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

A. Given:

\[
A + B \xrightleftharpoons[k_{-1}]{k_1} C \rightarrow P
\]

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. Steady State Approximation:

If \([C]\) stays low...

\[
\frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_2[C]
\]

\[
\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[C] \approx 0
\]

Solving for \([C]\)...

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

Therefore...

\[ \frac{d[P]}{dt} = \frac{k_1k_2}{k_{-1} + k_2} [A][B] \]

This is indistinguishable from...

\[ A + B \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} C \overset{k_2}{\rightarrow} P \]
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

2. Simple Equilibrium Approximation:

If $k_1 \gg k_2$...

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

Therefore...

$$\frac{d[P]}{dt} = k_2[C] = k_2K_{eq}[A][B]$$

*Apparent* predictions...

$$\frac{d[P]}{dt} \propto [A]$$

and...

$$\frac{d[P]}{dt} \propto [B]$$
However, \([C]\) does not necessarily stay low (i.e., \(k_1[B] >> k_{-1}\)). 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 \(C\) is the observable reactant; increasing \([B]\) cannot appreciably increase \([C]\).

- Why does the so-called “simple equilibrium approximation” fail to clearly predict this?
3. Alternative Equilibrium Approximation:

Let \([A_T]\) = total concentration of \(A\) in all forms. Therefore,

\[
[A_T] = [A] + [C]
\]

Similarly...

\[
[B_T] = [B] + [C]
\]

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

\[
[B] \approx [B_T] \approx \text{constant}
\]

Since...

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

Solving for \([C]\)...
\[
[C] = \frac{K_{eq}[B][A_T]}{1 + K_{eq}[B]}
\]

Therefore...
\[
d[P]/dt = k_2[C] = \frac{k_2K_{eq}[B][A_T]}{1 + K_{eq}[B]}
\]

Let...
\[
d[P]/dt = k_{obsd}[A_T]
\]

such that...
\[
k_{obsd} = \frac{k_2K_{eq}[B]}{1 + K_{eq}[B]}
\]

\[(1)\]
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

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

- This is most likely at high [B].
- $C$ becomes the observable form, the mechanism reduces to...

$$C \quad \overset{k_2}{\rightarrow} \quad P$$

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

$$k_{obsd} = \frac{k_2K_{eq}[B]}{1 + K_{eq}[B]}$$
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

b. **Limiting Case 2**: \( K_{eq}[B] \ll 1 \) (i.e., \([C]/[A] \ll 1\))

- This is most likely at low \([B]\).
- \(A\) remains the observable form. The mechanism reduces to...

\[
A + B \overset{k_2K_{eq}}{\underset{k_{-1}}{\rightleftharpoons}} P
\]

\[
d[P]/dt = k_2K_{eq}[A_T][B]
\]

\[
k_{obsd} = \frac{k_2K_{eq}[B]}{1 + K_{eq}[B]}
\]
c. **Combined Cases 1 and 2**: “Saturation Kinetics”

Let...

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

such that...

\[ f(x) = k_{\text{obsd}} \quad x = [B] \quad a = k_2K_{\text{eq}} \quad b = K_{\text{eq}} \]
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

Alternatively, rearranging eq (1) gives...

\[
\frac{1}{k_{\text{obsd}}} = \frac{1}{k_2K_{\text{eq}}[B]} + \frac{1}{k_2}
\]

\[\text{slope} = \frac{1}{(k_2K_{\text{eq}})}\]
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

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

\[
\frac{1}{k_{\text{obsd}}} \approx \frac{1}{k_2}
\]

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

\[
\frac{1}{k_{\text{obsd}}} \approx \frac{1}{k_2 K_{\text{eq}}} \cdot \frac{1}{[B]}
\]
IX. 2nd-Order /1st-Order Pre-equilibrium, 1st-Order Reaction:

4. **Conflict of Approximations:**

The simple equilibrium approximation gives...

\[ \frac{d[P]}{dt} = k_2 K_{eq} [A][B] \]

The alternative equilibrium approximation gives...

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

How can this be? Neither approximation includes extraneous assumptions.

- The simple approximation predicts that...

\[ \frac{d[P]}{dt} \propto [C] \propto [A][B] \]

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