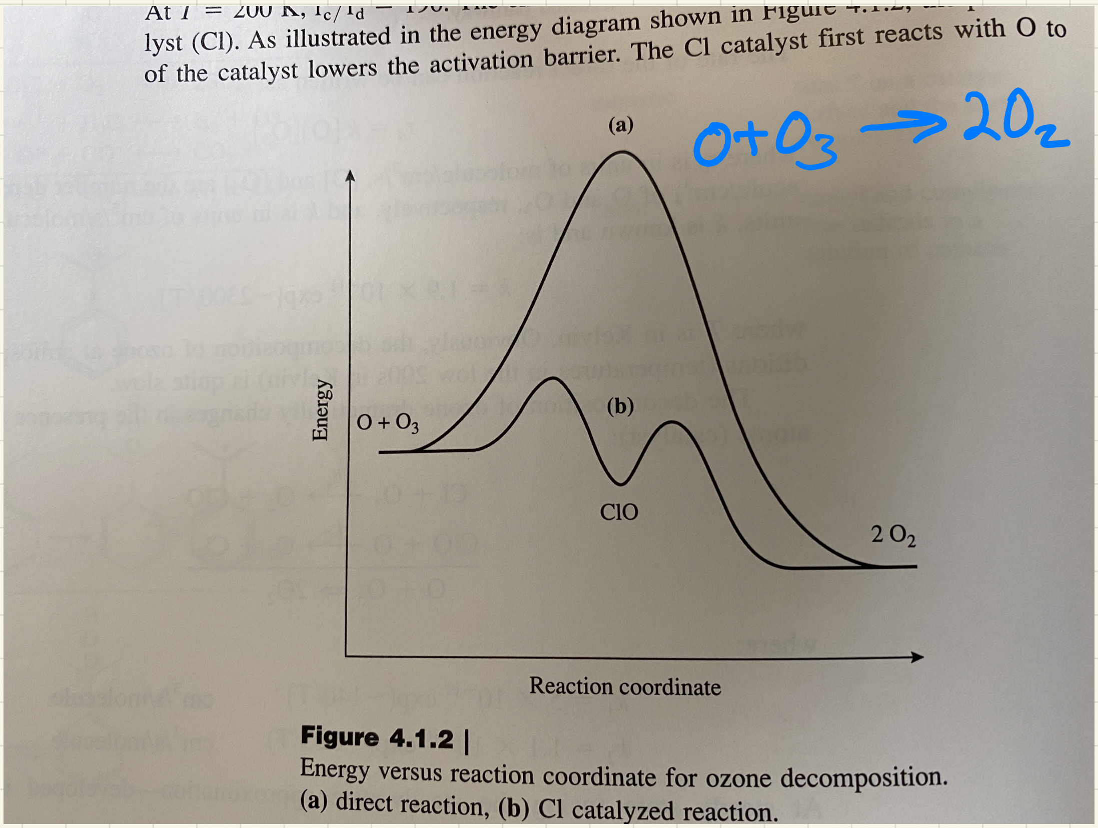
CBE 40445

9/9/20

ANALYSIS OF COMPLEX REACTION SCHEMES . . .

OZONE DECOMPOSITION



At T = 200 K, r_c/r_d = 190.

lyst (Cl). As illustrated in the energy diagram shown in Figure 4.1.2,

of the catalyst lowers the activation barrier. The Cl catalyst first reacts with O to

$O + O_3 \rightarrow 2O_2$

Figure 4.1.2 |
Energy versus reaction coordinate for ozone decomposition. (a) direct reaction, (b) Cl catalyzed reaction.

$r = k[O][O_3]$

$k = 1.9 \times 10^{-11} \exp\left(-\frac{2300}{T}\right)$

"SLOW" !!

IF CHLORINE IS PRESENT...

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$

$$ClO + O \xrightarrow{k_2} O_2 + Cl$$

$$O + O_3 \rightarrow 2O_2$$

$$k_1 = 5 \times 10^{-11} \exp\left(-\frac{140}{T}\right)$$

$$k_2 = 1.1 \times 10^{-10} \exp\left(-\frac{220}{T}\right)$$

$\frac{cm^3}{s \text{ MOLECULE}}$

CAN SHOW . . .

$$r_c = \frac{k_1 k_2 [O][O_3]\left([Cl]+[ClO]\right)}{k_1[O_3] + k_2[O]}$$

BUT $[O] \ll [O_3]$ $\quad k_1 \mathrel{\hat{=}} k_2$

$$r_c = k_2\left([O][Cl]+[ClO]\right)$$

CATALYZED DIRECT $\quad \dfrac{r_c}{r_d} = k_2 \dfrac{\left([Cl]+[ClO]\right)}{k_3[O_3]}$

ALSO $\quad \dfrac{[Cl]+[ClO]}{[O_3]} \sim 10^{-3}$

$$\frac{r_c}{r_d} = \frac{k_2}{k} \times 10^{-3} = 6 \times 10^{-3} \exp\left(\frac{2050}{T}\right)$$

@ T=200K, $\dfrac{r_c}{r_d} = 200$

FINALLY... THE REAL NAME OF THE CHAPTER...

THE STEADY-STATE APPROXIMATION

CONSIDER

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

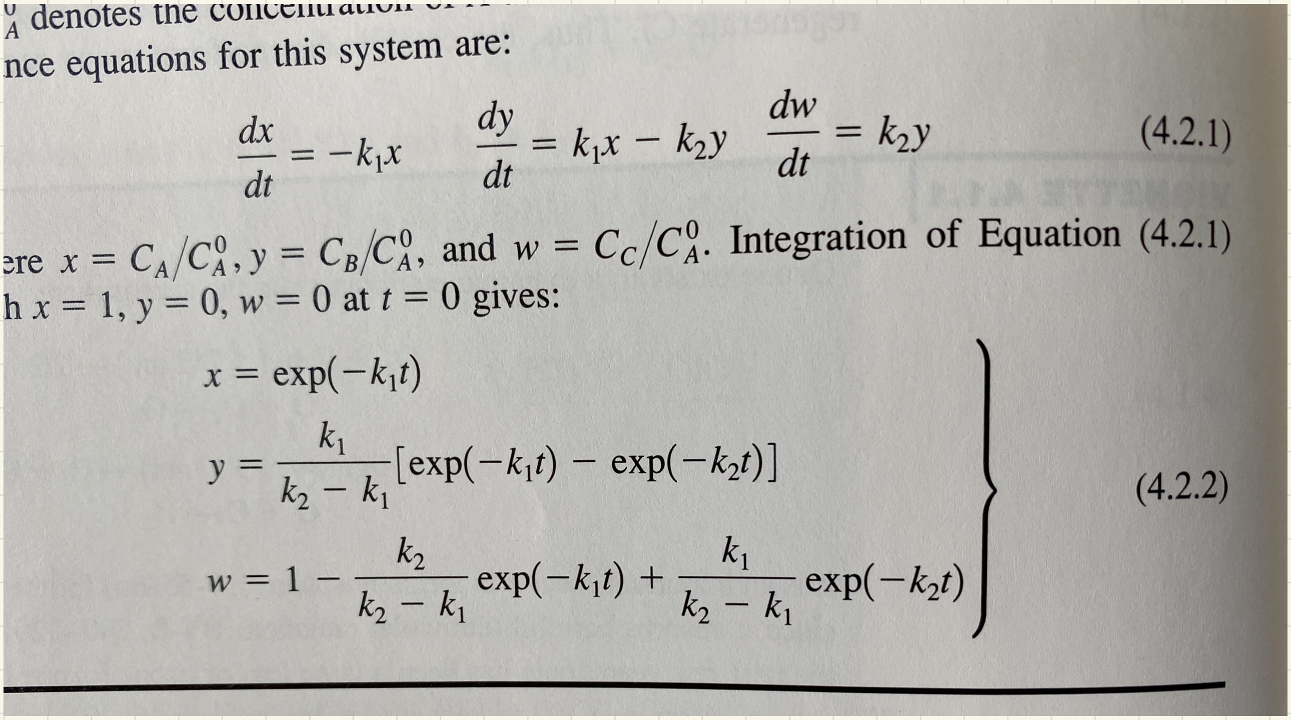
$C_A(t=0) = C_{A0}$, $C_{B0} = 0$, $C_C^0 = 0$

$$x \equiv \frac{C_A}{C_A^0} \qquad y = \frac{C_B}{C_A^0} \qquad w = \frac{C_C}{C_A^0}$$

$$\frac{dx}{dt} = -k_1 x$$

$$\frac{dy}{dt} = k_1 x - k_2 y$$

$$\frac{dw}{dt} = k_2 y$$



^0_A denotes the concentratio

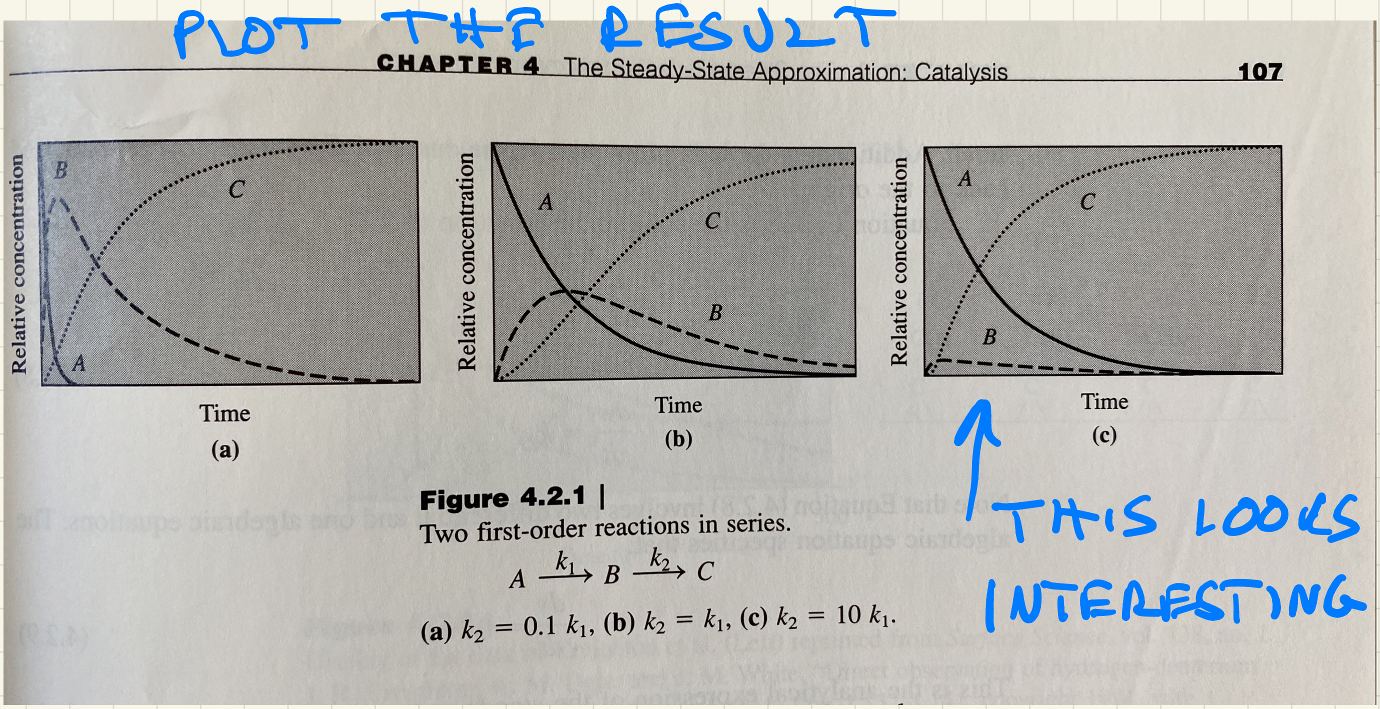
nce equations for this system are:

$$\frac{dx}{dt} = -k_1 x \qquad \frac{dy}{dt} = k_1 x - k_2 y \qquad \frac{dw}{dt} = k_2 y \tag{4.2.1}$$

ere $x = C_A/C_A^0$, $y = C_B/C_A^0$, and $w = C_C/C_A^0$. Integration of Equation (4.2.1)
h $x = 1$, $y = 0$, $w = 0$ at $t = 0$ gives:

$$\left.\begin{aligned} x &= \exp(-k_1 t) \\ y &= \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \\ w &= 1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t) \end{aligned}\right\} \tag{4.2.2}$$

BEING GOOD CHEMICAL ENGINEERS WE PLOT THE RESULT



CHAPTER 4 The Steady-State Approximation: Catalysis **107**

(a) (b) (c)

Figure 4.2.1 |
Two first-order reactions in series.

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

(a) $k_2 = 0.1\ k_1$, (b) $k_2 = k_1$, (c) $k_2 = 10\ k_1$.

THIS LOOKS INTERESTING

NOT MUCH B, AND DOESN'T CHANGE..

$(k_2 >> k_1)$

$$x = \exp(-k_1 t)$$

$$y = \frac{k_1}{k_2} \exp(-k_1 t)$$

$$w = 1 - \exp(-k_1 t)$$

THIS IS THE SOLUTION TO!

$$\frac{dx}{dt} = -k_1 x$$

$$0 = k_1 x - k_2 y$$

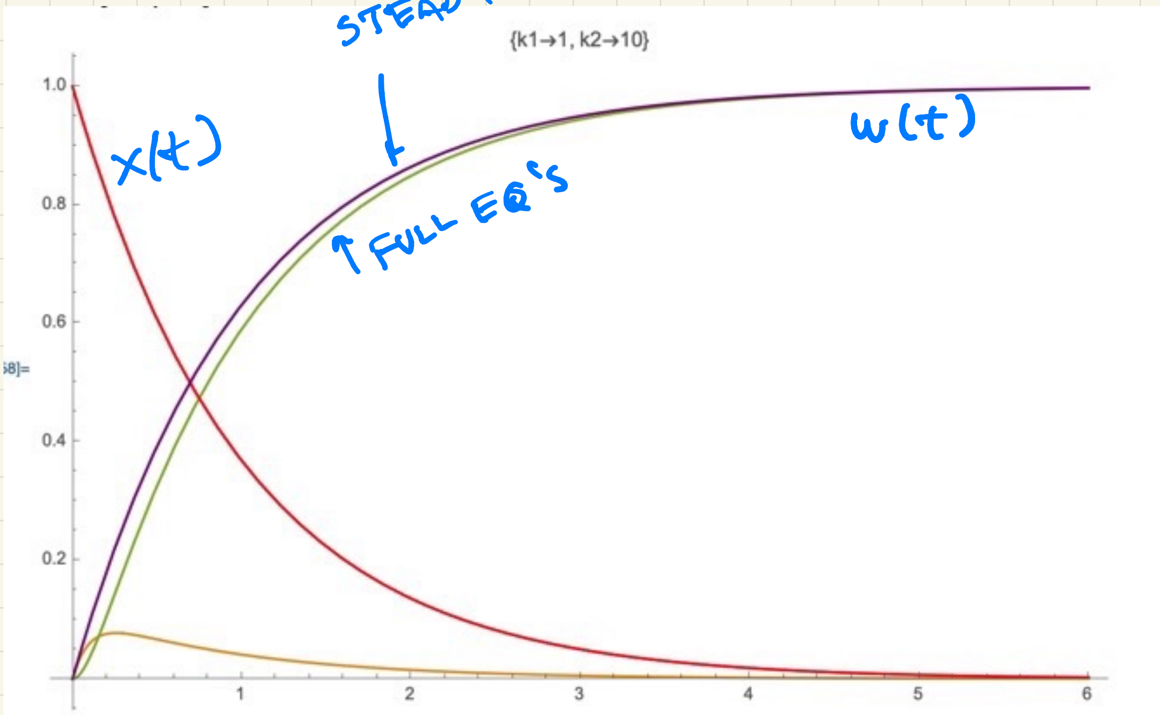
$$\frac{dw}{dt} = k_2 y$$

THUS WE PRESUME!

$$\frac{dy}{dt} = 0$$ "STEADY-STATE" ASSUMPTION.

WE WILL USE ("TRYOUT") THIS SIMPLIFICATION FOR REACTION INTERMEDIATES ...

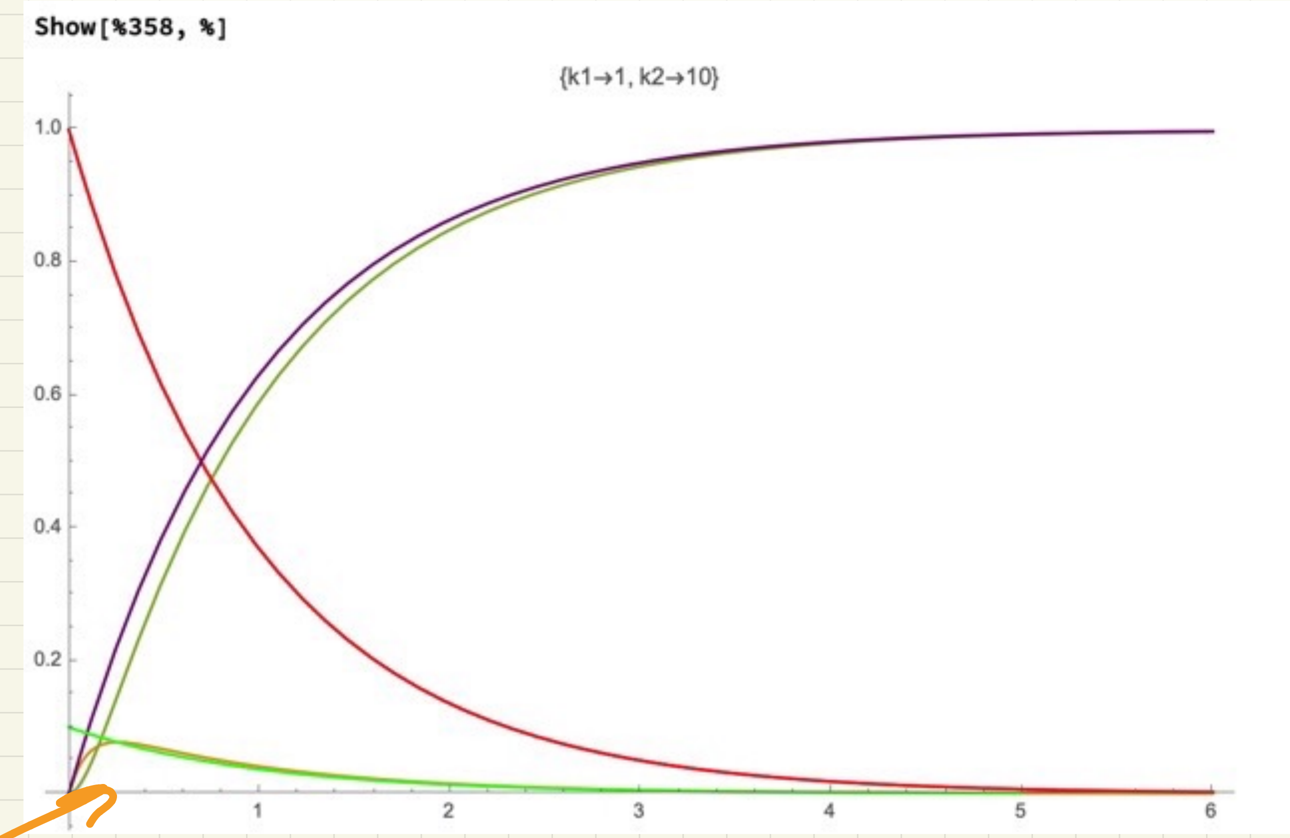
STEADY-STATE APPROXIMATION



$x(t)$

$w(t)$

↑ FULL EQ's



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IF WE INCLUDE $y(t) = \frac{k_1}{k_2} \exp\left(-k_1 t\right)$

CONCLUSION: IF THIS "ASSUMPTION" HELPS TO SIMPLIFY AND "ELUCIDATE" COMPLEX MECHANISMS . . . GO AHEAD & TRY !!

CAVEAT: THERE IS AN INDUCTION TIME: "RELAXATION TIME" WHILE THIS APPROXIMATION DOESN'T WORK BECAUSE THE CONCENTRATION IS BUILDING UP TO THE STEADY-STATE

LET'S TAKE A QUICK LOOK!

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

WE WANT TO CONSIDER THIS REACTION

WITH $\frac{dC_B}{dt} = 0$, $k_2 >> k_1$

STEADY STATE CONCENTRATION

FIRST ALLOW THAT C_B IS NOT AT C_B^*

$$C_B = C_B^*(1+\bar{\varepsilon})$$

THEN

$$\frac{dC_B}{dt} = C_B^*\frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt}$$

FROM REACTION MECHANISM

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

FROM PREVIOUS ANALYSIS THE STEADY STATE OF C_B

$$C_B^* = \frac{k_1}{k_2} C_A$$

$$\Rightarrow \frac{dC_B^*}{dt} = \frac{k_1}{k_2}\frac{dC_A}{dt} = -\frac{k_1^2}{k_2}\dot{C}_A$$

USING $\frac{dC_A}{dt} = -k_1 C_A$

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

NOW FROM ABOVE:

$$\frac{dC_B}{dt} = C_B^*\frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt}$$

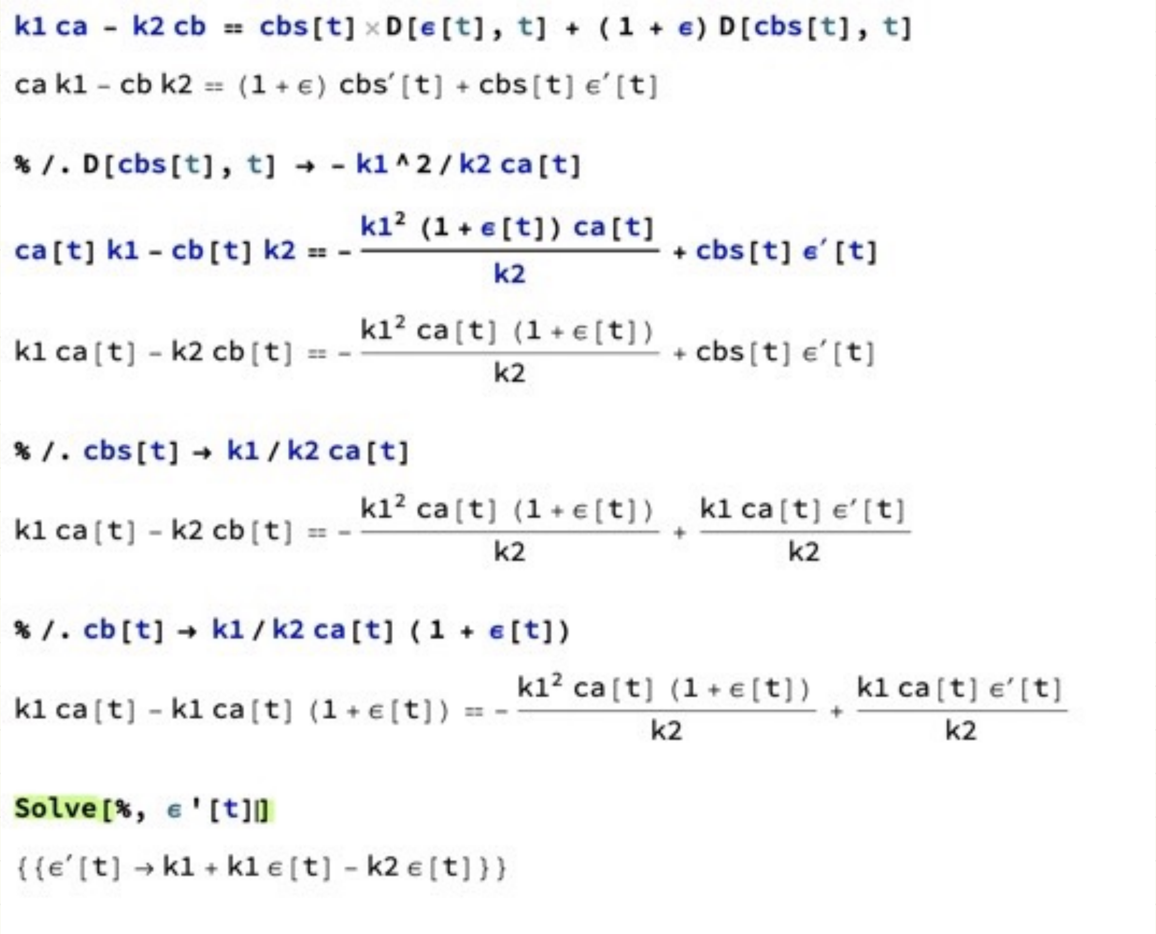
$$C_B^*\frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\frac{dC_B^*}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{k_1 C_A}{k_2}\frac{d\bar{\varepsilon}}{dt} + (1+\bar{\varepsilon})\left(-\frac{k_1^2}{k_2} C_A\right) = k_1 C_A - k_2 C_B$$

$$\Rightarrow \frac{d\bar{\varepsilon}}{dt} + (k_2 - k_1)\bar{\varepsilon} - k_1 = 0$$

$\varepsilon = -1 \quad C_B = 0$

$t = 0$



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k1 ca - k2 cb == cbs[t] × D[ϵ[t], t] + (1 + ϵ) D[cbs[t], t]
```

$$ca\,k1 - cb\,k2 == (1+\epsilon)\,cbs'[t] + cbs[t]\,\epsilon'[t]$$

```
% /. D[cbs[t], t] → - k1 ^ 2 / k2 ca[t]
```

$$ca[t]\,k1 - cb[t]\,k2 == -\frac{k1^2\,(1+\epsilon[t])\,ca[t]}{k2} + cbs[t]\,\epsilon'[t]$$

$$k1\,ca[t] - k2\,cb[t] == -\frac{k1^2\,ca[t]\,(1+\epsilon[t])}{k2} + cbs[t]\,\epsilon'[t]$$

```
% /. cbs[t] → k1 / k2 ca[t]
```

$$k1\,ca[t] - k2\,cb[t] == -\frac{k1^2\,ca[t]\,(1+\epsilon[t])}{k2} + \frac{k1\,ca[t]\,\epsilon'[t]}{k2}$$

```
% /. cb[t] → k1 / k2 ca[t] (1 + ϵ[t])
```

$$k1\,ca[t] - k1\,ca[t]\,(1+\epsilon[t]) == -\frac{k1^2\,ca[t]\,(1+\epsilon[t])}{k2} + \frac{k1\,ca[t]\,\epsilon'[t]}{k2}$$

```
Solve[%, ϵ'[t]]
```

$$\{\{\epsilon'[t] \to k1 + k1\,\epsilon[t] - k2\,\epsilon[t]\}\}$$

$$\varepsilon = -\frac{1}{\overline{K}-1}\left\{\overline{K} - \exp\left((\overline{K}-1)k_2 t\right)\right\}$$

$$K \equiv k_1/k_2 < 1$$

AT SUFFICIENTLY LARGE TIME:

$$\overline{\varepsilon} = \overline{K} \quad .$$

THIS TIME IS OBTAINED FROM:

$$\exp(-k_2 t) \sim \exp(-4)$$

$$t \mathrel{\hat{=}} \frac{4}{k_2}$$

EXAMPLE OF ENZYME CATALYSIS

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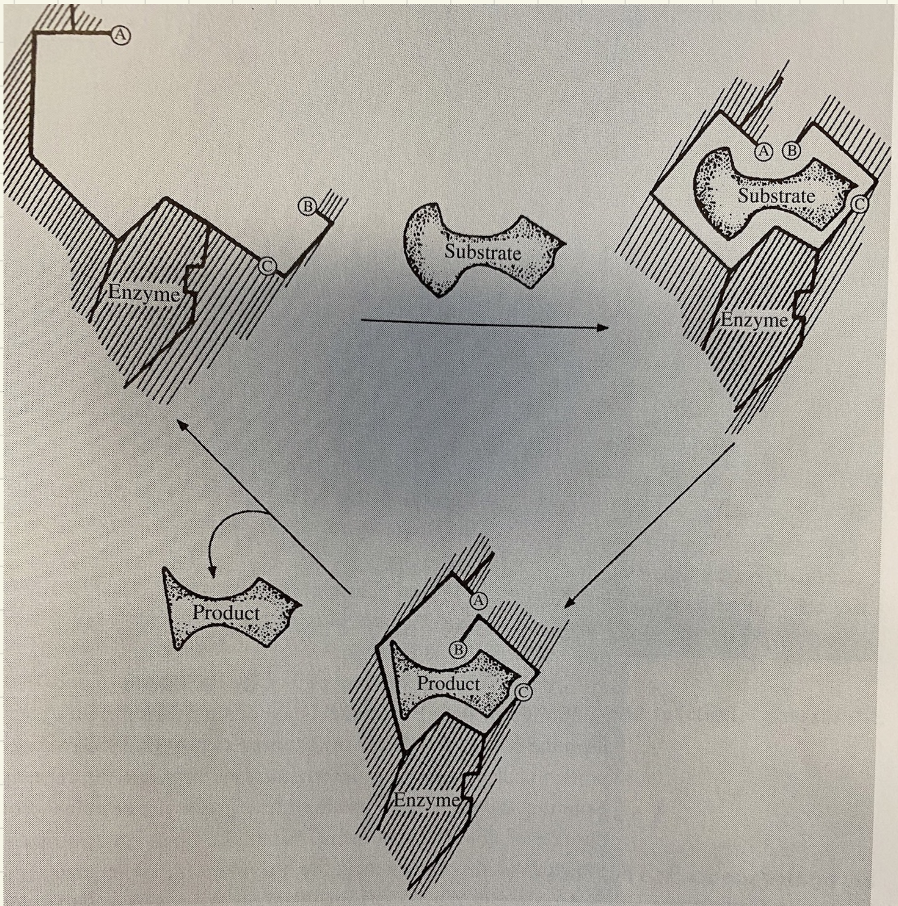
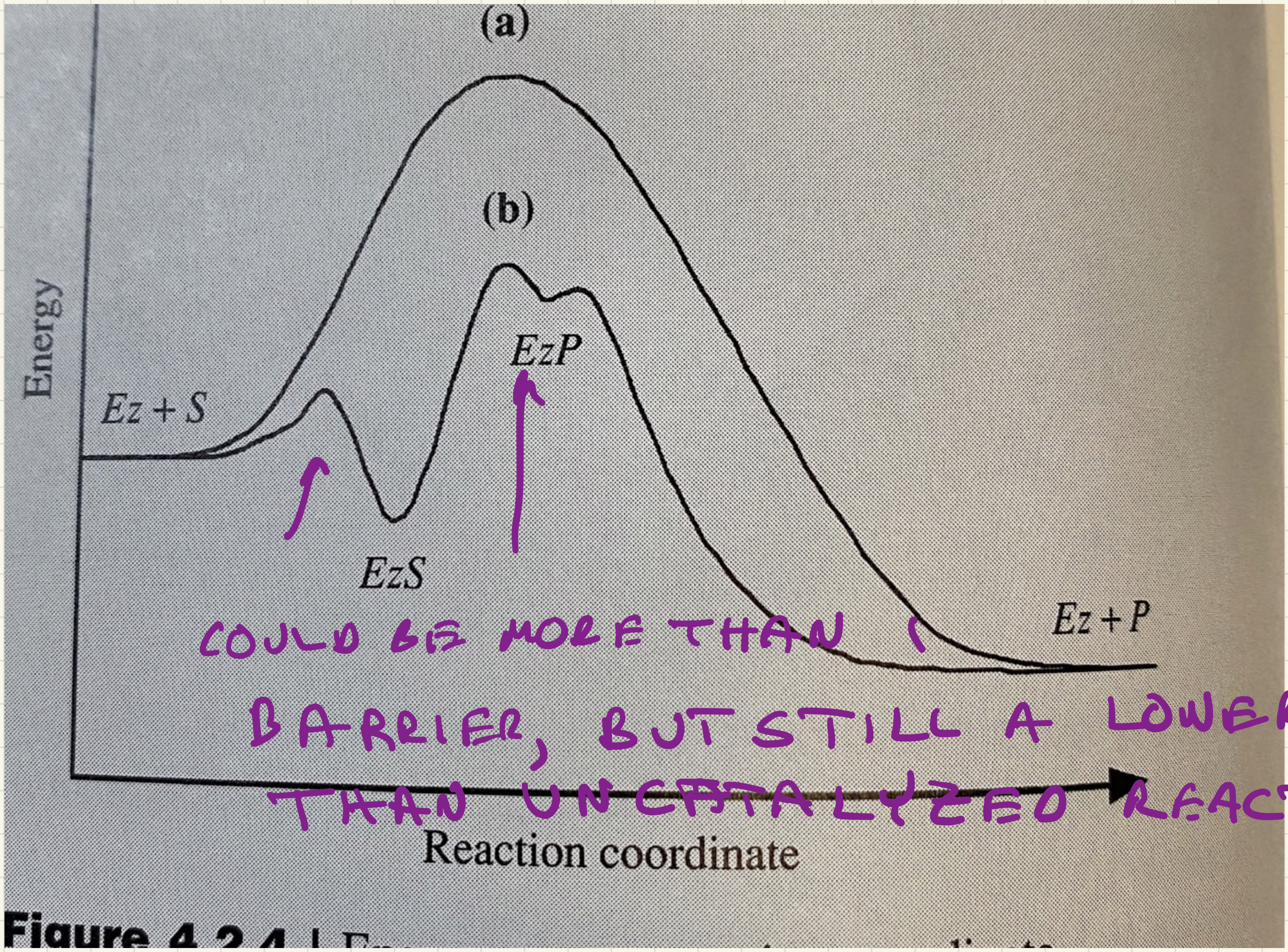


Figure 4.2.3 | Schematic model of the induced fit mechanism for enzyme catalysis. *A*, *B*, and *C* are particular functional groups in the enzyme binding site that must be properly aligned with the bound substrate for reaction to occur. The substrate binding induces a conformational change in the enzyme after which reaction of the bound complex takes place. Other conformational changes occur during the reaction of the substrate to produce the bound product. Desorption of the product returns the enzyme to its unbound conformation. [Adapted from D. E. Koshland, Jr., *Angew. Chem. Int. Ed. Engl.*, **33** (1994) 2375, with permission of WILEY-VCH Verlag GmbH and the author.]

confines substrates and prevents the escape of reaction intermediates. Domain closure must



COULD BE MORE THAN 1 BARRIER, BUT STILL A LOWER E THAN UNCATALYZED REACTION

Figure 4.2.4 | E

$$Ez + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EzS \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} EzP \xrightarrow{k_3} Ez + P$$

$$\frac{dC_S}{dt} = -k_1 C_{Ez} C_S + k_{-1} C_{EzS}$$

$$\frac{dC_{EzS}}{dt} = k_1 C_{Ez} C_S - k_{-1} C_{EzS} - k_2 C_{EzS} + k_{-2} C_{EzP}$$

$$\frac{dC_{EzP}}{dt} = k_2 C_{EzS} - k_{-2} C_{EzP} - k_3 C_{EzP}$$

$$\frac{dC_P}{dt} = k_3 C_{EzP}$$

BUT MANY CASES ARE SUCH THAT $k_3 >> k_2 + k_{-1}$

$$Ez + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} EzS \xrightarrow{k_3} Ez + P$$

$$\frac{dC_S}{dt} = -k_1 C_S C_{Ez} + k_{-1} C_{EzS}$$

$$\frac{dC_{EzS}}{dt} = k_1 C_S C_{Ez} - k_{-1} C_{EzS} - k_3 C_{EzS}$$

$$\frac{dC_P}{dt} = k_3 C_{EzS}$$

$$C_E^0 = C_{Ez} + C_{EzS}$$

$$\frac{dC_{EzS}}{dt} = 0 = k_1 C_S C_{Ez} - k_{-1} C_{EzS} - k_3 C_{EzS}$$

$$C_{EzS} = \frac{k_1 C_S C_{Ez}}{k_{-1} + k_3} = \frac{C_S C_{Ez}}{K_m}$$

$$K_m \equiv \frac{k_{-1} + k_3}{k_1}$$

PART OF RATIONALE!
WE CAN'T GET
ALL CONSTANTS
ANYWAY!

$$C^0_{EZ} = C_{EZ} + C_{EZS}$$

$$C_{EZS} = \frac{C_S C_{EZ}}{K_m}$$

$$C_{EZS} = \frac{C^0_{EZ} C_S - C_{EZS} C_S}{K_m}$$

SOLVE

$$C_{EZS} = \frac{C^0_{EZ} C_S}{K_m + C_S}$$

WHICH GIVES...

$$\frac{dC_P}{dt} = \frac{k_3 C^0_{EZ} C_S}{K_m + C_S}$$

OR

$$\frac{dC_P}{dt} = -\frac{dC_S}{dt} = \frac{\Lambda_{MAX} C_S}{K_m + C_S}$$

$$\Lambda_{MAX} = k_3 C^0_{EZ}$$

STANDARD
FORM