

# A First Course on Kinetics and Reaction Engineering

## Unit 15. Integral Data Analysis

### Overview

As noted in Unit 14, the design equations (reactor models) for the perfectly mixed batch reactor and for the PFR are differential equations, and as a result, the equations cannot be fit directly to experimental data. Unit 14 described the use of differential data analysis to address this problem. This unit considers the alternative approach: integral data analysis. In an integral kinetics data analysis, the differential equation is first solved to obtain an algebraic equation<sup>1</sup>, and then that algebraic equation is fit to the experimental data. The method of half-lives, a special form of integral analysis, is also described.

### Learning Objectives

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

- half-life

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:

- Analyze batch reactor and plug flow reactor kinetics data using an integral data analysis
- Use the half-life method to determine reaction order

### Information

For the purposes of this unit, it is assumed that kinetics data have been collected using either an isothermal, perfectly mixed batch reactor or an isothermal, steady state PFR. It is further assumed that prior to generation of the data, the reactor was tested to ensure that it conformed to the assumptions of the corresponding ideal reactor model, and that only one chemical reaction was taking place. Under these circumstances, all that is needed to model the reactor is a single mole balance design equation. For a batch reactor, this design equation takes the form given in equation (15.1) and for a PFR it takes the form shown in equation (15.2).

$$\frac{dn_i}{dt} = Vr_{i,j} \quad (15.1)$$

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} r_{i,j} \quad (15.2)$$

In order to test the suitability of a potential rate expression, that rate expression must be substituted into the appropriate mole balance design equation. The resulting equation cannot be fit to the experimental data using linear least squares because it is a differential equation, not a linear algebraic

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<sup>1</sup> Actually, the equation that results from solving the differential equation may include transcendental functions such as logarithms, in which case it is not an algebraic equation in the strictest sense of the term. Nonetheless, in this unit they will be referred to as algebraic equation, in contrast to the original differential equations.

equation. However, if the differential mole balance design equation is solved analytically, an algebraic equation results, and that algebraic equation can be fit to the experimental data. In this unit the rate expressions being tested using batch reactor kinetics data will be limited so that the algebraic equation that results from solving the differential model equation can be linearized. In this way, the model can then be fit to the experimental data using linear least squares fitting. It will be shown presently that the solution to the PFR mole balance design equation often can't be linearized, but for many cases there is a simple alternative to linear least squares fitting. Unit 16 will address the situation, for any of the ideal reactor types, where the reactor model equation cannot be linearized. In any case, once the model has been fit to the kinetics data, it is necessary to decide whether the fit is sufficiently accurate, and if it is, to calculate the parameters in the rate expression and their uncertainties from the fitting results.

Note that in equation (15.1) the dependent variable is  $n_i$  and the independent variable is  $t$ , and in equation (15.2) the dependent variable is  $\dot{n}_i$  and the independent variable is  $z$ . When the rate expression is substituted into these equations it is likely that it will contain variable quantities that change as the independent variable ( $t$  or  $z$ ) changes. For example, rate expressions will commonly include concentrations or partial pressures of one or more species, and the concentration or partial pressure of each reactant and product will change over time in a batch reactor or along the length of a plug flow reactor. Before equation (15.1) or equation (15.2) can be analytically integrated, the right hand side of the equation must be re-written so that no variables other than the dependent ( $n_i$  or  $\dot{n}_i$ ) and independent ( $t$  or  $z$ ) variables appear on the right hand side, along with constants. Generally this will require using a mole table, definitions for composition and reaction progress variables, and possibly the ideal gas law, as discussed in Units 1 and 13, and below.

The most common ways that composition appears in rate expressions is as concentrations or as partial pressures. In addition, for a PFR, the volumetric flow rate may be introduced into the rate expression in the process of expressing concentrations or partial pressures in terms of the molar flow rate. In such cases it is important to recognize that the volumetric flow rate in an isothermal, isobaric PFR can vary if the reaction taking place results in a change in the total molar flow rate. Thus, it is useful to recall how these quantities are related to the dependent variables,  $n_i$  or  $\dot{n}_i$ . The relationships for flow systems were already discussed in Unit 13, so only a summary will be presented here in the form of equations (15.3) through (15.10), which apply to a flow reactor (CSTR or PFR).

$$C_i = \frac{\dot{n}_i}{\dot{V}} \quad (15.3)$$

$$\dot{V}^0 = \dot{V} \quad (\text{incompressible liquids}) \quad (15.4)$$

$$\dot{V} = \frac{\dot{n}_{tot} RT}{P} \quad (\text{ideal gas}) \quad (15.5)$$

$$\dot{n}_{tot} = \sum_{\substack{i=all \\ species}} \dot{n}_i \quad (15.6)$$

$$y_i = \frac{\dot{n}_i}{\dot{n}_{tot}} \quad (15.7)$$

$$P_i = y_i P = \frac{\dot{n}_i P}{\dot{n}_{tot}} \quad (15.8)$$

$$\tau = \frac{V}{\dot{V}^0} \quad (15.9)$$

$$SV = \frac{1}{\tau} = \frac{\dot{V}^0}{V} \quad (15.10)$$

In most cases, the reaction volume,  $V$ , for a batch reactor is a constant. For gases it equals the total volume of the reactor, while for liquids it is the total volume less any headspace. The only situation where the liquid volume would change would be a non-ideal solution where there is a non-zero  $\Delta V$  of mixing; in that case one would need an equation that relates the solution volume to its composition. In this course it is almost always assumed that the liquid phase volume does not vary with composition. For a CSTR, the pressure is assumed to be constant, and here we will assume the pressure drop to be negligible in any PFR that was used to generate kinetics data. In contrast, the pressure in a batch reactor may change over time if a gas phase system is being studied and if the total number of moles changes due to the reaction. Hence, the most commonly used relationships in the integral analysis of batch reactor data are given in equations (15.11) through (15.13).

$$C_i = \frac{n_i}{V} \quad (15.11)$$

$$P_i = \frac{n_i RT}{V} \quad (15.12)$$

$$P = \frac{n_{tot} RT}{V} \quad (15.13)$$

You may recall that the differential analysis of PFR data is only possible if the reactor was operated differentially. The reason was that the independent variable,  $z$ , typically is not varied during PFR experiments. Usually a single reactor of fixed length is used, and the composition is only measured at the reactor inlet and outlet, hence  $z$  is the same in every experiment. This also causes a problem in integral data analysis. Put briefly, the algebraic equation obtained by solving the differential model equation often cannot be linearized to a form suitable for linear least squares fitting. If the potential rate expression being tested only contains a single rate coefficient, there is a very easy way to fit the algebraic equation to the experimental data. This is illustrated in Example 15.4, and it is discussed in Supplemental Unit S3. If the rate expression contains two or more unknown parameters and cannot be linearized to a form suitable for

linear least squares fitting, it will be necessary to use the methods described in Unit 16 to analyze the PFR kinetics data.

**Half-life method.** There is a variation on integral analysis that can be used to quickly determine the order of a reaction. It involves measuring the “half-life” of the reaction using a batch reactor. The half-life method is most commonly applied when the rate depends, in a power-law fashion, upon the concentration of a single reactant (let’s say A), as expressed in equation (15.14). The half-life,  $t_{1/2}$ , is the amount of time that it takes for the concentration of the reactant to decrease to one-half of its initial value. This rate expression can be substituted into the batch reactor design equation, equation (15.1), giving equation (15.15). Assuming a constant reaction volume, substituting the definition of concentration as given in equation (15.11) leads to equation (15.16).

$$r_A = -k(C_A)^\alpha \quad (15.14)$$

$$\frac{dn_A}{dt} = -kV(C_A)^\alpha \quad (15.15)$$

$$\frac{dn_A}{dt} = -kV\left(\frac{n_A}{V}\right)^\alpha = -kV^{1-\alpha}n_A^\alpha \quad (15.16)$$

Equation (15.16) can be solved by separating the variables and integrating. In the present case, the lower limit of integration is that the moles of A equal  $n_A^0$  at  $t$  equals zero, and the upper limit of integration is that the moles of A equal  $0.5(n_A^0)$  at  $t$  equals the half-life,  $t_{1/2}$ . If the reaction order,  $\alpha$ , is equal to one, the result is given in equation (15.17); for reaction orders other than one, equation (15.18) results.

$$t_{1/2} = \frac{0.693}{k} \quad (\text{first order kinetics}) \quad (15.17)$$

$$t_{1/2} = \frac{(2^{\alpha-1} - 1)}{k(\alpha - 1)(C_A^0)^{\alpha-1}} \quad (\alpha \neq 1) \quad (15.18)$$

Equations (15.17) and (15.18) suggest that the reaction order,  $\alpha$ , can be determined by measuring the half-life in a series of experiments using different initial concentrations of A. If the half-life is the same for all initial concentrations, the reaction is first order. Otherwise, a log-log plot of the half-life vs. the initial concentration should yield a straight line, and the slope should equal  $1-\alpha$  as can be seen in equation (15.19) where the logs of both sides of equation (15.18) were taken. (Note that  $k$  and  $\alpha$  are constants as long as all the experiments are performed at the same temperature.)

$$\ln(t_{1/2}) = \ln\left(\frac{(2^{\alpha-1} - 1)}{k(\alpha - 1)}\right) + (1 - \alpha)\ln(C_A^0) \quad (\alpha \neq 1) \quad (15.19)$$