<u>Integrating Rate Laws Using the Finite Difference Approximation</u>

In molecular dynamics, you used the finite difference approximation to integrate Newton's equation of motion for an anharmonic oscillator. The finite difference method can also be used to integrate kinetic rate laws. In fact, the finite difference approach is used by Stella. So learning how to integrate molecular dynamics equations also teaches you how to solve chemical kinetics problems.

For example, the first order rate law is:

$$-\frac{d[A]}{dt} = k\,[A] \qquad 1$$

Now approximating the derivative with finite differences gives:

$$-\frac{\Delta[A]}{\Delta t} = k\,[A] \qquad 2$$

Multiplying by $-\Delta t$ gives:

$$\Delta A = -\,k\,[A]\,\Delta t \qquad 3$$

where

$$\Delta A = [A](t) - [A](t-\Delta t) \qquad 4$$

with $[A](t)$ the concentration of A at time t and $[A](t-\Delta t)$ the concentration of A in the preceding time interval. Substituting eq. 4 into eq. 3 with some rearrangement gives:

$$[A](t) = [A](t-\Delta t) - k\,[A]\,\Delta t \qquad 5$$

or simplifying the notation gives

$$[A]_2 = [A]_1 + k\,[A]_1\,\Delta t \qquad 6$$

<u>The trick in using the finite difference approach is to use a Δt that is small enough.</u> In practice, you should run your calculation with two different Δt values and compare. If the runs differ significantly, choose an even smaller Δt and run again. This advice holds for Stella models, too.

Stella also uses some more sophisticated techniques to decrease the errors inherent in a finite difference integration, but the form of eq. 5 is still the basis. You can view the finite difference equations in Stella by clicking on the triangular shaped button that is just above the χ^2 symbol on the left hand border of the main window.

Table I is an example spreadsheet to show how well the finite difference approximation works, based on eq. 6. The exact column is from the exact integrated time dependence:

$$[A] = [A]_o\, e^{-kt} \qquad 7$$

If you would like an extra credit opportunity, you can write a finite difference spreadsheet for a consecutive reaction. Use the same rate constants as you did for your Stella model.

Table I. Comparison of the finite difference approximation to the exact solution of a first order rate law. k=0.3 sec^{-1} and Δt = 0.1 sec. Closer agreement is obtained with smaller Δt values.

t	[A]=[A]-k[A]dt	exact
0	1.000	1.000
0.1	0.970	0.970
0.2	0.941	0.942
0.3	0.913	0.914
0.4	0.885	0.887
0.5	0.859	0.861
0.6	0.833	0.835
0.7	0.808	0.811
0.8	0.784	0.787
0.9	0.760	0.763
1	0.737	0.741
1.1	0.715	0.719
1.2	0.694	0.698
1.3	0.673	0.677
1.4	0.653	0.657
1.5	0.633	0.638
1.6	0.614	0.619
1.7	0.596	0.600
1.8	0.578	0.583
1.9	0.561	0.566