OK, so you were blown away by the chemical kinetics lecture? Here's a brief summary:

For a reaction

\[ A + B + C \ldots \rightarrow P_1 + P_2 \ldots \]

the rate will depend on the concentration of at least one of the reactants (unless it is a 'zero order' reaction) to some power \( n_i \):

\[ \frac{dP}{dt} = k[A]^{n_A}[B]^{n_B}[C]^{n_C} \ldots \]

Some of the \( n_i \) could be zero, in which case the reaction rate is independent of the concentrations of those components (and 'zero order' in those reactants), so you can leave those terms out of the equation. The overall order of the reaction is the sum of the exponents of the concentration terms: \( \sum n_i \) and the order in any of the reactants is equal to the value of its \( n_i \).

There are two general methods for determining the order of a chemical reaction:
1) use measurements of initial rates
2) use an integrated rate equation

**Initial rates**

Start with a simple reaction: \( A \rightarrow P \)

The rate is measured by disappearance of \( A \) or appearance of \( P \) as a function of time, or

\[ \frac{-d[A]}{dt} = \frac{d[P]}{dt} = k[A]^n. \]

Determining the order of the reaction and the value of the rate constant can be done easily. Just run the reaction, measuring the decrease in \( [A] \) for a very short time, so that \([A]\) is approximately constant and equal to \([A]_0\); use this as the nominal reactant concentration. However, the concentration of \( A \) does decrease as the reaction proceeds. Measure \( [A] \) at various times, plot \( [A] \) versus \( t \), and the slope of the line \( \frac{d[A]}{dt} \) will be \(-k[A]_0^n\). (Remember that by definition, the derivative is the slope of the line tangent to the curve at a particular point; that point is \([A] = [A]_0\), \( t = 0 \). So, the initial rate is a direct measure of the derivative and you don't have to integrate the equation).

From one slope alone, you can't get either \( k \) or \( n \) because all you know is the product of \( k \) times \([A]_0^n \). But, you could run the reaction again with a different \([A]_0\) and see what happens. \( k \) is constant, so any change in the initial rate (i.e., slope) must come from \([A]_0^n \). Say that you double \([A]_0\) in the second run. If there was no change in the rate, \( n \) must be zero. If the rate is proportional to \([A]_0\), meaning that \( n = 1 \), the rate should double. If the rate goes up by a factor of four when you double \([A]_0\), then \( n = 2 \). If there are two reactants, you have to run the experiment again (i.e., three times), holding \([A]_0\) constant but varying \([B]_0\).

Once you know \( n \), just choose one of the rates, and plug in the values of \([A]_0\), \([B]_0\), etc. that produced that rate, plug in the \( n_i \), and solve for \( k \).

**Integrated rate equations**

In the initial rate approach, you just measured the very early part of the reaction, before \([A]\) became appreciably different from \([A]_0\), but you had to run the experiment again in order to change \([A]\). If you had just let the reaction go, \([A]\) would have changed all by itself. But then the reaction is harder to analyze because \([A]\) keeps changing and, unless the reaction is zero order in \( A \), the rate keeps changing, too. The question is how does the rate change as \([A]\) changes; does it vary as \([A]\), as \([A]^2\), as \([A]^3\) ...? You can use an integrated rate equation to figure it out, but the equation is different
for reactions of different order. Let's consider a few cases individually. We will only consider a uni-
reactant reaction (or assume that the reaction is zero order in any other reactants). So the general
equation is
\[-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k\cdot[A]^n\]
for all cases.

**Zero order reactions.** In this case, \(n = 0\) (duh). So, the equation is
\[-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k\cdot[A]^0.\]
It's easier if we can measure \([A]\), but if you have to measure \([P]\), let \([P] = [A]_0 - [A]\) so that there
will be an \([A]\) on the right side of the equation, and we can forget about \([P]\). What we want to do is
to integrate the equation (add up all of the incremental changes) between the start of the reaction and
some time \(t\) when we measure \([A]\) (or \([P]\)). So, write it like this:
\[-\frac{d[A]}{dt} = k\cdot[A]^0\]
then rearrange it to
\[\frac{d[A]}{[A]^0} = -k\cdot dt\]
The integral is
\[\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^0} = -k \int_0^t dt\]
which is very easy. Since \([A]^0 = 1\), the left side of the equation is just the integral of the derivative,
or \([A]\), evaluated from \([A]_0\) to \([A]\) and similarly for the right side:
\[[A] - [A]_0 = -k (t - 0) = -kt\]
So, a plot of \([A] - [A]_0\) versus \(t\) should be a straight line of slope = -k. You could also plot \([A]\) versus
\(t\) and get the same slope, but with an intercept of \([A]_0\). It doesn't matter. The point is, if you get a
straight line, the reaction is zero order.

**First order reactions.** Now the equation is
\[-\frac{d[A]}{dt} = k\cdot[A]\]
Again, we'll integrate is from the initial point, \([A] = [A]_0\) at time = 0, to \([A]\) at time = \(t\). First
rearrange the equation:
\[\frac{d[A]}{[A]} = -k\cdot dt\]
then integrate
\[\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt\]
If you remember that the integral of \(d(\text{cabin})\) over \((\text{cabin})\) is \(\log\) \(\text{cabin}\), the integral on the left is easy,
and the integral on the right is the same as before:
\[\ln [A] - \ln [A]_0 = \ln \frac{[A]}{[A]_0} = -kt\]
So, a plot of \(\ln \frac{[A]}{[A]_0}\) versus \(t\) should be a straight line if and only if the reaction is first order in \([A]\)
and zero order in anything else. The slope of the line is -k.
Second order reactions with one reactant. Let's skip all the explanations, which should be clear by now, and go right to the integral:

\[ \frac{d[A]}{[A]^2} = -k \frac{t}{0} \]

The only difference between this equation and the first order equation is the squared term in the denominator. So, the integral will be different, too. The \([A]^{-1} d[A]\) case is a special one whose integral equals a logarithm. All other powers follow a general rule that comes from the differentiation rule:

\[ d(u^n) = n u^{(n-1)} du. \]

To anti-differentiate, we go backwards:

\[ \int u^n du = \frac{1}{n+1} u^{(n+1)}. \]

In our case, \(n = -2\), so the left side of the integral is \(\frac{1}{1+(-2)} [A]^{-1}\) and the complete equation is

\[ -[A]^{-1} = -kt \]

Evaluated between \([A]_o\) and \([A]\), and 0 and \(t\), we get

\[ \frac{1}{[A]} - \frac{1}{[A]_o} = -kt \]

or

\[ \frac{1}{[A]} = \frac{1}{[A]_o} + kt \]

So, a plot of \(1/[A]\) versus \(t\) will be a straight line with slope = \(k\) and an intercept of \(1/[A]_o\) (if and only if the reaction is second order in \([A]\)).

This equation would work for a second order bi-reactant reaction that was first order in \([A]\) and first order in \([B]\), as long as the stoichiometry between \(A\) and \(B\) were 1 and \([A]_o = [B]_o\). In this case, \(A\) and \(B\) behave indistinguishably, starting at the same concentration and disappearing at the same rate; their concentrations are always equal. If either the stoichiometry were not one or the initial concentrations were different, you'd have to write a relation between \([A]\) and \([B]\) by linking them to the product formed:

\[ [A] = [A]_o - [P], [B] = [B]_o - m[P], \]

where \(m\) is the ratio of \(B\) used up per molecule of \(A\), assuming that you get one molecule of \(P\) per molecule of \(A\). In this case, you need to express \([B]\) in terms of \([A]\) so that the integral would have only \([A]\), \(k\) and \(t\). \([B]_o\) is a constant and it will be in the equation, too. Want to try it? If you do, you will find that the equation will not work in the special case of \([A]_o = [B]_o\), but you can use the simpler approach we went through above.

Pseudo zero order behavior

Keep in mind that the concentration of a reactant might not change during the course of the reaction because it is a catalyst or because its concentration is very large compared to the concentrations of other reactants; in the case of \(H^+\), the reaction mixture may be buffered. In this case, the order of the reaction in this component will not be apparent. The concentration of a reactant has to change during the reaction, or it will not play a role in the time course of the reaction; it just becomes part of the rate constant and the reaction is 'pseudo zero order' in that component. However, in the initial rates method, you can alter the concentration of any species you want (except perhaps solvent), so you can establish the order in any component (except maybe solvent).