Chemical Kinetics I: The Dry Lab

Up until this point in our study of physical chemistry we have been interested in equilibrium properties; now we will begin to investigate non-equilibrium properties and how the state variables of a non-equilibrium system change with time. In the case of chemical reactions, we are often concerned with the time rate of change of the concentrations of the reactants, products, and intermediates during the reaction. Knowledge of these rates of change provides deep insight into the mechanism by which a reaction proceeds. The only way to gain this knowledge is experimentally, by measuring the concentrations of the reactants, products, and intermediates during the course of a reaction. While such investigations are among the most difficult in all of chemistry, we are concerned here with the principles that govern these rates of change.

For a simple one step reaction it can often be shown that the time rate of change of the reactants or products is proportional to a quantity called the rate constant, \( k \) i.e. for the hypothetical reaction,

\[
A_2 \rightarrow 2A
\]

\[
\frac{d[A_2]}{dt} = k[A_2]^n,
\]

where \([A_2]\) indicates the concentration of \(A_2\) and the power \(n\) to which this concentration is raised is called the “order” of the reaction.

The quantity \(k\) often can be expressed by the general form

\[
k = AT^n e^{-\frac{E^*}{RT}}
\]

where \(E^*\) is the activation energy of the reaction and \(A\) is a constant. The quantity \(AT^n\) is related to the number of reacting molecules with energy \(E^*\) that can actually react to become products. Now if we are working with a reaction at constant temperature, then
$k$ is simply a constant. We are interested in the effects of changes in the magnitude of $k$ and $n$ on the rates of reactions. In this effort you will be using a sophisticated piece of software designed by the folks at IBM called the Chemical Kinetics Simulator. You may find this piece of software useful in your future courses or work.

In order to get familiar with this software you should first run the tutorial in Chapter two of the CKS manual. This is probably most easily done if you work in pairs. You may or may not prefer to bring up the Manual’s pdf file on one computer, while on the other you run the simulation. As you run this simulation think about what the various user supplied inputs represent physically. If you are not sure, ask.

Once you have completed the tutorial, complete the following investigations into the effects of changing $k$ and $n$ on simple reactions and then on a series of linked reactions each characterized by its own values of $k$ and $n$:

1) First set up the simple dissociation reaction

$$A_2 \rightarrow 2A$$

Treat the “form of the rate constant” (in the CKS software) as temperature independent. Now pick a rate constant (of order $10^{-3}$), also under “form of the rate law” click on the button to “use special rate law” and then “set rate law”. Make sure the value 1.00 is highlighted, if not, then enter this value. You have now designated kinetics of this reaction as first order. Set your initial concentration of $A_2$ to 1.0 mole per liter and that of $A$ to zero. Now run the simulation and inspect the plot of concentrations versus time for your reactions. Make sure you adjust your axes so that you have some resolution of the change in concentrations with time (about 200 seconds). Here and for the rest of the lab, you can export the plot results to an Excel spreadsheet for further analysis or to examine specific values. To do this, click on “Save” in the Plot window, and save as “Text”.

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1a) How long does it take for the concentration of $A_2$ to reach half of its initial concentration? How long does it take for the concentration of $A_2$ to reach a quarter of its initial concentration?

1b) Change the value of $k$ while keeping the reaction first order. What effect does this have on the length of time it takes to reach half and quarter initial concentrations?

1c) Based on your observations and knowledge of the rate law, what do you expect the functional form of the time dependence of $[A_2]$ to be? Check your expectations using Excel.

1d) Using the same values of $k$ but changing the value of $n$ from 1.00 to 2.00 repeat the calculations. Note that it takes considerably longer for the reaction to proceed to completion. Explain this on molecular grounds. Now, again determine how long it takes for the concentration of $A$ to reach half and quarter initial concentrations.

1e) The time it takes for a reaction to reach half-way to the final concentration is called the reaction half-life. If the final concentration is zero, half-way to the final concentration corresponds simply to half the initial concentration. Explain why the reaction half-life can be used to determine the rate constant of a first order reaction. Derive an equation that gives this relationship.

2) Make the reaction reversible, i.e.

$$A_2 \rightleftharpoons 2A$$

Fixing the reaction constant of the forward reaction and its order to be first, change the rate of the reverse reaction and its order. Under what conditions, if any, does the overall reaction, in terms of the time-dependence of the concentrations or behavior of the half-lives, appear to be first order? (Note that in this case, the final concentrations are not zero.)
3) Add the following second step to the reaction so that the overall reaction is:

\[ A_2 \leftrightarrow 2A \]

\[ A + A_2 \rightarrow A_3 \]

The net reaction above can be thought of as the conversion of \( A_2 \) to \( A_3 \), with the species \( A \) appearing as an intermediate. In some cases, the concentration of intermediates reaches a plateau sometime in the course of the reaction. This situation is called “steady-state” in the concentration of the intermediate. Steady-state may occur even if the concentration of intermediates is small, and so you may need to adjust the scale of your axes to determine if steady-state is occurring.

Alter the reaction parameters of the second reaction. What conditions are necessary in order to develop an observable intermediate concentration of \( A \)? What conditions are necessary in order to develop a steady-state concentration of \( A \)? Are there any conditions under which the overall reaction appears to be first order?

4) Finally, investigate the effects of activation energy on the rate of reaction. Use the simple reaction that we started with for this purpose, i.e.

\[ A_2 \rightarrow 2A \]

For this reaction treat the “form of the rate constant” as temperature dependent. For the value of the “A Factor” enter 1.0 e10, for the temperature exponent enter 0.0, and for the activation energy enter 17 Kcal/mole. Run the simulation and note the amount of time required to reach a concentration of \( A \) to be a half mole per liter. Now change the activation energy and note the time required to reach the same concentration.

How sensitive is the reaction rate to changes in the activation energy?
Using your insights from this simulation, explain how it is possible to dramatically alter the products resulting from competing reactions by small changes in the activation energies of these reactions. What do you expect the corresponding sensitivity to temperature changes to be?