Bchm 102-2005
Assignment #1 solutions:

1. Rate equations according to the dimerization scheme:

$$\frac{dw}{dt} = \frac{dc}{dt} = -k_1 w(t)c(t) + k_{-1}h(t) \qquad \frac{dh}{dt} = k_1 w(t)c(t) - k_{-1}h(t)$$

Note that these are not all independent – there is always a relationship among w, c, and h.

2. What IS this relationship for the conditions of the problem? Each oligo is initially added at a concentration D, for a total concentration of DNA of 2D. As the reaction proceeds, this total concentration of DNA strands is given by:

Total DNA strands = w(t) + c(t) + 2h(t)

,since each molecule of helix consists of 2 oligo strands. Therefore, since the total number of DNA strands remains constant,

$$2D = w(t) + c(t) + 2h(t)$$

3. For the particular case here, $w(0)=c(0)=D$, $h(0)=0$, and $k_{-1}=0$. Also $w(t)=c(t)$ throughout the time-course. Also, the conservation of mass above demands that:

$$w(t) + h(t) = D$$

Thus, the equations become:

$$\frac{dw}{dt} = -k_1 w^2 \qquad \frac{dh}{dt} = k_1 w^2 = k_1 (D-h)^2$$

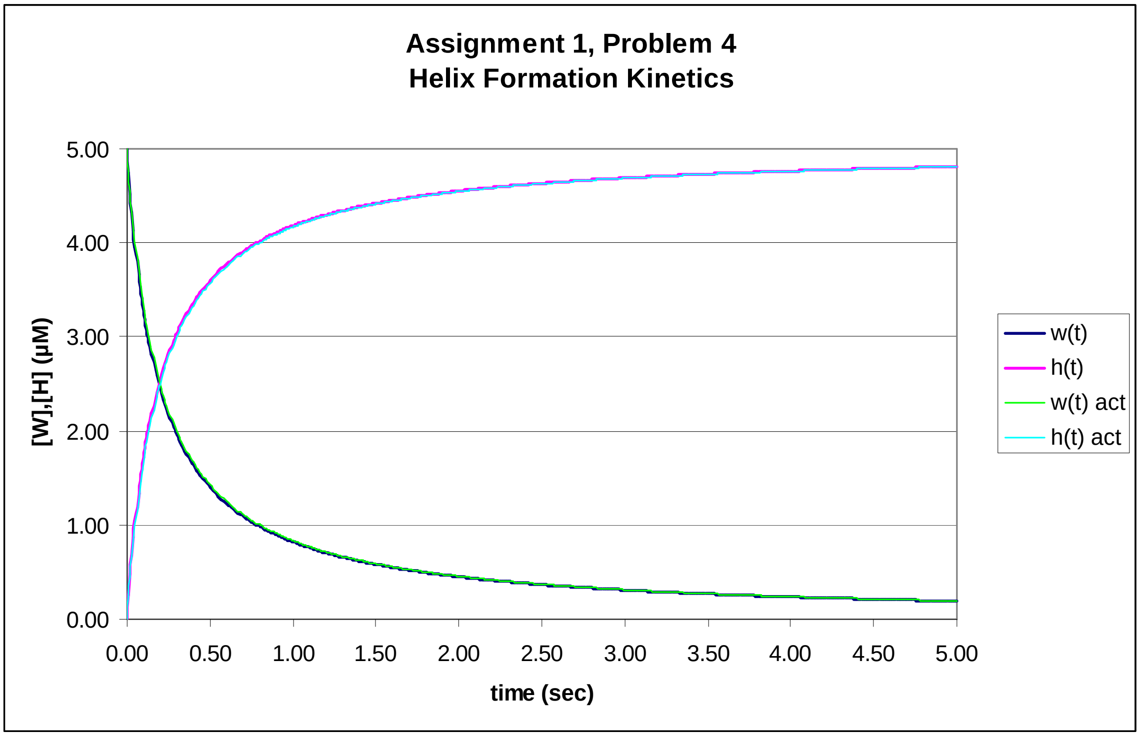
Now we can solve either of these, since each carries the same information. (For each W consumed one H is formed.) The W equation just looks easier, so let's try that. Of course, once we've solved it, we'll immediately know h(t), since h(t)=D - w(t), right? The W equation is easily rearranged to get all *w(t)* on the left and all *t* on the right:

$\frac{dw}{w^2} = -k_1 dt$, which can be immediately integrated: $\int_{w(0)}^{w(t)} w^{-2} dw = -k_1 \int_0^t dt$

(Notice that I have explicitly placed definite limits on the integrals; this is just a convenient way of incorporating the initial conditions of the problem.) This integrates to:

$= -\left[\frac{1}{w(t)} - \frac{1}{w(0)}\right] = \frac{1}{D} - \frac{1}{w(t)} = -k_1(t-0)$, or:

$w(t) = C(t) = \frac{D}{1+k_1 Dt} = \frac{1}{\frac{1}{D} + k_1 t}$ and $h(t) = D - \frac{1}{\frac{1}{D} + k_1 t}$ ===> **The solution!**



k1	1.00E+00	$\mu M^{-1}s^{-1}$
k2	0	s^{-1}
D	5.00E+00	µM
Dt	0.01	S

Time(s)	w(t)	h(t)
0	5	0
0.01	4.75	0.25

,where w(t) is '=R[-1]C-R[-1]C^2*k1*dt' and h(t) is '=D-RC[-1]'

The Excel file that you can play with is here.

5. Now start with c(t) = constant = C_0. Also, for these conditions, the conservation of mass is: *w(t)+h(t)=D*. Remember that it is no longer true that *w(t)=c(t)*! Now,

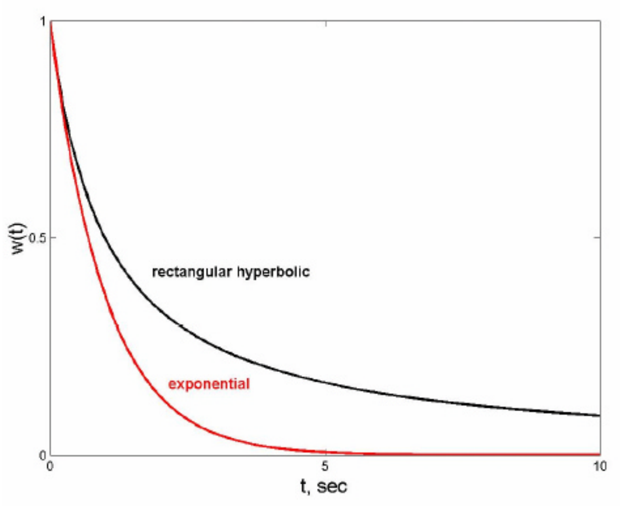
$$\frac{dw}{dt} = -k_1 w(t) C_0$$

(Note that there is still a dependence on c(t), except that it is a constant)

and again, we can separate variables and integrate:

$$\int_D^{w(t)} \frac{dw}{w} = \ln\frac{w(t)}{D} = -k_1 C_0 t \text{ or, } w(t) = De^{-k_1 C_0 t} \text{ and } h(t) = D(1 - e^{-k_1 C_o t})$$

Another way to think about this is to substitute $k_1^{'} = k_1 C_0$ in which case you get a familiar form $\frac{dw}{dt} = -k_1^{'} w(t)$.



Now, this is interesting – the functional forms of the timecourses in (3) and (5) are totally different depending on the details of the experiment, even though the rate equations governing them are identical! In (3), w(t) falls via a "rectangular hyperbolic" timecourse, which approaches its final values quite slowly (try it out!); in (5), w(t) still falls, but by a more familiar exponential timecourse, which attains its final value quickly. Think about the "why" of this difference; if you can see why the same differential equation produces such different results, you'll have understood something important.

6. The new conditions are, $W + C \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} H$, *w(0)=c(0)=0, h(0)=*$H_0$. So, the rate equation for helix dissociation is

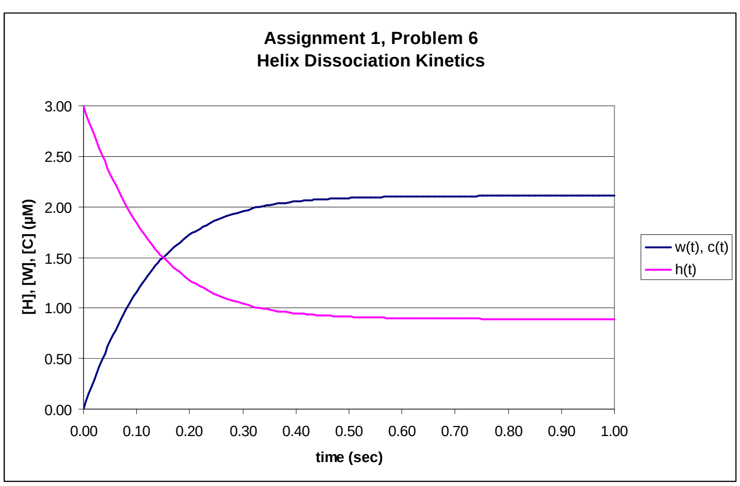
$$\frac{dh}{dt} = -k_{-1}h(t) + k_1 w(t)c(t) = -k_{-1}h(t) + k_1 w(t)^2$$

Applying conservation of mass, $w(t)=H_0-h(t)$, we get:

$$\frac{dh}{dt} = -k_{-1}h(t) + k_1 (H_0 - h(t))^2$$

, which we do not know how to solve because it contains $h(t)^2$ term.

We *can*, however, look at the timecourse of this reaction using Excel:



Timecourse of h(t) falls in the range of 0.1-1 sec. This makes sense, since $k_{-1}=5s^{-1}$.

The Excel file that you can play with is here.