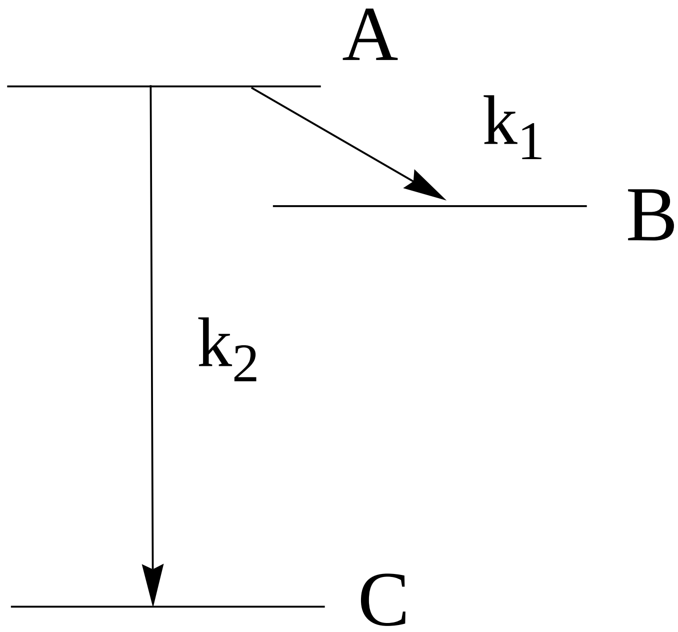
Parallel First Order Reactions



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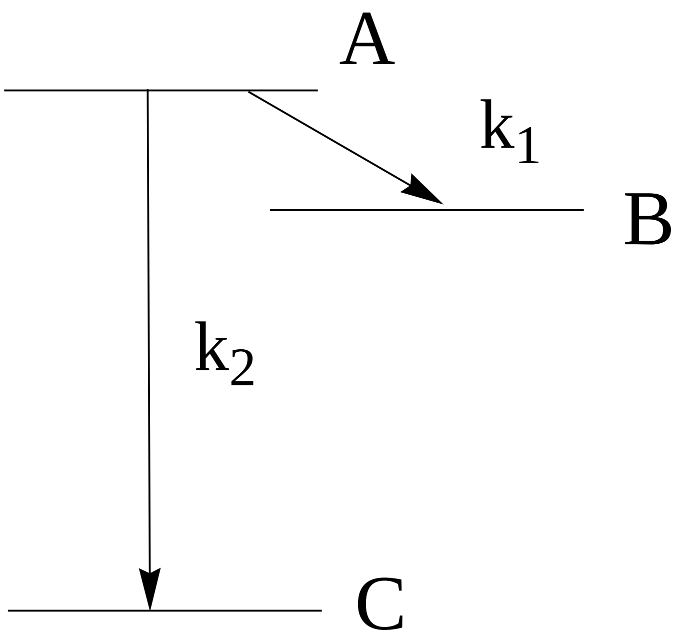

- $A \rightarrow B$ and $A \rightarrow C$ so that:
- $d[A]/dt = -(k_1+k_2)[A]$
- $d[B]/dt = k_1[A]$
- $d[C]/dt = k_2[A]$

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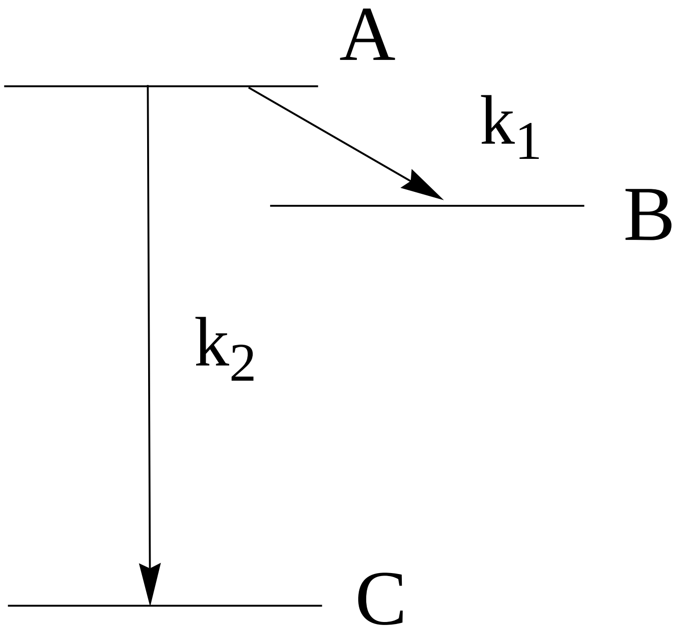

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- Solve for [A] first:

$$[A] = [A]_0 \exp\{-(k_1 + k_2)t\}$$

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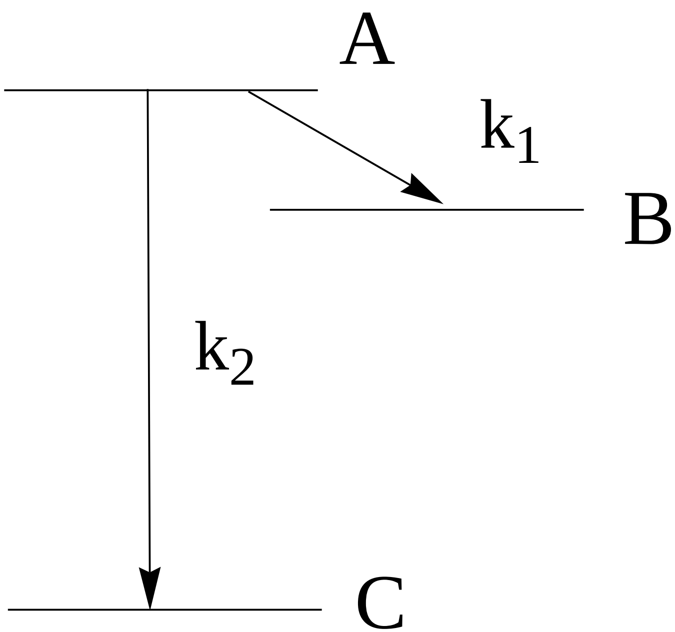

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$$[A] = [A]_0 \exp\{-(k_1 + k_2)t\}$$

then

$$\frac{d[B]}{dt} = k_1[A]_0 \exp\{-(k_1 + k_2)t\}$$

$$\frac{d[C]}{dt} = k_2[A]_0 \exp\{-(k_1 + k_2)t\}$$

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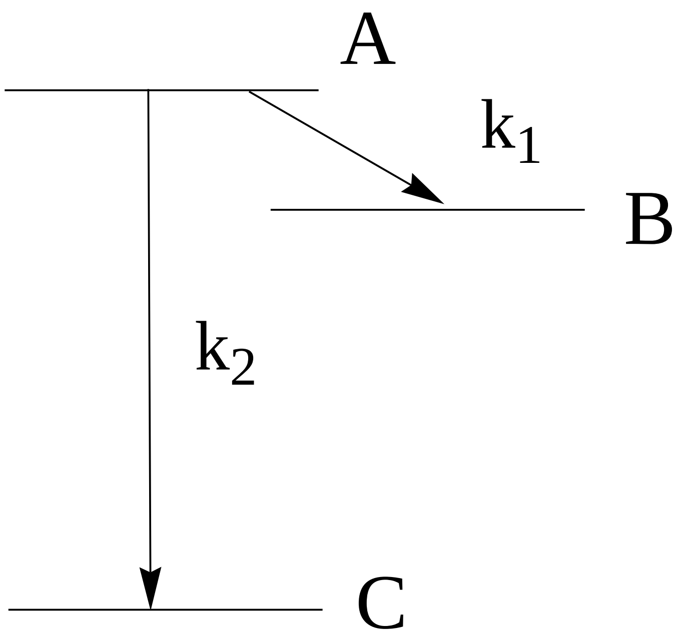

- The solutions are:

$$[B] = \frac{k_1[A]_0}{k_1 + k_2}\left(1 - \exp\{-(k_1 + k_2)t\}\right)$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2}\left(1 - \exp\{-(k_1 + k_2)t\}\right)$$

- The production of B and C occurs with a constant proportion:

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

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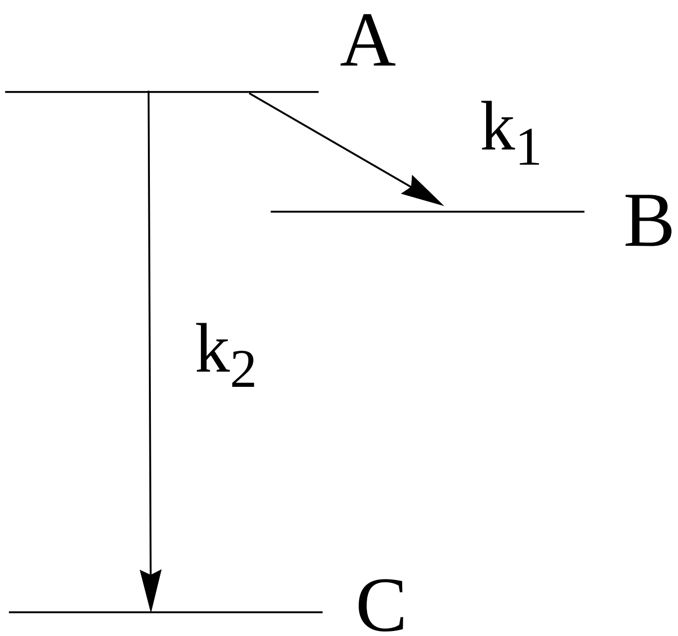
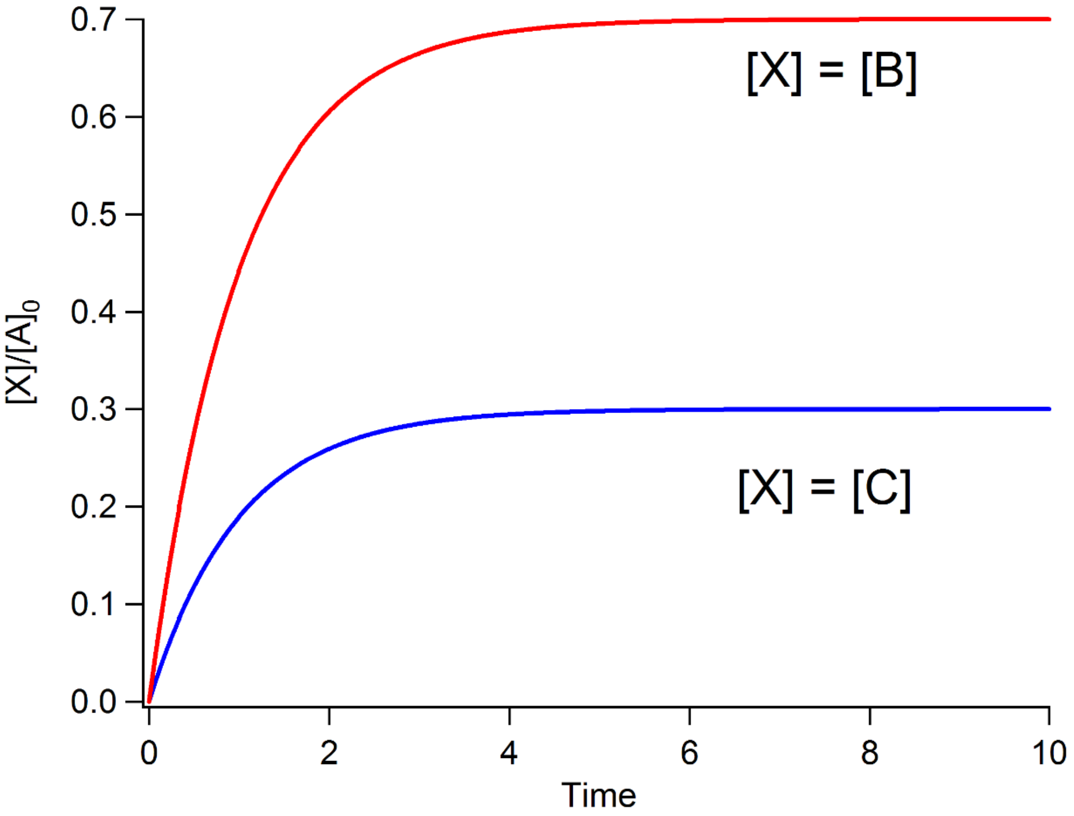
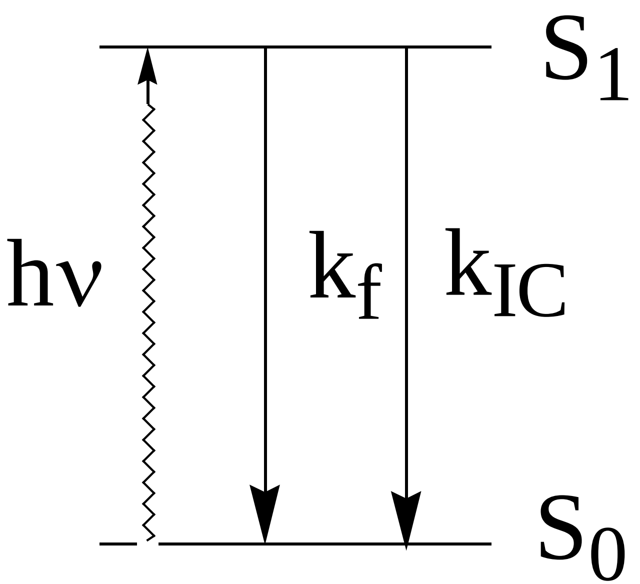




Example from fluorescence Competing or parallel processes

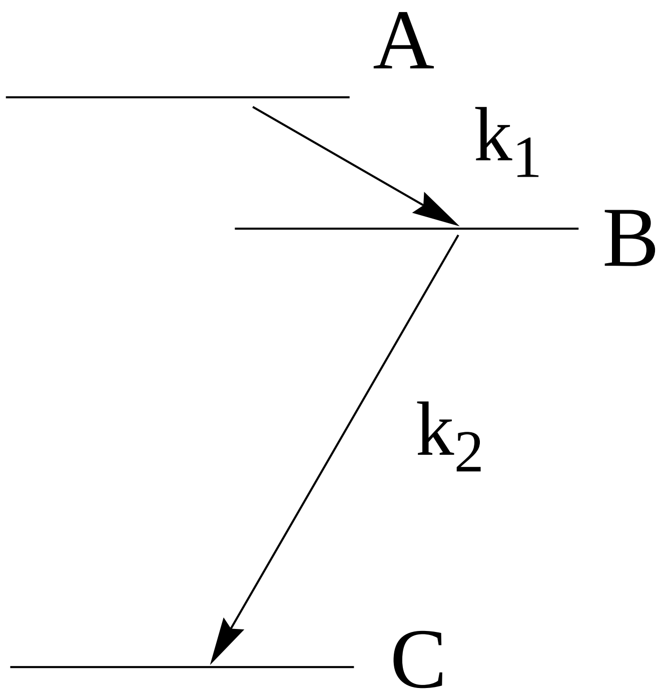


Photoexcitation followed by return to the S_0 ground state.

- Decay of the singlet S_1 state can occur either radiatively by fluorescence (k_f) or by internal conversion (k_{IC}).
- $d[S_1]/dt = -(k_f + k_{IC})[S_1]$
- The overall decay rate constant is the sum of the rate constants. The fluorescence quantum yield is

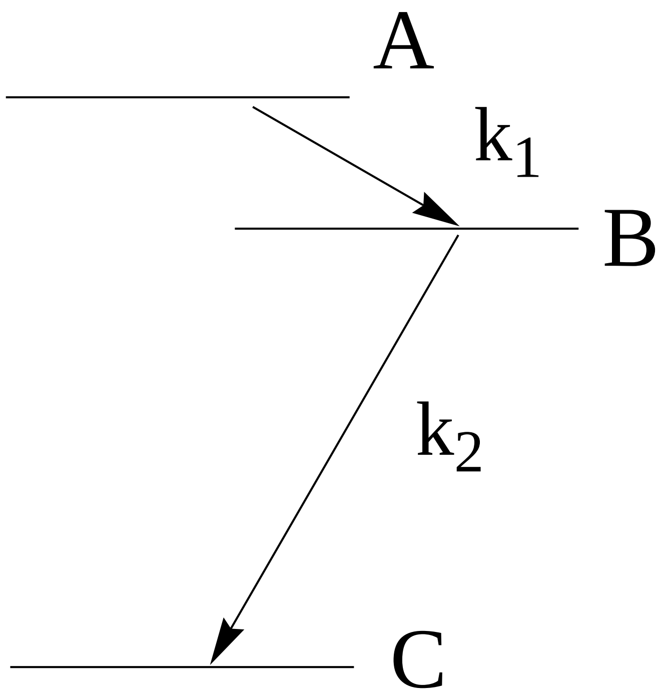
$$\Phi = \frac{k_f}{k_f + k_{IC}}$$

Sequential first-order reactions
Consecutive elementary reactions



- A $\rightarrow$ B $\rightarrow$ C rate equations are:
- $d[A]/dt = -k_1[A]$
- $d[B]/dt = k_1[A] - k_2[B]$
- $d[C]/dt = k_2[B]$
- Either k_1 or k_2 can be the rate limiting step.

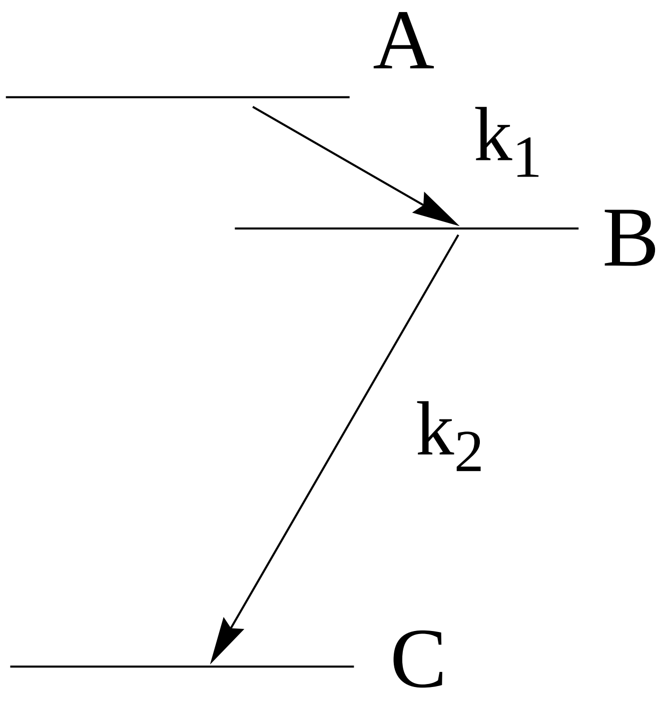
Sequential first-order reactions
Consecutive elementary reactions



- First solve eqn. for A

$$[A] = [A]_o e^{-k_1 t}$$

Sequential first-order reactions
Consecutive elementary reactions



- First solve eqn. for A

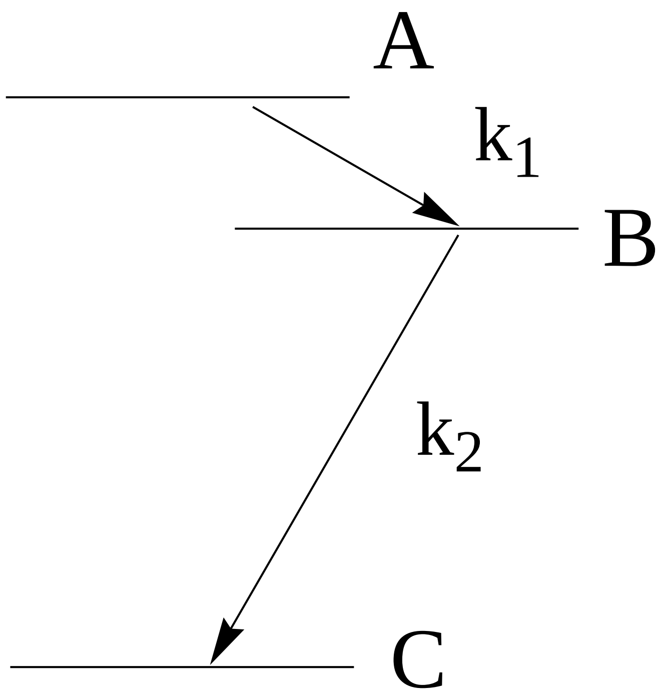
$$[A] = [A]_o e^{-k_1 t}$$

- Substitute into eqn. for B

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] = k_1[A]_o e^{-k_1 t} - k_2[B]$$

$$[B] = \frac{k_1[A]_o}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Sequential first-order reactions
Consecutive elementary reactions



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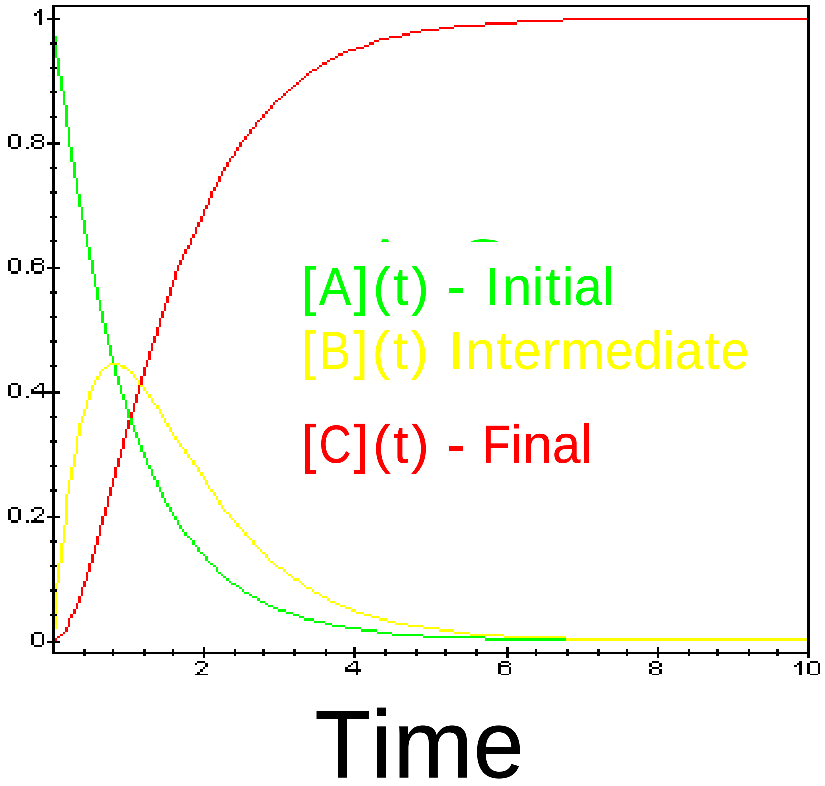
$$[B] = \frac{k_1[A]_o}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

- Similarly for C

$$[C] = [A]_o\left(1 - \frac{1}{k_2 - k_1}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right)$$

Populations as a function of time



- The population as a function of time is given by the solutions to the sequential first order reactions.
- The case shown is intermediate with $k_2 = 1.5k_1$.
- The population of B grows and reaches a maximum and then decays.

Rate determining step

- If $k_2 >> k_1$ then the first ($A \rightarrow B$) step becomes the rate-limiting step.
- If the $A \rightarrow B$ step is rate limiting then little or no B will be observed even though it is formed on the reaction path.
- If $k_1 >> k_2$ then the second ($B \rightarrow C$) step becomes the rate limiting step.
- If the $B \rightarrow C$ step is rate limiting then there will be a significant build-up of the intermediate state B.