# A First Course on Kinetics and Reaction Engineering

## Unit 11. Laboratory Reactors

### Overview

Rate expressions are generated by selecting a mathematical function to be tested to see whether it is acceptable, gathering kinetics data in a laboratory reactor, substituting the function to be tested into a model for the laboratory reactor, fitting the resulting laboratory reactor model to the experimental data and assessing the fit. The first section of this part of the course examined different ways to select a mathematical function for testing. In Section B, the focus shifts to the experimental tasks associated with generating a rate expression. This unit introduces three very common laboratory reactor types and the models for them. Unit 11 describes each of these three most-common reactor types. For each of them, the assumptions used to model them are enumerated, and the preferred way of operating them is described. The model equations corresponding to the preferred operational mode are then presented, followed by some discussion of actual equipment of that type. The unit concludes by describing some tests that can be used to gauge how well an actual laboratory reactor conforms to the assumptions used to model it.

### Learning Objectives

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

- perfectly mixed batch reactor (batch reactor)
- continuously stirred tank reactor (CSTR, perfectly mixed flow reactor)
- plug flow reactor (PFR)
- adiabatic reactor
- isothermal reactor
- steady-state reactor
- age function
- residence time distribution function (age distribution function)
- stimulus
- response
- tracer
- step change stimulus
- impulse stimulus
- fluid element

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- age function for an ideal CSTR
- age function for an ideal PFR

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:

- Write the mole balance design equation for a perfectly mixed batch reactor model, a perfectly mixed, steady state flow reactor and a steady state plug flow reactor
- Describe the assumptions inherent in the perfectly mixed batch reactor model, the steady state flow reactor model and the steady state plug flow reactor model
- Give an example of a laboratory reactor that can be modeled as a perfectly mixed batch reactor, a perfectly mixed flow reactor and a plug flow reactor
- Given a description of a laboratory reactor and how it is operated, determine whether it can be modeled as a perfectly mixed batch reactor, a perfectly mixed flow reactor, a plug flow reactor, or none of these ideal reactors
- State the upper and lower bounds for the age function
- Use experimental stimulus/response data (for either a step change or an impulse) to construct the corresponding age function and use the result to determine the reactor can be accurately modeled as one of the ideal flow reactor types
- Describe the conditions under which a reactor might pass the age function test, but nonetheless, the assumption of perfect mixing would not be valid
- Describe less sophisticated tests that can be used to determine the ideality of the flow in a reactor

## Information

At first it is surprising to learn that the vast majority of reactors used for the purpose of studying reaction kinetics are of three basic types. Laboratory reactors come in a variety of sizes, shapes and configurations, but even though they often appear to be completely different, most of them can be modeled as either perfectly mixed batch reactors, continuous flow stirred tank reactors or plug flow reactors. The reason for this is that the reactors are classified on the basis of the equations that are used to model them, and not solely upon their appearance.

***Perfectly mixed batch reactors*** are often referred to simply as batch reactors, but the assumption of perfect mixing is implicit. A perfectly mixed batch reactor is one that does not have any feed flowing into it, nor any product effluent being removed from it. The contents of the reactor are assumed to be perfectly mixed. That is, if you simultaneously sampled the fluid at many different locations within the reactor, the samples would all have the exact same composition and they would be at the exact same temperature. In a batch reactor, the composition and temperature will change over time (temporally), but at any one moment in time the composition and temperature will be uniform throughout the fluid volume (spatially).

Typically the reactants are first loaded into the reactor; this is also called charging the reactor. If the charge to the reactor has not been pre-heated, then once the reagents are in the vessel, it may be necessary to heat the contents to a temperature where reaction will take place. If the reaction being studied involves two or more reactants, they can be pre-heated to the desired temperature before adding them to the reactor. Alternatively, it may be necessary to add catalyst to start the reaction. As soon as the reactor is ready (i. e. charged and at the desired temperature) the initial composition is analyzed. The kinetics experiment is taken to begin at the instant the initial composition is analyzed. The reaction is allowed to proceed for a measured length of time. Periodically during this interval the elapsed time the composition is recorded. If the temperature of the reaction mixture is constant throughout this length of time, it is said that the reactor is being operated isothermally. *Isothermal operation is the preferred method for collecting experimental kinetics data when using a perfectly mixed batch reactor*. Note that isothermal operation will usually require adding or removing heat at a rate that varies during the course of processing the batch. Adiabatic operation, where no heat is added or removed during the processing of the batch, is less desirable for gathering experimental rate data.

If the laboratory batch reactor can be accurately modeled as being both perfectly mixed and isothermal, then the kinetics data analysis only requires a single design equation (assuming only one reaction takes place). The design equation, that is, the reactor model, is nothing more than a mole balance on one of the participating species. The mole balance design equation for such a perfectly mixed, isothermal batch reactor is given in equation (11.1). In equation (11.1) $n_i$ denotes the number of moles of species $i$ present in the reactor, $t$ denotes the time, $V$ is the volume within which reaction occurs and $r_{i,j}$ is the rate per unit volume of the only reaction, $j$, taking place with respect to species $i$. Note that $n_i$ changes with time; the design equation is a differential equation. The left-hand side of equation (11.1) represents the accumulation of moles of $i$ in the reactor and the right hand side represents the rate of generation of moles of $i$ in the reactor. By definition, there are no input or output terms in the batch reactor mole balance.

$$\frac{dn_i}{dt} = Vr_{i,j} \tag{11.1}$$

Real, physical examples of a batch reactor can be as simple as a well-stirred beaker or flask immersed within a constant temperature bath. Figure 11.1 shows such a flask. It also shows an electronically controlled stirring motor (A), the shaft of which extends into the flask where it causes the rotation of a stirrer (B). Reagents can initially be placed in the flask through one neck (C) while a thermometer passes through a second neck and is immersed in the reacting fluid. Coolant or heating fluid flows through a jacket that surrounds the reacting fluid. The coolant enters and leaves the jacket through two ports (E). When the reaction is done, the contents of the reactor can be drained through stopcock D.

An agitator, like that in the reactor of Figure 11.1 often is not very effective for mixing of gases. For gases, one might use a recirculation loop reactor, which can be modeled as a perfectly mixed batch reactor if operated appropriately. Figure 11.2 gives a simple schematic diagram of a recirculation loop reactor. In-line mixing devices can be placed in the flow path to promote thorough mixing of the fluid. The reactor must be operated at a very high recirculation rate, and the pump and other components must be operated at a constant temperature. If heterogeneous catalytic reactions are being studied, a packed catalyst bed can be inserted somewhere within the loop. In this case, the amount of reactant converted during a single pass through the bed should be very small so that the compositions at the beginning and at the end of the bed are essentially equal. In this way the composition will change with time, but within

*Figure 11.1. A simple round-bottomed flask that can be used as a perfectly mixed batch reactor. (In this photograph, the agitator, B, appears to be flipped upside down.)*

the reactor, composition will be essentially uniform everywhere in the loop, just as the batch reactor model assumes. A recirculation reactor such as that shown in Figure 11.2 is particularly useful for the study of a single gas phase reaction that involves a change in the total number of moles. In such a system, if the initial composition, temperature and pressure are known, the composition at any other time can be found from a measurement of the total pressure. Thus kinetics data can be measured simply by recording the total pressure as a function of time.

The stopped flow reactor, shown schematically in Figure 11.3, is a batch reactor that is especially useful for the study of rapid, liquid-phase, bimolecular reactions. Solutions containing the reactants are fed in separate streams to a small mixing chamber. This chamber is designed so that the fluids enter as high velocity jets. The high velocity of these jets causes instantaneous, perfect mixing when the jets enter the reactor. Downstream from the mixing chamber, but still near to it, a detector is located. Typically the detector is a spectrophotometer. This device shines radiation of a given frequency through the fluid and measures how much of the radiation is absorbed. The frequency of the radiation is chosen so that only one of the reactants or products absorbs the radiation. In this way the response from the spectrophotometer is directly proportional to the amount of the one reactant or product that absorbs the radiation. In a typical experiment the fluids begin flowing and a steady state is established. The flow is then stopped instantaneously, and the response of the

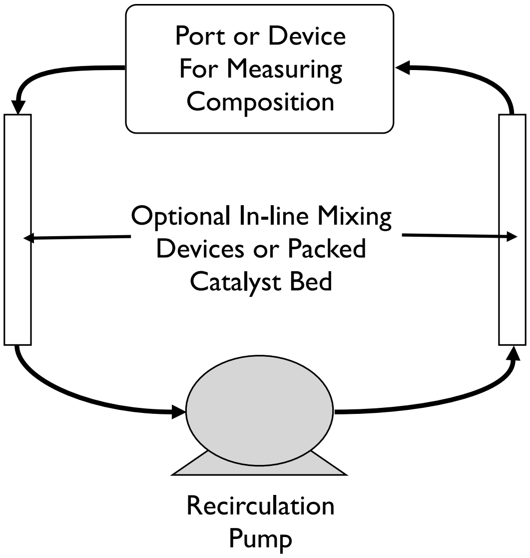

*Figure 11.2. A recirculation loop can be used as a perfectly mixed batch reactor.*

spectrophotometer is recorded as a function of time. The instant the flow stops, the volume through which the radiation passes becomes a very small batch reactor.

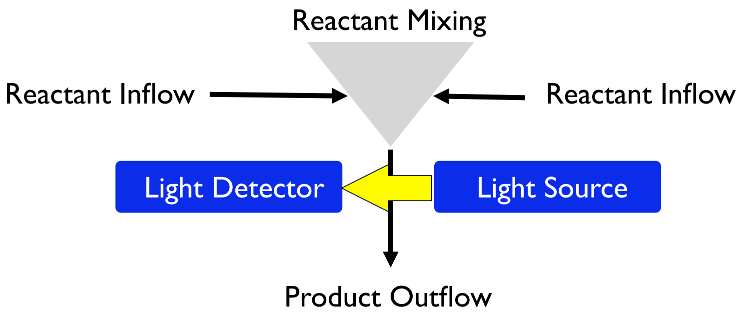

*Figure 11.3. Schematic representation of a stopped-flow reactor.*

***The continuously stirred tank reactor*** is also called a perfectly mixed flow reactor, a perfect mixer, or by the acronym for continuously stirred tank reactor, CSTR. As with the batch reactor, the most important assumption made in the modeling of a perfectly mixed flow reactor is that the contents of the reactor are perfectly mixed. The difference between a batch reactor and a CSTR is that in a CSTR, reagents are fed into the reactor continuously at a known rate of flow and with known temperature and composition. The flow into the reactor may be as a single stream or as two or more separate streams. In addition, a product stream is continuously removed from the reactor. If the total mass flowing into the reactor equals the total mass flowing out of the reactor, and if each of the flow rates, compositions, and temperatures does not change with time, the reactor is said to be operating at steady state. Put differently, when a reactor is operating at *steady state*, then at any one point in the reactor the environmental variables do not change with time, all flows into and out of the reactor are constant, and the volume of fluid within the reactor is constant. Like a batch reactor, a CSTR can be operated as an isothermal reactor (the temperature is constant) or as an adiabatic reactor (no heat is added or removed).

When a perfectly mixed reactor is used to collect kinetics data for the purpose of generating a rate expression, *it is most preferable to operate the reactor at steady state*. As long as the reactor temperature is known for each experiment and assuming that only one chemical reaction is taking place, this permits the use of a single, mathematically simple design equation in the kinetics data analysis. That design equation is nothing more than a mole balance on one of the species participating in the reaction. The design equation for a steady state, perfectly-mixed flow reactor (a CSTR) is given in equation (11.2). *Equation (11.2) assumes that a single reaction, $j$, is taking place*, that it is homogeneous and that the rate will be normalized per unit volume of reacting fluid. In equation (11.2) $\dot{n}_i$ denotes the net, steady-state molar flow rate of species $i$ (a superscript $0$ denotes the net inlet molar flow rate while the absence of a superscript denotes the net outlet molar flow rate), $V$ denotes the volume within which reaction occurs and $r_{i,j}$ denotes the rate per unit volume of reaction $j$ with respect to species $i$. Looking at equation (11.2), it is easy to see that the left-hand side is the moles of $i$ out minus the moles of $i$ in, and the right hand side is the generation of moles of $i$. That is, equation (11.2) is a mole balance on species $i$; there is no accumulation term because it's been assumed that the reactor is operating at steady state.

$$\dot{n}_i - \dot{n}_i^0 = V r_{i,j} \tag{11.2}$$

Any real laboratory reactor that is going to be modeled as a perfectly mixed flow reactor must be designed so that the composition is uniform throughout the reactor. There are several ways in which this can be accomplished. The batch laboratory reactor shown in Figure 11.1 could be converted into a CSTR simply by allowing reactants to flow in continuously (at a constant temperature and flow rate) at neck C and simultaneously allowing fluid to drain from stopcock D at the exact same total mass flow rate. This is probably the simplest design for a homogeneous liquid phase reaction. If a reactor like that shown in Figure 11.1 was converted to a CSTR as just described, one would need to carefully balance the inlet and outlet flow rates so that the amount of fluid in the reactor remained constant (to fulfill the assumption of steady-state). An alternative design would be to use a stirred flask or tank with a large diameter tube leaving from its side. This overflow tube would become the outlet stream from the reactor. The inlet flow rate could be varied over a range of values, and as long as the liquid level in the reactor did not rise above the overflow tube, it would not be necessary to adjust the outlet flow rate in order to maintain steady state.

If the reaction takes place in the gas phase, a stirred tank type of design is not always effective, especially at low pressures. A conventional agitator may not be able to mix gases fast enough to satisfy the criterion of perfect mixing. One alternative is to let the gases flow into the reactor at high velocity through jets in the reactor sides. The kinetic energy of the molecules as they enter provides the mixing within the reactor. Another possibility is to use a recirculation loop as the reactor, as shown schematically in Figure 11.4. In-line mixing devices can be placed within the loop to promote mixing. With this reactor design, the flow velocity within the loop is much higher than that in the feed and effluent lines. Care must be taken so that the temperature is not changed within the pump or elsewhere in the recirculation loop. Also, the system must be designed so that a negligible amount of reaction takes place within the feed and effluent lines, because these are not perfectly mixed. The most common way to do this is to keep the feed and effluent lines much cooler than the recirculation loop. A variation on this design can be used when dealing with heterogeneous catalytic reactions. A small, fixed catalyst bed is inserted within the loop. Conditions are selected so that the conversion of the reactants upon passing through the catalyst bed is very small. In this way, the compositions before and after the catalyst bed are nearly identical, and the reactor satisfies the criterion of essentially perfect mixing. In order to keep the conversion across the bed low, it will be necessary to use high flow rates within the loop, so it is natural for the recirculating flow to be much larger than the flow in either the feed or effluent lines. As the feed enters the loop, it is immediately

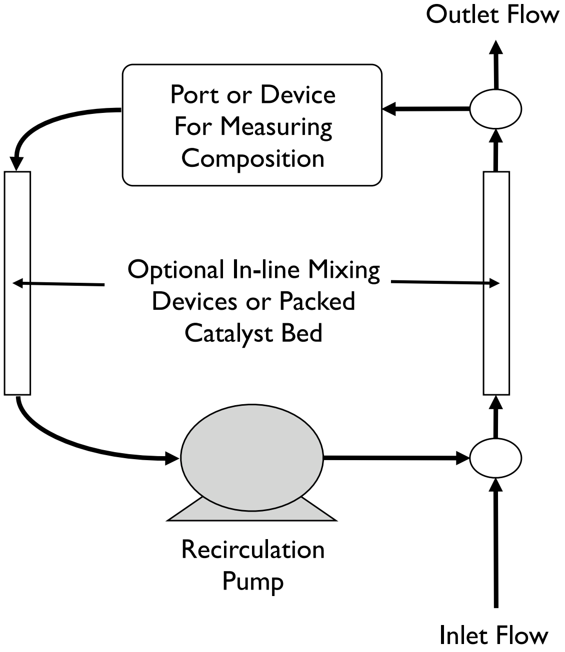

*Figure 11.4. A recirculation loop can be used as a CSTR.*

diluted to the mean loop composition, just as the fluid flowing into a continuous flow stirred tank reactor is immediately diluted when it enters the tank.

When a gas phase reaction is catalyzed by a solid, it isn't practical or desirable to try to stir the reactor contents. An autoclave (high pressure reactor) can be used to combine the recirculation and the packed bed of catalyst. This particular reactor geometry has come to be known as a Berty reactor. A schematic diagram is given in Figure 11.5a. In that figure, the catalyst is held as a stationary cylindrical packed bed indicated in light blue that is coaxial with the cylindrical autoclave. An impeller (gray) spins at the bottom of the autoclave drawing gas at a very high velocity from the bottom of the catalyst bed and directing it back to the top of the catalyst bed as indicated by the dark blue arrows. The outer vessel is made of thick steel so it can withstand high pressures and temperatures, and there are gas feed and outlet lines. The recirculation rate within the reactor is much, much greater than the feed and outlet flow rates. Alternatively, the agitator shaft can have baskets attached to it, and the catalyst can be placed within these baskets. The baskets are then rotated rapidly and serve as the agitator. This design is commonly known as a Carberry reactor as shown schematically in Figure 11.5b. In that figure, the baskets filled with catalyst are indicated in gray and are shown attached to a shaft that causes them to spin rapidly within the autoclave. In addition to satisfying the perfect mixing criterion, these reactors also eliminate some diffusion problems that can cause difficulty when measuring heterogeneous catalytic reaction rates. These diffusional problems are discussed in Unit 12.

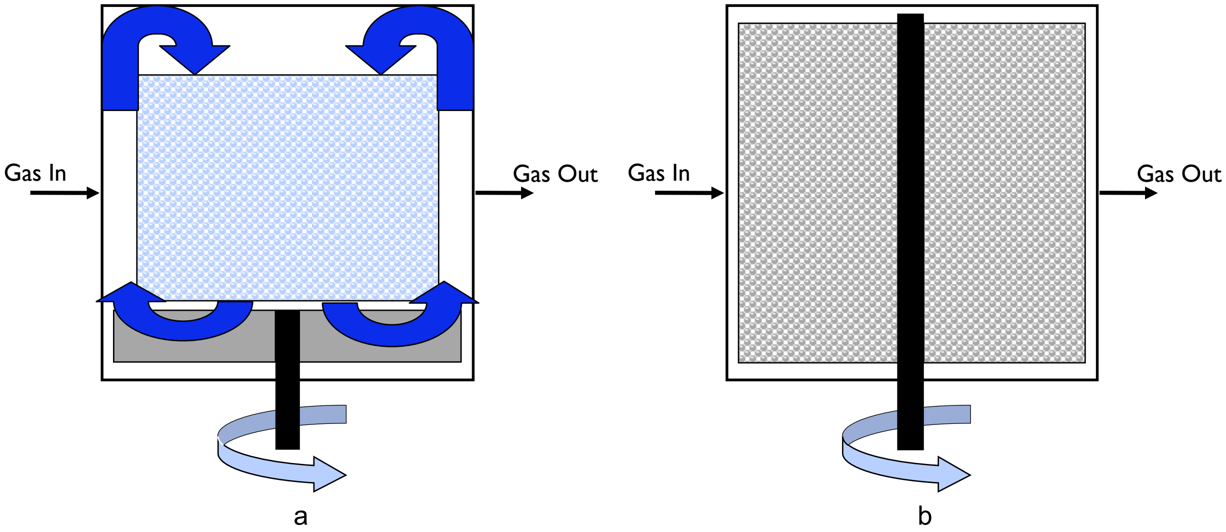

*Figure 11.5. Schematic representation of autoclaves configured as (a) Berty and (b) Carberry reactors.*

***The plug flow reactor*** is commonly referred to by the acronym, PFR. A PFR has feed continuously flowing into it and product continuously flowing out of it. It can be operated isothermally (the temperature is the same everywhere within the reactor) or adiabatically (no heat is added or removed). The distinguishing feature of a plug flow reactor, from which its name is derived, is the fluid velocity profile within it. A plug flow reactor is a simple tube or pipe operating so that the axial component of the velocity of the flowing fluid is the same at all radial positions. That is, the velocity right along the wall of the reactor is equal to the velocity along the centerline of the reactor. Put differently, instead of the parabolic velocity profile associated with laminar flow, a PFR has a flat velocity profile, and instead of there being “no-slip” at the wall, there is “complete slip.” Figure 11.6 illustrates plug flow.

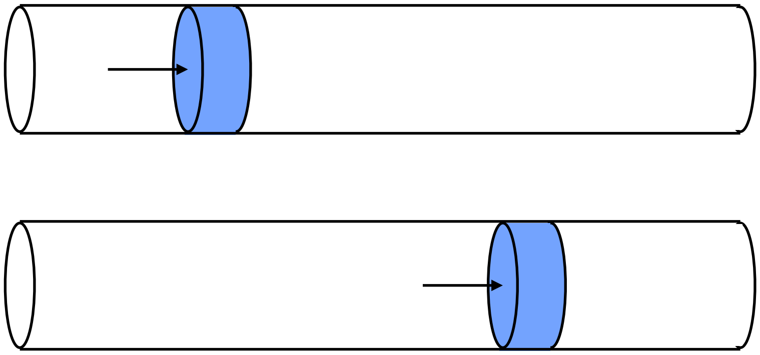

*Figure 11.6 Under plug flow conditions, the blue slug of fluid seen in the upper illustration would move through the tube as if it were a single unit so that a short time later the system would appear as shown in the lower illustration.*

In a plug flow reactor it is further assumed that there is no mixing in the axial direction. A disk shaped slug of fluid like that shown in Figure 11.6 would not mix with the fluid in front of it, nor with that flowing behind it as it moved through the reactor. It would emerge from the reactor as a disk. This kind of flow is sometimes also called piston flow or slug flow. While there is *no mixing in the axial direction*, it is assumed that the fluid is *perfectly mixed in the radial direction*. Again, if an infinitesimally thick fluid disk was placed in the inlet to the reactor, that disk would maintain a uniform temperature and composition as it flowed through the reactor. (The temperature and composition may change as the disk flows through the reactor, but within the disk they are uniform.) Thus the ideal plug flow reactor is assumed to be totally unmixed in the axial direction and, at the same time, to be perfectly mixed in the radial direction.

When the composition, temperature, pressure and flow rate remain constant when monitored at any fixed axial position, the reactor is said to be at steady state. These quantities will have different values at different locations, but *at any one location* they will not change with time if the reactor is at steady state. If the temperature is the same *throughout* the reactor, the reactor is said to be isothermal. When a plug flow reactor is used to collect kinetics data for the purpose of generating a rate expression, *it is most preferable to operate the reactor isothermally, isobarically (constant P) and at steady state*. Assuming only one reaction takes place, this again permits the use of a single mole balance design equation in the kinetics data analysis. As for the perfectly mixed batch reactor, it is an ordinary differential equation, given in equation (11.3). Equation (11.3) makes the further assumption that the PFR is indeed tubular with a constant inside diameter designated as $D$. In equation (11.3) $z$ is the axial distance from the reactor inlet and the other variables are defined as before. Note particularly that $\dot{n}_i$ appearing in this equation, like that in equation (11.2) is the molar flow rate of species $i$ whereas $n_i$, used in equation (11.1), is the moles of species $i$ (in this course, a dot over a variable indicates a flow rate of the quantity).

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} r_{i,j} \tag{11.3}$$

A plug flow reactor can be as simple as a length of tubing operated at sufficiently high flow rate that the flow is highly turbulent leading to plug flow. For catalytic reactions, such a tube can be packed with solid catalyst particles. Figure 11.6 shows such a reactor. The reactor itself is a glass tube (B) passing along the axis of a split-shell furnace (A). In the picture the furnace is open so the reactor tube can be seen. Looking carefully near the center of the furnace, a small packed bed of white catalyst material can be seen within the tube. A thermocouple can be seen entering a “T” fitting below the furnace; the thermocouple extends through the fitting and up into the reactor to the bottom of the catalyst bed. This thermocouple is used to make sure the reactor is operating isothermally; an electronic temperature controller monitors the temperature and adjusts the power to the furnace so that the temperature stays constant.

***Other considerations***. The discussion of the three types of laboratory reactors presented here has assumed that only one chemical reaction is taking place and that the objective is to obtain a rate expression for that single chemical reaction. If there were two or more chemical reactions taking place, the general procedure described at the start of this unit would still apply, but instead of using a *single* mole balance design equation to model the reactor, it would be necessary to write mole balance design equations for a number of species equal to the number of mathematically independent reactions taking place. This situation will not be considered in this course, but again, the procedure remains the same, apart from being considerably more complicated mathematically.

It should also be noted that laboratory reactors can be used for purposes other than generating a rate

*Figure 11.6. A laboratory plug flow reactor.*

expression. Weekman [1] has written a very nice paper regarding laboratory reactors in industrial use wherein he discusses two different objectives, each requiring a different kind of reactor. The first objective is determination of intrinsic reaction kinetics. This is the perspective of the material presented in this unit. The other objective Weekman considers is gathering data for design and scale-up purposes, where the demands upon the reactor are different, and consequently different types of reactors may be used.

Another important consideration in the selection of a reactor is the material of construction. One obvious area of concern is the strength of the material. If the reactor is to be operated at elevated temperatures and or pressures, the material from which the reactor is fabricated must be able to withstand these conditions. Similarly, if corrosives are present in the reaction mixture, the reactor must be constructed from materials that are impervious to the action of the corrosive chemicals.

Still another problem can arise for a homogeneous non-catalytic reaction if the reactor is made from a metal that catalyzes the reaction being studied. In this case, the measured kinetics will be those of the catalyzed reaction, not of the homogeneous non-catalytic reaction. Sometimes an inert (non-catalytic) coating or plating can be applied to the internal surfaces of the reactor if it is not possible to identify a material of construction that is not catalytic.

***Testing the models for laboratory reactors***. Clearly, if the procedure for generating a rate expression described at the beginning of this unit is going to work, then the models used to represent the laboratory reactors must offer an accurate description of those reactors. Put differently, if the laboratory reactor used to generate kinetics data does not satisfy the assumptions used to model it, then the process of generating a rate expression will fail. Laboratory reactors can be tested to determine whether or not they satisfy the assumptions inherent in the corresponding design equations used to model them. The remainder of this unit will describe tests that can be performed before any kinetics measurements are made. These tests characterize fluid flow within the reactor under the assumption that the flow will be the same whether or not reaction is taking place. Then, in Unit 12, additional tests will be described that can be performed while kinetics measurements are being made.

There are a few simple ways of testing for perfect mixing in a batch reactor or a CSTR. For example, one can inject an impulse of dye or tracer into the reactor and then simultaneously sample from several locations within the reactor over time. In this way the length of time necessary for the reactor composition to become uniform can be estimated. The reactor could not be modeled as perfectly mixed for any reaction that will take place on a time scale comparable to or smaller than this time. For gas phase systems, a smoke test is often used to visualize the mixing within the reactor and to identify regions that are not well-mixed. Similar experiments can be performed with liquid phase systems using colored dyes. In order to use a smoke or dye test, the reactor walls must be transparent. Then all one does is to introduce smoke or dye into the system through a small nozzle and watch how quickly and completely it mixes to uniformly fill the reactor volume. These kinds of tests typically do not yield a precise measure of the mixing time for the reactor, and they are probably more useful for identifying flow distribution issues where one zone or location in the reactor is not mixed as quickly as the rest of the reactor.

For laboratory *flow* reactors, there is a more quantitative way to characterize the flow within the reactor. Suppose that there was some way by which the molecules entering a reactor at one instant in time could be labeled or marked. Suppose further that the molecules entering before that instant or after that instant were not labeled and that the labeling did not affect how the molecules flowed through the reactor system. Immediately after the instant when the entering molecules were labeled, one could start monitoring the outlet from the reactor system and recording the elapsed time at which each labeled molecule exited. The elapsed time at which one molecule exited the reactor is called the residence time for that one molecule. It is the length of time during which that molecule “resided” within the reactor, or equivalently, it is the “age” of that molecule. After sufficiently long time had passed, the resulting data could be used to determine, for example, that 5% of the labeled molecules had a residence time of less than 4 minutes, 10% had a residence time of less than 4.5 minutes, etc. That is, the resulting data could be used to determine the distribution of residence times among the labeled molecules. If the reactor operates at steady state, then the distribution of residence times for the labeled molecules is the same as the distribution of residence times for fluid that enters the reactor at any arbitrary instant in time.

Two related mathematical functions can be used to characterize the distribution of residence times of the fluid flowing through a reactor. The first is called the *age function*, $F(\lambda)$; given a value, $\lambda$, of the fluid “age” or residence time, $F(\lambda)$ is equal to the fraction of the fluid leaving a flow system at any instant that has an age or residence time less than $\lambda$. Clearly then $F(0) = 0$ since fluid can’t leave a system without having been inside that system. Additionally, $F(\infty) = 1$ for a steady-state process, because there is no accumulation at steady-state, so all fluid eventually leaves. The second function used to characterize the distribution of residence times of the fluid flowing through a reactor is the age distribution function, or, equivalently, *residence time distribution function* $dF(\lambda)$. In order to reduce confusion between the two functions, herein $F(\lambda)$ will be called the age function and $dF(\lambda)$ will be called the residence time distribution (RTD) function. Given a value, $\lambda$, of the fluid “age” or residence time, $dF(\lambda)$ is equal to the fraction of the fluid leaving a flow system at any instant that has an age or residence time between $\lambda$ and $\lambda + d\lambda$. Obviously, the age function and the RTD function are related to each other. For any fluid age, $\lambda$, the corresponding value of the RTD function can be found from the age function as shown in equation (11.4). Conversely, for any fluid age, $\lambda$, the corresponding value of the age function can be found by summing the RTD function over all ages from zero to $\lambda$. Assuming the RTD function to be continuous, the summation takes the form of the integral given in equation (11.5), where $y$ is used as a dummy age variable for the integration.

$$dF(\lambda) = F(\lambda + d\lambda) - F(\lambda) \tag{11.4}$$

$$F(\lambda) = \int_{y=0}^{y=\lambda} dF(y) \tag{11.5}$$

The key point, for present purposes, is that as a consequence of the flow assumptions used in their derivation, the CSTR and PFR models each lead to very specific age functions and RTD functions. Thus, a more quantitative way to test whether a laboratory reactor conforms to the assumptions of either an ideal CSTR or an ideal PFR is to measure the age function or the RTD function of the laboratory reactor and see whether it is equal to that for an ideal reactor. In this unit, we will focus on measuring and comparing the age function of a laboratory reactor to the age function for either an ideal CSTR or an ideal PFR. If the two age functions *do not agree*, then the laboratory reactor clearly does not obey the assumptions made in the ideal reactor model. In that case, before gathering experimental kinetics data, it would be necessary to either (a) modify the the reactor or the way it is being operated so that the measured and predicted age functions agree or (b) develop a different reactor model that is accurate and then use that different model when analyzing the resulting kinetics data. There are situations, discussed later in this unit, where, even though the measured age function matches that of an ideal CSTR, the CSTR design equation still is not an accurate model for the reactor. Thus, agreement between the measured age function and that for an ideal reactor model should be considered a necessary, but not sufficient criterion for accepting the ideal reactor model.

The age function is measured by applying a “*stimulus*” to the inlet of the reactor, and then measuring the “*response*” at the outlet from the reactor. For flow systems, the most common types of stimuli are a step change in the concentration of a “tracer” and an impulse in the concentration of a tracer. A *tracer* is something that flows as a part of the fluid, but that can be easily identified at the outlet of the system. Examples of tracers include colored dyes and radioactive isotopes.

To create a *step change stimulus* one might suddenly adjust the opening of a valve that admits the tracer into the system. An ideal step change stimulus involves an instantaneous change in the inlet tracer concentration; the tracer concentration at the inlet is constant at one level before the step change and constant at a different level after the step change. The change in tracer concentration can be either positive or negative, and the tracer concentration itself need not be zero either before or after the change. Figure 11.7 shows a plot of the inlet tracer concentration versus time during the application of a step change stimulus where at time $t_0$, the tracer weight fraction increases from $w_0$ to $w_f$.

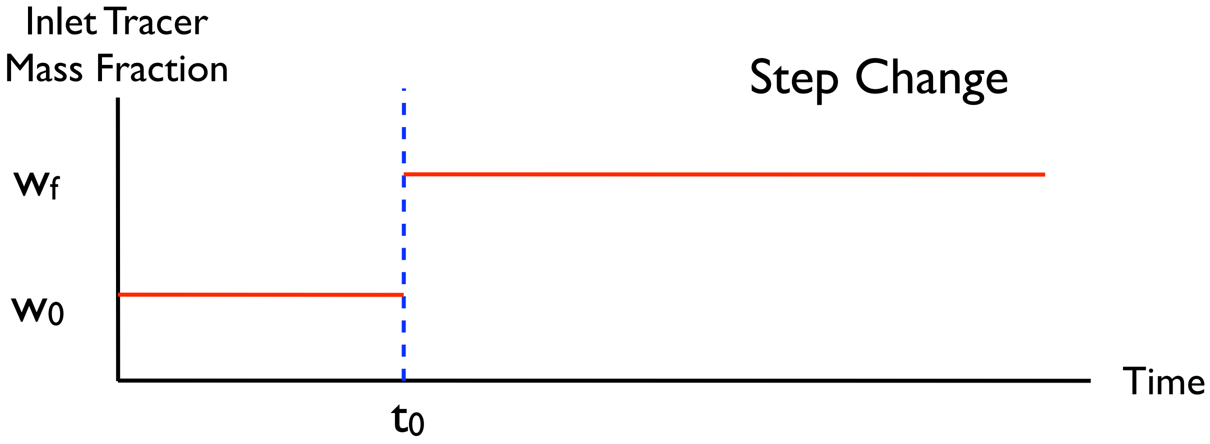

*Figure 11.7 Inlet tracer mass fraction versus time for a step change stimulus.*

To create an *impulse stimulus*, one might suddenly and instantaneously inject a known quantity of tracer into the feed to the reactor. Ideally, the injection requires no time at all, and the inlet concentration versus time is as shown in Figure 11.8.

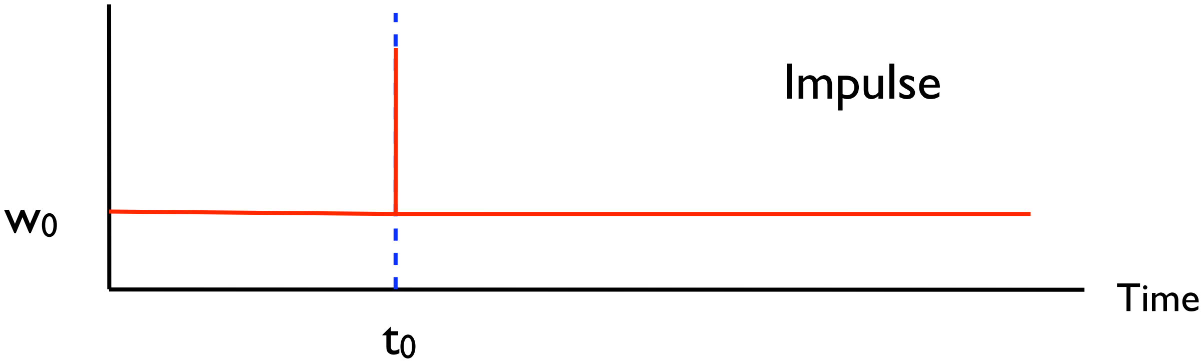

*Figure 11.8 Inlet tracer mass fraction versus time for an impulse stimulus.*

The stimulus is applied at the *inlet* to the reactor. For either of these stimuli, the response is the concentration of tracer at the *outlet* from the reactor as a function of elapsed time since the application of the stimulus. In order to derive the relationship between the age function and the experimentally observed response to a stimulus, it is convenient to define a fluid element. A *fluid element* can be defined as a very small amount of fluid that stays together as a unit for the whole time it is inside the reactor system. Fluid elements are hypothetical constructs that are convenient for the purpose of predicting system responses; they are not real entities.

*To measure the age function using the response to a step change stimulus*, let $t_0$ denote the point in time when the step change is applied to the inlet tracer concentration. Suppose that before the imposition of the step change, the system had been at steady state for sufficiently long that the tracer concentration was equal throughout the reactor. That is, let $w_0$ denote the weight fraction of tracer at the inlet, everywhere in the reactor, and at the outlet prior to $t_0$. Let the weight fraction of tracer at the inlet change to $w_f$ at $t = t_0$ (this is the step change stimulus as plotted in Figure 11.7).

Now suppose that at any time, $t'$, (later than $t_0$) a sample of fluid from the outlet of the system is taken and the mass fraction of tracer in that sample is measured and found to equal $w_{t'}$. Hypothetically, the sampled fluid will be a mixture of two kinds of fluid elements:

- fluid elements that have been inside the system for a length of time greater than or equal to $t' - t_0$. Since these fluid elements entered before the step change, their tracer weight fraction is $w_0$. These might be described as “aged” fluid elements.

- fluid elements that have been inside the system for a length of time less than $t' - t_0$. Since these fluid elements entered after the step change, their tracer weight fraction is $w_f$. These might be described as "young" fluid elements.

Because $F(\lambda)$ is defined as the fraction of the sampled fluid with an age less than $\lambda$, then $1 - F(\lambda)$ must be the fraction of the sampled fluid with an age greater than or equal to $\lambda$. Realizing this, the overall composition of the sampled fluid can be related to the compositions of the two kinds of fluid elements as given in equation (11.6) where $m_{sample}$ denotes the mass of the sampled fluid, $m_{young}$ is the mass of "young" fluid elements in the sampled fluid and $m_{aged}$ is the mass of "aged" fluid elements in the sampled fluid. The latter quantities can be related to the total mass of the sample by applying the definition of the age function. That is, the mass of young fluid elements in the sampled fluid, $m_{young}$, is equal to the total mass of the sampled fluid, $m_{sample}$, times the fraction of the sampled fluid that is "young," $F(\lambda)$ and similarly, $m_{aged}$ is equal to $m_{sample}$ times $1 - F(\lambda)$. This is done in equation (11.7) which can be rearranged to give an expression for the age function, equation (11.8), noting that $t' - t_0$ is simply the age, $\lambda$.

$$m_{sample} w_{t'} = m_{young} w_f + m_{aged} w_0 \tag{11.6}$$

$$m_{sample} w_{t'} = m_{sample} F\left(t' - t_0\right) w_f + m_{sample}\left[1 - F\left(t' - t_0\right)\right] w_0 \tag{11.7}$$

$$F\left(t' - t_0\right) = F\left(\lambda\right) = \frac{w_{t'} - w_0}{w_f - w_0} \tag{11.8}$$

<u>*To measure the age function using the response to an impulse stimulus*</u>, let the steady-state weight fraction of tracer be $w_0$, and let the impulse stimulus be applied to the feed at $t = t_0$, as plotted in Figure 11.8. The weight fraction of tracer in the outlet stream, i. e. the response, can then be recorded as a function of time, $w_{out}(t)$. The total steady-state mass flow rate can be represented as $\dot{M}$, and $m_{tot}$ can be used to represent the total mass of tracer in the impulse. It is assumed that the tracer flows in the exact same way as the other fluid, so the distribution of the tracer residence times is the same as the distribution of the residence times of any other fluid. Any "excess" tracer present in the outlet (i. e. any amount above the steady state level of $w_0$) is assumed to be from the impulse. The total amount of "excess" tracer, $m_{t'}$, that has come out of the reactor by some time $t'$ is then found using equation (11.9), that is, by adding up the excess over time.

$$m_{t'} = \dot{M} \int_{t_0}^{t'} \left(w_{out}\left(t\right) - w_0\right) dt \tag{11.9}$$

Dividing $m_{t'}$ by $m_{tot}$ gives the fraction of the tracer that came out in a time less than $\lambda = t' - t_0$ , and since the tracer is assumed to flow in identical manner to the total fluid, this is also equal to the fraction of the fluid which has a residence time less than $\lambda$. Hence, equation (11.10) can be used to find the age function from data for the response to an impulse stimulus in the same manner that equation (11.8) is used for the response to a step change stimulus.

$$F\left(t' - t_0\right) = F\left(\lambda\right) = \frac{\dot{M}\int\limits_{t_0}^{t'}\left(w_{out}\left(t\right) - w_0\right)dt}{m_{tot}} \tag{11.10}$$

It is perhaps worth mentioning that one might not know the total mass of tracer added in the impulse, $m_{tot}$. Ideally, one would simply weigh the tracer before injecting it into the system. However, if this was not done, one can note that if you add up all of the “excess” that ever comes out of the system, it must equal the total mass added in the impulse. Thus, equation (11.11), where the upper limit is infinity, can be used to find the total mass of the tracer.

$$m_{tot} = \dot{M}\int\limits_{t_0}^{\infty}\left(w_{out}\left(t\right) - w_0\right)dt \tag{11.11}$$

Knowing how to measure the age function for a real laboratory reactor, one next needs to know the age functions for an ideal CSTR and for an ideal PFR. The age function for an ideal steady-state, isothermal CSTR can be found from a mass balance. Consider a CSTR operating for a long time at steady state with an inlet and outlet tracer mass fraction of $w_0$ and a total mass flow rate of $\dot{M}$ . Let $w_f$ denote the new inlet tracer mass fraction after a step change stimulus has been applied at time $t = 0$, and let $w_{out}$ denote the *instantaneous* outlet tracer mass fraction (i. e. the response). Thus, $w_f$ is a constant while $w_{out}$ varies over time. A mass balance on the tracer is given in equation (11.12), and the initial condition needed to solve it is given as equation (11.13). In these equations $\rho_{fluid}$ is the density of the flowing fluid and $V_{fluid}$ is the steady state volume of fluid contained in the CSTR; both of these quantities are also constant. Noting that the average residence time, $\bar{t}$ , is given by equation (11.14), the mass balance can be solved for the response, equation (11.15). Recall that equation (11.8) is used to calculate the age function from the response to a step change stimulus. Noting that $t$ in equation (11.15) is the time since the application of the step change (i. e. $t = \lambda$), substitution of equation (11.15) into equation (11.8) gives, after simplification, the *age function for an ideal CSTR*, equation (11.16).

$$\dot{M}w_f = \dot{M}w_{out} + \rho_{fluid}V_{fluid}\frac{dw_{out}}{dt} \tag{11.12}$$

$$w_{out}\left(0\right) = w_0 \tag{11.13}$$

$$\bar{t} = \frac{\rho_{fluid} V_{fluid}}{\dot{M}} \tag{11.14}$$

$$w_{out}\left(t\right) = w_f - \left(w_f - w_0\right)\exp\left\{\frac{-t}{\bar{t}}\right\} \tag{11.15}$$

$$F_{CSTR}\left(\lambda\right) = 1 - \exp\left\{\frac{-\lambda}{\bar{t}}\right\} \tag{11.16}$$

The age function for a steady-state, isothermal PFR can also be found mathematically from a mass balance. However, the nature of the assumptions about the flow in a PFR makes it trivial to deduce the age function. Consider the application of an impulse of tracer to the inlet of a PFR. Every fluid element within the "slug" of tracer moves at the exact same constant velocity along the length of the reactor. The slug's linear velocity, $v$, is given by equation (11.17), where $A$ denotes the cross-sectional area of the tubular reactor. Eventually, the slug travels the length of the reactor, $L$. The time it takes for this to happen is just the distance $L$ divided by the velocity, and equation (11.18) shows that this simply equals the average residence time, $\bar{t}$. (The volume of the PFR, $V_{PFR}$ is just its cross-sectional area, $A$, times its length, $L$).

$$v = \frac{\dot{M}}{\rho_{fluid} A} \tag{11.17}$$

$$t_{\text{travel distance L}} = \frac{L}{v} = \frac{L}{\frac{\dot{M}}{\rho_{fluid} A}} = \frac{\rho_{fluid} A L}{\dot{M}} = \frac{\rho_{fluid} V_{PFR}}{\dot{M}} = \bar{t} \tag{11.18}$$

For all times prior to when the slug reaches the end of the reactor ( $\bar{t}$ ), no tracer has come out. All of the fluid that is coming out during this period has an age greater than the elapsed time, so the fraction with an age less than the elapsed time is zero. Then, just when the elapsed time equals $\bar{t}$, all of the tracer comes out. From this elapsed time onward, all the fluid leaving the reactor will have an age less than the elapsed time, so the fraction becomes equal to unity. Hence, the age function is given by equation (11.19); it is just a step change from zero to one at $\lambda = \bar{t}$.

$$\begin{aligned} F_{PFR}\left(\lambda\right) &= 0 \text{ for } \lambda < \bar{t} \\ F_{PFR}\left(\lambda\right) &= 1 \text{ for } \lambda \geq \bar{t} \end{aligned} \tag{11.19}$$

With this knowledge, one can test whether it is safe to model a laboratory reactor as an ideal CSTR or an ideal PFR. This is done by measuring $F(\lambda)$ versus $\lambda$ for the laboratory reactor. A plot can then be made from the data. On the same axes, $F(\lambda)$ for the ideal CSTR or PFR vs. $\lambda$ can be plotted. *If the two* *plots differ significantly, then the laboratory reactor cannot be modeled as an ideal CSTR or PFR*. In this latter situation, you need to do one of two things *before you begin to gather experimental kinetics data*. You either need to modify the reactor (or the way it is operated) so that it can be safely modeled as an ideal CSTR or PFR or you need to develop a different design equation that does model it accurately. In the latter case you can follow the same procedure used earlier and develop the expected age function for your new reactor model and then see whether it matches the experimentally measured age function.

Unfortunately, for a CSTR, when the experimentally measured age function ***does match*** the age function predicted from the ideal reactor model, *this still does not guarantee that the laboratory reactor can be modeled as an ideal CSTR*. The reason for this is that measuring the age function does not fully characterize the mixing within a reactor. It is possible for a reactor to appear to be very well-mixed at a macroscopic level while the mixing is quite poor at a microscopic level. In essence, the test being used here will give a favorable result as long as the time scale for mixing the fluid within the reactor is very small compared to the amount of time the fluid spends in the reactor. When we start performing kinetics experiments, there is a third time scale that becomes important, namely the time scale for reaction to occur. If the chemical reaction is very fast compared to the time scale for mixing the fluid in the reactor, then a significant amount of reaction will take place before the fluid is well-mixed. In this case, the reactor should not be modeled as an ideal CSTR because on the time scale that the reaction is taking place, it is not perfectly mixed, even though the experimental and ideal age functions are in complete agreement.

Thus, the agreement of age functions of the laboratory reactor and the ideal reactor model is a necessary, but not sufficient, criterion for ensuring the validity of modeling the laboratory reactor as ideal. It is most likely to fail when studying very fast chemical reactions. The age function test should be performed nonetheless, but one should not become complacent if the test is successful.

## References Cited

[1] Weekman, V.W., Laboratory Reactors and Their Limitations. AIChE Journal, 1974. 20(5): p. 833.