# A First Course on Kinetics and Reaction Engineering Example 12.4

# **Problem Purpose**

This example illustrates the planning of experiments for the generation of kinetics data.

# **Problem Statement**

A research chemist in your company has discovered a solvent that allows 5-hydroxymethylfurfural (HMF) to be converted to levulinic acid (LA) and formic acid (FA), reaction (1), without the formation of any other side products. (When other solvents are used, some of the HMF is converted to a brown tarry substance commonly referred to as "humins.") You have been asked to generate a rate expression for reaction (1) in the new solvent. You have a stirred tank batch reactor in your lab that is fitted with a temperature controller that is effective in maintaining constant temperature in the reactor. The new solvent becomes a solid at 40 °C, and the solvent decomposes at 165 °C. It has a negligible vapor pressure over this range of useful temperatures. It is anticipated that the reaction will be run at a temperature between 60 °C and 160 °C and that reagent concentrations will typically lie between 0.05 and 1 M. The chemist has mentioned to you that the reaction requires hours when run at temperatures near the solvent freezing point, but it only takes seconds to minutes when run at the upper limit of the solvent's stability range. Reaction (1) is exothermic with a heat of reaction of approximately 149 kJ/mol.

$$C_6H_6O_3 + 2 H_2O \rightarrow C_5H_8O_3 + HCOOH$$

(1)

Specify the experiments you would ask your technician to perform in order to generate data that could be used to find a suitable rate expression for this reaction. For simplicity sake, assume that very small samples can be removed from the reactor, quenched (the reaction stopped) and analyzed for composition in a negligibly small amount of time.

### **Problem Solution**

Note: In the range of temperatures and compositions being studied here, some of the water and some of the formic acid are expected to exist as gases with the remainder being in solution. This will be ignored in the experimental plan described here; to account for it, the initial amounts of these materials would need to be adjusted to account for the amounts that vaporize.

Ideally the execution of your experimental plan should accomplish three things: it should verify that the reactor can be accurately modeled as an ideal batch reactor, it should provide some information that will help you when it comes time to guess the mathematical form of the rate expression and it should generate a large amount of data that spans the temperature and composition range within which the rate expression will be used. The experimental plan listed below will accomplish these objectives.

# I. Experiments to Verify the Ideality of the Reactor

A batch reactor will be used, so the primary assumption to be tested is that the reactor is perfectly mixed. This will be true if the characteristic time for mixing is small compared to the characteristic time for

reaction. The time for reaction will be shortest at the highest temperatures where the research chemist has suggested the time will be "seconds to minutes." Several experiments should be run at a temperature of 160 °C using stoichiometric amounts of the reactants at high initial concentration (1 M HMF and 2 M H<sub>2</sub>O). This should correspond to the greatest initial rate of reaction. Each of the experiments in this series should use a different agitator speed, and the contents of the reactor should be sampled every half second for the first minute or two. (Experiments where sampling occurs very frequently for a short period at the start of the experiment.) The concentration of one of the products should be plotted versus time, using one set of axes to plot the results of all the runs. At the highest agitation rates, the data from the runs should superimpose, suggesting that perfect mixing is an acceptable assumption. In runs with lower agitation rates, the product concentration versus time curve may be observed to deviate toward lower product concentrations. This is suggestive that the rate of mixing is beginning to affect the observed results, and that mixing can no longer be modeled as perfect. All subsequent experiments should be conducted at an agitation rate well within the range where the plots superimposed.

If none of the experimental runs overlap, that suggests that the reaction is too fast to be studied in the present reactor, at least if that reactor is to be modeled as a batch reactor. In this case, repeat the experiments just described at a lower temperature (150 °C) and determine whether the kinetics can be studied at that temperature. Repeat this until you find a temperature where the initial rate data overlap; this will indicate the minimum agitator speed and the maximum temperature for the kinetics studies. In the following it will be assumed that kinetics can be measured at 160 °C.

# II. Experiments to Provide Clues to Guessing a Rate Expression.

There are three kinds of information we'd like to generate in these experiments: the reversibility of the reaction, the temperature dependence of the reaction rate, and the concentration dependencies of the reaction rate. This reaction is exothermic, so we expect the equilibrium conversion to decrease as the temperature increases. To assess the reversibility of the reactant, perform an experiment at the highest temperature (160 °C) using stoichiometric amounts of the reactants (e. g. 1 M HMF and 2 M H<sub>2</sub>O). Allow the reaction to proceed, sampling periodically until the composition is no longer changing. If no detectable HMF and H<sub>2</sub>O remain, the reaction is irreversible; if the amounts of these species becomes constant, but non-zero, with time, the reaction is reversible. To estimate the temperature dependence of the rate, initial rate experiments (as described above) should be performed at three temperatures (e. g. 60 °C, 110 °C and 160 °C), using the same initial composition in all three cases (e. g. 1 M HMF and 2 M H<sub>2</sub>O). To estimate the concentration dependencies of the rate, perform five initial rate experiments, all at the same temperature (e. g. 110 °C). A base experiment should use a stoichiometric initial composition (e. g. 1 M HMF and 2 M H<sub>2</sub>O). In the other four experiments the initial concentration of one reagent should be changed. For example, the remaining four experiments might use the following four sets of initial compositions:

- + 0.8 M HMF, 2.0 M H\_2O, 0 M LA and 0 M FA
- + 1.0 M HMF, 1.8 M  $H_2O,\,0$  M LA and 0 M FA
- + 1.0 M HMF, 2.0 M H\_2O, 0.2 M LA and 0 M FA

### • 1.0 M HMF, 2.0 M H<sub>2</sub>O, 0 M LA and 0.0 M FA.

Notice that in the experiments just described for estimating the temperature and concentration dependencies of the rate, the experiments were performed in groups where only one variable changed in each experiment of the group. By holding all but one variable the same in two experiments, the results provide some indication of how the changed variable affects the experimental outcome. Thus, for example, comparing the results of the base experiment described above to the results of experiment 1 would provide some measure of how the concentration of HMF affects the experiment, because these two experiments used the same temperature and the same concentrations of H<sub>2</sub>O, LA and FA. Similarly comparing the base experiment to experiment 2 would provide insight into how the concentration of H<sub>2</sub>O affects the experimental result, and so on.

#### III. Experiments to Generate the Main Data Set.

We would like to generate a large data set wherein the temperature used in the experiments ranges from 60 °C to 160 °C, the concentration of HMF varies (say from 0.05 to 1.0 M), the concentration of H<sub>2</sub>O varies (again say from 0.05 to 1.0 M), the concentration of LA varies (say from 0 to 1.0 M) and the concentration of FA varies (say from 0 to 1.0 M). Suppose we selected temperatures of 60, 85, 110, 135 and 160 °C and initial concentrations of each species of 0.05 (for the reactants, 0.0 for the products), 0.2, 0.4, 0.6, 0.8 and 1.0 M. If we tried to vary each of these individually (as was done in part II), it would require nearly 6500 experiments. We probably don't have enough time to do that many experiments, so we'll perform some sub-set of these. It is beyond the scope of this course to consider which of these experiments to perform; there are many good textbooks on experimental design that will offer approaches to selecting the specific experiments to perform. See, for example, Box, Hunter and Hunter, "Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building," Wiley, New York, 1978. In addition, as you perform the experiments, you may find that certain variables or ranges of variables can be neglected because no difference is observed in the kinetics or because the rate is very, very low.

As pointed out in the information reading, reaction kinetics are more strongly affected by temperature than by concentrations. For this reason, we might want to perform our experiments in "blocks." One block of experiments would all use a common temperature (e. g. 75 °C), but the concentrations would vary as above. A second block would use a different common temperature (e. g. 100 °C), again with concentrations varying as above. Third and fourth blocks might use additional common temperatures (e. g. 125 and 150 °C, respectively), again with concentrations varying as above. A fifth block might vary all the variables, but with temperature different from the four blocks. This "blocked" experimental design would facilitate separate analysis of each of the four blocks using common temperatures to find how the rate depends upon the concentrations, and then using the results of that analysis, the full data set could be used to find how the rate depends upon temperature.