

Mechanisms + Reaction Networks

How is it that a 1st order reaction happens at all? What gives the umph to push over the top?



Lindemann-Einhsiedel model

- 1 $A + M \xrightarrow{k_1} A^* + M$ activation
- 1 $A^* + M \xrightarrow{k_{-1}} A + M$ deactivation
- 2 $A^* \rightarrow [I] \rightarrow \text{products}$ reaction

$$\begin{aligned}r_A &= -r_1 + r_{-1} \\&\quad - k_1 C_A C_M + k_{-1} C_{A^*} C_M\end{aligned}$$

$$\begin{aligned}r_{A^*} &= r_1 - r_{-1} - r_2 \\&= k_1 C_A C_M - k_{-1} C_{A^*} C_M - k_2 C_{A^*}\end{aligned}$$

$$\begin{aligned}r_p &= r_2 \\&= k_2 C_{A^*}\end{aligned}$$

Could write differential equations & solve all of these simultaneously.

But, if C_{A*} is small & \sim invariant, might be useful to approximate

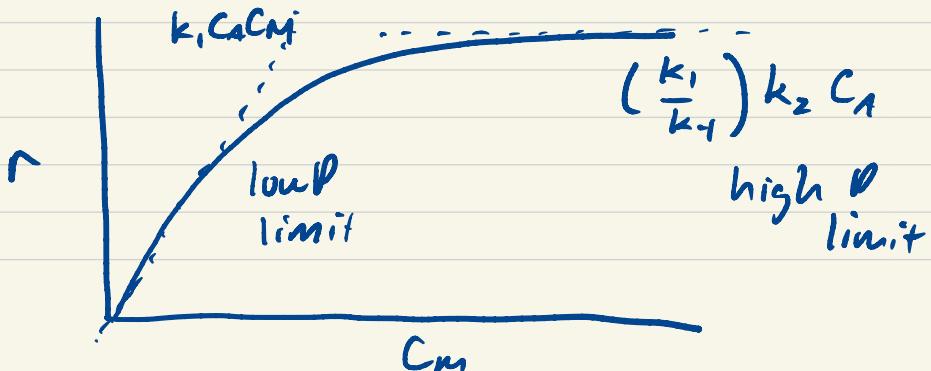
Suppose $r_{A*} \approx 0$, then

$$C_{A*} \approx \frac{k_1 C_A C_m}{k_1 C_m + k_2}$$

Can then write

$$r_p = -r_A = \frac{k_1 k_2 C_A C_m}{k_1 C_m + k_2}$$

example of quasi steady state approx.
(or pseudo)



Exhibits first order behavior in "high" P , limit, plenty of collisions to excite/de-excite & rate "limited" by k_2

Second order in low P , or "fall-off" region. Rate limited by activating collisions.

Typical behavior of gas-phase reactions & our first example of simplifying a reaction network.

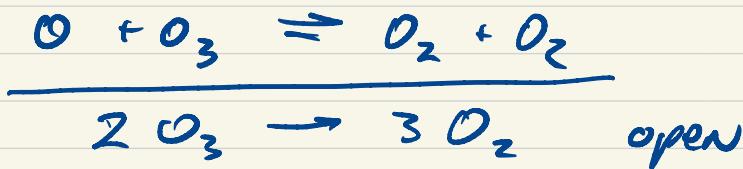
Illustrates why simplifications are often helpful.

Recall our postulates

1. reactions occur through a sequence of elementary steps
2. observed reactions involve a linear combination of elementary steps
3. elementary steps have a distinct molecularity reflective of how they occur physically
4. elementary steps may create intermediates that are produced and consumed through progression through steps
Often called "active centers"

Two familys of rxn networks

"Open" - sequence of steps from reactants to products that consume every intermediate that is created



Or even simpler



"Closed" - sequence in which some intermediates persist



$\text{Cl}\cdot$ is not generated by the cycle

would be initiated e.g. by



Once formed, many cycles possible
before terminated by



Example of catalysis by $\text{Cl}\cdot$:
 O_3 depletion...

Rate will depend on concentration
of $\text{Cl}\cdot$, controlled externally

One common approximation
is irreversibility. If eg

$$r_1 \gg r_{-1}$$

$$\frac{dC_{CO_3}}{dt} \approx -k_1 C_{CO_3} C_{CO_2}$$

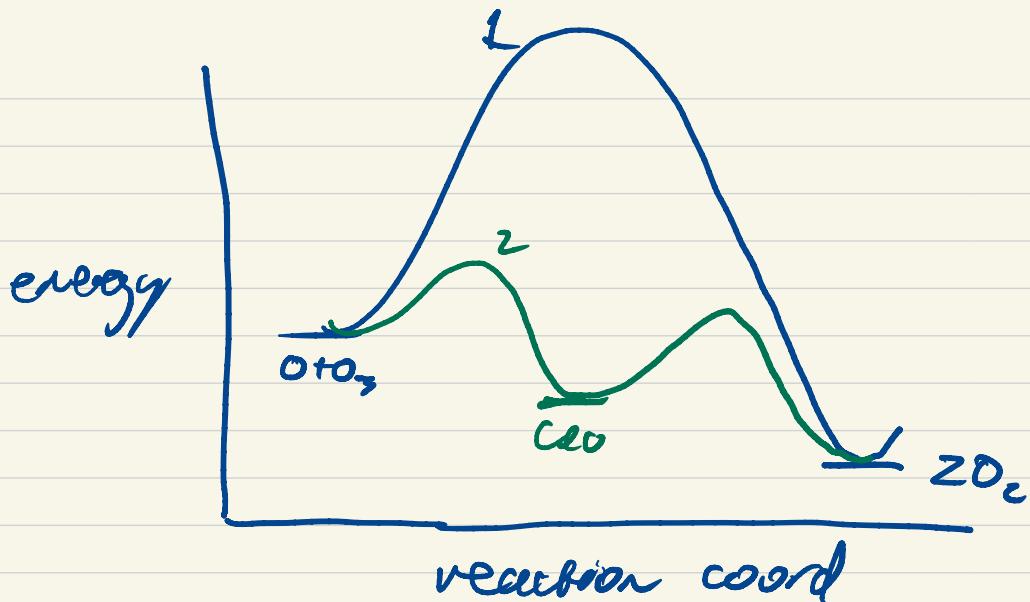
Why? Relative rate constants
" concentrations

Similarly

$$\frac{dC_O}{dt} \approx -k_2 C_{CO_2} C_O$$

$$\frac{dC_{CO_2}}{dt} = k_1 C_{CO_3} C_{CO_2} - k_2 C_{CO_2} C_O$$

Next simplification motivated by an
analytical model:



$$r_1 \gg r_2$$

Can write mass balances on all species.

$$\frac{dC_{O_3}}{dt} = -k_1 C_{CeO} C_{O_3} + k_{-1} C_{CeO} C_{O_3}$$

$$\frac{dC_O}{dt} = -k_2 C_{CeO} C_O - k_{-2} C_{CeO} C_{O_2}$$

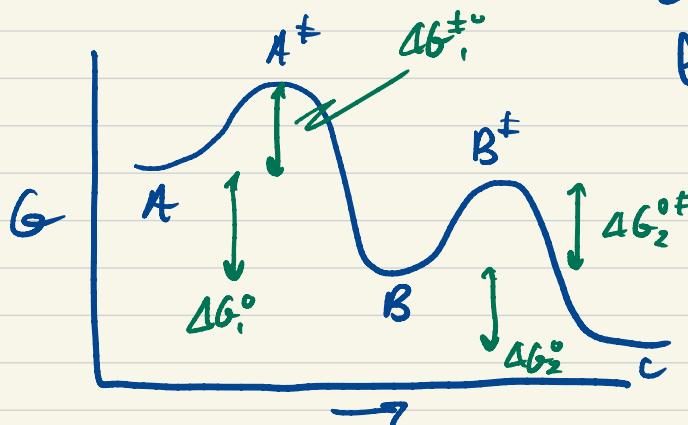
$$\frac{dC_{CeO}}{dt} = r_1 - r_{-1} - r_2 + r_{-2}$$

In principle all integrable, but insightful to simplify

Simplest possible reaction network

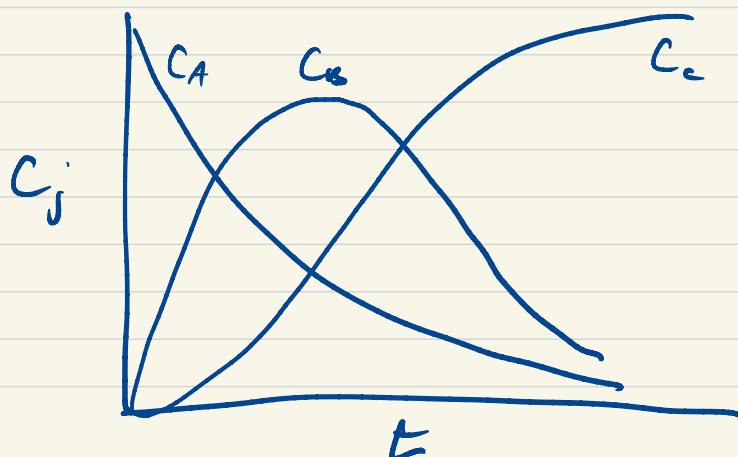


concept of
free energy
surface ..

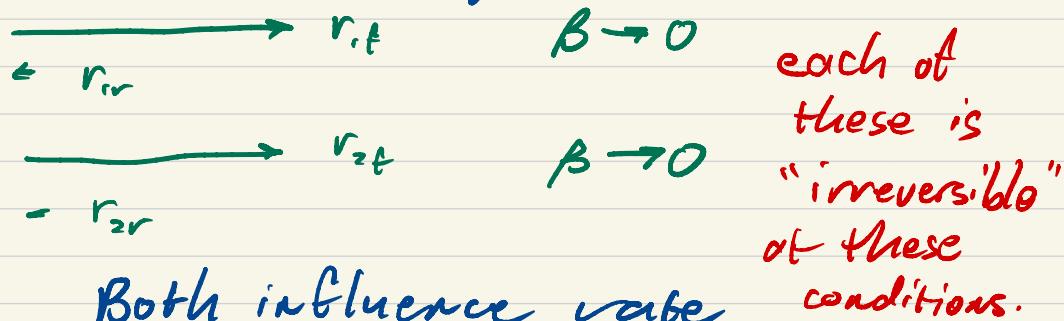


Look at $A \rightleftharpoons B \rightleftharpoons C$ plot w/ $k_1/k_{-1} = k_2/k_{-2}$
 $(125, -75) (125, -75)$ $\Delta G_1^\circ = \Delta G_2^\circ$

Integrate numerically:



can observe species rates
each reaction step has a rate



Both influence rate
instantaneous selectivity

$$S_j = \frac{r_j}{\sum r_j}$$

overall selectivity

$$S_j = \frac{c_j}{\sum c_j}$$

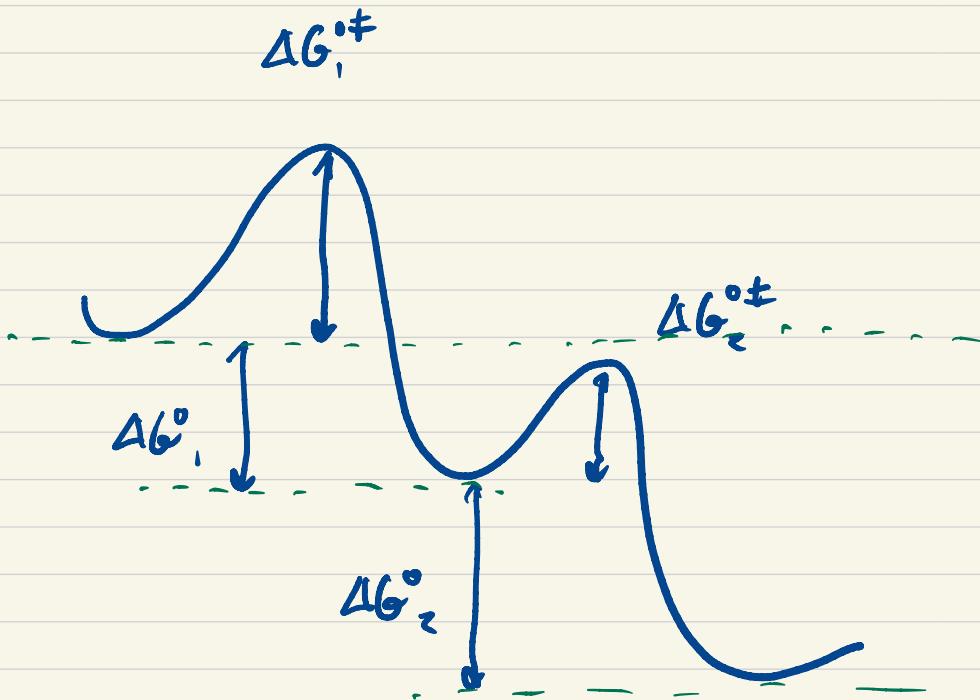
Yield

$$Y_j = \frac{c_j}{c_{j0}}$$

Values depend on how long
we run reaction

From a mechanistic perspective, often interested in which steps influence/control rate.

Concept of rate determining step.



Degree of rate control

$$\left(\frac{\partial \ln r}{\partial G_i} \right)$$

Now let ΔG_1 , ΔG_2 get smaller,
 C_c becomes Equilibrium limited

Now let

(125, -75) (100, -75)

Motivates PSSR

Useful to look @ rxn network
in irreversible limit, analytically
solvable:



$$\frac{dC_A}{dt} = -k_1 C_A \quad \text{1st order}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

$$C_A = C_{A0} e^{-k_1 t}$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

1st order inhomogeneous

homogeneous

$$C_B = \alpha e^{-k_2 t}$$

particular

$$C_B = \beta e^{-k_1 t} \quad \downarrow \text{substitute}$$

$$-k_1 \beta e^{-k_1 t} + k_2 \beta e^{-k_1 t} = k_1 C_{A0} e^{-k_1 t}$$

$$\beta = \frac{k_1}{k_2 - k_1} C_{A0}$$

Combine

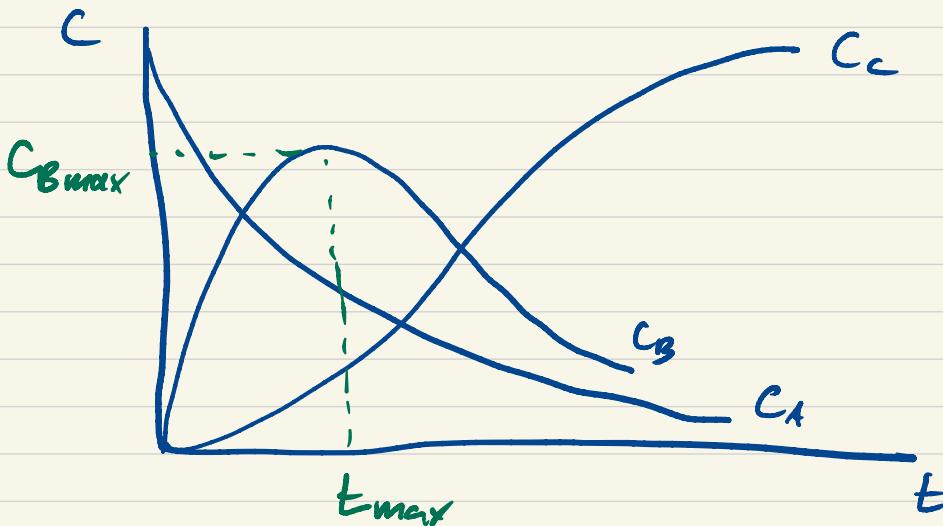
$$C_B = \alpha e^{-k_2 t} + \frac{k_1}{k_2 - k_1} C_{A0} e^{-k_1 t}$$

$$C_B(t=0) = 0 \quad \text{boundary condition}$$

$$0 = \alpha + \frac{k_2}{k_2 - k_1} C_{A0}$$

$$\Rightarrow C_B(t) = C_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$C_C(t) = C_{A0} - C_B - C_A$$



Characteristic time t_{\max} determined by k_1 & k_2

Characteristic time t_{max} determined by k_1 & k_2

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$= k_1 C_{A0} e^{-k_1 t} - k_2 C_{B0} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$= 0 \quad \text{independent of } C_{B0}!$$

$$\Rightarrow t_{max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$C_B(t_{max}) = C_{B0} \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

What happens in limit $k_2 \gg k_1$?

$$C_B(t_{max}) \rightarrow 0 !!$$

B behaves like an intermediate, consumed as fast as created

$$\frac{C_B(t_{max})}{C_{B0}} \rightarrow \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}} \rightarrow \sim 1$$

$$\frac{r_B}{-r_A} = 1 - \frac{k_2}{k_2 - k_1} (1 - e^{-(k_2 - k_1)t})$$

$$k_2 - k_1 = \frac{1}{t_{\max}} \ln \frac{k_2}{k_1}$$

$$\frac{r_B}{-r_A} = \frac{-k_1}{k_2 - k_1} + \frac{k_2}{k_2 - k_1} \cdot \frac{k_2}{k_1} e^{-t/t_{\max}}$$

$$k_2 \gg k_1$$

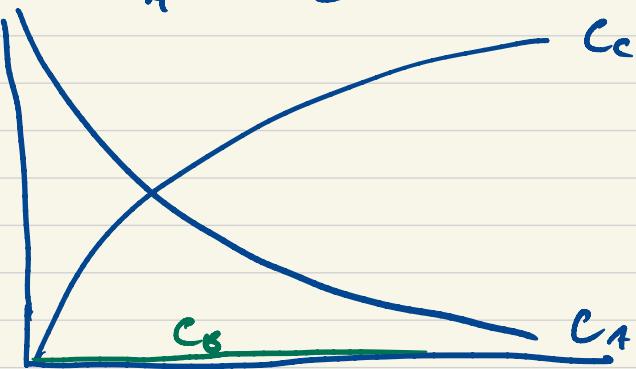
$$\frac{r_B}{-r_A} \approx -\left(\frac{k_1}{k_2}\right) + \frac{k_2}{k_1} e^{-t/t_{\max}}$$

$\frac{t}{t_{\max}}$	$\frac{1 - C_A/C_{A0}}{1.4 \times 10^{-5}}$	$\frac{r_B/-r_A}{0}$
1		
1.1	1.5×10^{-5}	-7.5×10^{-7}
2	2.8×10^{-5}	-1.0×10^{-6}
1000	0.014	"
50000	0.50	"
500000	0.999	"

In the limit $k_2 \gg k_1$, C_B reaches its maximum rapidly, stays at the same value, and to a very good approximation has a net rate

$$r_B = k_1 C_A - k_2 C_B \approx 0$$

$$\Rightarrow -r_A = r_C$$



Basis of pseudo steady state approximation.

$$r_j = \frac{dC_j}{dt} \approx 0 \quad C_j \rightarrow 0$$

B is a reactive intermediate, to be distinguished from a regular intermediate.

Applying the PSSA changes one
diff eq into an algebraic

Go back to

SKIP



PSSA on ClO ...

$$\frac{dC_{ClO}}{dt} = k_1 C_{Cl} C_{O_3} - k_2 C_{ClO} C_0 \approx 0$$

$$\Rightarrow C_{ClO} = \frac{k_1 C_{Cl} C_{O_3}}{k_2 C_0}$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_{Cl} C_{O_3}$$

$$\frac{dC_{O_2}}{dt} = k_2 C_0 \cdot \frac{k_1 C_{Cl} C_{O_3}}{k_2 C_0}$$

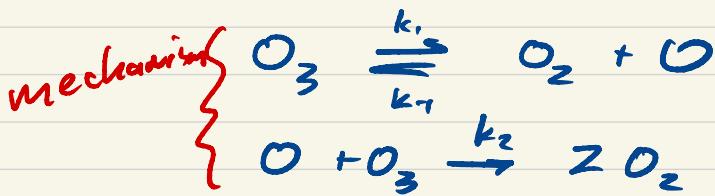
$$= k_1 C_{Cl} C_{O_3}$$

Could recast...

$$C_{Cl} + C_{ClO} = C_{Cl,o}$$

$$C_{Cl,o} - C_{Cl} = \frac{k_1 C_{Cl} C_{O_3}}{k_2 C_0}$$

more interesting



PSSA on O

$$r_O = k_1 C_{\text{O}_3} - k_{-1} C_O C_{\text{O}_2} - k_2 C_O C_{\text{O}_3} = 0$$

$$\Rightarrow C_O = \frac{k_1 C_{\text{O}_3}}{k_{-1} C_{\text{O}_2} + k_2 C_{\text{O}_3}}$$

$$-r_{\text{O}_3} = k_1 C_{\text{O}_3} - (k_{-1} C_{\text{O}_2} + k_2 C_{\text{O}_3}) \cdot \frac{k_1 C_{\text{O}_3}}{k_{-1} C_{\text{O}_2} + k_2 C_{\text{O}_3}}$$

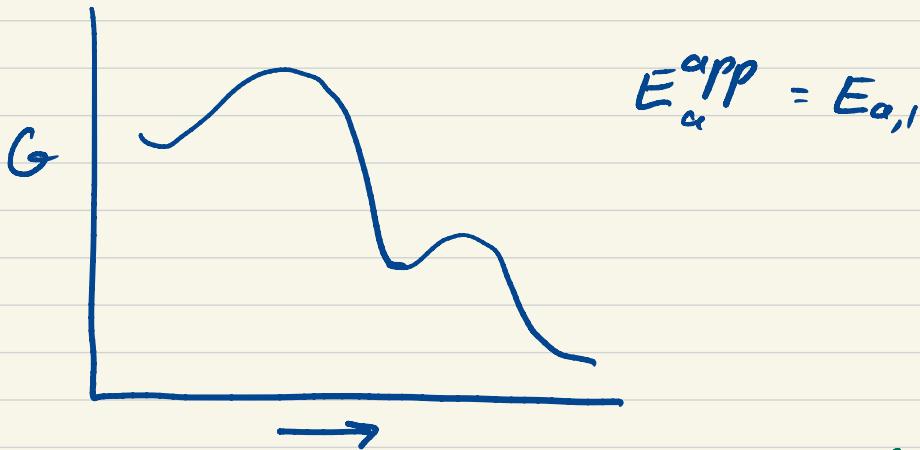
$$\Rightarrow -r_{\text{O}_3} = \frac{2 k_1 k_2 C_{\text{O}_3}^2}{k_{-1} C_{\text{O}_2} + k_2 C_{\text{O}_3}}$$

non-linear in $C_{\text{O}_2} + C_{\text{O}_3} !!$

$$r_2 \gg r_{-1}$$

limit $k_2 C_{O_3} \gg k_{-1} C_{O_2}$

$$-r_{O_3} = 2 k_1 C_{O_3} \quad \text{apparent 1st order}$$



$$r_{\text{net}} = r_f (1 - \beta)$$

$$\begin{array}{c} \longrightarrow r_{1,t} \\ \longleftarrow r_{1,r} \\ \longrightarrow r_{2,t} \end{array} \quad \begin{array}{c} \beta_1 \rightarrow 0 \\ \beta_2 \rightarrow 0 \end{array} \quad \begin{array}{c} \text{vector} \\ \text{representation} \end{array}$$

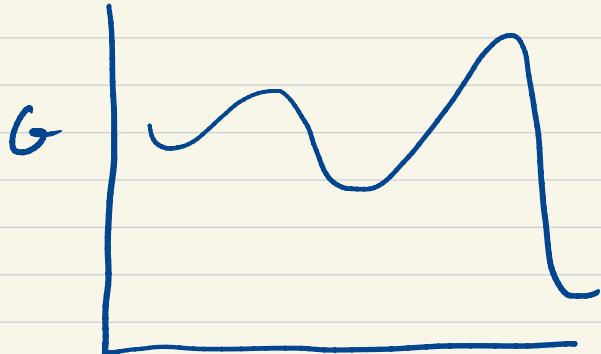
Recall PSSA implies $r_{\text{net},1} = r_{\text{net},2}$

$$\text{Must have } r_{2,t} = r_{1,t} - r_{1,r}$$

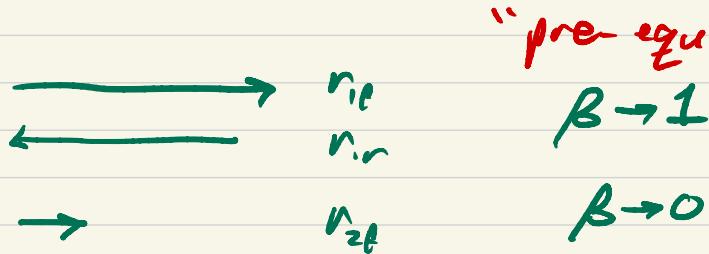
Degree of rate control?

limit $k_2 C_{O_3} \ll k_{-1} C_{CO_2}$

$$-r_{O_3} = 2 \left(\frac{k_1}{k_{-1}} \right) k_2 \frac{C_{O_3}^2}{C_{CO_2}}$$



$$E_a^{app} = \Delta H_f + E_{q,c}$$



In pre-equilibrium, set rate of α step to 0, $r_i = 0$.

Implies reaction occurs on timescale much more rapid than others.

Other mechanism examples



PSSA species

8 independent species

→ 8 diff eqs

PSSA eliminates 3, down to 5

ODEs + 3 algebras

Ethane pyrolysis



$$r_{CH_3} = 2r_1 - r_2 = 0$$

$$r_{C_2H_5} = r_2 - r_3 - r_5 = 0$$

$$r_H = r_3 - r_4 - r_5 = 0$$

∴

$$r_{C_2H_4} = k_3 \left(\frac{k_1}{2k_3} + \sqrt{\left(\frac{k_1}{2k_3} \right)^2 + \frac{k_1 k_4}{k_3 k_5}} \right) C_{C_2H_6}$$

$$\approx k C_{C_2H_6} !!$$

apparent 1st order under conditions
that approximations hold

Convenient: Gram. & design perspective
Reduces parameters to be found.

Polymerization mechanism

$\text{CP}_x \text{Zr-H}$



$$r_i = k_1 C_{\text{MH}} C_e$$

$$r_p = k_2 C_e \sum_i C_{\text{MR}_i}$$

$$r_t = k_3 \sum_i C_{\text{MR}_i}$$

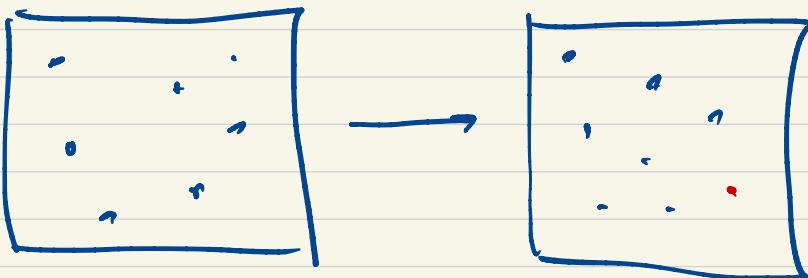
$$\text{At SS. } r_i = r_t$$

$$k_1 C_{\text{MH}} C_e = k_3 \sum_i C_{\text{MR}_i}$$

$$r_p = k_2 \left(\frac{k_1}{k_3} \right) C_{\text{MH}} C_e^2$$

$$\text{DOP} = 1 + \frac{k_2}{k_3} C_e \dots$$

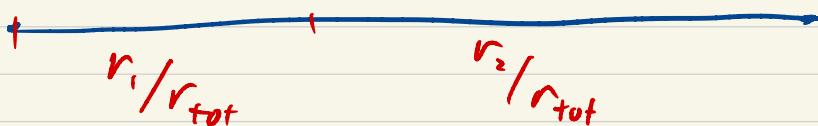
stochastic model



Gillespie model

$$r_i = f(k, N_j)$$

$$r_{\text{tot}} = \sum_i r_i$$



Poisson dist random selection of r

$e^{-r_{\text{tot}} \gamma}$ is probability a rxn has not occurred in time γ ↗

$$\gamma = -\ln(\text{random}) / r_{\text{tot}}$$

power emerges when location as well as concentration determine rates