Lecture 14
Recall from last lecture... WARNING: Linear Algebra Ahead

Two-state kinetics

$$A \rightleftharpoons B$$
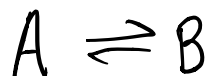
p_A: probability of A (trans)
p_B: probability of B (gauche)
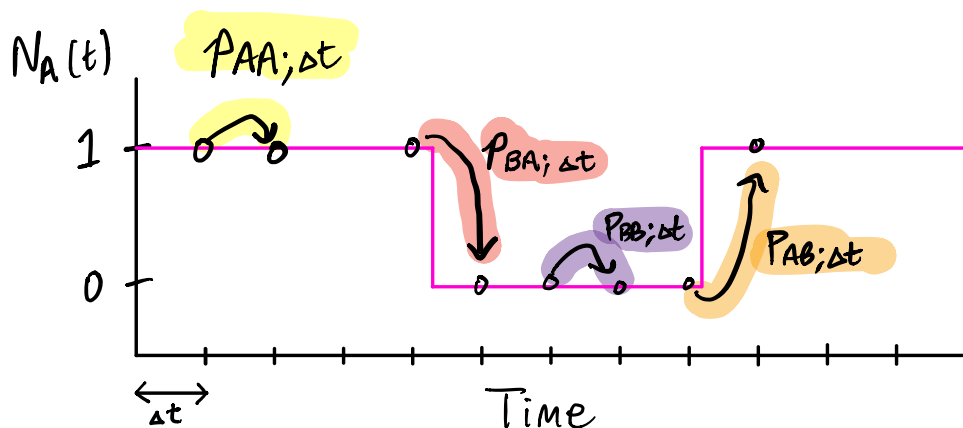
In matrix form after a (discrete) time Δt:

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

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

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

$\Uparrow$

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

Suppose I start with some $c_A(0), c_B(0)$, what is $c_A(t), c_B(t)$?

$c_A(t) \equiv c_A^{eq} + \Delta C(t)$
$c_B(t) \equiv c_B^{eq} - \Delta C(t)$

$$\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix} + \Delta C(t)\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\frac{d}{dt}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix} = \mathbb{W}\begin{pmatrix} c_A(t) \\ c_B(t) \end{pmatrix}$$

$$= \mathbb{W}\begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix} + \Delta C(t)\,\underline{\mathbb{W}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$= \begin{pmatrix} -k_{BA} c_A^{eq} + k_{AB} c_B^{eq} \\ k_{BA} c_A^{eq} - k_{AB} c_B^{eq} \end{pmatrix} + \Delta c(t) \begin{pmatrix} -k_{BA} - k_{AB} \\ k_{BA} + k_{AB} \end{pmatrix}$$

$$= \underline{0} \begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix} - \underbrace{(k_{AB} + k_{BA})}_{\substack{\uparrow \\ \text{eigenvalue}}} \Delta c(t) \underbrace{\begin{pmatrix} 1 \\ -1 \end{pmatrix}}_{\substack{\text{eigenvector} \\ \text{of } \mathbf{W}}}$$

(This is handwavy)

$$\frac{d}{dt} \mathbf{c} = \mathbf{W} \mathbf{c} \implies \frac{d\mathbf{c}}{\mathbf{c}} = \mathbf{W} dt$$

⟩ Integrate both sides

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

⟩ Exponentiate both sides

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

$$\implies \mathbf{c}(t) = \exp[\mathbf{W} t] \mathbf{c}(0)$$

A matrix exponential!

$$\exp[\mathbf{W} t] = \mathbb{1} + \mathbf{W} t + \frac{1}{2} t^2 \mathbf{W}^2 + \dots$$

$$\exp\left[\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix} t\right] = ?$$

I love a good basis

$\mathbb{W}$ has eigenvalues ν_0 and ν_1 with associated left and right eigenvectors

$$\langle 0|\mathbb{W} = \langle 0|\nu_0 \qquad \mathbb{W}|0\rangle = \nu_0|0\rangle$$

$$\langle 1|\mathbb{W} = \langle 1|\nu_1 \qquad \mathbb{W}|1\rangle = \nu_1|1\rangle$$

$$\exp\left[\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix} t\right]$$

$$= |0\rangle\langle 0|e^{\nu_0 t} + |1\rangle\langle 1|e^{\nu_1 t}$$

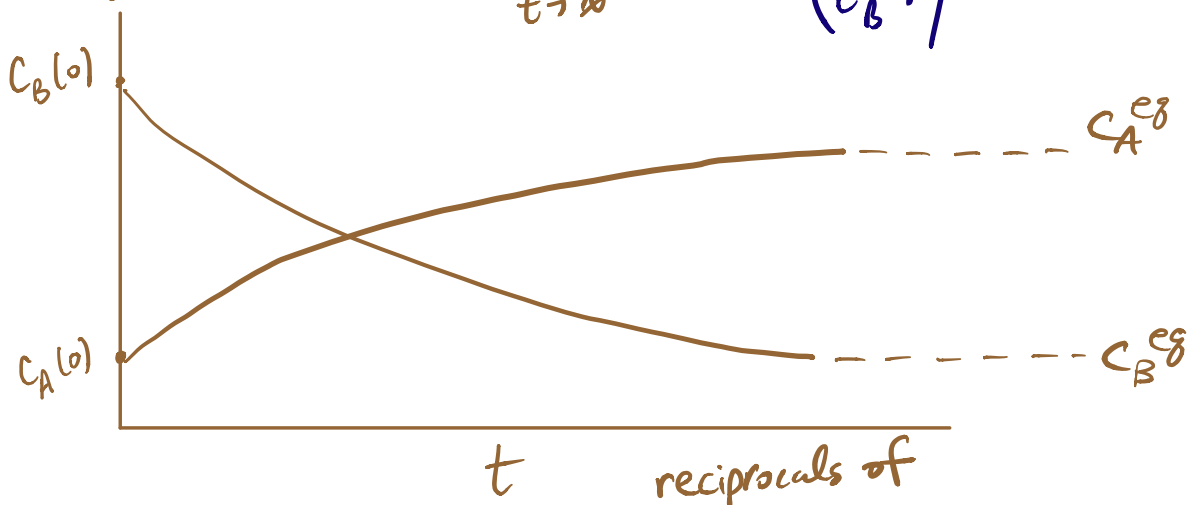$$c(t) = \left(|0\rangle\langle 0|e^{\nu_0 t} + |1\rangle\langle 1|e^{\nu_1 t}\right) c(0)$$

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

$$= \left[\begin{pmatrix} p_A^{eq} \\ p_B^{eq} \end{pmatrix} \left(c_A(0) + c_B(0) \right) \right.$$

$$\left. + \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB}+k_{BA})t} \left(c_A(0) - c_B(0) \right) \right]$$

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

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

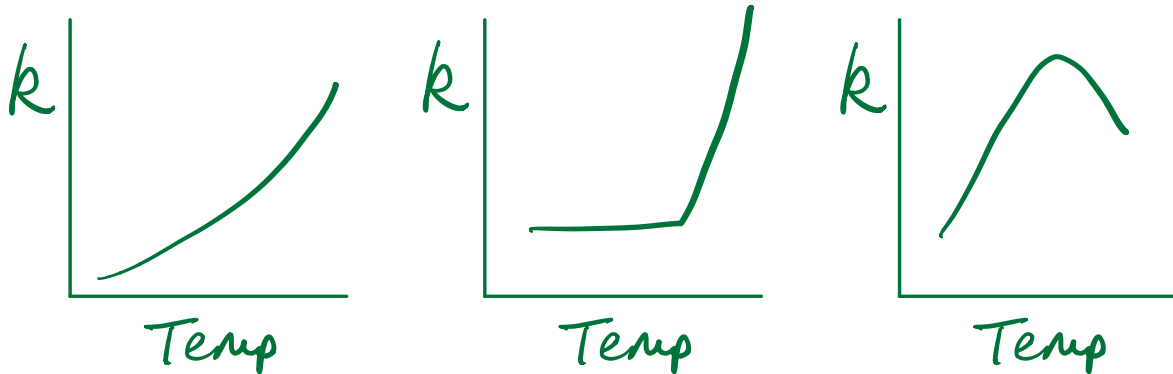Long time... ? $\lim\limits_{t \to \infty} \mathbf{c}(t) = \begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix}$

t reciprocals of
$\vee$

Relaxation timescales are eigenvalues of $\mathbb{W}$!

What determines k_{AB} and k_{BA}?
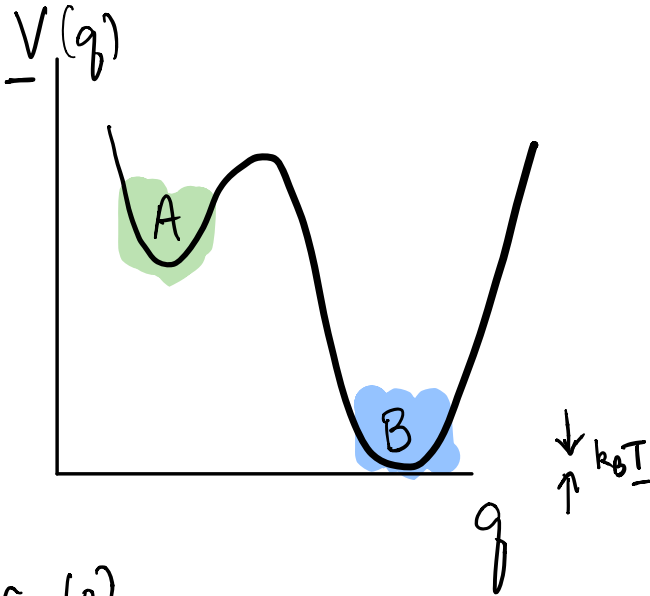
How are they related to $V(\phi)$?

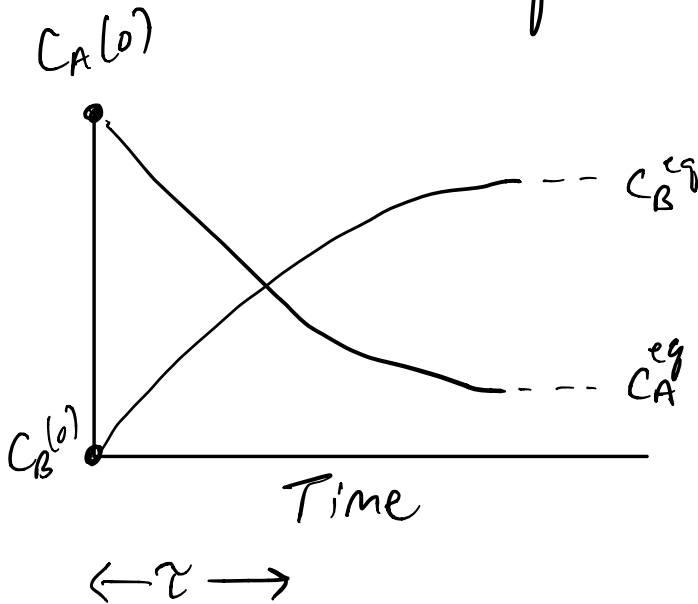How do they depend on temperature?

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

$$\underline{V}(q)$$

A

B

$$\downarrow \atop \uparrow k_B \underline{T}$$

q

Start in A with
100% probability.

$C_A(0)$

C_B^{eq}

C_A^{eq}

$C_B(0)$

Time

$\longleftarrow \tau \longrightarrow$

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

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

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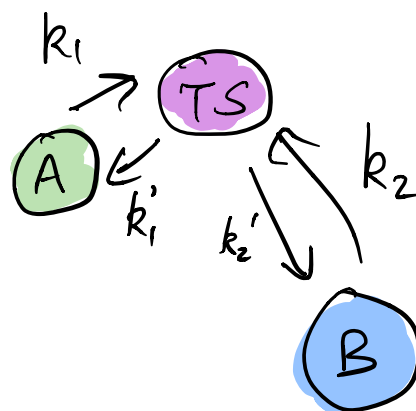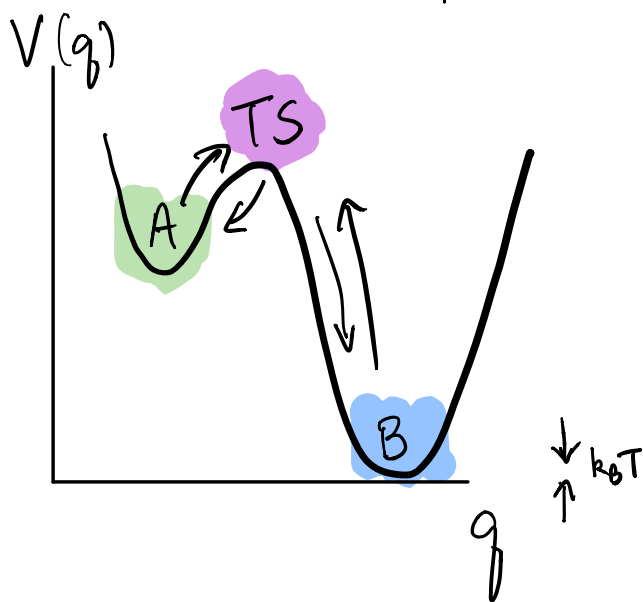
$$\frac{dc_A}{dt} = -k_1 c_A + k_1' c_{TS}$$

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

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

$$\frac{d\mathbf{c}}{dt} = \underbrace{\begin{pmatrix} -k_1 & k_1' & 0 \\ k_1 & -k_1'-k_2' & k_2 \\ 0 & k_2' & -k_2 \end{pmatrix}}_{\mathbb{W}} \mathbf{c}$$

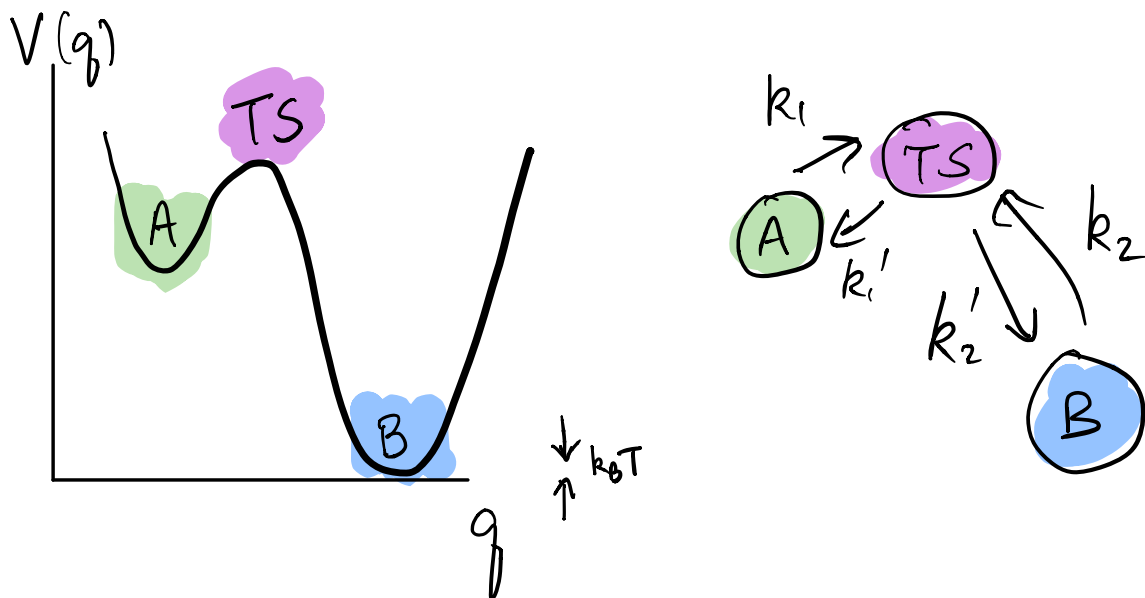$$\Rightarrow \quad \mathbf{c}(t) = \mathbf{c}^{eq} + \mathbf{x}\, e^{-t/\tau_1} + \mathbf{y}\, e^{-t/\tau_2}$$

where

$$\frac{1}{\tau_1} = \nu_1 = \frac{1}{2}\Bigg[-(k_1+k_1'+k_2+k_2') \\ + \sqrt{(k_1+k_1'+k_2+k_2')^2 - 4(k_1 k_2 + k_1' k_2 + k_1 k_2')} \Bigg]$$

and

$$\frac{1}{\tau_2} = \nu_2 = \frac{1}{2}\Bigg[-(k_1+k_1'+k_2+k_2') \\ - \sqrt{(k_1+k_1'+k_2+k_2')^2 - 4(k_1 k_2 + k_1' k_2 + k_1 k_2')} \Bigg]$$
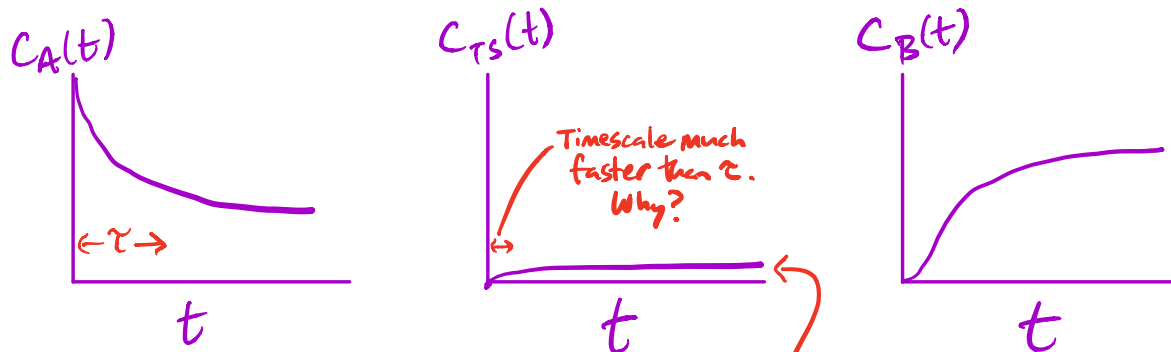
are the two non-zero eigenvalues of $\mathbb{W}$.

$V(q)$

TS

A

B

$\downarrow \uparrow k_B T$

q

k_1

TS

A

k_1'

k_2'

k_2

B

We really care about the limiting behavior when:

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

$$\Rightarrow \quad k_1 \ll k_1' \quad \& \quad k_2 \ll k_2'$$

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...

$c_A(t)$

$c_{TS}(t)$

Timescale much faster then τ. Why?

$c_B(t)$

$\leftarrow \tau \rightarrow$

t

t

t

$c_{TS}^{eq} << c_A^{eq}$

Why?

$c_A \downarrow$ with some τ $\underline{c_{TS}}$ $c_B \uparrow$ with some 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)

$$0 = \frac{dc_{TS}}{dt} = k_1 c_A - k_1' \underline{c_{TS}} + k_2 c_B - k_2' \underline{c_{TS}}$$

$$\Rightarrow \quad -(k_1' + k_2') \, c_{TS} + k_1 c_A + k_2 c_B = 0$$

$$\Rightarrow \quad c_{TS} = \frac{k_1 c_A + k_2 c_B}{k_1' + k_2'} \qquad \text{A steady-state concentration in the transition state}$$

Plug this c_{TS} into our rate equation for $\frac{dc_A}{dt}$

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

$$\Rightarrow \frac{dc_A}{dt} = -k_1 \, c_A + k_1' \left(\frac{k_1 c_A + k_2 c_B}{k_1' + k_2'} \right)$$

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

$$= \underbrace{\frac{-k_1 k_2'}{k_1' + k_2'}}_{\substack{k_{BA}^{\text{effective}}}} c_A + \underbrace{\frac{k_2 k_1'}{k_1' + k_2'}}_{\substack{k_{AB}^{\text{effective}}}} c_B \qquad \text{2-state kinetics!}$$

$$k_{BA}^{\text{effective}} = k_1 \, \frac{k_2'}{k_1' + k_2'}$$

Rate constant if we only had a 2-state model

Probability per unit time to go from $A \to TS$ given you start in A

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