A First Course on Kinetics and Reaction Engineering
Example 15.4

Problem Purpose

This problem shows how to test a single parameter rate expression using kinetics data from a PFR where the integrated form of the mole balance design equation cannot be properly linearized for the use of linear least squares fitting. It additionally illustrates how to handle a gas phase reaction where the total number of moles, and consequently the volumetric flow rate, varies along the length of an isothermal (constant T), isobaric (constant P) PFR.

Problem Statement

A rate expression is needed for the decomposition of phosgene, equation (1). A series of experiments were performed using a plug flow reactor with a diameter of 0.25 cm and a length of 10 cm. The feed in all cases was pure COS, and the reactor operated isothermally at 1500K and 1 atm. The feed rate was varied and the conversion of COS was recorded. The results are presented in the table below. Find a rate expression that is consistent with these data.

$$COS \rightarrow CO + S \qquad\qquad (1)$$

Inlet Flow Rate (cm³ min⁻¹)	fractional COS conversion
10	0.99
20	0.93
30	0.86
40	0.78
60	0.66
75	0.60
100	0.51

Problem Analysis

This problem gives PFR kinetics data for a gas phase reaction and asks us to test a specified rate expression using integral data analysis. To do this, we will write the mole balance design equation, substitute the rate expression, integrate to obtain an algebraic equation and fit the result to the experimental data. We will then assess the accuracy of the resulting fitted model and decide whether it is sufficiently accurate. It is important to note that the reaction that occurs in the gas phase, and it involves a change in the total number of moles. As a consequence, the total molar flow rate and the volumetric flow rate will change along the length of the reactor.

Problem Solution

The problem does not suggest a rate expression to test, so we are free to choose one. We'll start with the simple first order rate expression given in equation (2). Assuming that the experimental reactor

obeys the assumptions of an ideal plug flow reactor operated in the preferred isothermal, isobaric steady state manner, a single mole balance design equation will be sufficient to analyze the data, since only one reaction was taking place. The necessary mole balance design equation for an ideal PFR, written in terms of COS, is given in equation (3). Mole balances for CO or S could have been used equally well.

$$r_1 = k_1 P_{COS} \tag{2}$$

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

$$\frac{d\dot{n}_{COS}}{dz} = \frac{-\pi D^2}{4} r_1 \tag{3}$$

Substitution of the rate expression into the design equation leads to equation (4). Before this can be integrated, all variables must be expressed in terms of the dependent variable (here the flow rate of COS, $\dot{n}_{COS}$) and the independent variable (here z). Looking at equation (4), the reactor diameter and the rate coefficient are constants (the latter only because the reactor is isothermal), but the partial pressure of COS is expected to change as COS is converted by reaction (1). Thus, the partial pressure of COS must be re-expressed in terms of the molar flow rate of COS.

$$\frac{d\dot{n}_{COS}}{dz} = \frac{-\pi D^2}{4} k_1 P_{COS} \tag{4}$$

The partial pressure of COS is equal to the mole fraction of COS times the total pressure, equation (5). Substitution into the design equation gives equation (6). Looking at this equation, we see that the using it will indeed introduce the molar flow rate of COS, but it also introduces another variable quantity. That is, while the total pressure does not vary along the length of the reactor, the total molar flow rate will change along the length of the reactor. The reason for this is that each time one COS molecule reacts, two product molecules are produced. Therefore, we next need to write the total molar flow rate in terms of the molar flow rate of COS.

$$P_{COS} = \frac{\dot{n}_{COS}}{\dot{n}_{tot}} P \tag{5}$$

$$\frac{d\dot{n}_{COS}}{dz} = \frac{-\pi D^2}{4} k_1 \left(\frac{\dot{n}_{COS}}{\dot{n}_{tot}} P \right) \tag{6}$$

A mole table proves useful in relating one composition variable to another, as discussed in Unit 1. A mole table for the present system is presented below.

Species	Inlet molar flow rate	Molar flow rate after reaction
COS	$\dot{n}_{COS}^0$	$\dot{n}_{COS}^0 - \dot{\xi}_1$
CO	0	$\dot{\xi}_1$
S	0	$\dot{\xi}_1$
Total Moles	$\dot{n}_{COS}^0$	$\dot{n}_{COS}^0 + \dot{\xi}_1$

The third column of the mole table provides expressions for the molar flow rate of COS in terms of the extent of reaction and for the total molar flow rate in terms of the extent of reaction. Eliminating the extent of reaction between these two equations gives an expression for the total molar flow rate in terms of the molar flow rate of COS, equation (7).

$$\dot{n}_{COS} = \dot{n}_{COS}^0 - \dot{\xi}_1 \quad \Rightarrow \quad \dot{\xi}_1 = \dot{n}_{COS}^0 - \dot{n}_{COS}$$

$$\dot{n}_{tot} = \dot{n}_{COS}^0 + \dot{\xi}_1 = 2\dot{n}_{COS}^0 - \dot{n}_{COS} \tag{7}$$

Substitution of equation (7) into the mole balance design equation, equation (6), leads to equation (8). The only variables appearing in that equation are $\dot{n}_{COS}$ and z; all the other quantities are constants. Consequently we can attempt to separate the variables and integrate equation (8). Doing so leads to equation (9).

$$\frac{d\dot{n}_{COS}}{dz} = \frac{-\pi D^2}{4} k_1 \left(\frac{\dot{n}_{COS}}{2\dot{n}_{COS}^0 - \dot{n}_{COS}} P \right) \tag{8}$$

$$\int_{\dot{n}_{COS}^0}^{\dot{n}_{COS}} \frac{\left(2\dot{n}_{COS}^0 - \dot{n}_{COS}\right)}{\dot{n}_{COS}} d\dot{n}_{COS} = \int_0^L \frac{-\pi D^2 k_1 P}{4} dz$$

$$\dot{n}_{COS}^0 - \dot{n}_{COS} + 2\dot{n}_{COS}^0 \ln\left(\frac{\dot{n}_{COS}}{\dot{n}_{COS}^0}\right) = \frac{-\pi D^2 L k_1 P}{4} \tag{9}$$

We now need to fit equation (9) to the experimental data. If equation (9) could be linearized, then linear least squares could be used to perform the fitting. However, a careful examination of equation (9) reveals that it cannot be properly linearized for least squares without adding more terms or variables. It could be put into the form of a straight line with a slope of 1 and an unknown intercept, but linear least squares fitting requires a slope that is unknown. Fortunately, the rate expression being tested here has only one unknown parameter, the rate coefficient, k_1. As described in Supplemental Unit S3, there is a

simple alternative to linear least squares fitting that can be used when the model equation contains only one unknown parameter. To use this fitting method, the model equation is rearranged to give an expression for the unknown parameter. In this problem, that leads to equation (10). Equation (10) is then used to calculate a value of k_1 for each experimental data point. The resulting set of k_1 values is averaged and the standard deviation is computed. If the model and data were perfect, the value of k_1 would be exactly the same for every single data point. Allowing for some experimental error, an accurate model will result in a standard deviation of k_1 that is a very small fraction of the average value of k_1. In addition, the differences between the individual k_1 values and the average value will not show any systematic trends; they will be random. If these criteria are satisfied, then the fit can be accepted as sufficiently accurate and the best value for k_1 can be taken to equal the average value plus or minus the standard deviation.

$$k_1 = \frac{-4}{\pi D^2 LP}\left[\dot{n}_{COS}^0 - \dot{n}_{COS} + 2\dot{n}_{COS}^0 \ln\left(\frac{\dot{n}_{COS}}{\dot{n}_{COS}^0}\right)\right] \tag{10}$$

Looking at equation (10), one sees that the pressure, reactor diameter and reactor length are given in the problem statement, but the inlet and outlet molar flow rates of COS are not. Therefore those quantities will need to be calculated for each experimental data point. The problem states that the feed was pure COS, so the ideal gas law can be used to calculate the inlet molar flow rate with the other data given in the problem statement, equation (11). Once the inlet molar flow rate of COS is known, its outlet molar flow rate can be calculated using the fractional conversion of COS that is also given in the problem statement. This is done using equation (12).

$$\dot{n}_{COS}^0 = \frac{P\dot{V}^0}{RT} \tag{11}$$

$$\dot{n}_{COS} = \dot{n}_{COS}^0\left(1 - f_{COS}\right) \tag{12}$$

Performing the calculations, one finds the average value of k_1 to equal 1.5×10^{-3} mol cm^{-3} min^{-1} atm^{-1} with a standard deviation of 0.06×10^{-3} mol cm^{-3} min^{-1} atm^{-1}. The difference between the individual values of k_1 and the average were plotted as a function of the fractional conversion, Figure 1. The data do not display any systematic trends relative to the expected value of zero. (The deviations appear to be very large in the figure, but that is because the y-axis scale is quite small. Figure 1 should not be used to assess the magnitude of the errors; it should only be used to look for systematic trends.) Hence, the fit appears to be sufficiently accurate and equation (2) is a suitable rate expression. The best value for k_1 is $1.5 \pm 0.06 \times 10^{-3}$ mol cm^{-3} min^{-1} atm^{-1} (standard deviation of the data taken as uncertainty).
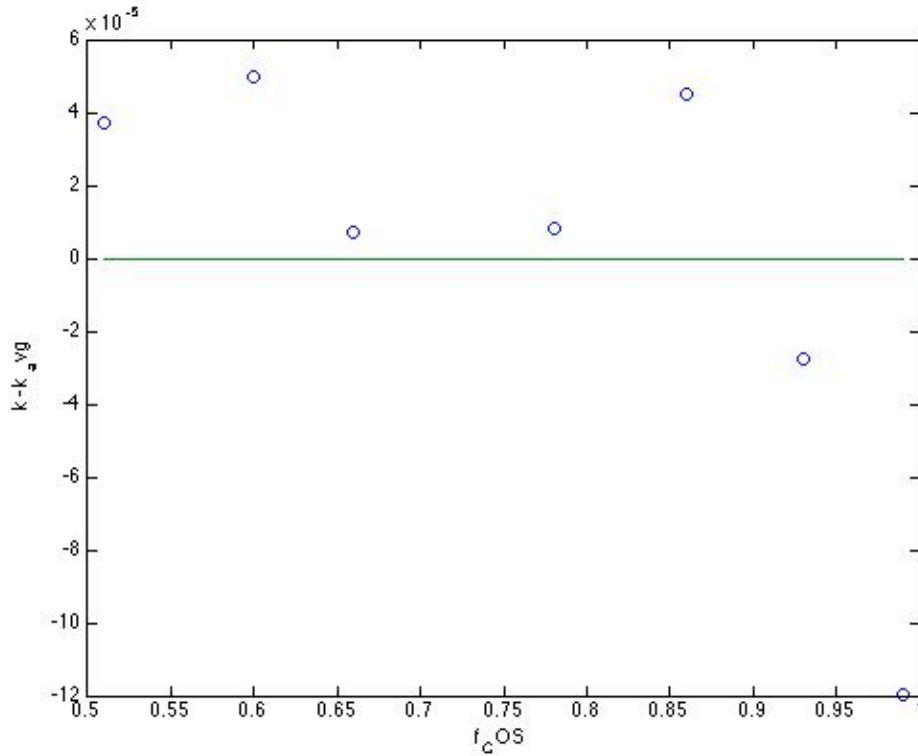
Figure 1. Deviation of individual k_1 values from the average as a function of conversion.

This example showed how the total molar flow rate can change when a PFR is used to gather kinetics data. That became important when the rate expression in terms of the partial pressure was substituted into the design equation. The same thing would have happened if the rate expression had used concentration instead of partial pressure. The concentration would be replaced using equation (13), introducing the volumetric flow rate, which will vary along the length of the reactor. Writing the volumetric flow rate in terms of the ideal gas law, equation (14), again introduces the total molar flow rate. Thus, when analyzing PFR kinetics data for a gas phase reaction, it is critical to check whether or not the total number of moles changes as a result of reaction. One cannot simply assume either the total molar flow rate or the volumetric flow rate to be constant.

$$C_{COS} = \frac{\dot{n}_{COS}}{\dot{V}}$$ (13)

$$\dot{V} = \frac{\dot{n}_{tot}RT}{P}$$ (14)

Calculation Details Using MATLAB

The calculations for this problem could easily be performed using a calculator. I used MATLAB for both the calculations and the plot. The code I used is provided as Example_15_4.m; it is also shown here in Listing 1. The code is a straightforward implementation of the calculation described above and will not be explained here. The plotting was done using standard MATLAB functions; consult the MATLAB documentation if it is unclear. The output from the code, apart from Figure 1, is shown in Listing 2.

```
% MATLAB file used in the solution of Example 15.4 of
% "A First Course on Kinetics and Reaction Engineering."

% Data provided in the problem statement, in consistent units
Diam=0.25; % cm
L=10.; % cm
T=1500; % K
P=1.0; % atm
Rgas=82.06; % (atm-cm^3)/(mol-K)
Vfr0=[10 20 30 40 60 75 100]'; % cm^3/min
fCOS=[0.99 0.93 0.86 0.78 0.66 0.60 0.51]';

% Calculate the inlet and outlet molar COS flow rates and k for each data
% point
n0COS = (P/Rgas/T)*Vfr0;
nCOS = n0COS.*(1-fCOS);
k = (-4/(pi()*Diam^2*L*P))*(n0COS - nCOS + 2*n0COS.*log(nCOS./n0COS));

% Calculate the average value of k and the standard deviation
k_avg = mean(k)
k_dev = std(k)

% Make a plot of (k - k_avg) vs. fCOS to see if there are systematic trends
plot(fCOS,(k - k_avg),'o',fCOS,zeros(length(fCOS),1),'-');
ylabel('k - k_a_v_g');
xlabel('f_C_O_S');
```

Listing 1. Contents of the file Example_15_4.m used to solve this problem using MATLAB.

```
>> Example_15_4

k_avg =

    0.0015


k_dev =

   5.9289e-05
```

Listing 2. Output from execution of code shown in Listing 1.