

L1: STEADY STATE APPROXIMATION

P1: INTRODUCTION TO KINETICS

Steady state Approximation (SSA) can turn a complex mechanism into a very simple equation for the rate formation of a product. Take



5 O_2 molecules don't just suddenly collide w/ a molecule of propane \rightarrow mechanism is made up of smaller intermediate steps.

Consider elementary step



$$\text{Rate of Elementary Step} = \frac{d[\text{C}]}{dt} = k[\text{A}][\text{B}], \quad k, t > 0$$

* orders in rate equation = coefficients in balanced reactions

ONLY when elementary step!

Arrhenius Equation $k = A e^{\frac{-E_a}{RT}}$

Then $k_1 = A e^{-E_a/RT_1}$ and $k_2 = A e^{-E_a/RT_2}$

(t = time
 T = temperature)

$$\ln k_1 = \ln A + \left(\frac{-E_a}{RT_1}\right) \quad \text{and} \quad \ln k_2 = \ln A + \left(\frac{-E_a}{RT_2}\right)$$

$$\ln A = \ln k_1 + \frac{E_a}{RT_1} \quad \text{and} \quad \ln A = \ln k_2 + \frac{E_a}{RT_2}$$

$$R = 8.314 \frac{\text{J}}{\text{mol K}}$$

$$\ln k_1 + \frac{E_a}{RT_1} = \ln k_2 + \frac{E_a}{RT_2}$$

$$\frac{E_a}{RT_1} - \frac{E_a}{RT_2} = \ln k_2 - \ln k_1$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}(T_2 - T_1)$$

A assumed to be temperature independent over (T_1, T_2)

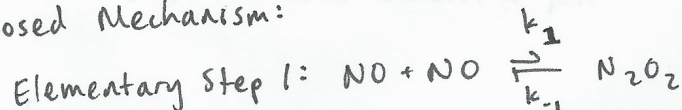
P2: STEADY STATE APPROXIMATION

Purpose: to identify rate law even when there is no obvious rate-limiting step.

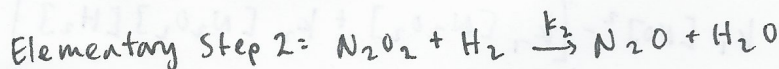
ex.



Proposed Mechanism:



k_1, k_{-1}, k_2



= rate constants

Derive a rate law for the formation of N_2O .

Which step is rate-limiting?

Case 1: Step 1 is RDS $\rightarrow \frac{d[N_2O]}{dt} = k_1 [NO]^2$

Rate is determined by how fast N_2O_2 intermediate can be produced.

Why is $[NO]$ squared in the rate law?

For every moment in time, there are $\binom{n}{2} = \frac{n(n-1)}{2}$ collisions possible

$$\lim_{n \rightarrow \infty} \frac{n(n-1)}{2} \approx \frac{1}{2} \lim_{n \rightarrow \infty} n^2 \text{ for sufficiently large } n$$

\therefore rate proportional to $n^2 = [NO]^2$

Case 2: Step 2 is RDS + Step 1 in rapid equilibrium $\rightarrow k_2 [N_2O_2][H_2] = \frac{d[N_2O]}{dt}$

Rewrite in terms of $[NO]$ and $[H_2]$ since N_2O_2 is an intermediate.

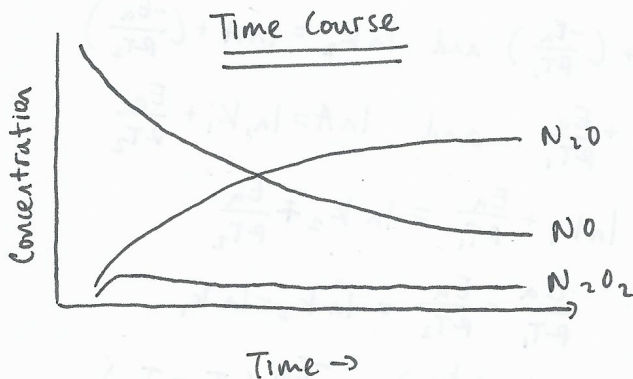
Since Step 1 is in equilibrium,

$$k_1 [NO]^2 = k_{-1} [N_2O_2] \quad (k_1 \neq k_{-1}^{-1})$$

$$[N_2O_2] = \frac{k_1}{k_{-1}} [NO]^2$$

$$\therefore \frac{d[N_2O]}{dt} = \frac{k_2 k_1}{k_{-1}} [NO]^2 [H_2]$$

Two cases have two rate laws \rightarrow combine them using SSA to approximate rate law.



SSA: $\frac{d[\text{intermediate}]}{dt} \approx 0 \rightarrow$ any intermediate produced is almost immediately consumed

$$\text{Net Rate of Formation of } N_2O_2 = \left(\text{Production Rate of } N_2O_2 \right) - \left(\text{Consumption Rate of } N_2O_2 \right) \approx 0$$

Step 1 Forward: produces N_2O_2

Step 1 Reverse: consumes N_2O_2

Step 2 Forward: consumes N_2O_2

So, we have

$$k_1 [NO]^2 - [k_{-1} [N_2O_2] + k_2 [N_2O_2][H_2]] = 0$$

$$k_1 [NO]^2 = [N_2O_2] (k_{-1} + k_2 [H_2])$$

$$[N_2O_2] = \frac{k_1 [NO]^2}{k_{-1} + k_2 [H_2]}$$

Plug back into $\frac{d[N_2O]}{dt} = k_2 [N_2O_2] [H_2]$

$$\boxed{\frac{d[N_2O]}{dt} = \frac{k_1 k_2 [NO]^2 [H_2]}{k_{-1} + k_2 [H_2]}}$$

Suppose Step 1 (For., Rev.) is very slow. ($k_1, k_{-1} \ll k_2$)

Then $k_{-1} + k_2 [H_2] \approx k_2 [H_2]$

You CANNOT cancel k_1 from numerator since it is multiplication and you don't know how much smaller k_1 is than k_2 .

Then $\frac{d[N_2O]}{dt} \approx \frac{k_1 k_2 [NO]^2 [H_2]}{k_2 [H_2]} = k_1 [NO]^2$

↳ same as case 1!

Suppose Step 2 is very slow ($k_2 \ll k_1, k_{-1}$)

Then $k_{-1} + k_2 [H_2] \approx k_{-1}$

↳ same as case 2!

$$\frac{d[N_2O]}{dt} \approx \frac{k_1 k_2 [NO]^2 [H_2]}{k_{-1}} = \frac{k_2 k_1}{k_{-1}} [NO]^2 [H_2]$$

SSA interpolates b/w two extremes → it's a far more powerful + general approach to kinetics, as it doesn't matter which step is slow.

Also, notice,

$$\frac{1}{\frac{d[N_2O]}{dt}} = \frac{1}{k_1 [NO]^2} + \frac{1}{\frac{k_2 k_1}{k_{-1}} [NO] [H_2]}$$

The steady state result is the harmonic sum of the rates obtained by assuming each step was slow.

Steady State Summary:

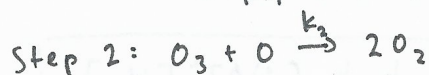
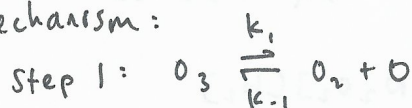
1. Write a rate law for intermediates if necessary.
2. Write a steady state equation for your intermediates by considering rates of production + consumption.
3. Use the equations to eliminate intermediates from the rate law.

P3: CRANKING IT UP

ex. consider the depletion of atmospheric ozone:



Proposed mechanism:



Derive $\frac{-d[O_3]}{dt}$. Assume steady state for all intermediates.

$$\frac{-d[O_3]}{dt} = \left(\begin{array}{c} \text{Rate of Decomposition} \\ \text{of } O_3 \end{array} \right) - \left(\begin{array}{c} \text{Rate of Production} \\ \text{of } O_3 \end{array} \right)$$

take notes on signs!

$$= k_1[O_3] + k_2[O_3][O] - k_{-1}[O_2][O]$$

[O] is an intermediate. Get rid of it using SSA.

$$\frac{d[O]}{dt} = \left(\begin{array}{c} \text{Rate of Production} \\ \text{of } O \end{array} \right) - \left(\begin{array}{c} \text{Rate of Consumption} \\ \text{of } O \end{array} \right)$$

$$\frac{d[O]}{dt} = k_1[O_3] - (k_{-1}[O_2][O] + k_2[O_3][O]) = 0$$

$$[O] (k_{-1}[O_2] + k_2[O_3]) = k_1[O_3]$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \rightarrow \text{Plug into expression for } \frac{-d[O_3]}{dt}$$

$$\frac{-d[O_3]}{dt} = k_1[O_3] + k_2[O_3][O] - k_{-1}[O_2][O]$$

$$= k_1[O_3] + [O] (k_2[O_3] - k_{-1}[O_2])$$

$$= k_1[O_3] + \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} (k_2[O_3] - k_{-1}[O_2])$$

$$= k_1[O_3] \left(\frac{k_{-1}[O_2] + k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]} \right) + \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} (k_2[O_3] - k_{-1}[O_2])$$

$$= \frac{k_1 k_{-1} [O_3] [O_2] + k_1 k_2 [O_3]^2 + k_1 k_2 [O_3]^2 - k_1 k_{-1} [O_3] [O_2]}{k_{-1} [O_2] + k_2 [O_3]}$$

$$\boxed{\frac{-d[O_3]}{dt} = \frac{2k_1 k_2 [O_3]^2}{k_{-1} [O_2] + k_2 [O_3]}}$$

Note that this rate law doesn't have any integer orders if you try to put in the form $\frac{-d[O_3]}{dt} = k [O_2]^m [O_3]^n$

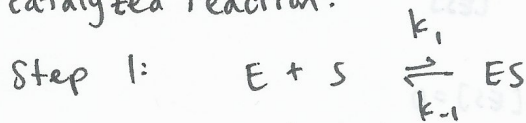
$[O_2]$ is in the denominator $\rightarrow O_2$ acts as an inhibitor of ozone depletion. As O_2 builds up, it competes w/ O_3 in looking for free oxygen atoms to bind with.

Also, since
$$\frac{-d[O_2]}{2 dt} = \frac{d[O_3]}{3 dt}$$

$$\frac{d[O_2]}{dt} = \frac{3 k_1 k_2 [O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$$

P4: ENZYME KINETICS - MICHAELIS-MENTEN EQUATION

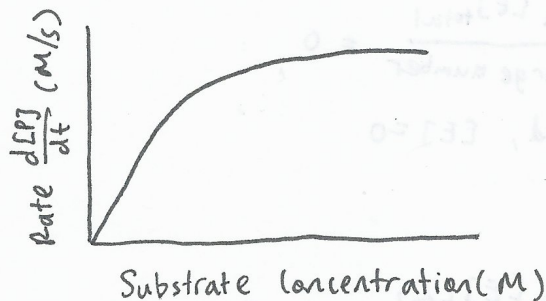
Basic enzyme-catalyzed reaction:



Enzyme E + Substrate S form Enzyme-Substrate complex (ES)



Enzyme converts substrate into product



1. $\frac{d[P]}{dt}$ eventually plateaus as active sites are saturated.
2. $\frac{d[P]}{dt}$ is linear when substrate concentration is small.

GOAL: DERIVE RATE LAW FOR FORMATION OF P

$$\begin{aligned} \frac{d[P]}{dt} &= \left(\begin{array}{c} \text{Net formation rate} \\ \text{of P} \end{array} \right) - \left(\begin{array}{c} \text{Net consumption rate} \\ \text{of P} \end{array} \right) \\ &= k_2 [ES] - 0 = k_2 [ES] \end{aligned}$$

We don't know $[E]$ or $[ES]$ at any given time because we don't know exactly how many free enzymes and how many substrate-bound enzymes there are. We only know $[E]_{\text{TOTAL}}$ because that's the amount we added to the reaction.

$$[E]_{\text{total}} = [E] + [ES]$$

$$\frac{[E]_{\text{total}}}{[E] + [ES]} = 1$$

$$\frac{d[CP]}{dt} = k_2 [ES] \cdot 1 = k_2 [ES] \frac{[E]_{\text{total}}}{[E] + [ES]}$$

$$= \frac{k_2 [E]_{\text{total}}}{\frac{[E]}{[ES]} + 1}$$

Since k_2 , $[E]_{\text{total}}$, and 1 are all constants,

$$\frac{d[CP]}{dt} \propto \frac{1}{\frac{[E]}{[ES]}}$$

When all enzyme is free, $[ES] = 0$

$$\lim_{[ES] \rightarrow 0^+} \frac{[E]}{[ES]} \rightarrow \infty$$

$$\text{Hence, } \frac{d[CP]}{dt} = \frac{k_2 [E]_{\text{total}}}{\text{large number}} = 0$$

When all enzyme is bound, $[E] = 0$

$$\frac{[E]}{[ES]} = 0$$

$$\text{Hence, } \frac{d[CP]}{dt} = \frac{k_2 [E]_{\text{total}}}{0 + 1} = k_2 [E]_{\text{total}}$$

SSA for $[ES]$ intermediate:

$$\frac{d[ES]}{dt} = 0 = \left(\text{Net production rate of ES} \right) - \left(\text{Net consumption rate of ES} \right)$$

$$0 = k_1 [E][S] - k_{-1} [ES] - k_2 [ES] = 0$$

$$[ES](k_{-1} + k_2) = k_1 [E][S]$$

$$\frac{[E]}{[ES]} = \frac{k_{-1} + k_2}{k_1 [S]}$$

↑ plug this into rate law obtained earlier.

$$\begin{aligned} \frac{d[P]}{dt} &= \frac{k_2 [E]_{\text{total}}}{1 + \frac{[E]}{[ES]}} = \frac{k_2 [E]_{\text{total}}}{1 + \frac{k_{-1} + k_2}{k_1 [S]}} \cdot \frac{[S]}{[S]} \\ &= \frac{k_2 [E]_{\text{total}} [S]}{[S] + \frac{k_{-1} + k_2}{k_1}} \end{aligned}$$

We define $K_m = \frac{k_{-1} + k_2}{k_1}$, where K_m is the "Michaelis constant".

We have also seen that maximum rate of product

formation is $\frac{d[P]}{dt} = k_2 [E]_{\text{total}}$ (all enzymes substrate bound)

So, we refer to $k_2 [E]_{\text{total}} = V_{\text{max}}$

$$\therefore \boxed{\text{Michaelis-Menten Equation: } \frac{d[P]}{dt} = \frac{V_{\text{max}} [S]}{[S] + K_m}}$$

At low substrate concentration, $[S] \ll K_m$, so

$$\frac{d[P]}{dt} \approx \frac{V_{\text{max}} [S]}{K_m} \rightarrow \text{linear relationship}$$

At high substrate concentration, $[S] \gg K_m$, so

$$\frac{d[P]}{dt} \approx \frac{V_{\text{max}} [S]}{[S]} = V_{\text{max}}$$

$$\lim_{[S] \rightarrow \infty} \frac{d[P]}{dt} = V_{\text{max}}$$

$$\text{When } [S] = K_m, \frac{d[P]}{dt} = \frac{V_{\text{max}} [S]}{2[S]} = \frac{1}{2} V_{\text{max}}$$

K_m = substrate concentration at which enzyme is operating at half of its maximum rate

END