A First Course on Kinetics and Reaction Engineering

Unit 13. CSTR Data Analysis

Overview

Unit 13 describes how to use kinetics data from a CSTR to determine whether or not a given mathematical function is acceptable as a rate expression. It is assumed that the data were generated using a laboratory reactor operating at steady state, and that the laboratory reactor is accurately described by the ideal CSTR model. If the rate expression is found to be sufficiently accurate, the analysis will additionally provide the best values, including uncertainties, for each of the parameters appearing in the rate expression. For illustrational purposes, the systems considered in Unit 13 are limited to situations where only one chemical reaction is taking place, and the rate expression being evaluated can be written in the form of a linear equation. If the reaction system being studied consists of two or more phases, it is further assumed that concentration and temperature gradients within the system are negligible.

Learning Objectives

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

- head space
- space time
- space velocity

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

- space time
- space velocity

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 equations relating the following quantities to each other: concentration, mole fraction, partial pressure, total pressure, temperature volumetric flow rate and molar flow rates
- use CSTR kinetics data to evaluate a rate expression, determine whether it is acceptably accurate, and find the best values, including uncertainties, of the parameters appearing in it

Information

As noted in Unit 11, when one reaction takes place in a steady state CSTR, a mole balance on one of the participating species is all that is needed to model the reactor. That mole balance design equation is reproduced here as equation (13.1). Equation (13.1) could be written for i being equal to each of species that is present, resulting in a set of equations. Those equations, however, would be related to each other through the reaction stoichiometry. Hence in practice it is only necessary to write as many species mole balance design equations as there are mathematically independent chemical reactions occurring within the reactor. In this unit we limit consideration to systems where only one reaction is taking place, so equation (13.1), written one time for i equal to any reactant or product, is all that is needed to model the CSTR used to generate the kinetics data.

$$\dot{n}_i - \dot{n}_i^0 = V r_{i,j} \tag{13.1}$$

A few things need to be recognized regarding the volume, V, that appears in equation (13.1). The total volume of the reactor may not equal the fluid volume for liquid phase systems. The reason is that, for a liquid system, the physical reactor often is not completely full to the very brim, but instead there is some small vapor space, also called *head space*, in the reactor vessel. That is, the total reactor volume is the sum of the fluid volume plus the head space. For gas phase systems there is no head space because a gas will expand to fill the entire volume. The volume that appears in the design equation, equation (13.1), is the volume within which the reaction takes place. For a liquid phase system with head space above the liquid, equation (13.1) assumes that the reaction only occurs in the liquid phase and not in the head space. Consequently in this case V represents the fluid volume within the reactor and not its total volume. That said, problems and examples from many kinetics and reaction engineering textbooks will very often say that the reactor used for data generation had a volume equal to some value, X. Unless the problem statement additionally provides the volume of the head space, this really means that the fluid volume in the reactor was X. Note also that it is implicitly assumed in equation (13.1) that the rate expression should be normalized per unit volume. In fact, if the reaction rate should be normalized using a different normalizing factor, such as the surface area of a heterogeneous catalyst within the reactor, then equation (13.1) must be modified. This was illustrated in Example 11.2.

Once the kinetics data have been collected, four steps remain in the procedure for generating a rate expression from those data. First, a rate equation is selected for testing and substituted into equation (13.1). Second, for each experimental data point, the values of each of the quantities that appear in the resulting equation, other than parameters from the rate expression, are calculated. This will often entail the use of a mole table, definitions of composition and reaction progress variables, the ideal gas law, etc. For each data point, it should be possible to substitute calculated or measured variables for all quantities appearing in the resulting equation, except for the parameters specific to the rate expression. That is, for each data point, everything appearing in the resulting equation should be known except for things like rate coefficients, power-law rate expression exponents, etc. The third step is to fit the equation to the experimental data. In this unit it will always be possible to write the equation being fit to the data in the form of a linear equation so that linear least squares can be used to perform the fitting. (If you are not familiar with fitting a linear equation using linear least squares, see Supplemental Unit S3.) The fitting process will yield values and uncertainties for each parameter that appears in the rate expression. The final step is to make a decision whether the resulting fit is adequate or not, that is, whether the fitted equation offers a sufficiently accurate representation of the experimental data. If the fit is satisfactory, the rate expression is accepted with the parameters equal to the values generated during the analysis. If the fit is not satisfactory, a different rate expression must be postulated and the process must be repeated. This continues until an adequate fit is obtained.

During the analysis of kinetics data as just described, there are a number of relationships that are very commonly required. The rate expression is a function of the environmental variables, specifically it is a function of temperature, pressure and composition. The most common ways that composition appears in rate expressions is as concentrations or, for gases, as partial pressures. The mole balance design equation, equation (13.1), uses the molar flow rate as a compositional variable. Thus it is useful to recall how the molar flow rate is related to concentration and partial pressure. The concentration and the molar flow rate of a species entering a reactor are related through equation (13.2), and those of a species leaving a reactor are related through equation (13.3). In these equations C_i denotes the concentration of species i, $\dot{n}_i$ denotes the molar flow rate of species i, $\dot{V}$ denotes the total volumetric flow rate, and a superscript 0 denotes a quantity measured in the reactor feed.

$$C_i^0 = \frac{\dot{n}_i^0}{\dot{V}^0} \tag{13.2}$$

$$C_i = \frac{\dot{n}_i}{\dot{V}} \tag{13.3}$$

The volumetric flow rate, $\dot{V}$, behaves differently for liquids and gases. In this course, reacting liquid phase systems can be considered to be incompressible with a constant density. In that case, the volumetric flow rate will be constant, as expressed in equation (13.4). For gas phase systems, the density can change due to changes in pressure, temperature, or total number of moles. The ideal gas law can be used to inter-relate all these effects as given in equations (13.5) and (13.6). It is important to note by examination of equations (13.5) and (13.6), that the volumetric flow rate of a gas phase reaction system generally will not be the same in the feed and the effluent unless the temperature, pressure and total molar flow rate are the same.

$$\dot{V}^0 = \dot{V} \qquad \text{(incompressible liquids)} \tag{13.4}$$

$$\dot{V} = \frac{\dot{n}_{tot} RT}{P} \qquad \text{(ideal gas)} \tag{13.5}$$

$$\dot{n}_{tot} = \sum_{\substack{i=all\\ species}} \dot{n}_i \tag{13.6}$$

The mole fraction, y_i, of a species is, by definition, related to the molar flow rates according to equation (13.7). A similar equation could be written for the mole fraction in the feed by adding a superscript 0 to each variable in equation (13.7). It is then easy to relate partial pressure to the molar flow rates using equation (13.8).

$$y_i = \frac{\dot{n}_i}{\dot{n}_{tot}} \tag{31.7}$$

$$P_i = y_i P = \frac{\dot{n}_i P}{\dot{n}_{tot}} \tag{31.8}$$

There are two terms which are sometimes used to describe the feed to a reactor. These are the *space time* (average residence time), τ, and the *space velocity*, SV, defined in equations (13.9) and (13.10), respectively. In these equations V represents the volume of the fluid in the reactor as discussed previously in conjunction with equation (13.1).

$$\tau = \frac{V}{\dot{V}^0} \tag{13.9}$$

$$SV = \frac{1}{\tau} = \frac{\dot{V}^0}{V} \tag{13.10}$$