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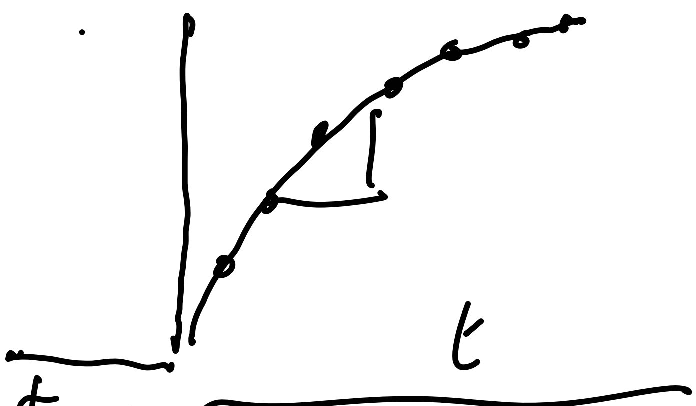
$$H^+ + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O, \quad k_2 = 1.4\times10^{11}\,\mathrm{L/mol\ s}, \quad k_1 = 2.5\times10^{-5}\,s^{-1}$$

$$D^+ + OD^- \rightarrow D_2O, \quad k_2 = 8.4\times10^{10}\,\mathrm{L/mol\ s}, \quad k_1 = 2.5\times10^{-6}\,s^{-1}$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\tau = \frac{1}{k_1 + k_{-1}}$$



$t = 0$

$$\tau = ? \quad \frac{1}{k_2[H^+]_{eq} + k_2[OH^-] + k_1}$$

Relaxation kinetics in modern day research

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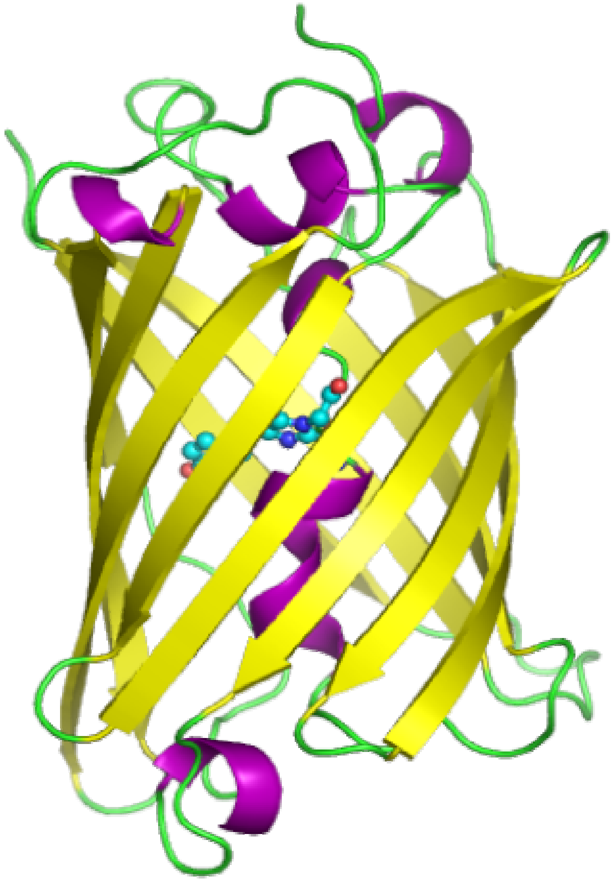
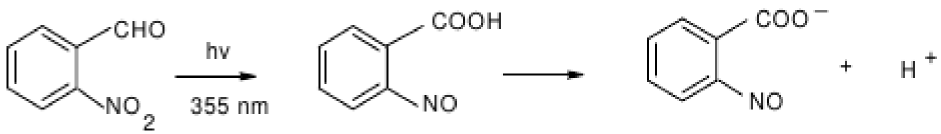
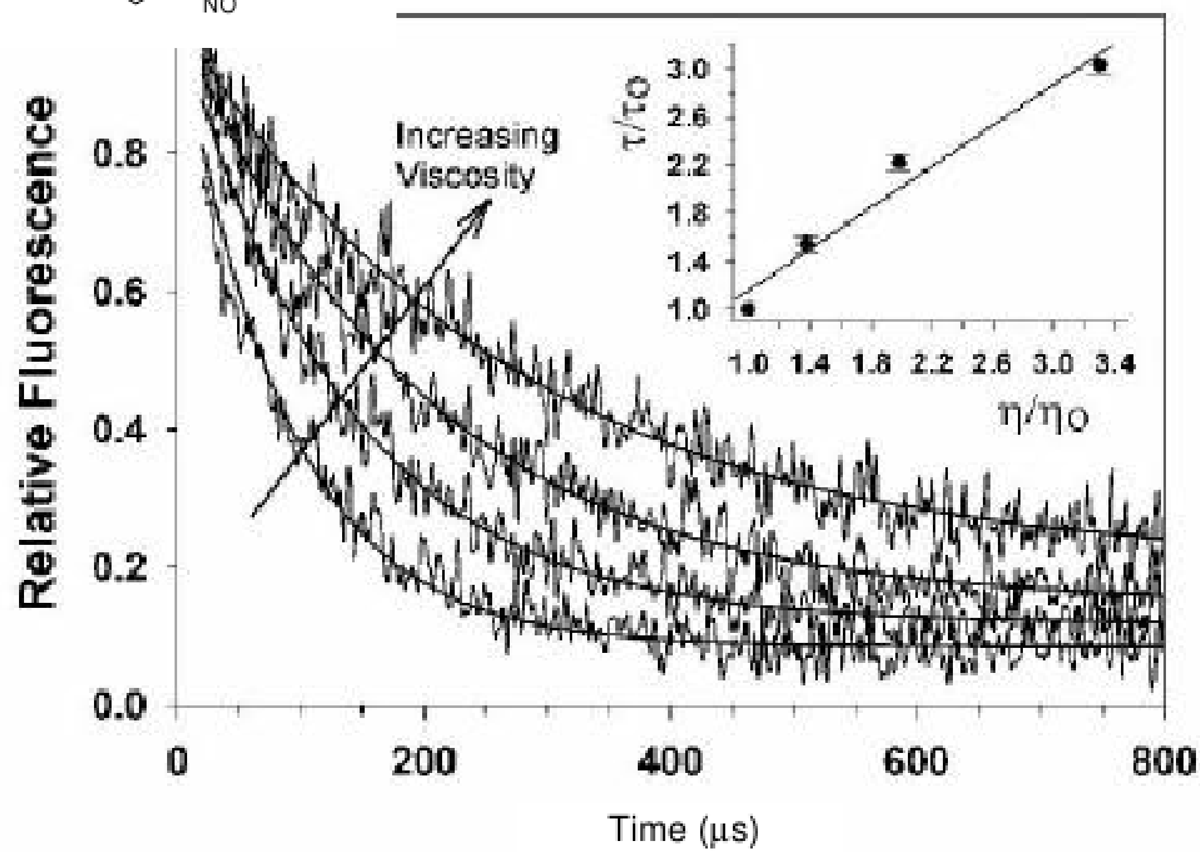
Structure of Green Fluorescent Protein



Relaxation kinetics through a light induced pH jump

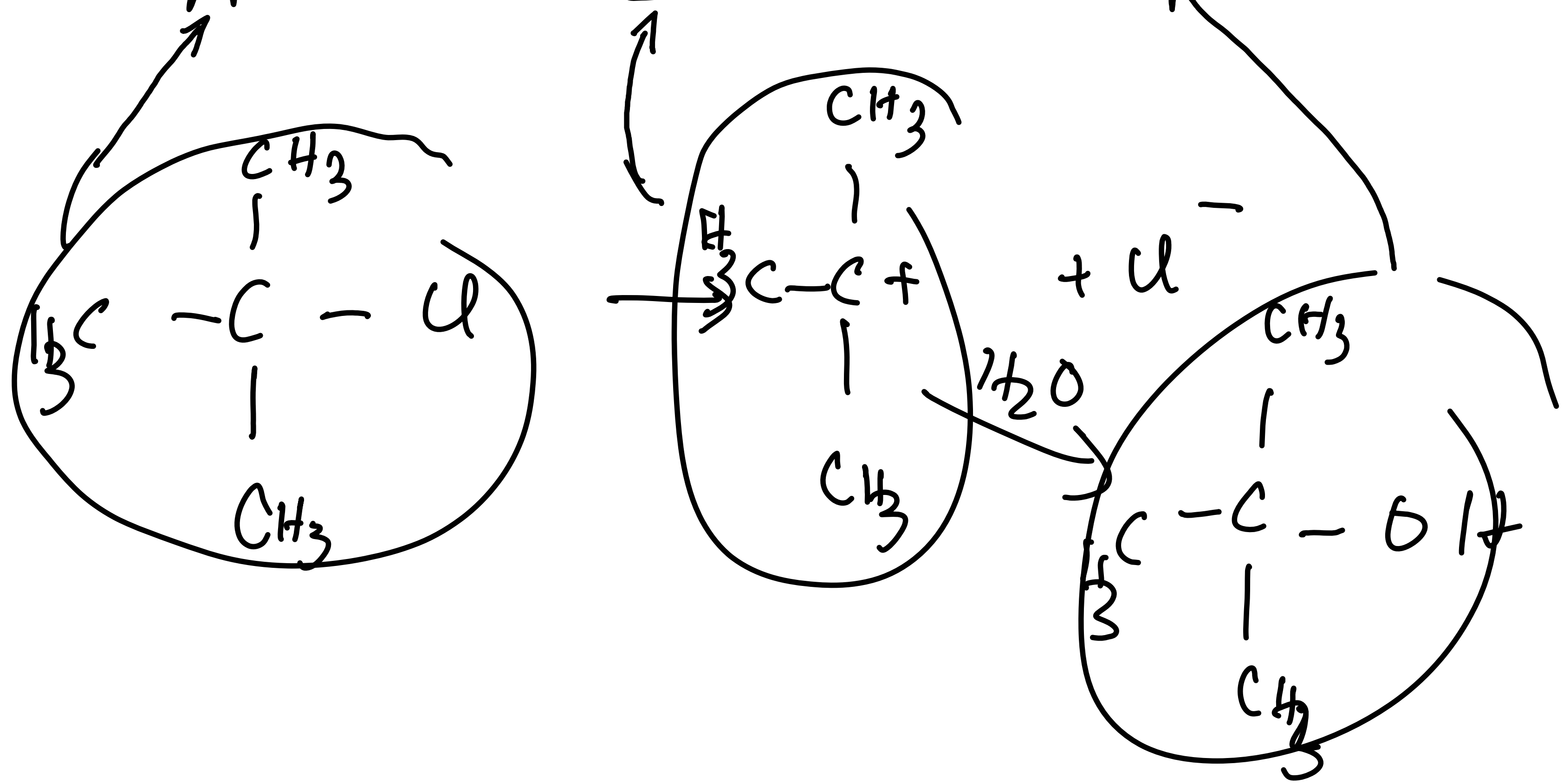


Kinetics of the fluorescence change in GFP after laser induced pH change from 8 to 5 as a function of viscosity. Time constants are 87, 134, 193, and 264 μs.



Consecutive Reactions

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$



$$\frac{d[A]}{dt} = -k_1 [A]$$

$$\frac{d[I]}{dt} = k_1 [A] - k_2 [I]$$

$$[A](t) = [A]_0 e^{-k_1 t}$$

$$\frac{d[P]}{dt} = k_2 [I]$$

Solution of a linear system of differential equation

$$\frac{d}{dt}\begin{bmatrix} A \\ I \\ P \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} \begin{bmatrix} A \\ I \\ P \end{bmatrix}$$

$$[P](t) = [A]_0 - [A] \quad [I]$$

$$\boxed{\frac{d[I]}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [I]}$$

$$\frac{d[I]}{dt} + k_2 [I] = k_1 [A]_0 e^{-k_1 t}$$

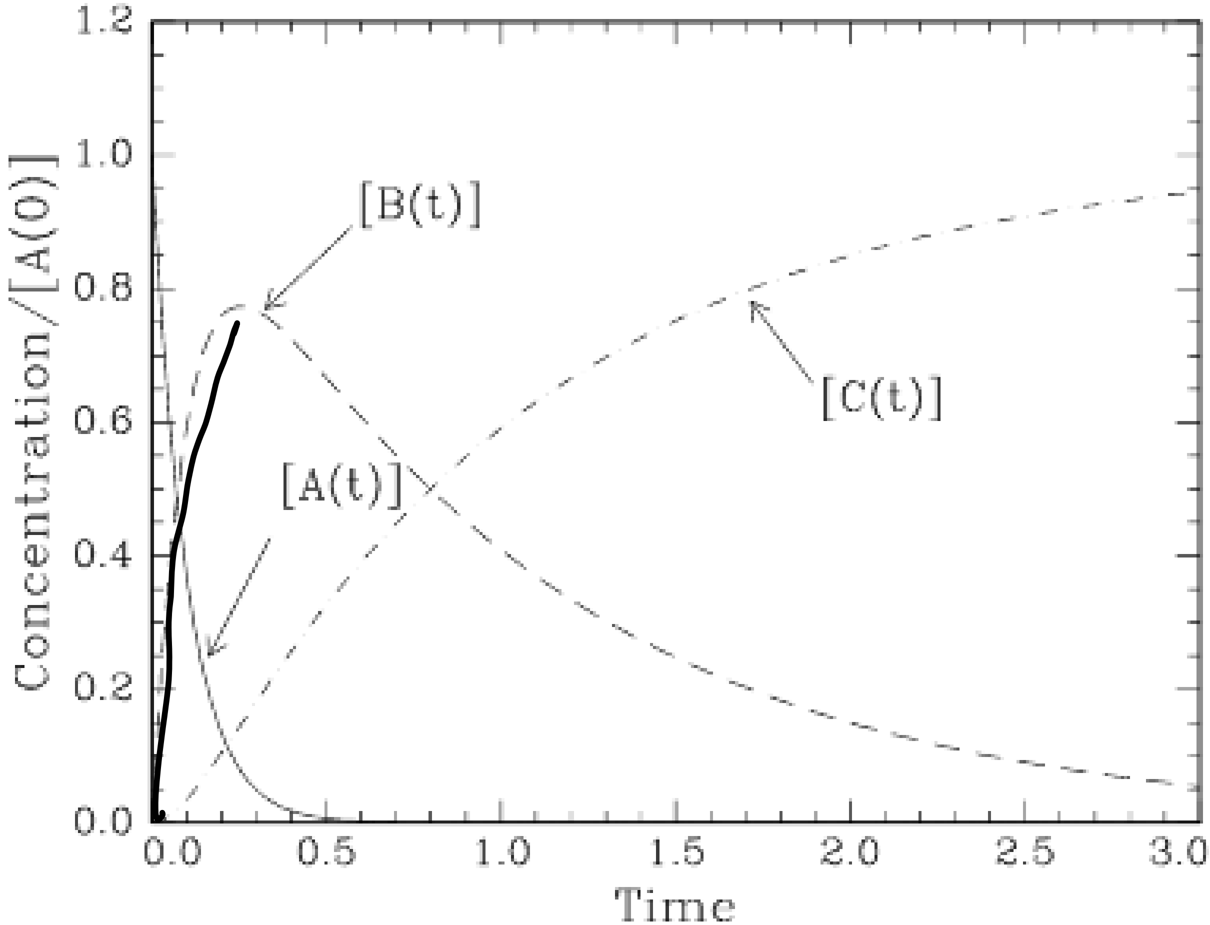
This equation may be converted into an exact differential equation by multiplying with an integrating factor. Do it yourself - look at your Calculus book, if needed.

The result is:

$$[I](t) = \frac{k_1[A]_0}{k_2-k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

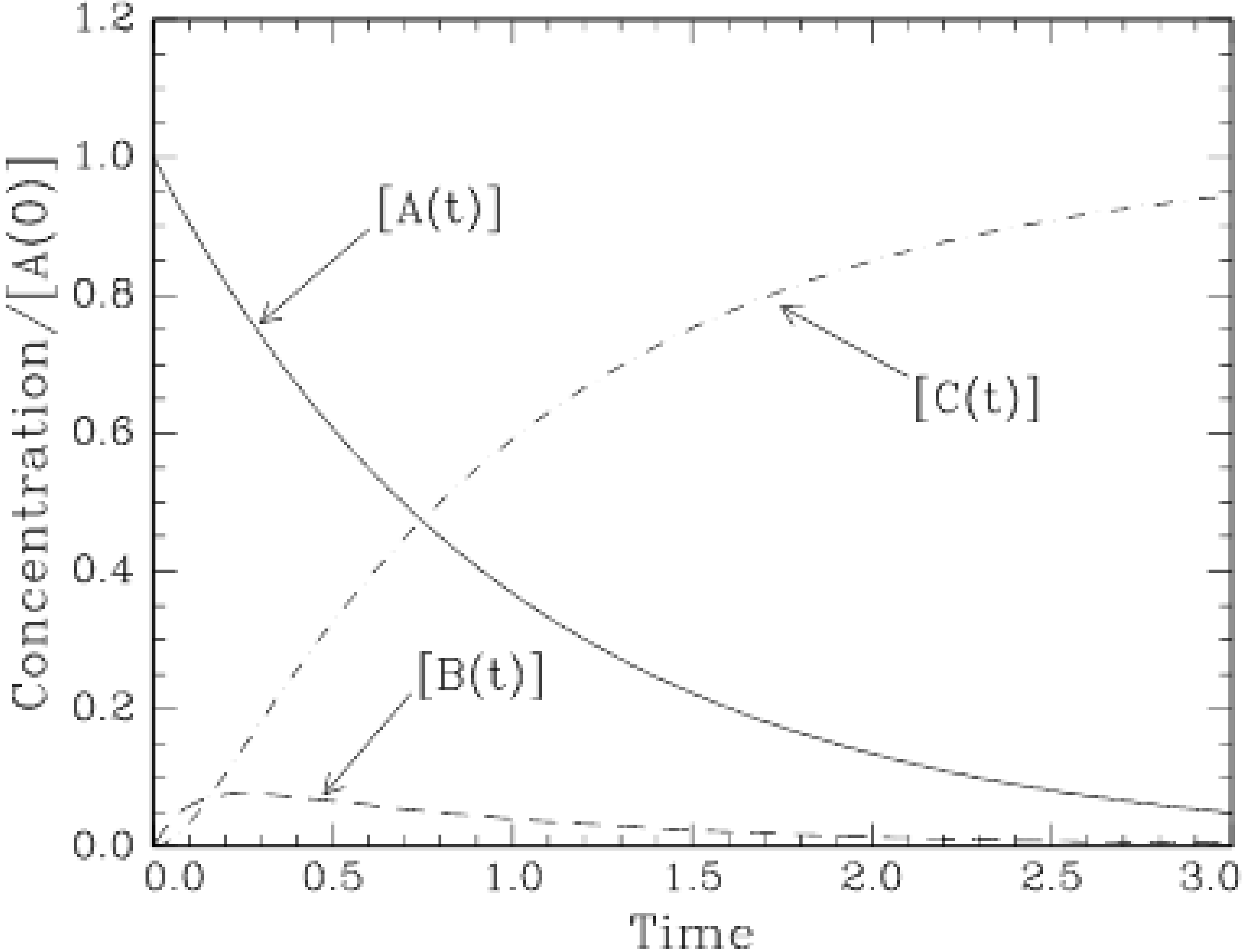
$[P](t)$ obtained by mass conservation $= [A]_0 - [I] - [A]$

Example plot for k1=10k2.



$k_1 = 10k_2$

$k_2 = 10 k_1$



[A(t)]
[C(t)]
[B(t)]
Concentration/[A(0)]
Time
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0

$$A \xrightarrow[\text{slow}]{k_1} I \xrightarrow[\text{fast}]{k_2} P$$

Derive the approximate forms in the two limiting situations:

(a) $k_1 \gg k_2$

(b) $k_2 \gg k_1$

$$[P]_b : \left(1 - e^{-k_1 t}\right)$$

Student question about ignoring backward reacrions. That is,why is it not

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P$$

Look at case (b):

$$\frac{d[I]}{dt} \approx 0 \quad [I \text{ is in steady state}]$$

Steady state approximation

$$k_1 [A] = k_2 [I]_{ss}$$

$$[I]_{ss} = \frac{k_1 [A]}{k_2}$$

$$\frac{d[P]}{dt} = k_2 [I]$$

$$[P](t) =$$