ChemE 2200 – Chemical Kinetics Lecture 7

Today:

The steady-state approximation, cont'd.

Analysis of series reactions $\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$

The pre-equilibrium approximation.

"Why is 'pre-equilibrium' a misnomer?"

Recap: If B is a reactive intermediate,
perhaps apply the steady-state approximation to B:

$$\frac{d[\mathrm{B}]}{dt} = 0$$

identify a reactive intermediate, or

identify a slow reaction.

Reading for Kinetics Lecture 8:

McQuarrie & Simon, Chp 29.6.

Homework 10 (assigned Wednesday, March 26)

Exercises 7 and 8 apply the
pre-equilibrium approximation,
the subject of today’s lecture.

Exercises 7 and 8 will not are
Not eligible for Quiz 10.

2^{nd} Prelim

Tuesday, April 15, 7:30 – 9:30 p.m.

245 and 128 Olin Hall

Covers –
Classical Thermodynamics

Covers –
Thermodynamics Lectures 1 through 12.
Homework Assignments 5 through 8.
Calculation Sessions 5 through 8.

You may use a hand-written, double-sided reference sheet
and your annotated “Equations of Thermodynamics” lecture handout.

Bring a ruler or straightedge.

Differential Rate Equations

$$A \xrightarrow{k} B$$

$$\frac{d[A]}{dt} = -k[A]$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

Differential Rate Equations, cont'd

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$$

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

Complexity of Differential Rate Equations Increases Linearly.

Integrated Rate Equations

$$\mathrm{A} \xrightarrow{k} \mathrm{B}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt}$$

$$[\mathrm{B}] = [\mathrm{A}]_0 (1 - e^{-kt})$$

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \left(\frac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_{-1} + k_1} \right)$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \left(\frac{k_1 (1 - e^{-(k_1 + k_{-1})t})}{k_{-1} + k_1} \right)$$

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$[\mathrm{C}] = [\mathrm{A}]_0 \left(\frac{k_1 (e^{-k_2 t} - 1) - k_2 (e^{-k_1 t} - 1)}{k_2 - k_1} \right)$$

Integrated Rate Equations, cont'd

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \left[\frac{k_1(\lambda_2 - k_2)}{\lambda_2(\lambda_2 - \lambda_3)} e^{-\lambda_2 t} + \frac{k_1(k_2 - \lambda_3)}{\lambda_3(\lambda_2 - \lambda_3)} e^{-\lambda_3 t} \right]$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \left[\frac{-k_1}{(\lambda_2 - \lambda_3)} e^{-\lambda_2 t} + \frac{k_1}{(\lambda_2 - \lambda_3)} e^{-\lambda_3 t} \right]$$

$$[\mathrm{C}] = [\mathrm{A}]_0 \left[\frac{k_1 k_2}{\lambda_2 \lambda_3} + \frac{k_1 k_2}{\lambda_2(\lambda_2 - \lambda_3)} e^{-\lambda_2 t} - \frac{k_1 k_2}{\lambda_3(\lambda_2 - \lambda_3)} e^{-\lambda_3 t} \right]$$

such that

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

$$\lambda_3 = \frac{1}{2}\left[k_1 + k_{-1} + k_2 - \left\{ (k_1 + k_{-1} + k_2)^2 - 4 k_1 k_2 \right\}^{1/2} \right]$$

Complexity of Integrated Rate Equations Increases Geometrically.

The Steady State Approximation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$$

Write the rate equations.

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}\boxed{[B]} \qquad (1)$$

$$\frac{d[B]}{dt} = \boxed{k_1[A] - k_{-1}[B] - k_2[B]} \qquad (2)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad (3)$$

Need to express [B] in terms of [A]. Apply the Steady-State Approximation to B.

$$\boxed{\frac{d[B]}{dt} = 0} = \boxed{k_1[A] - k_{-1}[B] - k_2[B]}$$

Solve for [B]: $\boxed{[B] = \dfrac{k_1[A]}{k_{-1}+k_2}}$ (4) Substitute for [B]

Substitute eqn (4) into eqn (1) and integrate.

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}\frac{k_1[A]}{k_{-1}+k_2} = \frac{-k_1k_2}{k_{-1}+k_2}[A]$$

Integrate 1st order rate equation

$$[A] = [A]_0 \exp\left[\frac{-k_1k_2}{k_{-1}+k_2}t\right] \qquad (5)$$

The Steady State Approximation, cont'd

From the previous slide:

$$[\mathrm{B}] = \frac{k_1\boxed{[\mathrm{A}]}}{k_{-1}+k_2} \qquad (4)$$

Substitute for [A]

$$\boxed{[\mathrm{A}]} = [\mathrm{A}]_0 \exp\left[\frac{-k_1 k_2}{k_{-1}+k_2}t\right] \qquad (5)$$

Substitute eqn (5) into eqn (4) to yield an integrated rate equation for [B].

$$\boxed{[\mathrm{B}]} = [\mathrm{A}]_0 \frac{k_1}{k_{-1}+k_2} \exp\left[\frac{-k_1 k_2}{k_{-1}+k_2}t\right] \qquad (6)$$

Substitute eqn (6) into eqn (3) and integrate.

Substitute for [B]

$$\frac{d[\mathrm{C}]}{dt} = k_2\boxed{[\mathrm{B}]} = [\mathrm{A}]_0 \frac{k_1 k_2}{k_{-1}+k_2} \exp\left[\frac{-k_1 k_2}{k_{-1}+k_2}t\right]$$

Separate 'n' integrate with $[\mathrm{C}]_0 = 0$.

$$[\mathrm{C}] = [\mathrm{A}]_0 \left(1 - \exp\left[\frac{-k_1 k_2}{k_{-1}+k_2}t\right]\right) \qquad (7)$$

The Steady State Approximation – Summary

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp \boxed{\left[\frac{-k_1 k_2}{k_{-1} + k_2} t \right]} \qquad (5)$$

$$[\mathrm{B}] = [\mathrm{A}]_0 \frac{k_1}{k_{-1} + k_2} \exp \boxed{\left[\frac{-k_1 k_2}{k_{-1} + k_2} t \right]} \qquad (6)$$

$$[\mathrm{C}] = [\mathrm{A}]_0 \left(1 - \exp \boxed{\left[\frac{-k_1 k_2}{k_{-1} + k_2} t \right]} \right) \qquad (7)$$

Looks like $\mathrm{A} \rightarrow \mathrm{C}$
with rate constant =

$$\frac{k_1 k_2}{k_{-1} + k_2}$$

The Steady State Approximation – Check

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Is [B]/[A] small?

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{\cancel{[\mathrm{A}]_0} \dfrac{k_1}{k_{-1}+k_2} \cancel{\exp\left[\dfrac{-k_1 k_2}{k_{-1}+k_2} t\right]}}{\cancel{[\mathrm{A}]_0} \cancel{\exp\left[\dfrac{-k_1 k_2}{k_{-1}+k_2} t\right]}} = \frac{k_1}{k_{-1}+k_2} \ll 1?$$

Requirement for the Steady-State Approximation:

$$\underbrace{k_{-1}+k_2}_{\propto \text{ rate B is consumed}} \gg \underbrace{k_1}_{\propto \text{ rate B is created}}$$

Is [B] at steady state?

$$\frac{d[\mathrm{B}]}{dt} = 0?$$

« 1? Yes, if

< 1

$$\frac{d[\mathrm{B}]}{dt} = -[\mathrm{A}]_0 \boxed{\frac{k_1^2 k_2}{(k_{-1}+k_2)^2}} \boxed{\exp\left[\frac{-k_1 k_2}{k_{-1}+k_2} t\right]} = 0?$$

When is the Steady-State Approximation applicable to $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$?

Case 1. $\underset{\text{small}}{k_{-1}} + \underset{\text{large}}{k_2} \gg \underset{\text{small}}{k_1}$ $\qquad A \underset{\text{slow}}{\overset{\text{slow}}{\rightleftarrows}} B \xrightarrow{\text{fast}} C$ Deductive

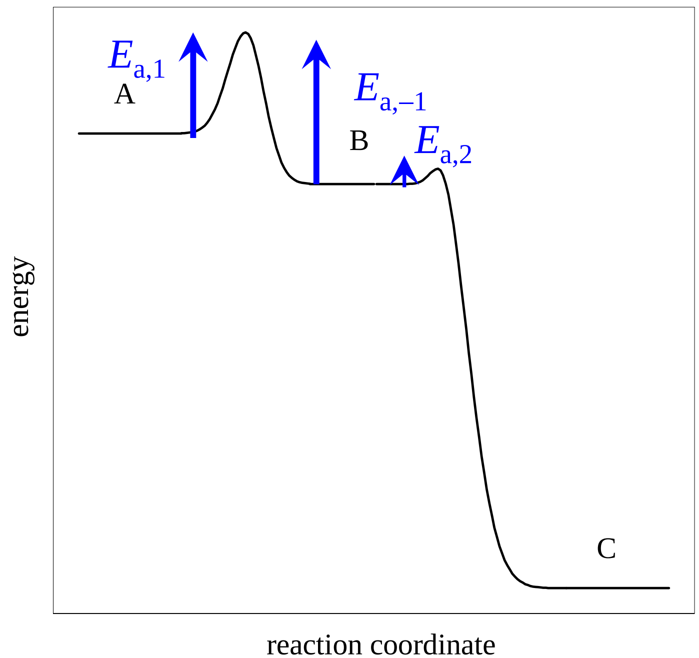
Inductive: $k_1 = 2$

$k_{-1} = 1$

$k_2 = 1000$

$$\text{rate constant} = \frac{k_1 k_2}{\cancel{k_{-1}} + k_2} \approx \frac{k_1 \cancel{k_2}}{\cancel{k_2}}$$

$$\text{rate constant} \approx k_1$$



$E_{a,-2} \gg E_{a,2}$

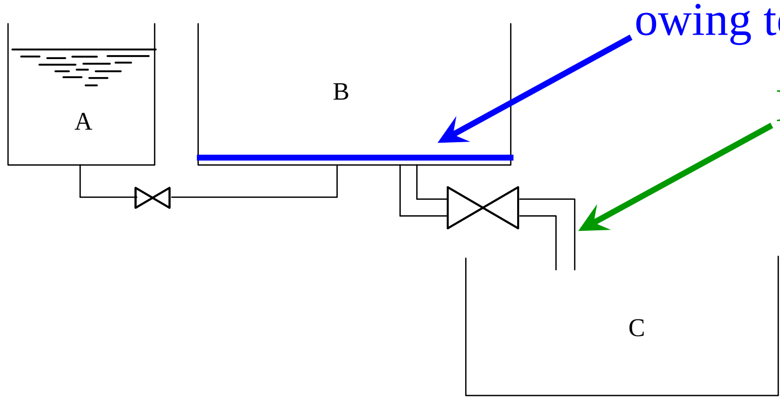
$\Rightarrow k_{-2} \approx 0$

$\Rightarrow B \rightarrow C$ is irreversible.

Tank analogy - amount in tank $\propto$ concentration

$[B]_0 = 0$, $[C]_0 = 0$

If a reaction is reversible, tanks are at the same level.



Level in B tank is always low, owing to large drain to tank C.

If this pipe is absent, $A \leftrightarrow B$ only.

If $k_2 = 0$, [A] and [B] reach equilibrium with [B] > [A].

When is the Steady-State Approximation applicable to $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$?

Case 2. $\underbrace{k_{-1}}_{\text{large}} + \underbrace{k_2}_{\text{small}} \gg \underbrace{k_1}_{\text{small}}$ $\quad A \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} B \xrightarrow{\text{slow}} C$

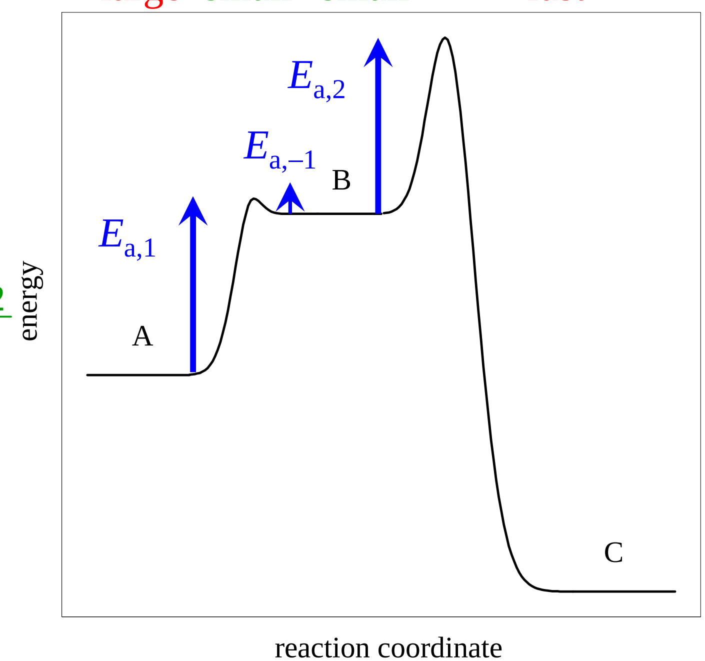
Inductive: $k_1 = 1$

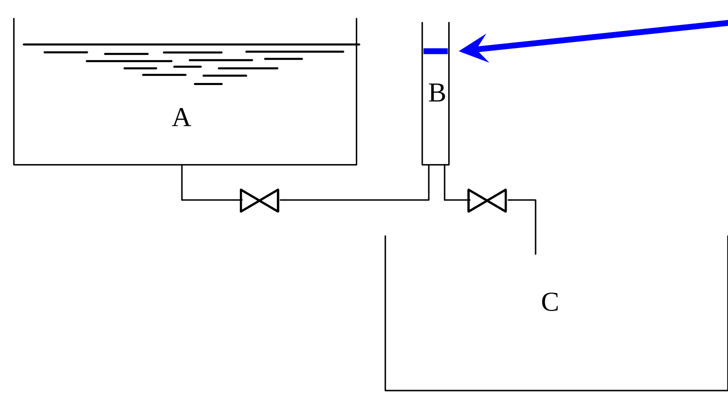
$k_{-1} = 1000$

$k_2 = 1$

$$\text{rate constant} = \frac{k_1 k_2}{k_{-1} + \cancel{k_2}} \approx \frac{k_1 k_2}{k_{-1}}$$

$$\text{rate constant} \approx K_{eq,1} k_2 \approx \frac{1}{1000} k_2$$





Fluid level in tank B nearly the same as fluid level in tank A, but [B] « [A].

$\frac{[B]}{[A]}$ is small because of thermodynamics

When is the Steady-State Approximation applicable to $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$?

Case 3. $\underset{\text{large}}{k_{-1}} + \underset{\text{large}}{k_2} \gg \underset{\text{small}}{k_1}$ $\qquad A \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} B \xrightarrow{\text{fast}} C$

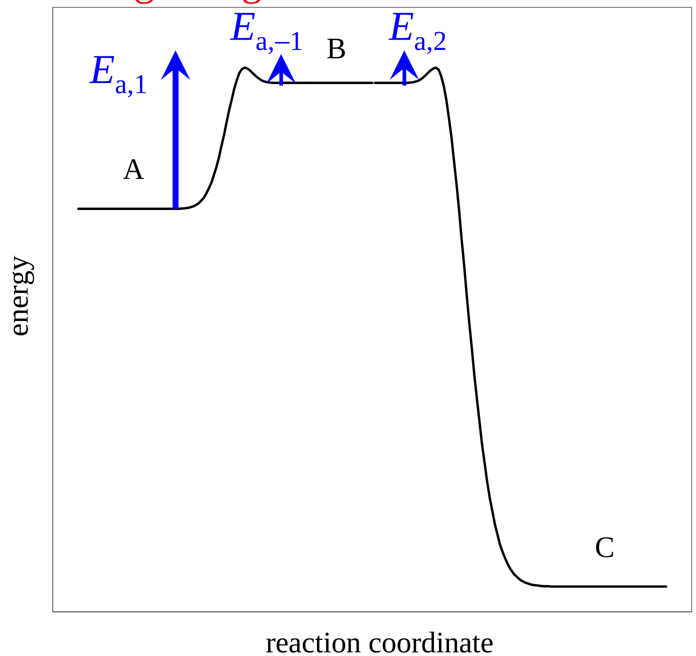
Inductive: $k_1 = 1$

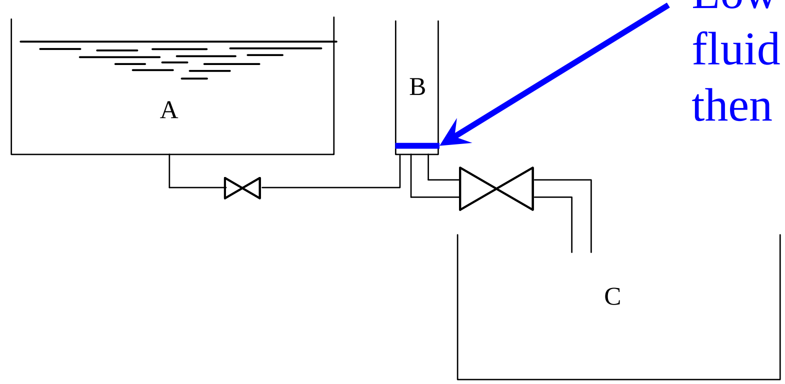
$k_{-1} = 1000$

$k_2 = 1000$

$$\text{rate constant} = \frac{k_1 k_2}{k_{-1} + k_2} \approx \frac{k_1 k_2}{k_2 + k_2}$$

$$\text{rate constant} \approx \frac{1}{2} k_1$$



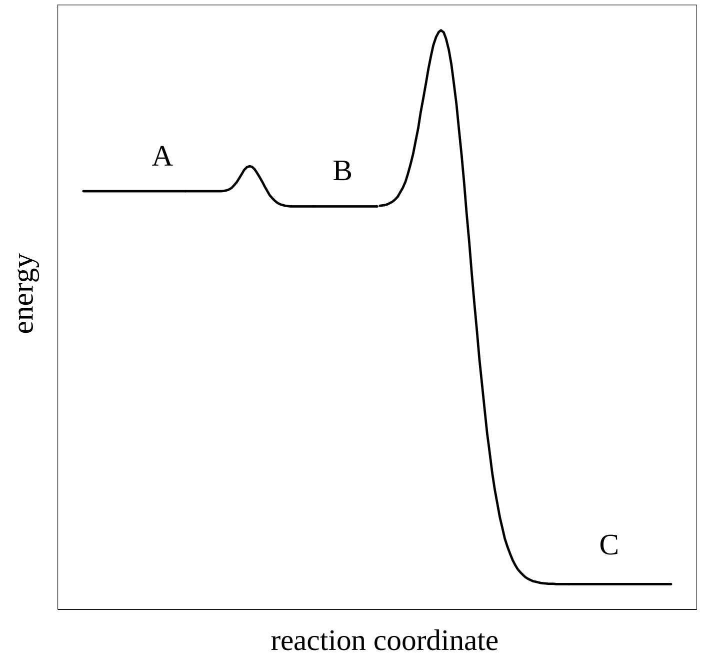


Low fluid level in tank B; fluid drains slowly from tank A, then drains rapidly to tank C.

When is the Steady-State Approximation applicable to $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$?

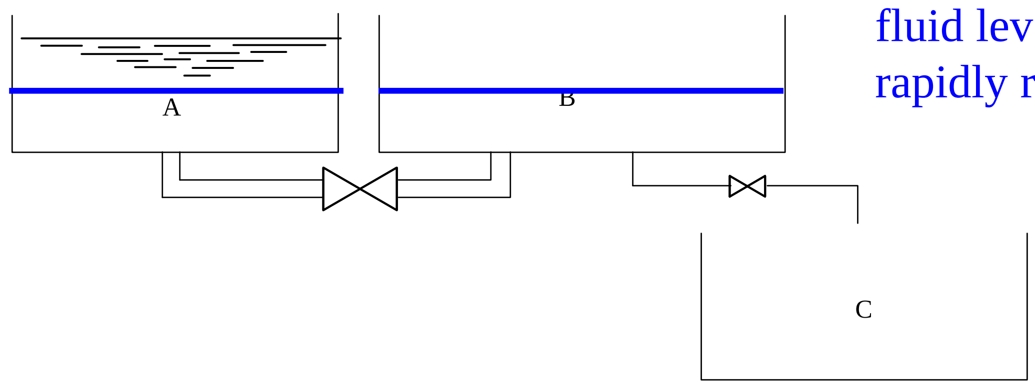
Case 4. $\underset{\text{large}}{k_{-1}} + \underset{\text{small}}{k_2} \cancel{\gg} \underset{\text{large}}{k_1}$ $\quad A \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} B \xrightarrow{\text{slow}} C$

Steady-State Approximation ***not*** applicable.



Reversible reaction that precedes the RLS is in equilibrium.

Apply the Pre-Equilibrium Approximation



fluid levels in tanks A and B rapidly reach same level.

$\frac{[B]}{[A]}$ is not small.

The Pre-equilibrium Approximation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C \qquad \text{with } k_1 + k_{-1} \gg k_2$$

Assume $k_1 = 2000$

$k_{-1} = 1000$

$k_2 = 1$

Write the rate equation for [B].

$$\frac{d[B]}{dt} = k_1\boxed{[A]} - k_{-1}[B] - k_2[B] \qquad (1)$$

substitute

Express [A] in terms of [B].

~0 for $t < 1/k_2$

$$[A]_0 + \overset{0}{\cancel{[B]_0}} + \overset{0}{\cancel{[C]_0}} = [A] + [B] + \cancel{[C]}$$

$$[A] = \boxed{[A]_0 - [B]} \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[B]}{dt} = k_1([A]_0 - [B]) - k_{-1}[B] - k_2[B]$$

$$= k_1[A]_0 - (k_1 + k_{-1} + \cancel{k_2})[B]$$

$k_1 + k_{-1} + k_2 \approx k_1 + k_{-1}$

$$\approx k_1[A]_0 - (k_1 + k_{-1})[B]$$

looks like $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

The Pre-equilibrium Approximation, cont'd

$$\frac{d[\mathrm{B}]}{dt} \approx k_1[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{B}]$$ looks like $\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$

$$\int_0^{[\mathrm{B}]} \frac{d[\mathrm{B}]}{k_1[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{B}]} = \int_0^t dt$$ separate 'n' integrate

$$-\frac{1}{k_1 + k_{-1}} \ln\left(k_1[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{B}]\right)\Big|_0^{[\mathrm{B}]} = t\Big|_0^t$$

$$\ln \frac{k_1[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{B}]}{k_1[\mathrm{A}]_0} = -(k_1 + k_{-1})t$$

$$k_1[\mathrm{A}]_0 - (k_1 + k_{-1})[\mathrm{B}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_{-1})t}$$

$$\boxed{[\mathrm{B}] = \frac{k_1}{k_1 + k_{-1}}[\mathrm{A}]_0\left(1 - e^{-(k_1+k_{-1})t}\right)} \qquad t < \frac{1}{k_2}$$

Use a mass balance to obtain an expression for [A].

$$[\mathrm{A}] = [\mathrm{A}]_0 - [\mathrm{B}] \qquad (2)$$

$$= [\mathrm{A}]_0 - \frac{k_1}{k_1 + k_{-1}}[\mathrm{A}]_0\left(1 - e^{-(k_1+k_{-1})t}\right)$$

$$\boxed{[\mathrm{A}] = \frac{1}{k_1 + k_{-1}}[\mathrm{A}]_0\left(k_{-1} + k_1 e^{-(k_1+k_{-1})t}\right)} \qquad t < \frac{1}{k_2}$$

The Pre-equilibrium Approximation, cont'd

Calculate the relative concentrations of A and B.

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{\dfrac{k_1}{\cancel{k_1 + k_{-1}}}\cancel{[\mathrm{A}]_0}\left(1 - e^{-(k_1+k_{-1})t}\right)}{\dfrac{1}{\cancel{k_1 + k_{-1}}}\cancel{[\mathrm{A}]_0}\left(k_{-1} + k_1 e^{-(k_1+k_{-1})t}\right)}$$

$$= \frac{k_1 - \overbrace{k_1 e^{-(k_1+k_{-1})t}}^{0}}{k_{-1} + \underbrace{k_1 e^{-(k_1+k_{-1})t}}_{0}} \qquad \text{assume } (k_1 + k_{-1})t \gg 1$$

$$\approx \frac{k_1}{k_{-1}} = K_{\mathrm{eq},1} \qquad \text{for } t > \frac{1}{k_1 + k_{-1}}$$

A and B approach equilibrium with a time constant (characteristic time) = $t = \dfrac{1}{k_1 + k_{-1}} \ll \dfrac{1}{k_2}$

The Pre-equilibrium Approximation, cont'd

For $t \gg \dfrac{1}{k_1 + k_{-1}}$ $\quad \boxed{k_1[\mathrm{A}] = k_{-1}[\mathrm{B}]}$ The pre-equilibrium approximation for rxn 1

$$\frac{d[\mathrm{B}]}{dt} = \cancel{k_1[\mathrm{A}] - k_{-1}[\mathrm{B}]} - k_2[\mathrm{B}] \approx -k_2[\mathrm{B}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] = k_2 K_{eq,1}\boxed{[\mathrm{A}]} \qquad (3)$$

need [A] in terms of [C]

mass balance $\rightarrow$ mol balance $\quad [\mathrm{A}]_0 + \cancelto{0}{[\mathrm{B}]_0} + \cancelto{0}{[\mathrm{C}]_0} = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]$

$[\mathrm{B}] = K_{eq,1}[\mathrm{A}]$

$$[\mathrm{A}]_0 = [\mathrm{A}] + K_{eq,1}[\mathrm{A}] + [\mathrm{C}]$$

$$\boxed{[\mathrm{A}] = \frac{[\mathrm{A}]_0 - [\mathrm{C}]}{1 + K_{eq,1}}} \qquad (4)$$

substitute

Substitute eqn (4) into eqn (3). $\quad \dfrac{d[\mathrm{C}]}{dt} = \dfrac{k_2 K_{eq,1}}{1 + K_{eq,1}}([\mathrm{A}]_0 - [\mathrm{C}])$

$$[\mathrm{C}] = [\mathrm{A}]_0\left[1 - \exp\left(-\frac{k_2 K_{eq,1}}{1 + K_{eq,1}}t\right)\right]$$

Did not assume $[\mathrm{C}] = 0$, so result not restricted to $t < 1/k_2$.

C is formed with a time constant (characteristic time) = $\tau = \dfrac{1}{k_2}\dfrac{1 + K_{eq,1}}{K_{eq,1}}$

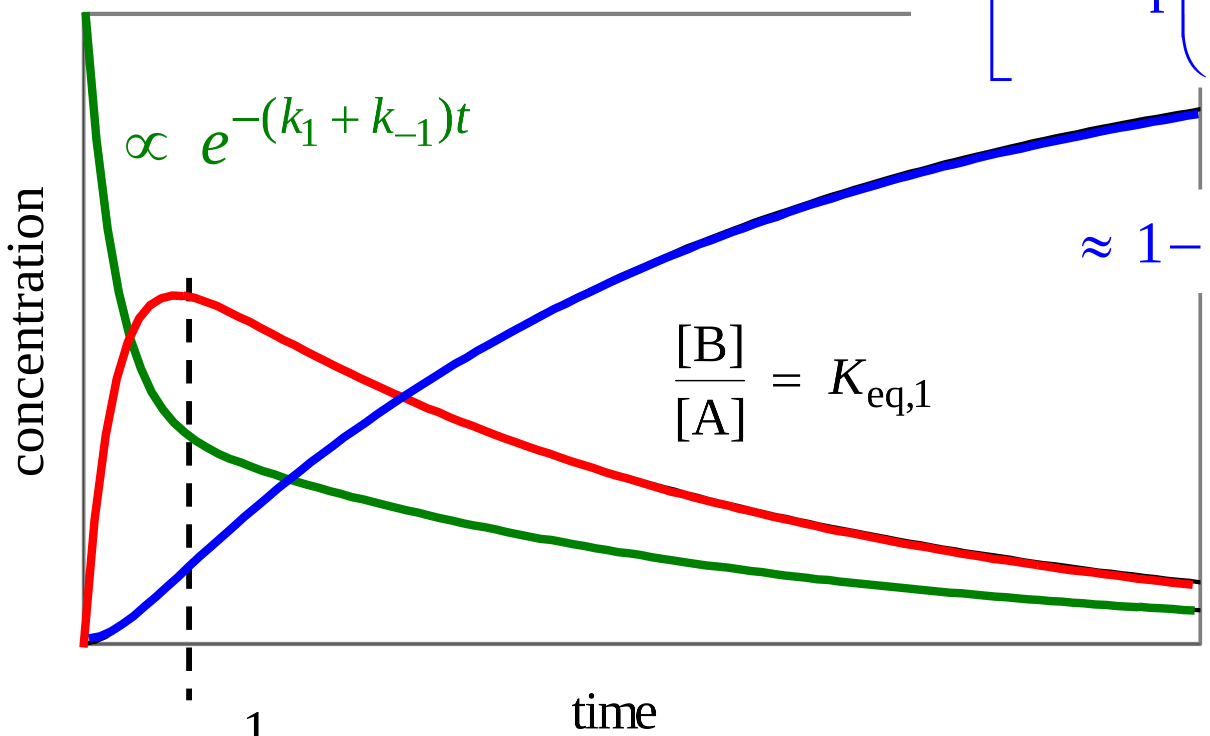
The Pre-equilibrium Approximation

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \quad \text{with} \quad k_1 + k_{-1} \gg k_2$$

$k_1 = 8$
$k_{-1} = 4$
$k_2 = 1$

$$\propto \left[1 - \exp\left(-\frac{k_2 K_{\mathrm{eq},1}}{1 + K_{\mathrm{eq},1}} t\right)\right]$$

[A], [B], [C]



$\approx 1 - e^{-k_2 t}$ for $K_{\mathrm{eq},1} \gg 1$

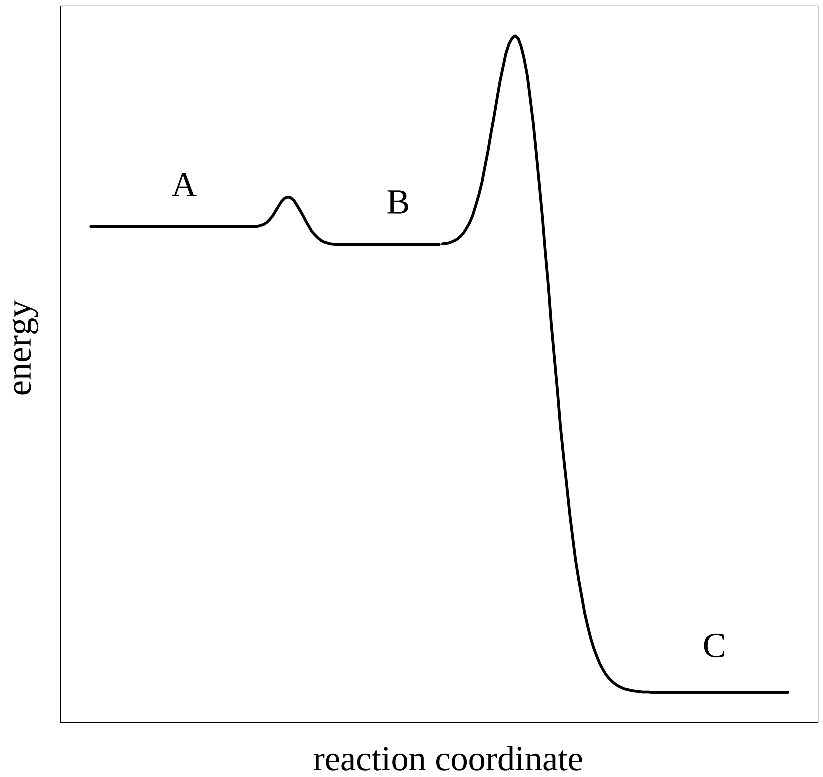
$$t = 3 \times \frac{1}{k_1 + k_{-1}}$$

note: $e^{-3} = 0.05$

Criterion for the Pre-equilibrium Approximation

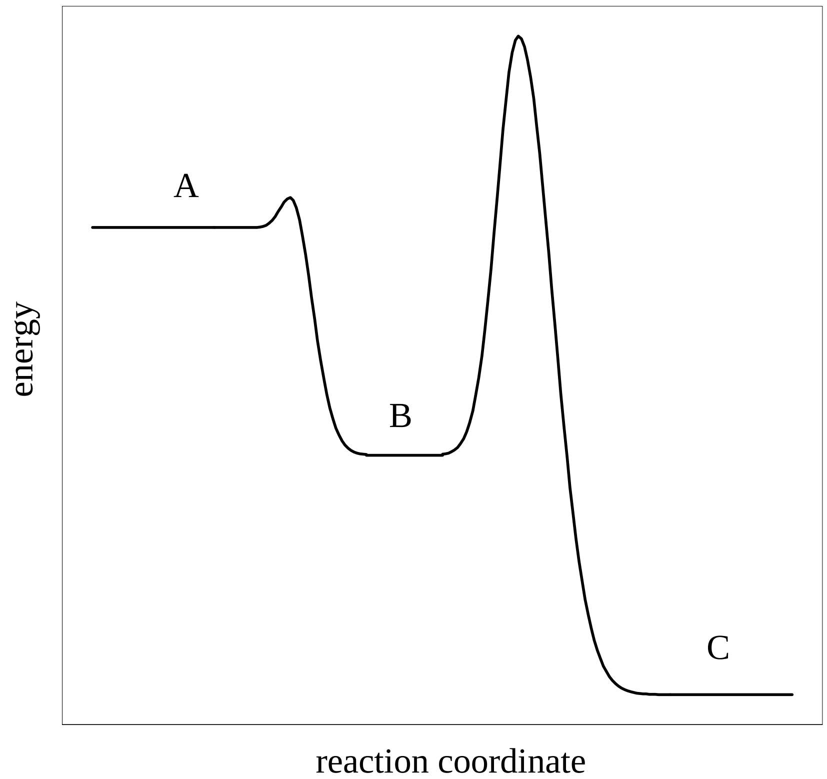
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C \quad \text{with} \quad k_1 + k_{-1} \gg k_2$$

rate for A $\leftrightarrow$ B » rate for B $\rightarrow$ C



$k_1 + k_{-1} \gg k_2$

large large small



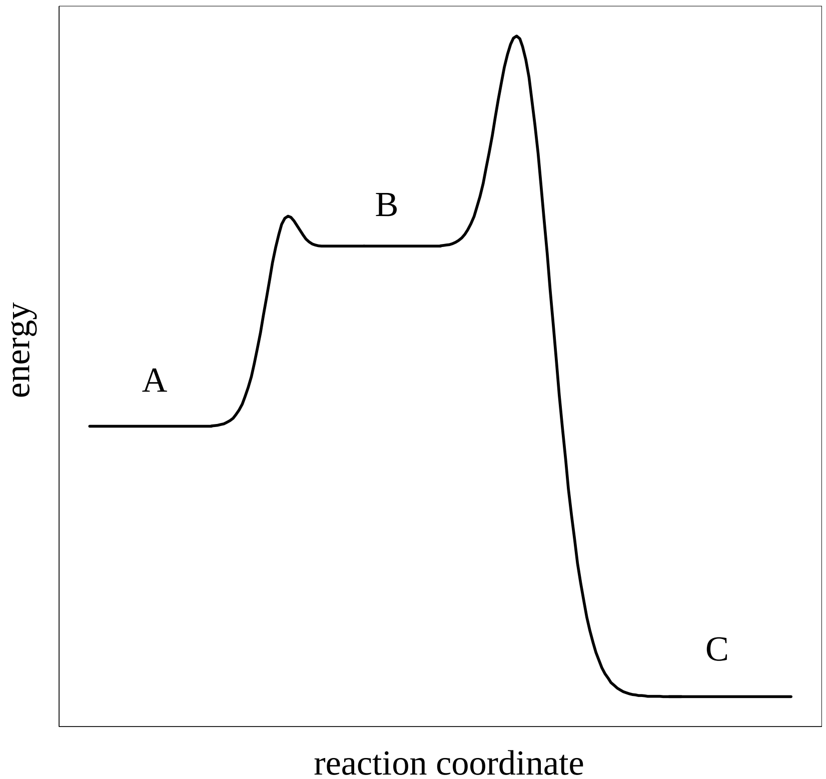
$k_1 + k_{-1} \gg k_2$

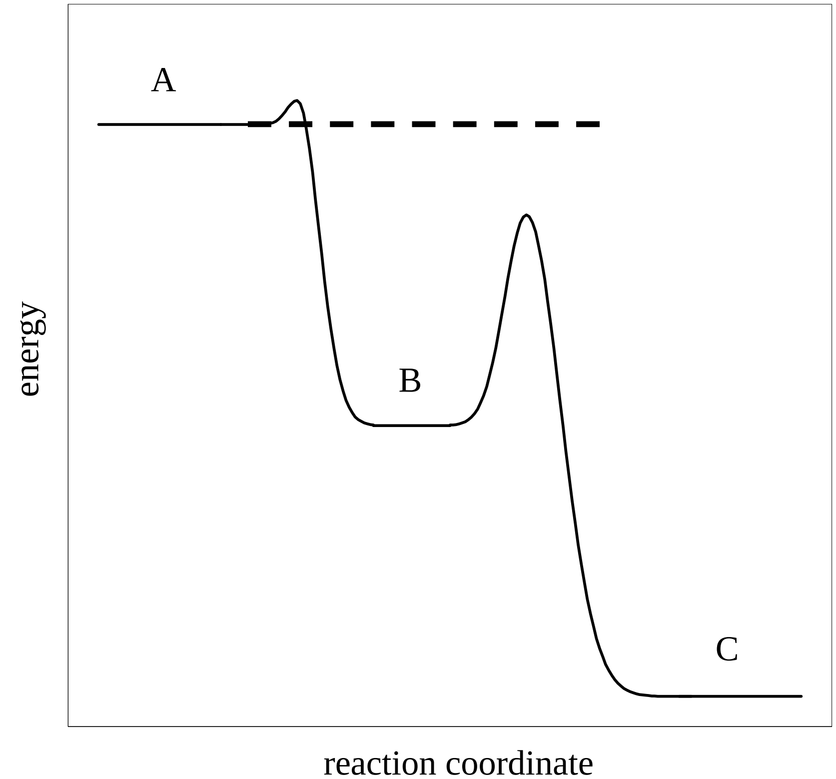
large small small

Criterion for the Pre-equilibrium Approximation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C \quad \text{with} \quad k_1 + k_{-1} \gg k_2$$

rate for A $\leftrightarrow$ B » rate for B $\rightarrow$ C





$k_1 + k_{-1} \gg k_2$

small large small

$k_1 + k_{-1} \gg k_2$

large very small small

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{C}$$

Criterion for the Pre-equilibrium Approximation?

$$\text{rate for A} \leftrightarrow \text{B} \gg \text{rate for B} \leftrightarrow \text{C}$$

$$k_1 + k_{-1} \gg k_2 + k_{-2}$$

$\underline{\textit{at least one}}$ of these $\gg$ $\underline{\textit{both}}$ of these

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{C}$$

Criterion for the Steady-State Approximation?

rate B is consumed » rate B is created

$$k_{-1} + k_2 \gg k_1 + k_{-2}$$

at least one of these » *both* of these