X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

A. Given

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C \xrightarrow{k_2} P$$
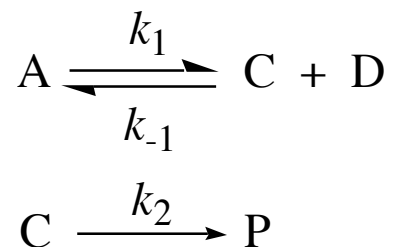
B. Rate Equation:

If we simplify by assuming [C] stays low...

$$d[P]/dt = k_2[C]$$
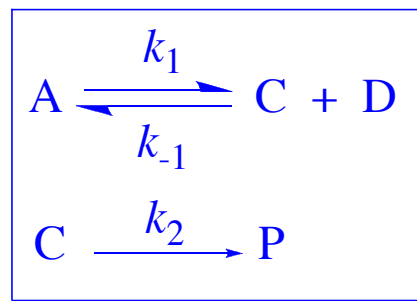
Since...

$$d[C]/dt = k_1[A] - k_{-1}[C][D] - k_2[C] \cong 0$$

Solving for [C]...

$$[C] = \frac{k_1[A]}{k_2 + k_{-1}[D]}$$

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

Therefore...

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

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C \xrightarrow{k_2} P$$

Or, dividing through by k_2...

$$d[P]/dt = \frac{k_1 [A]}{1 + (k_{-1}[D])/k_2}$$

• This alternative mathematical representation includes the branching ratio...
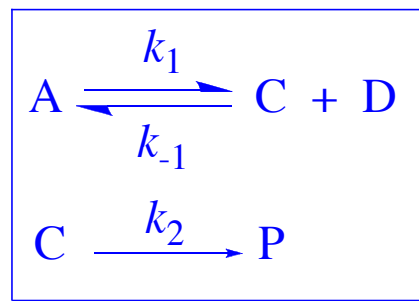
$$(k_{-1}[D])/k_2$$

The branching ratio reflects the partitioning of intermediate $\underline{C}$ to starting material ($k_{-1}[D]$) and to product (k_2). The transition from one limiting case to the other (i.e., non-limiting case) is observed when the branching ratio is near unity.

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

C. Limiting Cases:

1. Case 1: $k_2 \gg k_{-1}[D]$

$$d[P]/dt = k_1[A]$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$
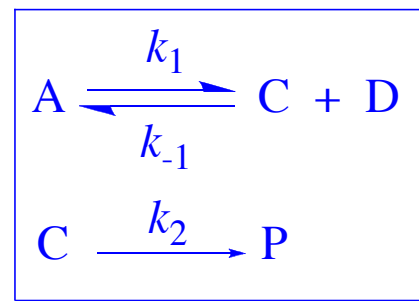
$$C \xrightarrow{k_2} P$$

• The rate of product formation from C is much greater than the rate that C returns to starting material. Therefore, the formation of C is rate limiting.

• This limiting behavior is most likely to be observed at low [D] (i.e., low conversion).

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

2. <u>Case 2</u>: $k_2 << k_{-1}[D]$

$$d[P]/dt = \frac{k_1 k_2}{k_{-1}} \cdot \frac{[A]}{[D]}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C \xrightarrow{k_2} P$$

• As [D] builds up, "autoinhibition" by <u>D</u> due to the back reaction becomes more likely.

• Determination of the "reaction order over time" -- the order in <u>A</u> derived from plots of <u>A</u> vs. t -- affords a quantitatively irrational order that acts like a high order.

• Determination of the "true reaction order" -- the order in <u>A</u> obtained by monitoring initial rates at variable $[A_0]$'s -- affords a clean 1st order in <u>A</u>.

• The problem is that the math gets nasty due to changing [D].

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

D. Flooding Technique:

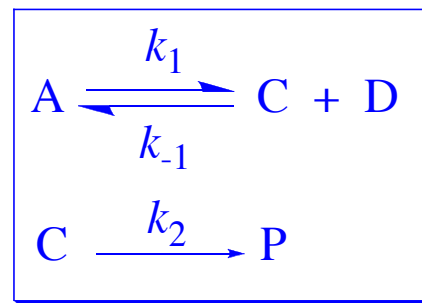1. Given: excess [D] added at the outset

$$[D] \cong [D_0]$$

2. Rate Equation:

$$d[P]/dt = k_{obsd}[A]$$

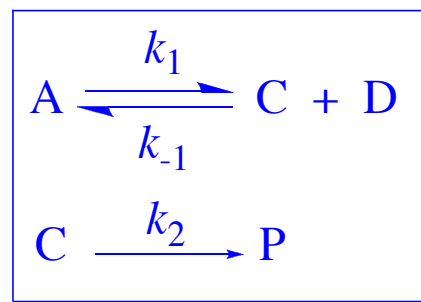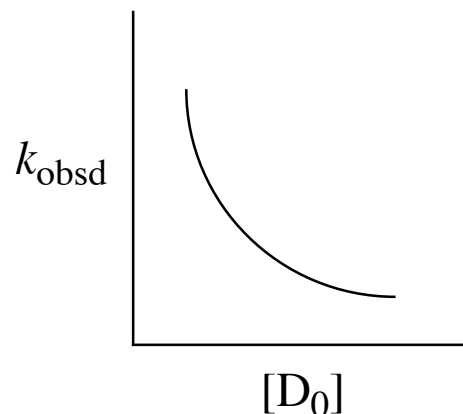such that...

$$k_{obsd} = \frac{k_1 k_2}{k_2 + k_{-1}[D_0]}$$

In the limit that $k_{-1}[D] \gg k_2$ (as expected with excess $\underline{D}$)...

$$d[P]/dt = \frac{k_1 k_2}{k_{-1}} \frac{[A]}{[D]} = k_{obsd}[A]$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C \xrightarrow{k_2} P$$

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

3. Graphics:

- A plot of k_{obsd} vs. $[D_0]$ is non-linear for all inverse orders in $\underline{D}$.
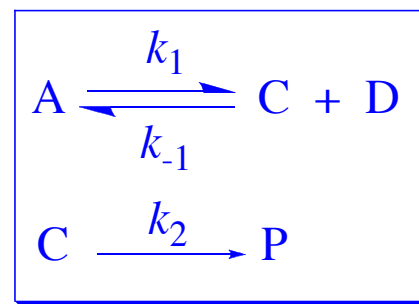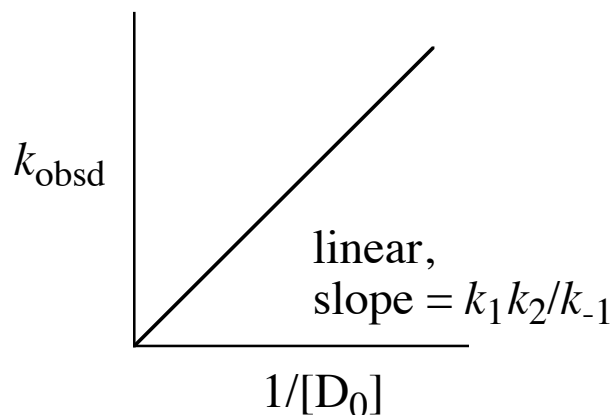
Let...

$$f(x) = ax^b$$

such that...

$$f(x) = k_{obsd} \qquad x = [D_0] \qquad a = k_1 k_2 / k_{-1} \qquad b = \text{order in } \underline{D}$$

- $\underline{b}$ will be negative for an inverse order.

X. 1st-Order/2nd-Order Pre-Equilibrium, 1st-Order Reaction:

For a more visually retrievable plot, we can turn to the graphical method. Thus...

linear,
slope $= k_1 k_2 / k_{-1}$

k_{obsd}

$1/[D_0]$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C \xrightarrow{k_2} P$$

• For $\underline{b} = -1$, a plot of k_{obsd} vs. $1/[D_0]$ will be linear.

• In the event that the reaction is inverse "nth" order, plots of k_{obsd} vs. $1/[D_0]^n$ will be linear.