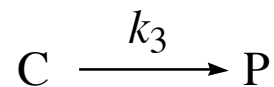
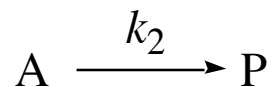
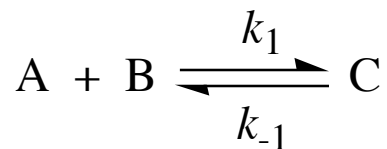
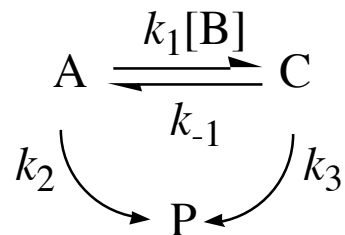


XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

A. Given:



Alternatively...



XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

B. Steady State Approximation:

1. Rate Equation:

Assuming $[B_0] \gg [A_0]$ and C does not become observable...

$$d[P]/dt = k_2[A] + k_3[C]$$

Since...

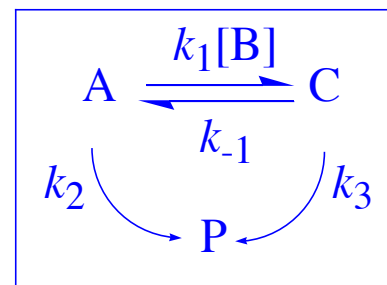
$$d[C]/dt = k_1[A][B] - k_{-1}[C] - k_3[C] \approx 0$$

Then...

$$[C] = \frac{k_1}{(k_{-1} + k_3)} [A][B]$$

and...

$$d[P]/dt = \frac{k_1 k_3}{(k_{-1} + k_3)} [A][B] + k_2[A]$$



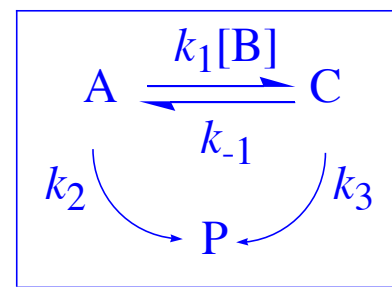
XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

Alternatively...

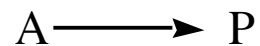
$$d[\text{P}]/dt = k_{\text{obsd}}[\text{A}]$$

such that...

$$k_{\text{obsd}} = \frac{k_1 k_3}{(k_{-1} + k_3)} [\text{B}] + k_2$$

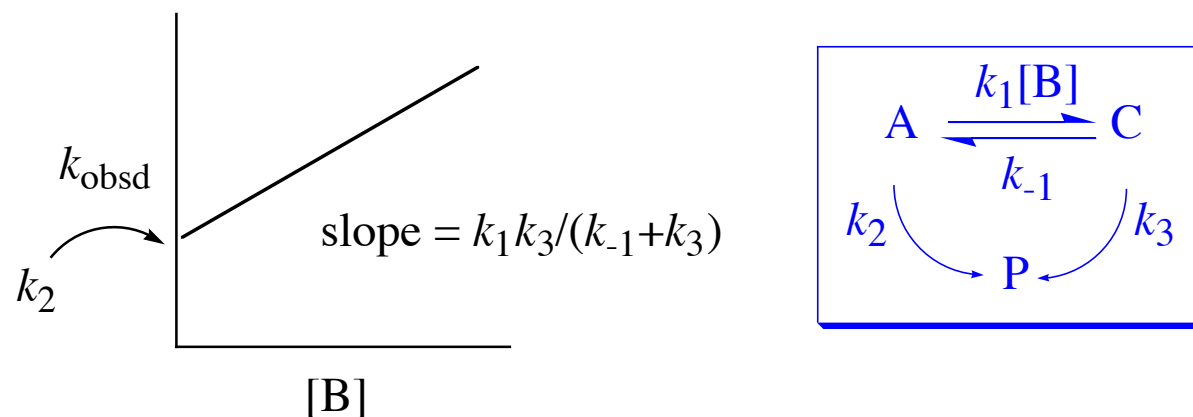


The mechanism reduces to...



XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

2. Graphics:



- The linearity shows 1st order in B. The non-zero intercept confirms the existence of a significant zeroth-order dependence.
- Be careful to include (0,0) origins on all plots of k_{obsd} vs. reagent concentrations to ensure detection of non-zero intercepts.



XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

C. Equilibrium Approximation:

1. Rate Equation:

If we assume that C may become observable at sufficiently high [B], then we apply the alternative equilibrium approximation...

$$d[P]/dt = k_2[A] + k_3[C] \quad (1)$$

Since...

$$[A_T] = [A] + [C] = \text{total concentration of } \underline{A} \text{ in all forms}$$

and, by the definition of equilibrium,...

$$k_1[A][B] = k_{-1}[C] \quad (2)$$

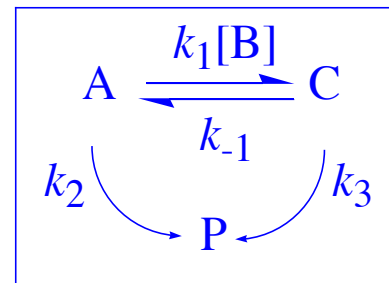
XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

Substituting for [A] in eq (2)...

$$k_1[B]\{[A_T] - [C]\} = k_{-1}[C]$$

and solving for [C]...

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



Similarly, substituting for [C] in eq (2) and solving for [A]...

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

Therefore...

$$d[P]/dt = \frac{k_{-1}k_2[A_T] + k_1k_3[A_T][B]}{k_{-1} + k_1[B]}$$

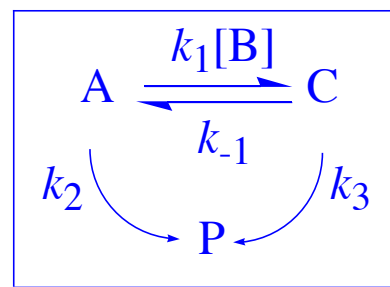
XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

or...

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

such that...

$$k_{\text{obsd}} = \frac{k_{-1}k_2 + k_1k_3[B]}{k_{-1} + k_1[B]}$$



Alternatively,...

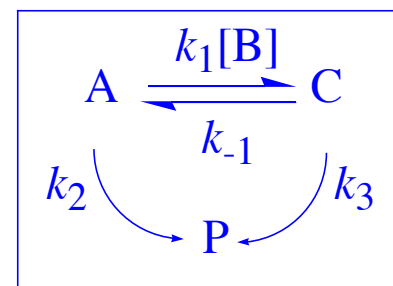
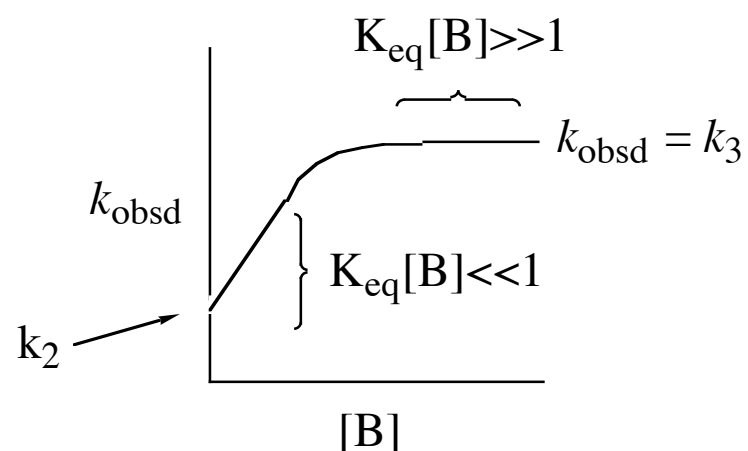
$$k_{\text{obsd}} = \frac{k_2 + k_3K_{\text{eq}}[B]}{1 + K_{\text{eq}}[B]}$$

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

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

2. Graphics:

a. Case 1: $k_2 < k_3$



$$k_{\text{obsd}} = \frac{k_2 + k_3 K_{\text{eq}} [B]}{1 + K_{\text{eq}} [B]}$$

The data are fit according to...

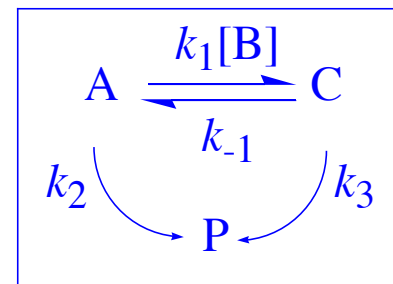
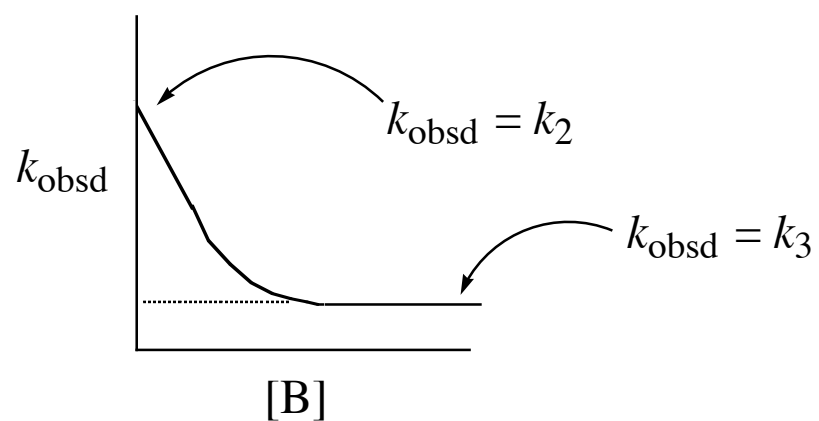
$$f(x) = \frac{a + bx}{1 + cx}$$

such that...

$$f(x) = k_{\text{obsd}} \quad x = [B] \quad a = k_2 \quad b = k_3 K_{\text{eq}} \quad c = K_{\text{eq}}$$

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

b. Case 2: $k_3 < k_2$

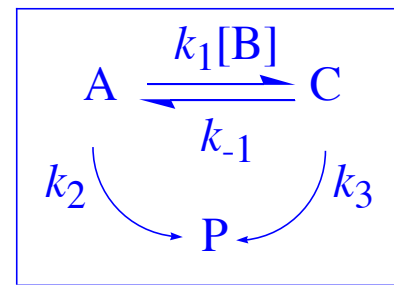
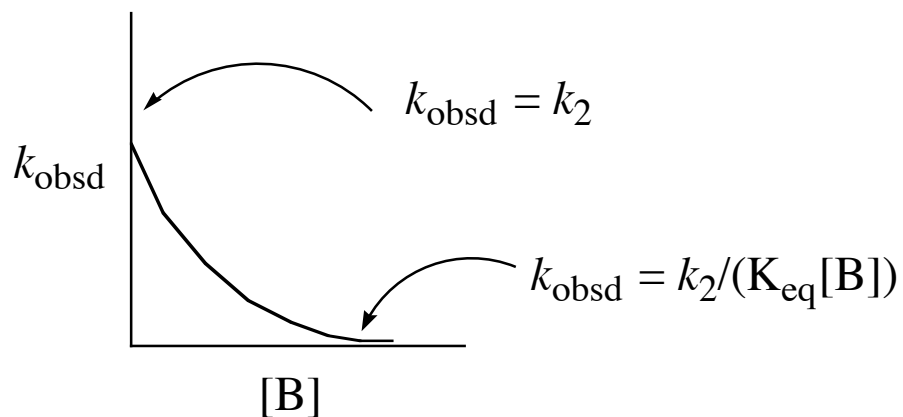


$$k_{\text{obsd}} = \frac{k_2 + k_3 K_{\text{eq}} [B]}{1 + K_{\text{eq}} [B]}$$

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

In the limit that $k_3 = 0$ (i.e., the complexed form is unreactive)...

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



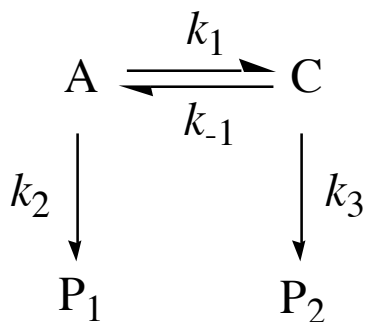
$$k_{\text{obsd}} = \frac{k_2 + k_3 K_{\text{eq}}[\text{B}]}{1 + K_{\text{eq}}[\text{B}]}$$

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

D. Addendum: The Curtin-Hammett Principle

The case study described above is loosely under the jurisdiction of what is commonly known as the Curtin-Hammett Principle. It is instructive to digress for a moment and look at the Curtin-Hammett Principle from the perspective of a kineticist.

1. Given

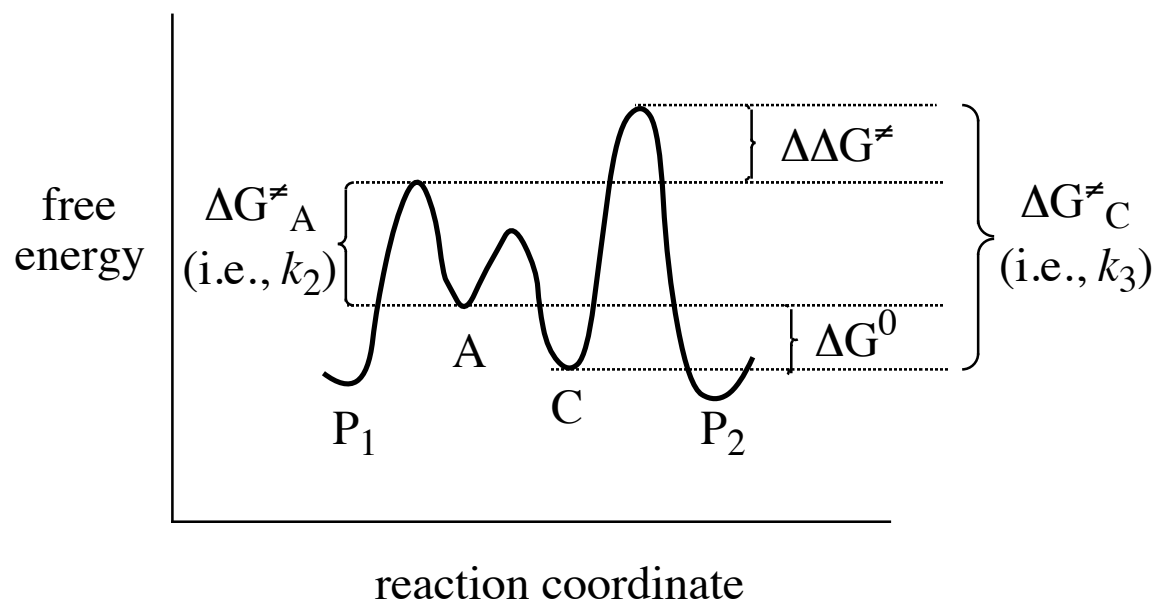


2. Early Articulation of the Curtin-Hammett Principle:

“Given two rapidly equilibrating species such that each can react to give their respective products, the product ratio depends only on the relative energy of the transition states...and will be independent of the position of the equilibrium.”

-Eliel

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:



Only $\Delta\Delta G^\ddagger$ matters according to the early articulation. However...

$$\Delta\Delta G^\ddagger = \Delta G^\ddagger_C - \Delta G^\ddagger_A - \Delta G^0$$

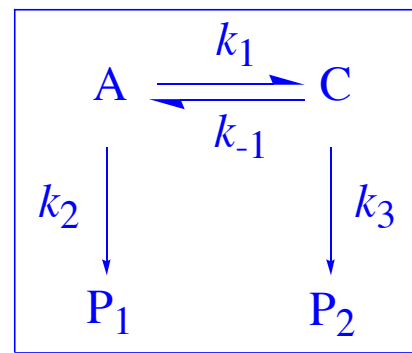
such that ΔG^\ddagger_A and ΔG^\ddagger_C reflect the relative reactivities of A and C, and ΔG^0 reflects the relative stabilities (concentrations) of A and C.

XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

3. Rate Equations:

$$d[P_1]/dt = k_2[A]$$

$$d[P_2]/dt = k_3[C]$$



To describe the product distribution we establish the proportions of the relative rates. Thus...

$$\frac{[P_1]}{[P_2]} = \frac{d[P_1]/dt}{d[P_2]/dt} = \frac{k_2[A]}{k_3[C]}$$

Since $[C]/[A] = k_1/k_{-1}$...

$$\frac{[P_1]}{[P_2]} = \frac{k_2}{k_3} \cdot \frac{k_{-1}}{k_1}$$



XIV. 2nd-Order Pre-Equilibrium, Parallel Reactions:

4. New and Improved Articulation of the Curtin-Hammett Principle:

“Given two rapidly equilibrating species such that each can react to give their respective products, the product ratio depends on their relative proportions and their relative reactivities.”

- See Seeman, J. I. *J. Chem. Educ.* **1986**, 63, 42.