Example 10.8 Testing the steady-state approximation.

The steady-state approximation contains an apparent contradiction: we set the time derivative of the concentration of some species (a reaction intermediate) equal to zero — implying that it is a constant — and then derive a formula showing how it changes with time. Actually, there is no contradiction since all that is required it that the rate of change of the "steady" species be small compared to the rate of reaction (as measured by the rate of disappearance of the reactant or appearance of the product). But exactly when (in a practical sense) is this approximation appropriate? It is often applied as a matter of convenience and justified *ex post facto* — that is, if the resulting rate law fits the data then the approximation is considered justified. But as this example demonstrates, such reasoning is dangerous and possible erroneous.

We examine the mechanism

$$A + B \xrightarrow{1} C$$

$$C \xrightarrow{2} A + B \tag{10.12}$$

$$C \xrightarrow{3} P$$

(Note that the second reaction is the reverse of the first, so we have a reversible second-order reaction followed by an irreversible first-order reaction.) The rate constants are k_1 for the forward reaction of the first step, k_2 for the reverse of the first step, and k_3 for the second step. This mechanism is readily solved for with the steady-state approximation to give

$$\frac{d[A]}{dt} = -k_e[A][B] \quad \text{with} \quad k_e = \frac{k_1 k_3}{k_2 + k_3} \tag{10.13}$$

(TEXT Eq. (10.38)). With initial concentrations of A and B equal, hence [A] = [B] for all times, this equation integrates to

$$\frac{1}{[A]} = \frac{1}{A_0} + k_e t \tag{10.14}$$

where A_0 is the initial concentration (equal to 1 in work to follow). We can use this as a diagnostic: if a graph of the reciprocal of the reactant concentration is linear, then the steady-state law, Eq. (10.xx) is correct.

In this example we shall solve the equations for this mechanism numerically in order to test the limits of the steady-state approximation. The differential equations are:

$$\frac{d[A]}{dt} = -k_1[A][B] + k_2[C]$$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C]$$

$$\frac{d[P]}{dt} = k_3[C]$$

For simplicity we assume [A] = [B] and designate these quantities as the first variable, y_0. The second variable is [C] = y_1 and the third is [D] = y_2. In entering the equations below, be careful to distinguish between "decorative" subscripts used for the rate constants — entered as "k.1:5" (for example) — and the index subscripts used for the vector **y**, entered as "y[0" (for example). Be sure you understand how the equations in the vector **D** follow from the differential equations above.

$$A + B = C \rightarrow P \qquad k_1 := 5 \qquad k_2 := 10 \qquad k_3 := 0.2 \qquad k_e := \frac{k_1 \cdot k_3}{k_2 + k_3}$$

$$y := \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad D(t,y) := \begin{bmatrix} -k_1 \cdot (y_0)^2 + k_2 \cdot y_1 \\ k_1 \cdot (y_0)^2 - k_2 \cdot y_1 - k_3 \cdot y_1 \\ k_3 \cdot y_1 \end{bmatrix} \qquad \begin{array}{l} tmax := 10 \\[6pt] npts := 100 \qquad \dfrac{1}{k_e} = 10.2 \\[6pt] \dfrac{npts}{tmax} = 10 \end{array}$$

The numbers above use rate constants with the same order of magnitude, but be careful: with rate constants of greatly different magnitude, these equations can easily become "stiff". Keep an eye on the ratio *npts/tmax*: it should be larger than k_e and any individual rate constant. If the steady-state law, Eq. (10.xx) is correct, then $1/k_e$ is the half life of the reaction; this calculation (shown above) can be used to determine *tmax* but, again, you must be careful: it is not appropriate in all circumstances.

The solution is shown below. The steady-state solution is calculated as *ss* for comparison (later); *ss* represents 1/[A] as predicted by the steady-state solution, Eq. (10.xx). Also we define a quantity *mult* whose utility is shown in the next box.

$$ans := rkfixed(y, 0, tmax, npts, D) \qquad\qquad i := 0 .. npts - 1 \qquad mult := 1$$

$$t := ans^{<0>} \qquad A := ans^{<1>} \qquad C := ans^{<2>} \qquad P := ans^{<3>} \qquad ss_i := 1 + k_e \cdot t_i$$

The box below shows the concentrations vs. time (left) and the reciprocal of [A] vs. time. (The intermediate, [C] is multiplied by *mult*: since this quantity is one, there is no effect, but other combinations of rate constants may give [C] too small to be seen on the same graph with the others, and increasing *mult* is a simple way to make it visible.)
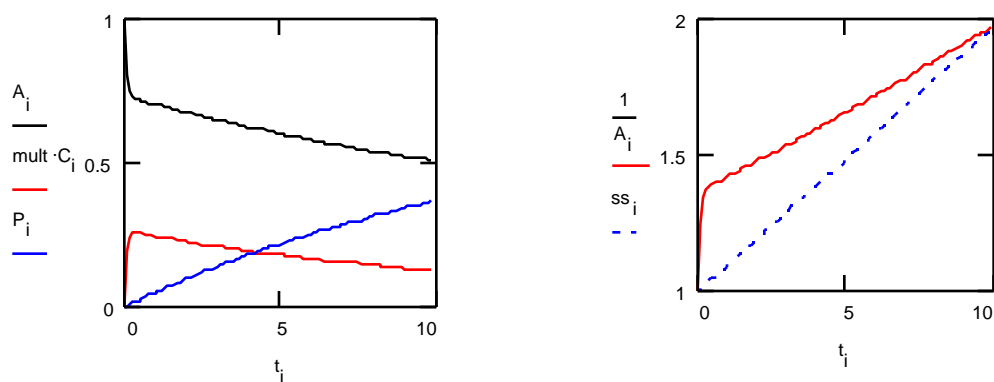
Comparison to the steady-state solution (*ss*, dashed line, above) makes it clear that the steady-state solution is not correct in this case, but would you realize that if you were dealing with real data? The calculated line (solid) is quite close to linear after the initial transient. Experimental considerations may prohibit you from obtaining measurements in the region of the transient — for example, mixing may be incomplete. Also, initial points are often deviant, and may be dropped from the analysis; we did exactly that in Example 10.1. Indeed, this example illustrates one reason that initial points may be deviant: a rate law may apply only after an initial transient.

Next, we will treat the calculated [A] as a data set, selecting points for analysis. We want to avoid the initial point since our objective is to see how well the second-order law works without that point.

$$k := 0 .. \frac{npts}{10} - 1 \qquad y_k := \frac{1}{A_{10 \cdot k + 10}} \qquad tx_k := t_{10 \cdot k + 10}$$

$$k_x := slope(tx, y) \qquad k_x = 0.062 \qquad k_e = 0.098$$

The box to the left demonstrates how to select every 10th point, starting with number 10, to be used as a data set for linear regression. Display the new arrays with "tx=" and "y=" to see what you have and to be certain it is what you want. The slope is the rate constant (*kx*) which is compared to the prediction, *ke*. The comparison is not good, but would we know that if we didn't know the answer? In the box below we calculate the error of the slope and compare the fitted line to the data with a graph.

$$time := 0 .. tmax \qquad y_{fit}(t) := intercept(tx, y) + k_x \cdot t$$
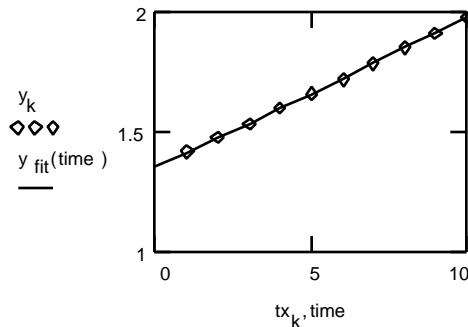
$$r := corr(tx, y) \qquad DF := 8$$

$$r = 0.999853$$

$$k := \frac{k_x}{|r|} \cdot \sqrt{\frac{1 - r^2}{DF}}$$

$$k_e = 0.0980$$
$$k_x = 0.0622$$
$$k = 0.0004$$

The graph looks very good; the residual graph (not shown) would show a clear systematic deviation, but with real data this could easily be obscured by experimental error (random scatter). The correlation coefficient (*r*) and standard deviation of the calculated rate constant ($_k$) are very good.

On one sense, this model is successful: it predicted a second-order rate law and, after the initial transient, that is what we find. For practical purposes, calling this a second-order rate with rate constant 0.0622 is quite correct. On the other hand, the relationship of the rate constant to the rates of the individual reactions is not at all what Eq. (10.xx) predicts. The steady-state approximation is not correct for this set of rate constants.

Try different rate constants; since there are 3 rate constant to vary (k_1, k_2 and k_3), to get meaningful comparisons it is best to keep something constant. For example, fix one of them and adjust the others, keeping k_e constant. Find conditions for which the steady-state law is exact: that is, it could not be distinguished from a simple second-order mechanism (A + B P) with any reasonable accuracy of the experimental data for [A]. Are there any conditions that give data that no reasonable person would ever mistake for a second order reaction?. What controls the length of the initial transient? In the end, you should be able to state in explicit, operational terms exactly what the conditions are for the steady-state approximation to be valid.