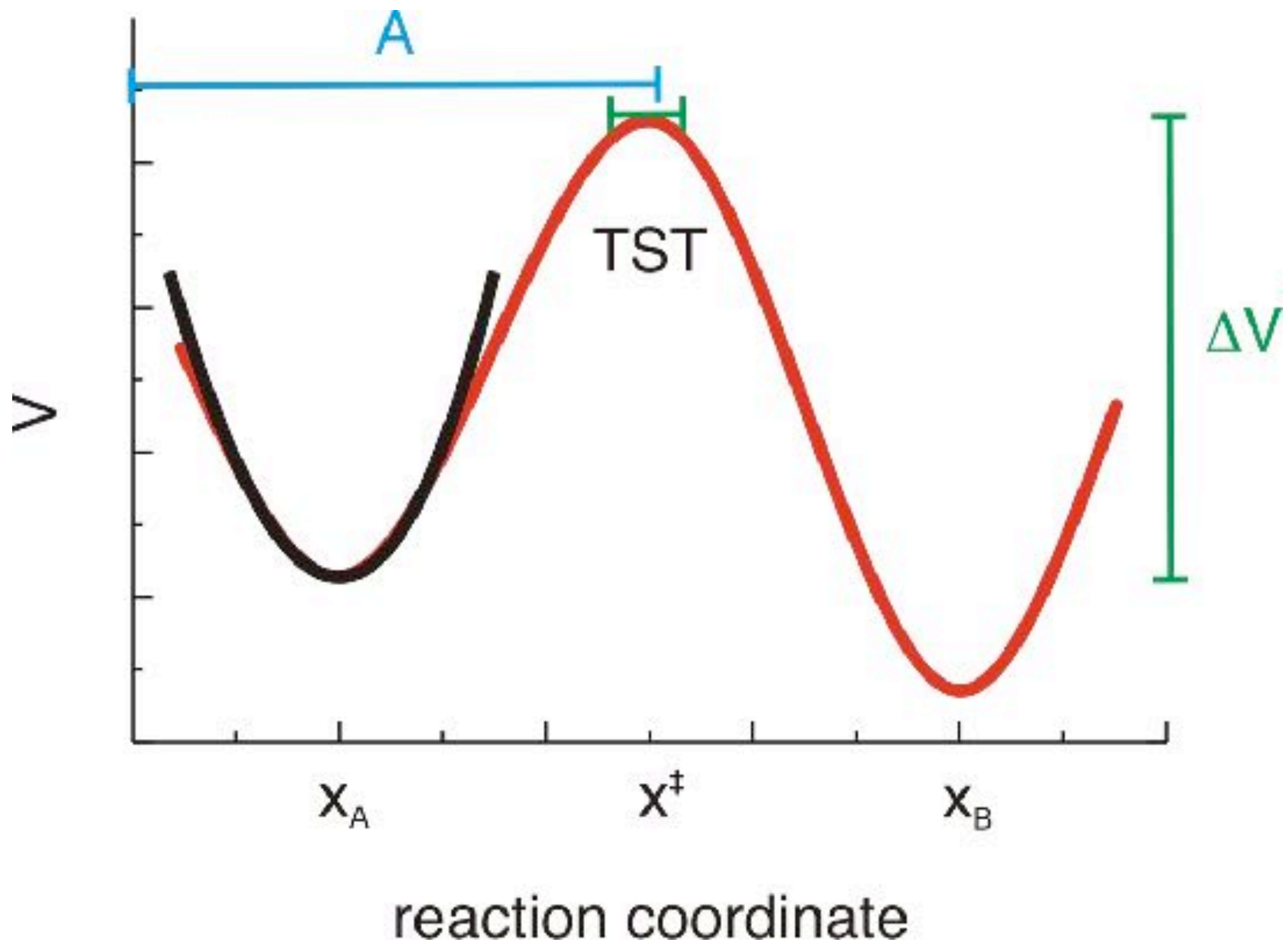
$$\omega_A = \sqrt{\frac{k_f}{m}}$$

partition function

$$q_A = \frac{1}{h}2\pi k_{\mathrm{B}}T\frac{1}{\omega_A}$$

Final result: Eyring equation

$$k_+ = \frac{\omega_A}{2\pi}\exp\left[-\frac{V(x^\ddagger)}{k_{\mathrm{B}}T}\right]$$



Eyring theory

harmonic approximation

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$$V(x) \approx \frac{1}{2} m\omega_A^2 (x - x_A)^2$$

$$\omega_A = \sqrt{\frac{k_f}{m}}$$

partition function

$$q_A = \frac{1}{h} 2\pi k_\mathrm{B} T \frac{1}{\omega_A}$$

Final result: Eyring equation

attempt frequency

$$k_+ = \frac{\omega_A}{2\pi} \exp\left[-\frac{V(x^\ddagger)}{k_\mathrm{B}T}\right]$$

probability to be at barrier (Boltzmann factor)