Determining Reaction Order
Initial Rates and the Method of Isolation

A fundamental challenge in Chemical Kinetics is the determination of the reaction order (or, in general, the Rate Law) from experimental information. We know that the rate law closely related to the reaction mechanism, and the knowledge of the mechanism of a given reaction allows us to control that reaction. But how does one actually determine a rate law? The first step is to control the conditions under which a reaction occurs, and then determine the rate of that reaction. If we measure the reaction rate just after we define the reaction conditions, then this is a measurement of the initial rate of the reaction.

Consider a reaction \( A + B \rightarrow \text{Products} \). An experimenter prepares a reaction mixture of 1.00 M of each of the reactants and measures the rate of reaction initially (at very early times, i.e. before the reactant concentrations have had a chance to change much due to the progress of the reaction) to be \( 1.25 \times 10^{-2} \) M/s. What is the rate constant for the reaction?

You CANNOT determine this from the above information, because first you have to know the reaction order!

Note: The reaction stoichiometry does NOT determine the reaction order except in the case of an ELEMENTARY reaction. (An elementary reaction is one in which the reaction takes place with a mechanism implied by the reaction equation. Most reactions are NOT elementary)

If the above reaction was elementary, then the rate law would be:
\[
\text{Rate} = k[A][B]
\]
and the reaction would be first order in A, first order in B and second order overall. The rate constant can then be determined from initial rate information easily:
\[
k = \frac{(1.25 \times 10^{-2} \text{ M/s})}{(1.00 \text{ M})^2}
\]
\[
k = 1.25 \times 10^{-2} \text{ l/mol.s}
\]

Remember: The units of the rate constant depend on the overall order of the reaction.

More information about the reaction rate law is needed than a single measurement of an initial rate! In order to determine the rate law experimentally, we must use more than one measurement of rate versus concentration!

The Method of Initial Rates

Consider a reaction \( A + B \rightarrow \text{Products} \) (this time we know the reaction is NOT elementary). An experimenter prepares several reaction mixtures and determines the initial reaction rates under these different conditions. The data obtained for several experimental runs is tabulated below:

<table>
<thead>
<tr>
<th>Run #</th>
<th>Initial ([A]_0)</th>
<th>Initial ([B]_0)</th>
<th>Initial Rate ((v_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00 M</td>
<td>1.00 M</td>
<td>1.25 x 10^{-2} M/s</td>
</tr>
<tr>
<td>2</td>
<td>1.00 M</td>
<td>2.00 M</td>
<td>2.5 x 10^{-2} M/s</td>
</tr>
<tr>
<td>3</td>
<td>2.00 M</td>
<td>2.00 M</td>
<td>2.5 x 10^{-2} M/s</td>
</tr>
</tbody>
</table>

What is the rate constant for this reaction?

ANS: Before we do anything, we must determine the order of the reaction with respect to every reactant, i.e. we must determine the rate law for the reaction. In the above example, the order can be easily determined by inspection.

Method: Find a pair of experimental runs that the concentration of only one reactant changes. This is called the method of isolation and a good experimental design always has one such pair of experimental runs. We can see that in runs 1 and 2, only the initial concentration of B has been varied. In fact, \([B]_0\) has doubled from run 1 to run 2 and the
reaction rate has also doubled. Therefore the reaction must be First Order in B.

Examination of runs 2 and 3 show that in these experimental runs the concentration dependence of A has been isolated. In this case the doubling of the initial concentration of A has No EFFECT on the reaction rate so the reaction must be Zeroth Order in A.

Thus the rate law for the reaction is

\[ \text{rate} = k[B]^1[A]^0 = k[B] \]

Now, the rate constant can be determined from any of the experimental runs. Let's use run #3:

\[ \text{rate} = 2.5 \times 10^{-2} \text{ M/s} = k (2.0 \text{ M}) \]

\[ k = 1.25 \times 10^{-2} \text{ s}^{-1} \]

Note that the initial rate of any experimental run (any prepared experimental condition) can now be determined (calculated) since we have the rate law and the rate constant.

A More Complicated Example

Consider a reaction \( A + B + C \rightarrow \text{Products} \) (this, too, is not an elementary reaction). Several initial conditions of this reaction are investigated and the following data are obtained:

<table>
<thead>
<tr>
<th>Run #</th>
<th>([A]_0)</th>
<th>([B]_0)</th>
<th>([C]_0)</th>
<th>(v_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.151 M</td>
<td>0.213 M</td>
<td>0.398 M</td>
<td>0.480 M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.251 M</td>
<td>0.105 M</td>
<td>0.325 M</td>
<td>0.356 M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.151 M</td>
<td>0.213 M</td>
<td>0.525 M</td>
<td>1.102 M/s</td>
</tr>
<tr>
<td>4</td>
<td>0.151 M</td>
<td>0.250 M</td>
<td>0.480 M</td>
<td>0.988 M/s</td>
</tr>
</tbody>
</table>

What is the initial rate of the reaction when all the reactants are at 0.100 M concentrations?

ANS: First we must determine the rate law for the reaction, then the rate constant and then evaluate the rate law under the desired conditions.

Method: Isolate the effect of the concentration of one of the reactants. In runs number 1 and 3, the only change of initial concentrations is that of reactant C, a change from 0.398 M to 0.525 M with a change in rate from 0.480 M/s to 1.102 M/s. These numbers are not so easy as to be able to guess the order by inspection, so let's think mathematically. If we define the order of the reaction in reactants A, B, and C as \(a\), \(b\), and \(c\), we can write down the rate law (with unknown orders)

\[ \text{rate} = k [A]^a [B]^b [C]^c \]

The ratio of the initial rates of runs 1 and 3 is then:

Note that we have chosen this ratio so that many terms on the right hand side cancel, i.e. \(k\) and the concentrations of species \(A\) and \(B\). The ratio reduces to:

Note that none of the numbers in this equation have any units anymore because we have divided them out in a dimensionless ratio. Now, how to solve for \(c\)? Take the natural log (i.e. \(\ln\)) of both sides of the equation

or
So the reaction is Third Order in reagent C!

To continue, we pick another pair of runs that have a change in the initial concentration of C and just one other reactant. Let us choose the runs 1 and 4. The ratio of the initial rates of these runs is:

Note that everything cancels, is known, or is the order b. So:

We can determine b as before by taking the ln of both sides of this equation:

and \( b = 1.00 \). The reaction is First Order in B!

Now that we know the order of Reactants A and B, we can use another pair of experimental runs to determine the remaining unknown order. We must use a pair of runs where the initial concentration of A changes, so we pick runs 1 and 2. As before, the ratio of initial rates is

The rate constant cancels as before and we can solve for a:

and, as usual, take the ln of both sides:

which results in \( a = 2.00 \) and the reaction is Second Order in A.

The rate constant for the reaction may now be evaluated from any of the experimental runs:

or

\[
 k = 1.57 \times 10^3 \quad \text{l}^3 / \text{mol}^2 \cdot \text{s}
\]

These units are appropriate for a reaction that is sixth order overall. Use another experimental run to check your answer. If the rate law is correct, every experimental run will give the same value of the rate constant.

And now for the finale. The rate of the reaction when all the reactants are 0.100 M is:

**Time Dependent Concentrations**
Suppose you encounter a reaction with some stoichiometry, say: A \( \rightarrow \) 2B + C and you are asked to determine the order of the reaction from data obtained for [A] as a function of time.

<table>
<thead>
<tr>
<th>time</th>
<th>[A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 min</td>
<td>1.000 M</td>
</tr>
</tbody>
</table>
How do you solve such a problem??:

This, unfortunately is not an initial rates problem. We have not been provided with data spaced close enough to get an instantaneous rate under known reactant concentrations. So we must directly test the integrated rate laws for validity.

The way we have been shown to test for a particular integrated rate law is to make a plot of the data that should show a straight line. Suppose you can't make a physical plot, but want to solve the problem anyway?

If the reaction above were zeroth order, the concentration versus time would be a straight line. This means the change in concentration (Δ[A]) divided by the elapsed time (Δt) would be a constant, for any pair of data points. Let's see if this is true for our data:

\[
\frac{(0.800 - 1.000)}{10} = -0.0200 \\
\frac{(0.6667 - 0.800)}{10} = -0.01333 \\
\frac{(0.5000 - 0.6667)}{20} = -0.00834
\]

These numbers are NOT constant, so the reaction is NOT zeroth order.

If the reaction is first order, a plot of the natural log of the concentrations versus time will be a straight line. Thus, the change in the natural log of the concentration (Δln([A])) divided by the elapsed time (Δt) will be constant.

\[
\frac{(\ln(0.800) - \ln(1.000))}{10} = -0.0223 \\
\frac{(\ln(0.6667) - \ln(0.800))}{10} = -0.0182 \\
\frac{(\ln(0.5000) - \ln(1.000))}{40} = -0.0173
\]

Note: doen't matter which points...

These numbers are NOT constant, so the reaction is NOT first order.

If the reaction is second order, a plot of the inverse concentration versus time will be linear. Thus, the change in inverse concentration (Δ(1/[A])) divided by the elapsed time (Δt) will be constant.

\[
\frac{(1/0.800 - 1/1.000)}{10} = 0.0250 \\
\frac{(1/0.6667 - 1/0.8000)}{10} = 0.0250 \\
\frac{(1/0.5000 - 1/1.000)}{40} = 0.0250
\]

The reaction IS second order with a rate constant of 0.0250 M⁻¹ min⁻¹