SECOND ORDER KINETICS

$$E + S \underset{k_r}{\overset{k_f}{\rightleftharpoons}} E\cdot S \underset{k_-}{\overset{k_{cat}}{\rightleftharpoons}} E + P$$

$$\begin{array}{c|c} & \begin{array}{cccc} E & S & E\cdot S & P \end{array} \\ \begin{array}{c} E \\ S \\ E\cdot S \\ P \end{array} & \begin{bmatrix} P_{EE} & & k_r\Delta t + k_{cat}\Delta t & \\ & P_{SS} & k_r \Delta t & \\ k_f \Delta t\cdot[S] & & P_{ES} & \\ & & & P_P \end{bmatrix} \end{array} \begin{bmatrix} E \\ S \\ ES \\ P \end{bmatrix}$$

THIS MATRIX CHANGES WITH TIME...

$$\frac{dES}{dt} = \underline{E\cdot S\cdot k_f} + \ldots$$

2ND ORDER REACTION

HOW DO WE DEAL w/ 2ND ORDER RXNS?

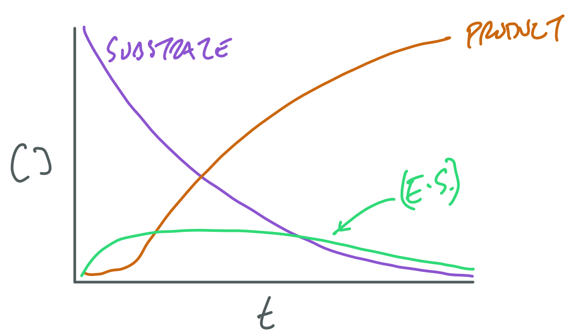
1) TURN INTO FIRST ORDER.

(A) IF k_- IS SMALL, IRREVERSIBLE

$$\frac{dE}{dt} = -k_f[E][S] + k_r[ES] + k_{cat}[ES] \cancel{- k_-[P][E]}$$

TRUE IF ΔG FOR RXN IS << Ø

(B) ASSUME [ES] IS AT STEADY STATE (OR, THAT E IS LIMITING FOR RXN).



$$\frac{dES}{dt} \sim Ø = k_f[E][S] - k_r[ES] - k_{cat}[ES]$$

$$Ø = k_f[E][S] - (k_r + k_{cat})[ES]$$

ALGEBRA

$$\frac{[ES]}{[E][S]} = \frac{k_f}{k_r + k_{cat}}$$

LOOKS LIKE AN EQUILIBRIUM CONSTANT...

$$[E]_0 = [E] + [ES]$$

$$\frac{[ES]}{([E]_0 - [ES])[S]} = \alpha$$

$$[ES] = \alpha [E]_0 [S] - \alpha [ES][S]$$

$$[ES] + [ES] \cdot \alpha [S] = \alpha [E]_0 [S]$$

$$\vdots$$

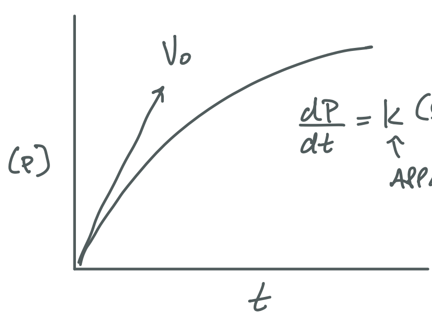
$$[ES] = \frac{\alpha [E]_0 [S]}{1 + \alpha [S]}$$

$$[ES] = \frac{[E]_0 [S]}{1/\alpha + [S]} \qquad K_m \equiv 1/\alpha$$

$$[ES] = \frac{[E]_0 [S]}{K_m + [S]}$$

$$\frac{dP}{dt} = k_{cat} \cdot [ES] = k_{cat} \cdot [E]_0 \cdot \left(\frac{[S]}{K_m + [S]}\right)$$

PURPOSE: STEADY STATE ASSUMPTION $\Rightarrow$ FIRST-ORDER IN $\underline{\underline{[S]}}$



$$\frac{dP}{dt} = k [S]_0$$

$\uparrow$ APPARENT FIRST-ORDER TERM.

__KEY POINTS:__ TO DISSECT COMPLICATED RXN:

1) FIND REACTIONS TO IGNORE (k_- IS SLOW, IGNORE IT)

2) FIND SIMPLIFYING CONDITIONS (STEADY STATE, FOR EXAMPLE) AND DESCRIBE THERE.

3) KNOW WHAT YOU ASSUMED AND WHEN IT DOES __NOT__ APPLY.

4) SIMULATE IT TO AVOID THIS.