

A First Course on Kinetics and Reaction Engineering

Unit 12. Performing Kinetics Experiments

Overview

Generating a valid rate expression for a reaction requires both a reactor and an accurate mathematical model for that reactor. Unit 11 introduced the three most common types of reactors and their models, and it described some tests that can be used to assess the accuracy of the models without running a chemical reaction. This unit describes additional tests for assessing the accuracy of the ideal reactor models while chemical reactions are taking place. It then discusses exactly what is meant by “kinetics data,” and presents typical approaches to generating kinetics data using a batch reactor, a CSTR and a PFR.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- bulk fluid
- boundary layer
- external transport limitations
- internal transport limitations

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Describe how to test the assumption of perfect mixing by variation of the agitator speed while a reaction takes place
- List the sequence of steps that must occur when a heterogeneous catalytic reaction takes place within a porous solid catalyst
- Explain the consequences of any step other than the reaction rate being the rate-limiting process during the collection of kinetics data
- Distinguish between internal versus external heat and mass transfer limitations
- Describe an experimental procedure for determining whether external mass transfer is rate-limiting during kinetics measurements
- Describe an experimental procedure for determining whether internal transport processes are rate-limiting during kinetics measurements
- Apply computational tests to determine whether external transport is rate-limiting during kinetics measurements
- Apply computational tests to determine internal transport processes are rate-limiting during kinetics measurements
- Describe a typical experimental kinetics run for an ideal batch reactor, CSTR or PFR, listing set variables and measured variables that will make up the resulting kinetics data set
- Specify a set of experiments to generate kinetics data to be used in generating a rate expression for a given reaction making use of either a perfectly mixed batch reactor, a CSTR or a PFR

Information

Unit 11 described how to measure the age function for a laboratory reactor and compare it to the age function that would be expected if the reactor obeyed the assumptions of an ideal CSTR or an ideal PFR. That test can't be applied to a batch reactor, however. Additionally, even if the age function matches that of an ideal CSTR, it is still possible that the mixing will be incomplete if a very fast reaction is being studied. When a reactor is going to be modeled as perfectly mixed (i. e. as a batch reactor or a CSTR), another test can be used to compare the speed of mixing to the rate of reaction. Specifically, the apparent rate of reaction can be measured in a series of experiments where the rate of spinning of the agitator is varied. At very low agitation rates, the apparent rate may be low because the reactants aren't mixed well enough. In that case, as the agitation rate is increased, the apparent rate of reaction should also increase until it eventually reaches a constant value. If the apparent rate reaches a point where it no longer changes upon further increase in the agitation rate, it may be assumed that the mixing has become sufficiently rapid that the chemical reaction is now the limiting factor. This is the desired regime of operation, and in all experiments for kinetics data collection, the agitation rate should be above the identified plateau value.

All three ideal reactor models assume some degree of spatial uniformity (perfect mixing); the batch reactor and the CSTR assume spatial uniformity in all three dimensions within the reactor and the PFR assumes spatial uniformity in the radial direction. The presence of two phases within a reactor may disrupt such spatial uniformity. This is true for almost any combination of phases (liquid-gas, liquid-liquid, solid-liquid, solid-gas, etc.). Whenever kinetics data are gathered using a two phase system, additional testing must be performed in order to ascertain whether the two-phase system displays the spatial uniformity that is assumed in the ideal reactor models. If it does not, then the ideal reactor models cannot be used in the analysis of any kinetics data that are generated.

This unit will only consider one type of two phase system: one where a porous solid catalyzes a reaction involving fluid phase reagents. When a fluid flows around solid particles, a hydrodynamic *boundary layer* forms between the bulk fluid and the external surface of the solid particles. Fluid in the boundary layer does not flow in the same way as the fluid far away from the solid, it is more quiescent. This can lead to a concentration gradient across the boundary layer, in which case the concentration at the external surface of the particles will not be the same as that sampled from the bulk fluid. When solid heterogeneous catalysts are used in a reactor, the reaction takes place on the surface of the solid. Thus, if a concentration gradient exists across the boundary layer and you are not aware of its existence, then you will be measuring a composition (that of the bulk fluid) that is different from the composition where the reaction is taking place (at the solid surface). If you were to use the data to generate a rate expression, the rate expression would be incorrect.

Figure 1 may help to illustrate the problem caused by the presence of concentration gradients during a heterogeneous catalytic reaction. First consider Figure 1a. The left side presents a highly magnified schematic representation of a location near a solid catalyst particle. The bulk flowing fluid is represented in light blue; this is the fluid that would be sampled in an experiment. In the location pictured, the concentration of a reactant of interest is equal to C_{bulk} . Close to the surface of the catalyst particle

there is a thin boundary layer, represented in the figure in pink. The figure makes this layer look very thick; that is only done for illustration purposes. Within the boundary layer where the fluid is relatively quiescent, the reactant moves via diffusion, not bulk fluid flow. If the concentration of the reactant could be measured at points along the black arrow in Figure 1a and then plotted as a function of the distance from the start of the boundary layer, the result would look like the graph on the right side of Figure 1a. The concentration of the reactant decreases steadily as one moves through the boundary layer perpendicular to the solid surface. No reaction takes place until the solid surface is reached, because the solid is needed to catalyze the reaction. Figure 1a shows how the reaction is taking place at a concentration denoted in red as C_{surf} . In an experiment, however, one would measure a concentration of C_{bulk} , and if the data were used to generate a rate expression, that rate expression would predict a rate at C_{bulk} that was really the rate at C_{surf} .

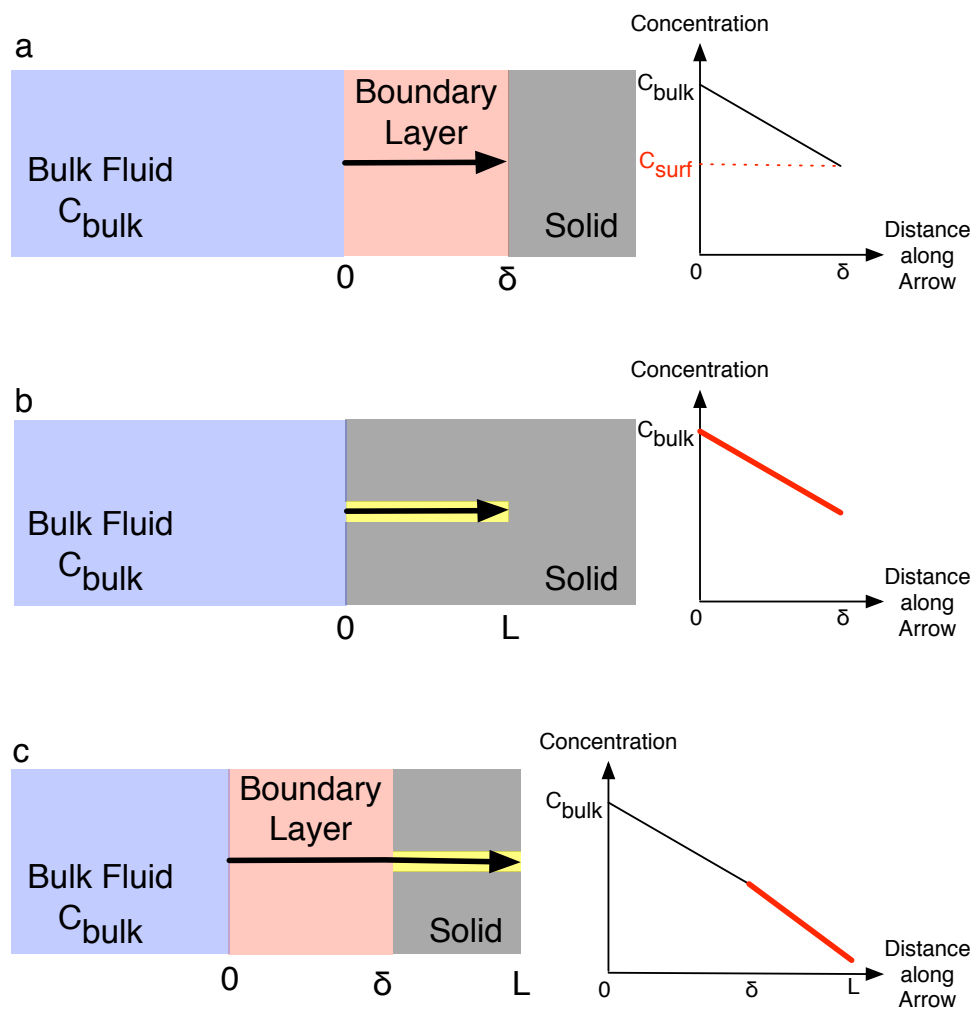


Figure 1. Schematic representations of (a) external mass transfer limitations, (b) internal mass transfer limitations and (c) combined external and internal mass transfer limitations.

If the solid is porous, as shown in Figure 1b, the situation is more complicated. Figure 1b assumes that the boundary layer is negligibly thin, but that the active sites for the reaction are primarily located within the pores of the solid, shown in yellow. Once again, there isn't any bulk fluid flow within these pores, and the reactant of interest has to move via diffusion along the path indicated by the thick black arrow. As before, this means that there will be a gradient in the concentration of the reactant at points lying along this path. The plot on the right side of Figure 1b shows that the concentration of the reactant decreases steadily. When compared to Figure 1a, the difference is that reaction is taking place over the whole range of concentrations indicated by the red line in the plot whereas in Figure 1a the reaction only took place at C_{surf} . Close to the entrance to the pore, the concentration is near C_{bulk} , and so near the pore entrance the reaction takes place at that concentration. A little farther into the pore, the concentration is a little lower, and so here the reaction takes place at a little lower concentration, and so on.

In fact, for a porous catalyst, both situations may exist simultaneously as illustrated in Figure 1c. The term “*external transport limitations*” is used to refer to a situation where concentration gradients between the bulk fluid and the external surface of the solid are sufficiently large to affect kinetics measurements. “*Internal transport limitations*” then refers to the situation where gradients within the pores of the solid are sufficiently large to affect kinetics measurements. The key point is that when gradients form, one measures a composition that does not correspond to the composition where the reaction is taking place, and this will lead to a rate equation that is wrong. The presence of gradients is not limited to concentrations; analogous temperature gradients may exist.

Considering a heterogeneous catalytic reaction taking place as depicted in Figure 1c, the events that must occur in order for reaction to take place include the following:

1. Reactants diffuse through the boundary layer separating the bulk fluid from the external surface of the catalyst.
2. Reactants diffuse into the catalyst pore structure.
3. Reaction takes place at a catalytically active site.
4. Products diffuse back through the catalyst pores to the external surface of the catalyst.
5. Products diffuse from the external surface of the catalyst through the boundary layer to the bulk fluid.

Heat must be transferred via an analogous process, but with the added complexity of radiation, direct particle-to-particle conduction, particle-to-wall conduction, etc. If you look at all the steps involved, only one (step 3 above) is a chemical reaction process; the rest are all physical transport processes. In order for the ideal reactor models to apply, all of those physical processes must occur with sufficient speed that the one reaction step is the sole factor that determines the overall rate. Put differently, we say that the chemical reaction step must be the rate-controlling step of the overall process. Gradients will always be present, but if the reaction step is rate-controlling, then the size of the gradients will be negligibly small.

Returning to the topic of generating a rate expression, the possibility of significant concentration gradients means that additional testing must be performed. Before any kinetics data are gathered for a porous heterogeneous system, it is necessary to test the reactor system for external concentration and temperature gradients and for internal concentration and temperature gradients. The tests are of two

types: computational and experimental. The conventional approach involves separate testing for external transport limitations and internal transport limitations. If concentration and temperature gradients are very small in both places, then the ideal reactor models can be used to analyze laboratory kinetics data. Similar precautions must be taken for other kinds of multiphase systems, e. g. liquid-liquid, gas-liquid, etc. This course will not consider all of these other systems from the perspective of validating reactor models, but instead it will limit consideration to testing reactors used for heterogeneous catalytic reactions.

Testing for External Transport Limitations. A common experimental test for external mass transfer limitations in a plug-flow (packed bed) reactor relies on the fact that for an ideal PFR, the conversion depends only upon the residence time within the reactor and not the linear velocity of the flowing fluid. The external mass transfer coefficient, in contrast, does depend upon the linear velocity of the flowing fluid. Thus, if the conversion changes when the linear velocity is changed while holding the residence time constant, this indicates that the apparent rate is being affected by the rate of external mass transfer. One approach to this test is to measure the conversion at varying fluid velocities with a fixed amount of catalyst and plot the conversion versus the residence time. The experiment is then repeated using a different amount of catalyst. In the absence of mass transfer limitations, the plots should superimpose. An alternative approach is to measure the conversion with a given amount of catalyst and at a given fluid flow rate. The conversion is then measured again using a different amount of catalyst, but with a flow rate that gives the same residence time as in the first experiment. In the absence of external mass transfer limitations, the conversions should be equal. Care should be taken in applying this test, however, because at the very low Reynolds numbers that are often used in laboratory reactors, the mass transfer coefficient depends very weakly upon the fluid velocity [1].

The Berty and Carberry reactors described in Unit 11 are designed to create very high linear fluid velocities through the catalyst bed. Consequently, by operating these reactors at sufficiently high rotational speeds, external heat and mass transfer limitations can be eliminated. For this reason, these reactors are sometimes referred to as gradientless reactors. It should be pointed out in this context, however, that the reactor design only eliminates external gradients; there still may be gradients within the pores of the catalyst particles. The agitator speed test described at the start of this unit should be applied when using a Berty or Carberry reactor.

When external mass transfer limitations are very severe, a first-order rate expression, equation (12.1) will be found to fit the experimental data very well. In this case it is more appropriate to refer to equation (12.1) as the apparent rate expression because the rate it refers to is the rate of external mass transfer and not the rate of reaction. The true rate expression can be first-order, but when external mass transfer limitations are severe, the apparent activation energy, E , will be very low (≤ 10 to 15 kJ mol^{-1}). True reaction rates typically have activation energies that are greater than this. This can serve as a warning indicator when kinetics data are being analyzed. If the reaction kinetics are observed to change to first order and the activation energy is simultaneously observed to become small, the kinetics data may contain experiments where external transport limitations existed.

$$r = k_0 \exp\left(\frac{-E}{RT}\right) C \quad (12.1)$$

There are also computational tests for external transport limitations that can be applied [2-5]. External temperature gradients can be safely ignored if equation (12.2) is satisfied and external concentration gradients can be safely ignored if equation (12.3) is additionally satisfied. In these equations ΔH is the heat of reaction, r is the rate of generation of a reactant, r_p is the radius of the catalyst particles, h is the heat transfer coefficient, T is the bulk fluid temperature, R is the ideal gas constant, E is the activation energy, C is the reactant concentration, k_c is the mass transfer coefficient, and n is the reaction order.

$$\frac{(-\Delta H)(-r)r_p}{hT} < 0.15 \frac{RT}{E} \quad (12.2)$$

$$\frac{(-r)r_p}{Ck_c} < \frac{0.15}{n} \quad (12.3)$$

Similarly, radial temperature gradients in the reactor can be ignored if equation (12.4) is satisfied, where λ is the thermal conductivity, r_r is the reactor radius and T_w is the wall temperature.

$$\frac{|\Delta H|(-r)r_r^2}{\lambda T_w} < 0.4 \frac{RT_w}{E} \quad (12.4)$$

The equations for the computational tests have been presented here without derivation. The cited references at the end of this document can be consulted to learn how these expressions were derived. Briefly, mass and energy balances are formulated for the fluid-catalyst system and re-arranged into a dimensionless form. An analysis is then performed to find the value of the dimensionless parameters in the balance equations where transport through the boundary layer affects the overall rate of the diffusion-reaction process by no more than 5% (or some other small percentage).

Testing for Internal Transport Limitations. Most heterogeneous catalysts are porous solids with very high specific surface areas. One gram of catalyst can have a surface area of hundreds of square meters. Most of this surface area is internal and corresponds to the walls of pores (picture the catalyst interior as looking like a microscopic sponge). The only way for reactants to reach the majority of the catalytic sites is to diffuse into the pore structure. If the rate of the reaction at the active sites is large, this can lead to the formation of significant concentration gradients within the pores. For present purposes, the goal is to be able to identify experimental conditions where these gradients are insignificantly small. As with external transport effects, the presence of significant internal transport limitations can be detected experimentally and computationally. As a general rule of thumb, external temperature gradients are more likely than internal temperature gradients while internal concentration gradients are more likely than external concentration gradients. This makes some sense because internally, heat can be conducted

through the solid part of the catalyst particles as well as through the fluid within the pores, whereas mass can only diffuse within the fluid in the pores.

One experimental test for the presence of internal heat or mass transfer limitations is to repeatedly measure the conversion using finer and finer catalyst particle sizes. In the absence of internal gradients, the conversion should not depend upon the particle size, but if gradients are present, their effects should diminish as the particle size is decreased. This happens because the diffusional path length becomes smaller as the particle size is decreased.

Koros and Nowak [6] suggest a test where the catalyst is prepared from two powders that are mixed and formed into catalyst pellets. One powder is inert while the other is catalytic. Two or more sets of pellets are prepared using different ratios of the powders. In the absence of internal gradients, the ratio of the observed rates should equal the ratio of amounts of the active powders used to prepare the catalysts. Madon and Boudart [7] describe a similar test where the catalyst comprises very small active catalyst nanoparticles supported on a porous oxide carrier.

There are also a few computational tests for the presence of intraparticle temperature or concentration gradients. For an isothermal reaction, equation (12.5) can be used to calculate ϕ_s where r_p is the particle radius, r is the reaction rate, D_{eff} is the effective diffusion coefficient and C is the reactant concentration. For a zero-order reaction, the effects of concentration gradients in the pores will be negligible if ϕ_s is less than 6. For first order reactions it should be less than 1, and for second order reactions it should be less than 0.3.

$$\phi_s = \frac{r_p^2 (-r)}{D_{eff} C} \quad (12.5)$$

Similarly, if equation (12.6) is satisfied, then temperature gradients within the catalyst particles should be negligibly small. In equation (12.6), ΔH denotes the heat of the reaction, λ is the thermal conductivity of the particles, R is the ideal gas constant, T is the temperature, and E is the activation energy.

$$\frac{r_p^2 (-r) \Delta H}{\lambda T} < 0.75 \frac{RT}{E} \quad (12.6)$$

Generation of Kinetics Data. Once a reactor has been selected and an accurate model for that reactor has been developed and validated, kinetics data can be generated. Whenever possible, one attempts to select a reactor that can be accurately modeled as one of the ideal reactor types (perfectly mixed batch, CSTR or PFR). In addition, if the reactor being used is accurately described by one of the ideal reactor types, the kinetics data will be easier to analyze if the preferred model of operation for that reactor type is employed. The preferred mode of operation is isothermal for a batch reactor, steady state for a CSTR and isothermal, isobaric and steady state for a PFR. Unless explicitly stated otherwise, it always will be assumed in this course that kinetics data have been generated using a laboratory reactor

that has been experimentally tested and shown to obey the assumptions of one of the three ideal reactor types and that has been operated in the preferred mode.

The paragraphs to follow describe, in general terms, the experimental procedure that would typically be used to generate kinetics data with each of the three reactor ideal reactor types. Before that, it should be pointed out that it is generally desirable to accumulate as large a set of data as possible. At the bare minimum, the range of temperatures, pressures and compositions used in the experiments should cover the range of those variables where the resulting rate expression will be used. In other words, it would be unwise to generate a rate expression using data from experiments at temperatures between 300 to 500 K if that rate expression was going to be used to design or model a reactor that operates between 400 and 650 K. In this respect, the problems you will find in most courses (including this one) and textbooks are grossly unrealistic. It's not uncommon to find a kinetics problem in a textbook that provides three to five data points and asks you to use those data to generate a rate expression. In a real world situation where you had to generate the data yourself, you might generate several hundred data points in order to find that same rate expression. As such, many textbook and course problems do an excellent job of illustrating the procedure for analyzing data, but they utilize an unrealistically small set of data to do so.

In general, it is good practice to design kinetics experiments statistically. You may have been exposed to factorial design of experiments in a lab course. Design of experiments will not be considered in this course; there are numerous books and publications available on the topic. That said, it is often a good idea to perform a few experiments wherein the concentration or partial pressure of each reactant and product is varied separately. The reason is that the procedure for generating a rate expression requires you to guess a mathematical form for the rate expression prior to testing it. A few simple experiments like this can guide you when guessing a mathematical form for the rate expression. For example, if you did two experiments where all compositions were the same except that the concentration of one reactant was doubled, and if the apparent rate quadrupled when that concentration doubled, then it would make sense to guess a mathematical form where the rate was proportional to that concentration squared instead of some other concentration dependence. The majority of the experimental data can still be gathered using a statistical design, with a few experiments like this to help in making a good guess for the mathematical form of the rate expression. Similarly, if you cannot perform an equilibrium analysis, it is a good idea to perform a few experiments using a very large residence time so that you can observe whether the reaction is irreversible (goes to completion) or not. If the reaction is reversible, it will (or at least it should) affect the mathematical form that you guess for the rate expression.

There's one other data-related factor to consider before describing procedures for generating data using the different reactor types. That has to do with the effects of temperature as compared to the effects of pressure and composition. Generally speaking, reaction rates are much more sensitive to temperature than to pressure or composition. As a consequence, it is quite common to collect "blocks" of data where all the experiments in any one block are run at the same temperature. This then permits the data to be analyzed in two steps. First each of the blocks are analyzed to ascertain the dependence upon pressure and composition, after which the full data set is analyzed to find only the temperature dependence using

the already-determined pressure and composition dependence. This is not a universal, nor a required practice, but it is quite common.

Typical procedure for generating kinetics data using a steady-state CSTR. This sub-section describes a single experiment (sometimes also called a run or an experimental run) using a CSTR. It further assumes that only one chemical reaction takes place in the reactor. Each CSTR run generates a single data point, so in order to generate a large data set, one typically performs a large number of experimental runs. The experiment begins with setting a constant inlet flow rate for each species along with a constant inlet temperature and pressure. Flow, pressure and temperature control devices are used to ensure that these quantities do not change over the course of the experiment. The temperature of the reactor contents is usually also set and some form of electronic temperature controller is used to hold it constant at the desired value. Note that the inlet flow is not required to contain only reactants, it is permissible, and often desirable, to include products in the inlet flow stream.

The temperature, pressure and composition of the outlet from the reactor are then monitored over time until they all cease varying with time and become constant. This indicates that the reactor has reached steady state. At this point it is wise to double check the inlet temperature, pressure and composition to make sure they haven't changed from their initial settings. The kinetics data point can then be recorded. It should include the inlet temperature, pressure and composition, the outlet temperature and some property of the outlet flow stream that can be used to determine its composition or the extent of reaction. There are a huge variety of properties that can be measured (concentration, electrical conductivity, absorption of light of a particular frequency, etc., etc., etc.). The key point is that the measurement must allow calculation of either the outlet concentration of a species or a reaction progress variable. (As noted, this assumes that there is only one reaction taking place; if there were two reactions, it would be necessary to measure two different quantities that could be related to the progress of the two reactions. Generally it is necessary to measure as many such quantities as there are mathematically independent reactions.) It is permissible to measure more than one property, of course, as this will allow for an independent check on the consistency of the data. That is, if you measure two properties and each property can be used to independently calculate the extent of reaction, the difference in the resulting extents of reaction gives an indication of the reliability of the data. To summarize, when only one reaction is taking place, an experimental data point consists of the measured values of the inlet temperature, pressure, composition and flow rate, the outlet temperature and the measured value of one property of the outlet stream from which the extent of reaction can be calculated.

Typical procedure for generating kinetics data using an isothermal, perfectly mixed batch reactor. Typically, the generation of kinetics data using a batch reactor also involves many separate experiments. However, each experiment using a batch reactor can generate more than one data point. To perform a batch reactor experiment, measured amounts of the desired reagents are put into the reactor (where they mix perfectly), and then as quickly as possible the reactor is set to the desired temperature. As soon as the reactor has stabilized at the desired (constant) temperature, its full composition is measured. This marks the starting time and starting conditions (temperature, pressure and composition) for this experiment. Periodically, after this, one records the elapsed time and simultaneously measures a

property that is related to the extent of reaction (see the discussion above for the CSTR). The temperature should also be measured as a check, but if the reactor is being operated isothermally, its value should remain constant. Any number of such measurements can be made, and each one yields a separate data point. Once the desired range of conversions has been spanned, or once the reaction has reached completion, the experiment is over. Subsequent experiments will typically utilize a different initial composition and/or a different temperature. When using a perfectly mixed batch reactor (and assuming only one reaction is taking place), a data point consists of the amount of material put in the reactor at the start of the experiment; the starting time, starting temperature, starting pressure and starting composition for the experiment; the elapsed time of the data point and the value of a property related to the extent of reaction measured at that time. As mentioned, each experiment can generate several such data points.

Typical procedure for generating kinetics data using an isothermal, steady-state PFR. From an operational viewpoint, the procedure for performing kinetics experiments using a PFR is exactly the same as the procedure used with a CSTR. Each experiment will yield a single data point, just as with the CSTR. Because the preferred operational mode of the PFR includes isothermal operation, it is not necessary to measure both the inlet and the outlet temperatures because by definition they will equal each other (if the reactor is truly isothermal). In Units 14 and 15 we will see that there are different ways to analyze PFR data. One method of data analysis is known as the differential method of analysis of PFR data. If one plans to use the differential method of analysis of the data, then an additional restriction is imposed during the experiments (or at least on those experiments to be analyzed differentially). This requirement is that the molar flow rate of each species present in the feed should not differ by more than ca. 5% from the flow rate of the same species at the outlet from the reactor. The reason for this restriction should become clear after studying Unit 14.

In concluding this unit, it is important to note that the procedures given here are typical, but there are hundreds of possible variations upon them that would also serve the desired purpose of generating data for subsequent kinetics analysis.

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