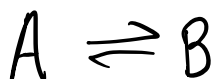


Lecture 16

Recall from last lecture...

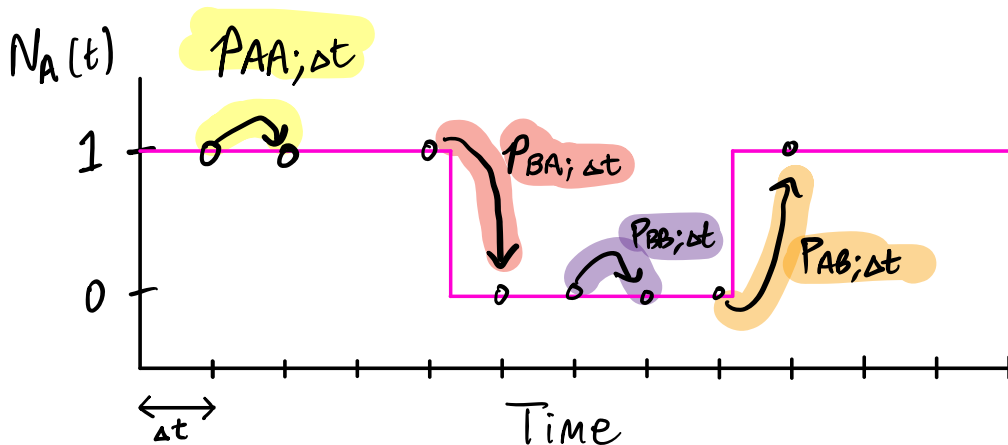
WARNING:
Linear Algebra Ahead

Two-state kinetics



p_A : probability of A (trans)

p_B : probability of B (gauche)



In matrix form after a (discrete) time Δt :

$$\begin{pmatrix} p_A(\Delta t) \\ p_B(\Delta t) \end{pmatrix} = \begin{pmatrix} P_{AA;\Delta t} & P_{AB;\Delta t} \\ P_{BA;\Delta t} & P_{BB;\Delta t} \end{pmatrix} \begin{pmatrix} p_A(0) \\ p_B(0) \end{pmatrix}$$

In matrix form after an infinitesimal time:

$$\frac{d}{dt} \begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix} = \begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix} \begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

(A coupled first order ODE)

We may prefer to think of concentrations

$$\frac{d}{dt} \begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \underbrace{\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}}_{\uparrow} \begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix}$$

\uparrow
 \mathbb{W} : the "rate matrix"

$$\frac{d}{dt} \mathbf{c} = \mathbb{W} \mathbf{c} \Rightarrow \frac{d\mathbf{c}}{\mathbf{c}} = \mathbb{W} dt$$

Integrate both sides

$$\Rightarrow \ln \mathbf{c} = \mathbb{W} t + \text{const.}$$

Exponentiate both sides

$$\Rightarrow \mathbf{c}(t) = \exp[\mathbb{W} t] \exp[\text{const.}]$$

$$\Rightarrow \mathbf{c}(t) = \exp[\underline{\mathbb{W}} t] \mathbf{c}(0)$$

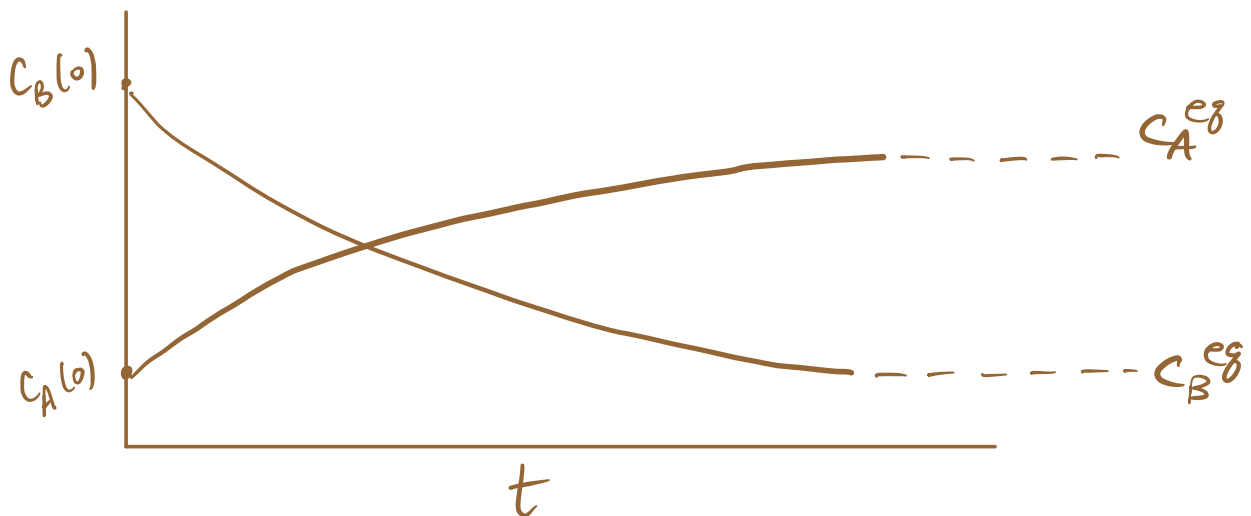
$$\mathbf{c}(t) = \left(|0\rangle \langle 0| e^{v_0 t} + |1\rangle \langle 1| e^{v_1 t} \right) \mathbf{c}(0)$$
$$= \left[\begin{pmatrix} P_A^{eq} \\ P_B^{eq} \end{pmatrix} (1 \ 1) e^{0t} + \begin{pmatrix} 1 \\ -1 \end{pmatrix} (1 \ -1) e^{-(k_{AB} + k_{BA})t} \right] \mathbf{c}(0)$$

$$= \left[\begin{pmatrix} P_A^{eq} \\ P_B^{eq} \end{pmatrix} (C_A(0) + C_B(0)) + \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB} + k_{BA})t} (C_A(0) - C_B(0)) \right]$$

$$c(t) = \left[\begin{pmatrix} C_A^{eq} \\ C_B^{eq} \end{pmatrix} + \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB} + k_{BA})t} (C_A(0) - C_B(0)) \right]$$

$\Delta C(t)$ from last time
decays with $\tau = (k_{AB} + k_{BA})^{-1}$

Long time ... ?

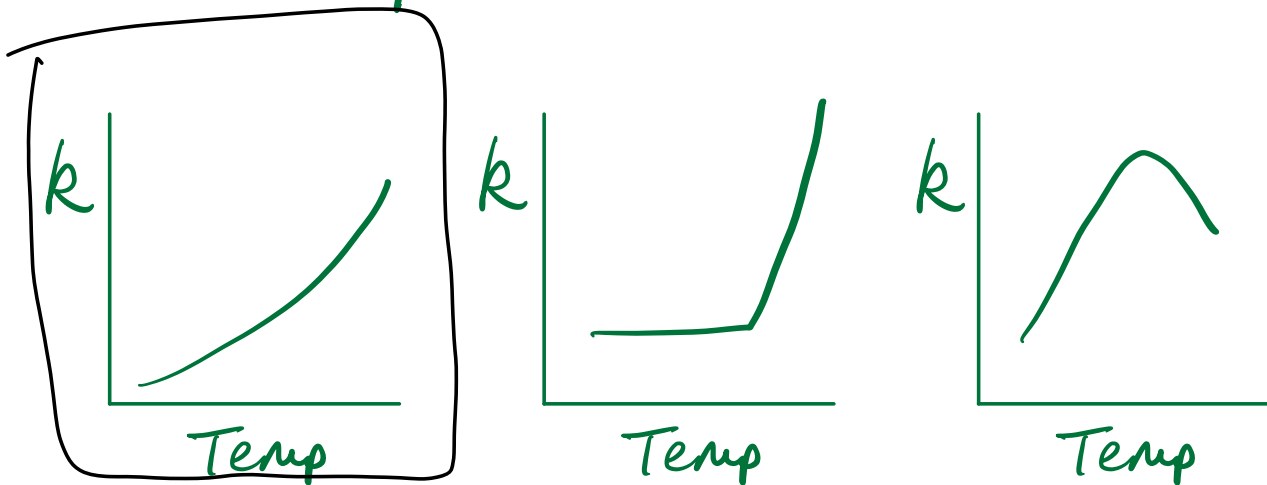


Relaxation timescales are ^{reciprocals of} eigenvalues of \mathbb{W} !

What determines k_{AB} and k_{BA} ?

How are they related to $V(\phi)$?

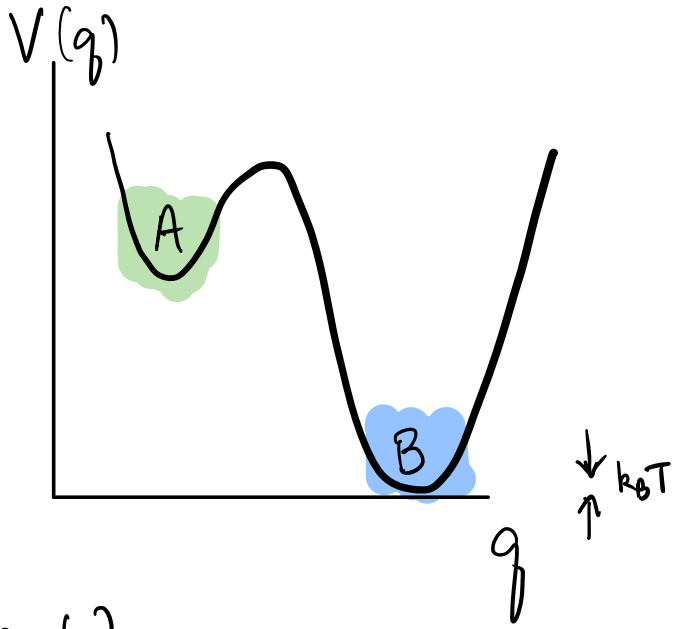
How do they depend on temperature?



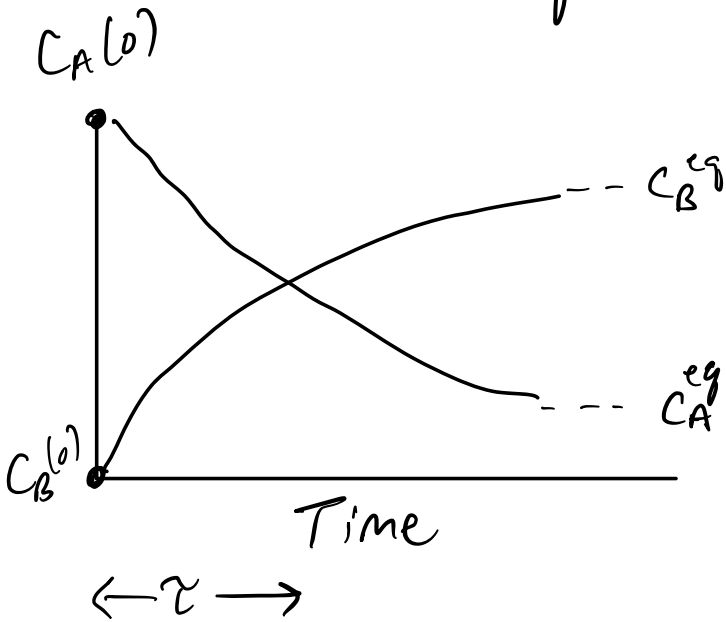
In general these are hard questions without general answers.

This type of exponential growth is common to rate processes involving an "activated complex"

Then the rate are estimated in terms of $V(\phi)$ (an activation barrier) and molecular collision rates, an approximation known as **transition state theory**.



Start in A with 100% probability.



$$\tau = (k_{AB} + k_{BA})^{-1}$$

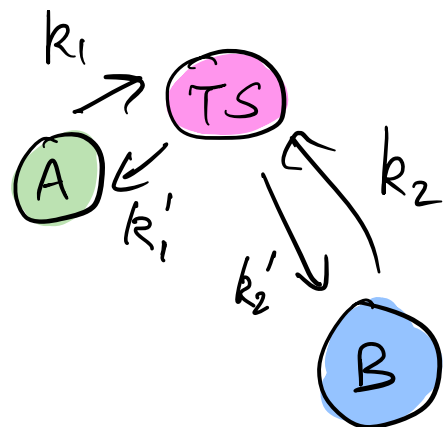
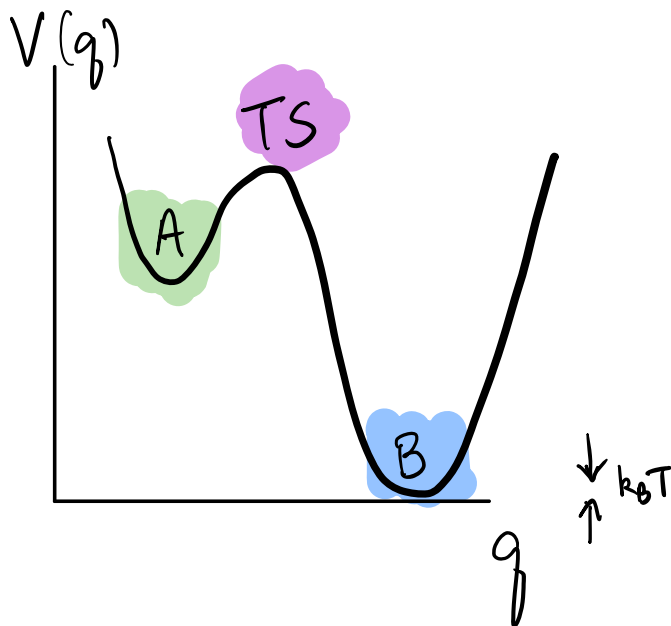
$$\frac{k_{BA}}{k_{AB}} = \frac{C_B^{eq}}{C_A^{eq}} \approx \frac{e^{-\beta V_B}}{e^{-\beta V_A}} = e^{-\beta(V_B - V_A)} \gg 1$$

Detailed Balance

The shape of $V(q)$ constrains the ratio of rates, but we have left out any notion of a barrier.

To bring that into the model...

3-state kinetics



$$\frac{dc_A}{dt} = -k_1 c_A + k_1' c_{TS}$$

$$\frac{dc_{TS}}{dt} = k_1 c_A - k_1' c_{TS} + k_2 c_B - k_2' c_{TS}$$

$$\frac{dc_B}{dt} = -k_2 c_B + k_2' c_{TS}$$

$$\frac{dc}{dt} = \underbrace{\begin{pmatrix} -k_1 & k_1' & 0 \\ k_1 & -k_1' - k_2' & k_2 \\ 0 & k_2' & -k_2 \end{pmatrix}}_{\text{LW}} c$$

$$\Rightarrow c(t) = c^{eq} + x e^{-t/\tau_1} + y e^{-t/\tau_2}$$

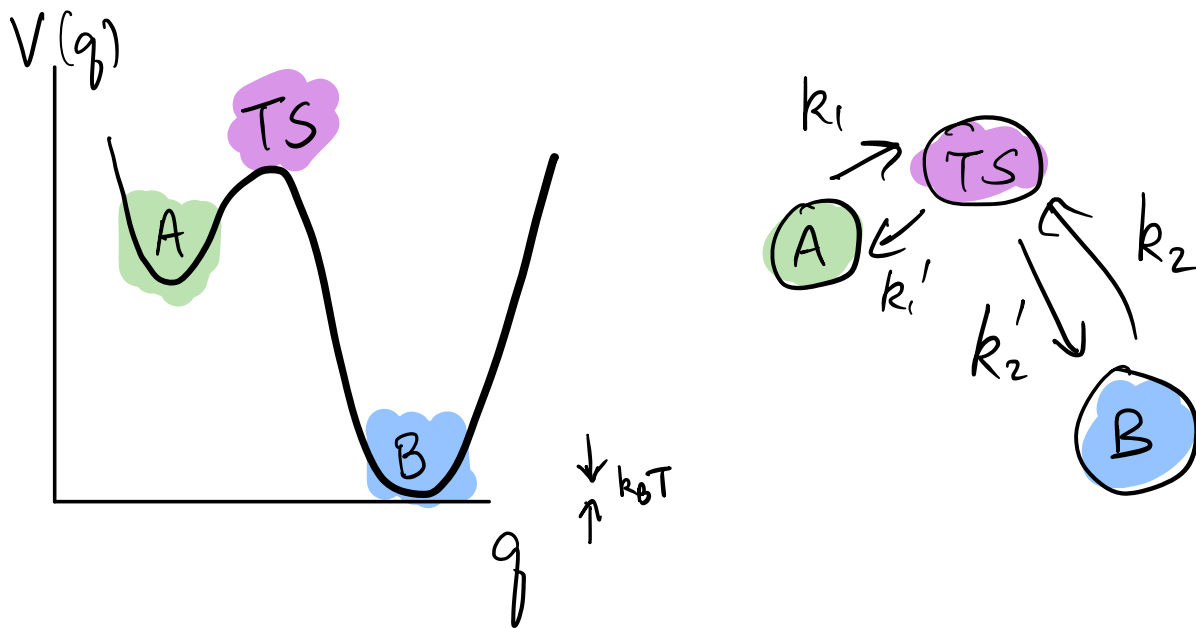
where

$$\frac{1}{\lambda_1} = \nu_1 = \frac{1}{2} \left[-(k_1 + k_1' + k_2 + k_2') + \sqrt{(k_1 + k_1' + k_2 + k_2')^2 - 4(k_1 k_2 + k_1' k_2' + k_1 k_2')} \right]$$

and

$$\frac{1}{\lambda_2} = \nu_2 = \frac{1}{2} \left[-(k_1 + k_1' + k_2 + k_2') - \sqrt{(k_1 + k_1' + k_2 + k_2')^2 - 4(k_1 k_2 + k_1' k_2' + k_1 k_2')} \right]$$

are the two nonzero eigenvalues of UV .



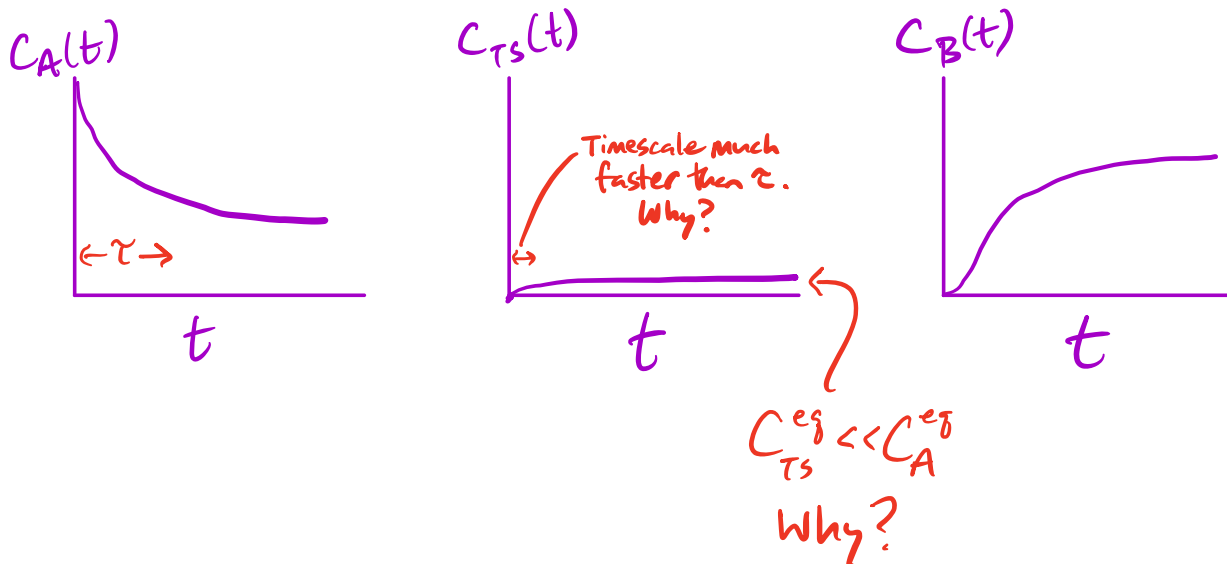
We really care about the limiting behavior when:

$$V_{TS} \gg V_A \text{ and } V_{TS} \gg V_B$$

$$\Rightarrow k_1 \ll k_1' \text{ + } k_2 \ll k_2'$$

Then there is a very good (and very common) approximation that would have simplified the math (not everyone is an ISP student who loves linear algebra).

Different timescales...



C_A ↓ with some τ

C_{TS}

C_B ↑ with τ

Concentration is essentially flat due to a balance between probability gained from A and lost to B

$$\frac{dC_{TS}}{dt} \approx 0$$

Steady State Approximation (effectively throwing away the fastest timescale)

$$\frac{dC_{TS}}{dt} = k_1 C_A - k_1' C_{TS} + k_2 C_B - k_2' C_{TS} = 0$$

$$\Rightarrow -(k_1' + k_2') C_{TS} + k_1 C_A + k_2 C_B = 0$$

$$\Rightarrow C_{TS} = \frac{k_1 C_A + k_2 C_B}{k_1' + k_2'}$$

A steady-state concentration in the transition state

Plug this C_{TS} into our rate equation for $\frac{dC_A}{dt}$

$$\frac{dC_A}{dt} = -k_1 C_A + k_1' \left(\frac{k_1 C_A + k_2 C_B}{k_1' + k_2'} \right)$$

$$= -k_1 \left(1 - \frac{k_1'}{k_1' + k_2'} \right) C_A + \frac{k_1' k_2}{k_1' + k_2'} C_B$$

$$= \underbrace{\frac{-k_1 k_2'}{k_1' + k_2'}}_{k_{BA} \text{ effective}} C_A + \underbrace{\frac{k_2 k_1'}{k_1' + k_2'}}_{k_{AB} \text{ effective}} C_B$$

2-state kinetics!

$$\underbrace{k_{BA}^{\text{effective}}}_{\text{Rate constant if we only had a 2-state model}} = k_1 \underbrace{\frac{k_2'}{k_1' + k_2'}}_{\text{Probability per unit time to go from A} \rightarrow \text{TS given you start in A}}$$

Preference for falling right versus left at the top of the barrier.

Approximate solution becomes very good when visiting TS is rare. ($k_1 \ll k_1' + k_2 \ll k_2'$)

Steady-state approximation ($\frac{dc_{TS}}{dt} = 0$) leads to an effective two-state kinetics between A + B.

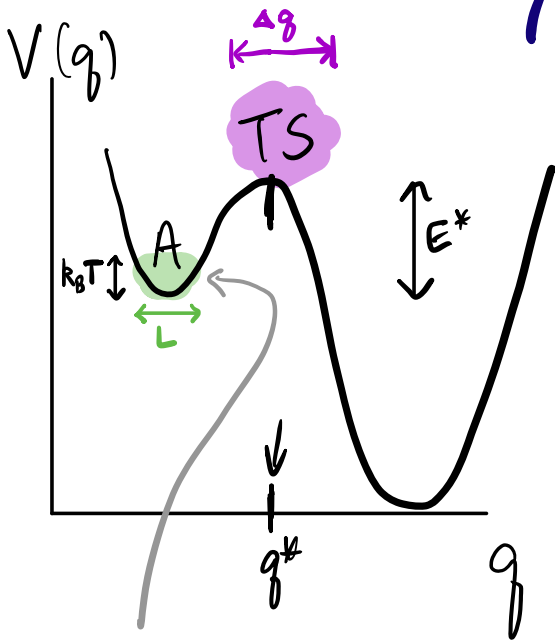
$$\frac{d}{dt} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = \begin{pmatrix} \frac{-k_1 k_2'}{k_1' + k_2'} & \frac{k_2 k_1'}{k_1' + k_2'} \\ \frac{k_1 k_2'}{k_1' + k_2'} & -\frac{k_2 k_1'}{k_1' + k_2'} \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

$$= \begin{pmatrix} -k_{BA}^{\text{eff}} & k_{AB}^{\text{eff}} \\ k_{BA}^{\text{eff}} & -k_{AB}^{\text{eff}} \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix}$$

So $c_{TS} = 0$? Then why include it at all?

Just because $c_{TS} \approx 0$, doesn't mean it is not important because the only way to go from $A \rightleftharpoons B$ is to pass through TS.

Transition State Theory: A way to try to estimate a rate using a free energy.



Highly likely states are confined to this region.

$$\frac{\text{Probability of TS}}{\text{Probability of A}} = \frac{\Delta q e^{-\beta E^*}}{L}$$

velocity v



Average time to get across a distance Δq :

$$\frac{\langle |v| \rangle}{\Delta q}$$

$$k_{BA}^{(TST)} = \frac{\Delta q e^{-\beta E^*}}{L} \frac{\langle |v| \rangle}{\Delta q} \frac{1}{2}$$

$$= \frac{e^{-\beta E^*}}{L} \frac{\langle |v| \rangle}{2}$$

$$= \frac{Q_{TS}}{Q_A} \frac{\langle |v| \rangle}{2}$$

Probability density at TS surface given confinement to region A.

∴ Rates often go like

$$k = A e^{-E^*/k_B T}$$

Arrhenius Rates

↑
"Prefactor"
No T-dependence

↑
An "activation energy"

Activated processes have a separation of timescales.

