IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

A. Given:

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

B. Rate Equation:

• It is often easier to derive rate expressions by focusing upon the rate of product formation rather than starting material disappearance.

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

1. <u>Steady State Approximation</u>:

If [C] stays low...

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

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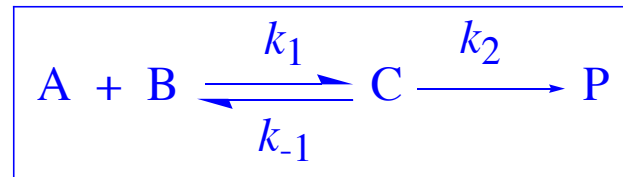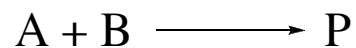
$$d[C]/dt = k_1[A][B] - k_{-1}[C] - k_2[C] \cong 0$$

Solving for [C]...

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

Therefore...

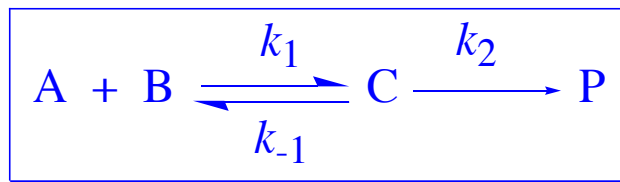$$d[P]/dt = \frac{k_1 k_2}{k_{-1} + k_2}[A][B]$$

This is indistinguishable from...

$$A + B \longrightarrow P$$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

2. <u>Simple Equilibrium Approximation</u>:

If $k_{-1} >> k_2$...

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

$$K_{eq} = [C]/\{[A][B]\}$$

Therefore...

$$d[P]/dt = k_2[C] = k_2 K_{eq}[A][B]$$

Apparent predictions...

$$d[P]/dt \propto [A]$$

and...

$$d[P]/dt \propto [B]$$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

However, [C] does not necessarily stay low (i.e., $k_1[B] \gg k_{-1}$). If so...

$-d[A]/dt \neq d[P]/dt$

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

• $d[P]/dt$ will be independent of [B] (i.e., the excess reagent) if $\underline{C}$ is the observable reactant; increasing [B] cannot appreciably increase [C].

• Why does the so-called "simple equilibrium approximation" fail to clearly predict this?

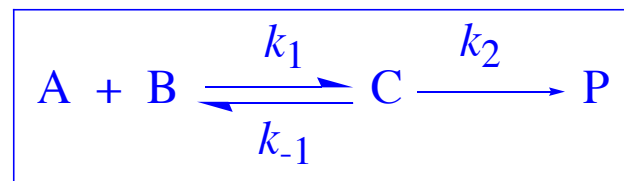## IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

3. <u>Alternative Equilibrium Approximation</u>:

Let $[A_T]$ = total concentration of <u>A</u> in all forms. Therefore,...

$$[A_T] = [A] + [C]$$

Similarly...

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

$$[B_T] = [B] + [C]$$

If $[B_T] \gg [A_T]$ (pseudo-1st-order conditions), then...

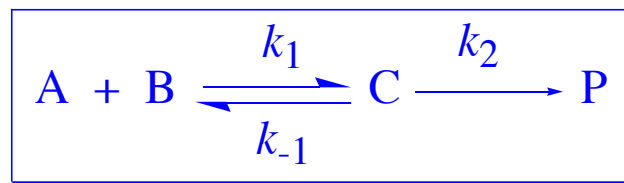$$[B] \cong [B_T] \cong \text{constant}$$

Since...

$$[C] = K_{eq}[A][B] = K_{eq}\{[A_T] - [C]\}[B]$$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

Solving for [C]...

$$[C] = \frac{K_{eq}[B][A_T]}{1 + K_{eq}[B]}$$

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

Therefore...

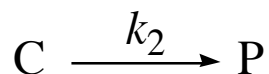$$d[P]/dt = k_2[C] = \frac{k_2 K_{eq}[B][A_T]}{1 + K_{eq}[B]}$$

Let...

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

such that...

$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]} \qquad (1)$$
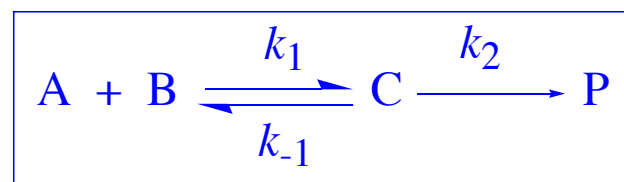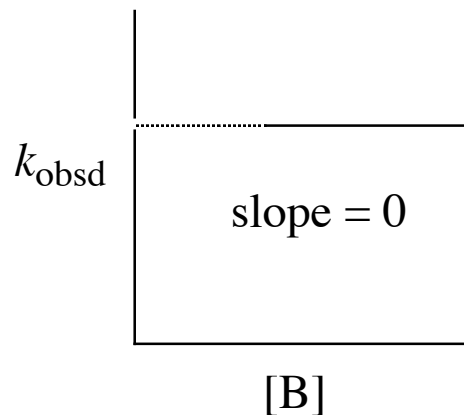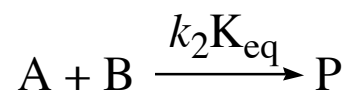
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

a. <u>Limiting Case 1</u>: $K_{eq}[B] \gg 1$ (i.e., $[C]/[A] \gg 1$)

• This is most likely at high $[B]$.

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

• <u>C</u> becomes the observable form, the mechanism reduces to...

$$C \xrightarrow{k_2} P$$

$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]}$$
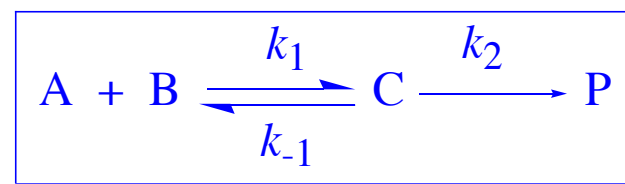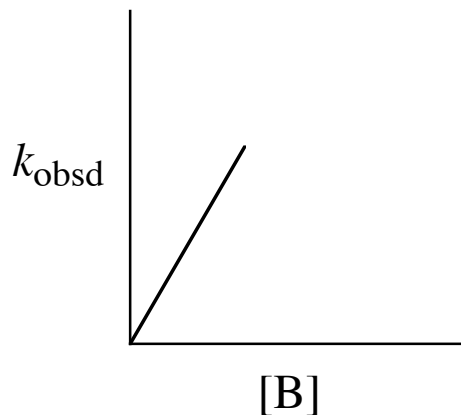
$$d[P]/dt = k_2[C] = k_2[A_T]$$

k_{obsd}

slope $= 0$

$[B]$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

b. <u>Limiting Case 2</u>: $K_{eq}[B] << 1$ (i.e., $[C]/[A] << 1$)

• This is most likely at low [B].

• <u>A</u> remains the observable form. The mechanism reduces to...

$$A + B \xrightarrow{k_2 K_{eq}} P$$

$$d[P]/dt = k_2 K_{eq}[A_T][B]$$

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

$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]}$$

k_{obsd} vs [B]

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

c. <u>Combined Cases 1 and 2</u>: "Saturation Kinetics"

k_{obsd} vs $[B]$ plot:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \overset{k_2}{\longrightarrow} P$$
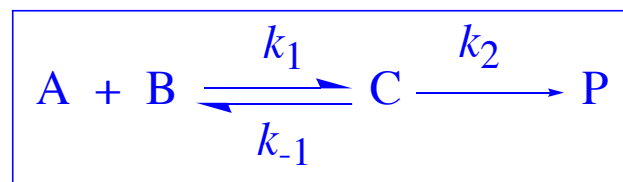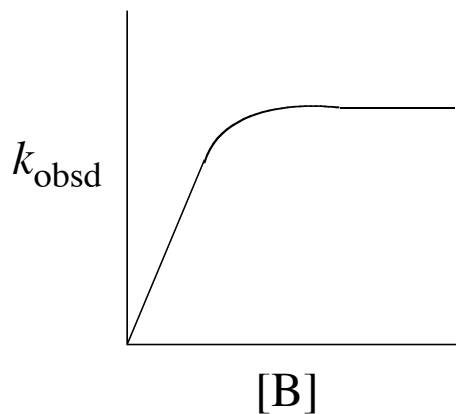
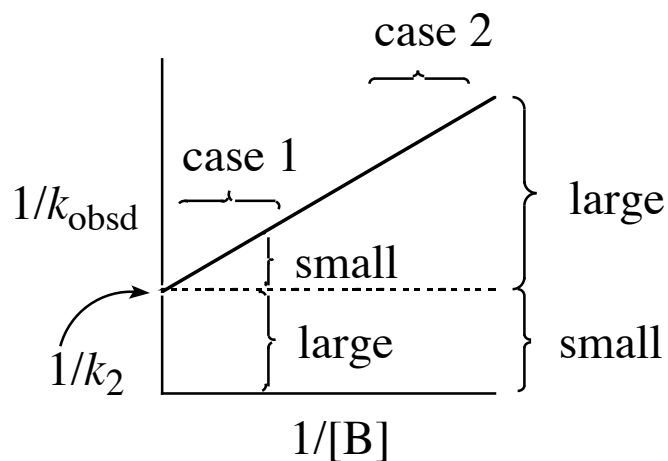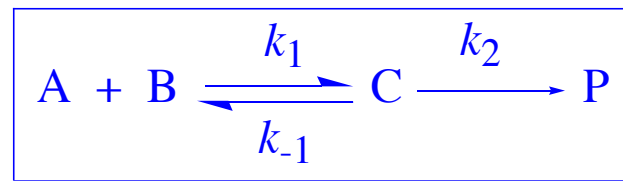$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]}$$

Let...

$$f(x) = \frac{ax}{1 + bx}$$

such that...

$$f(x) = k_{obsd} \qquad x = [B] \qquad a = k_2 K_{eq} \qquad b = K_{eq}$$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

Alternatively, rearranging eq (1) gives...

$$\frac{1}{k_{obsd}} = \frac{1}{k_2 K_{eq}[B]} + \frac{1}{k_2}$$

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

$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]}$$

case 2

case 1

$1/k_{obsd}$ ⎱ large

small

large ⎱ small

$1/k_2$

$1/[B]$

slope $= 1/(k_2 K_{eq})$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

Case 1: high [B] (i.e., low 1/[B]) and observable C

$$\frac{1}{k_{obsd}} \cong \frac{1}{k_2}$$

Case 2: low [B] (i.e., high 1/[B]) and observable A

$$\frac{1}{k_{obsd}} \cong \frac{1}{k_2 K_{eq}} \bullet \frac{1}{[B]}$$

IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

4. Conflict of Approximations:

The simple equilibrium approximation gives...

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

$$d[P]/dt = k_2 K_{eq}[A][B]$$

$$k_{obsd} = \frac{k_2 K_{eq}[B]}{1 + K_{eq}[B]}$$
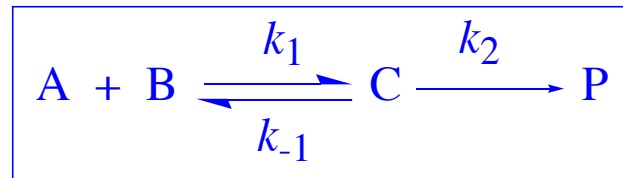
The alternative equilibrium approximation gives...

$$d[P]/dt = \frac{k_2 K_{eq}[B][A_T]}{1 + K_{eq}[B]}$$

How can this be? Neither approximation includes extraneous assumptions.

• The simple approximation predicts that...

$$d[P]/dt \propto [C] \propto [A][B]$$

but not [A] or [B] alone. [A] and [B] are correlated.