First Order Kinetics vs Second Order Kinetics

Students may report the dye bleaching reaction we study in the laboratory to be either first or second order in the dye. Why is it possible to obtain these ambiguous results?

The criterion we use to distinguish the order is specific and quantitative. Namely:

- we measure the dye concentration (or its absorbance, to which the concentration is directly proportional) as a function of time.
- We plot the reciprocal of the dye concentration vs time
- We plot the logarithm of the dye concentration vs time

If the plot of the logarithm vs time gives a more linear plot, we deduce that the order is 1

If the plot of the reciprocal vs time is more linear, we deduce that the order is 2

Our measure of “linearity” in each case is value of $R^2$, the “goodness of fit” criterion for the least squares linear fit to the experimental data.

The experimental data are subject to a variety of sources of error. These will generally produce plots that deviate somewhat from perfect straight line plots. I.e., the values of $R^2$ that we obtain have two contributions.

- A theoretical contribution due to the underlying ideal mathematical relationships between concentration and time that model first and second order kinetics
- A contribution due to experimental error

Let us ignore the second contributions to $R^2$ and ask how different the $R^2$ values are in the absence of experimental error.

To do so, we consider two cases: one in which a reaction is truly first order, and the second in which the reaction is truly second order. We ask how far from linearity is the plot for the inapplicable order (e.g., the second order plot when the reaction is truly first order) in each case?

What other characteristic of the experiment may have a bearing on this question? We know that in both first and second order kinetics, the concentration of the substance decreases in a non-linear but monotonic way. The distinction between these two will certainly depend on the time period over which they are measured.

**Case 1: Truly first order reaction.**

For such a reaction, the time dependence of concentration is given by

$$\frac{c}{c_0} = e^{-kt}$$
In the exercise, we make discrete measurements of \( c \) at specified intervals of time. Let us fix the number of measurements we make at that used in the experiment, namely, eight. We fix the total time over which we make the measurements by choosing a time increment, \( \Delta t \), between measurements measured in half-lives of the reaction. (E.g., if \( \Delta t = 0.25 \), 8 measurements will follow the reaction for 2 full half–lives.) The half–life of a first order reaction is given by \( t_{1/2} = \ln 2 / k \). In terms of \( (c/c_0) \) and \( (t/t_{1/2}) \), the first order concentration dependence becomes:

\[
\frac{c}{c_0} = e^{-\ln 2 \left( \frac{t}{t_{1/2}} \right)}
\]

We examine the values of \( R^2 \) and the slopes of the plots of the best, least squares, linear plots of the logarithm and the reciprocal of \( c/c_0 \) as a function of time, \( t/t_{1/2} \), and summarize the results as a function of the number of half lives over which we follow the reaction.

The results of such an analysis\(^1\) are as follows:

<table>
<thead>
<tr>
<th># half-lives</th>
<th>(-\ln (c/c_0))</th>
<th>( R^2 )</th>
<th>( 1/(c/c_0) )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.693</td>
<td>1.000</td>
<td>0.995</td>
<td>0.991</td>
</tr>
<tr>
<td>2</td>
<td>0.693</td>
<td>1.000</td>
<td>1.470</td>
<td>0.964</td>
</tr>
<tr>
<td>3</td>
<td>0.693</td>
<td>1.000</td>
<td>2.233</td>
<td>0.923</td>
</tr>
<tr>
<td>4</td>
<td>0.693</td>
<td>1.000</td>
<td>3.484</td>
<td>0.875</td>
</tr>
</tbody>
</table>

As can be seen from the table, the value of \( R^2 \) does not change for the log plot but for the reciprocal plot, it depends on the number of half-lives over which we follow the reaction. If our total time of observation is small, e.g. a single half life, \( R^2 \) will make it difficult to distinguish first from second order kinetics. Adding the likelihood that some experimental error will be introduced would confound the circumstances even more. Only if we follow the reaction for more than three half–lives, does the intrinsic \( R^2 \) become less than 0.900.

We note also that while the slope of the logarithm plot is constant over the range, the slope of the least squares straight line approximation to the reciprocal data varies over a large range – a factor of about 3.5.

What about the reverse case?

**Case 2: Truly second order reaction.**

For such reactions, the concentration dependence on time is given by

\[
\frac{c}{c_0} = 1 / (1 + c_0 kt)
\]

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\(^1\) These calculations are based on a spreadsheet available at: http://www.ic.sunysb.edu/Class/che133/spreadsheets/1stvs2nd.xlsx
A second order reaction does not have a single, constant, half-life. To get measures of time comparable to what we have done in Case 1, we define a *virtual* second order half-life as the time it takes for the initial concentration to fall to \( \frac{1}{2} \) of its original value. That time depends on both the original concentration, \( c_0 \), and the rate constant \( k \), namely \( t_{1/2} = \frac{1}{c_0 k} \). If we again use \( t_{1/2} \) as our scale of time, the second order rate law gives:

\[
\frac{1}{c/c_0} = 1 + \left( \frac{t}{t_{1/2}} \right)
\]

We again tabulate the slopes and \( R^2 \) for data spanning a number of half-lives.

<table>
<thead>
<tr>
<th># half-lives</th>
<th>(-\ln(c/c_0))</th>
<th>(R^2)</th>
<th>slope</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.686</td>
<td>0.990</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>0.536</td>
<td>0.976</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>3</td>
<td>0.444</td>
<td>0.963</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>0.382</td>
<td>0.951</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

The table shows that, unlike in Case 1, the goodness of fit criterion, \( R^2 \), degrades slowly as the number of half-lives increases. Following the reaction for four half-lives still gives an \( R^2 \) of 0.95. Based on the goodness of fit criterion, we are likely to interpret what are truly second order kinetics as first order!

Again, we note that the slope of the appropriate, reciprocal plot is insensitive to the number of half-lives while the slope of the “other”, logarithm plot decreases to almost half its value as the time scale is expanded to 4 half-lives.

Our efforts to “linearize” the process cannot hide the similarity in the initial values of the early parts of the underlying graphs of exponentials and reciprocals, as can be seen in the figure below.
With the reminder that in the above analysis, we have ignored contributions to $R^2$ due to experimental error, it is easy to see why the determination of the correct rate order requires considerable care in the kinetics measurements.

It also shows that, excluding large experimental uncertainties, for short observation periods, we are more likely to interpret the kinetics as first order than as second order.