A First Course on Kinetics and Reaction Engineering

Activity 14.1

Problem Purpose

This activity provides an opportunity to practice the estimation of derivatives using the polynomial and finite differences methods and to use the results in a differential data analysis. It also illustrates how susceptible the approximation methods are to noise in the data, especially the finite differences methods.

Problem Statement

A rate expression is needed for the reaction A → Y + Z, which takes place in the liquid phase. It doesn't need to be highly accurate, but it is needed quickly. Only one experimental run has been made, that using an isothermal batch reactor. The reactor volume was 750 mL and the reaction was run at 70 °C. The initial concentration of A was 1M, and the concentration was measured at several times after the reaction began; the data are listed below.

t (min)	C_A(M)
1	0.874
2	0.837
3	0.800
4	0.750
5	0.572
6	0.626
7	0.404
8	0.458
9	0.339
10	0.431
12	0.249
15	0.172
20	0.185

(a) Plot the data, fit a 2nd, 3rd, 4th and 5th order polynomial to the data and plot the polynomials. Choose the best polynomial and use it to estimate $\frac{dn_A}{dt}$ for each experimental data point.

(b) Use forward, backward and central differences to estimate $\frac{dn_A}{dt}$ for each experimental data point. When using central differences, use a forward difference for the first data point and a backward difference for the last data point.

(c) Find the best value for a first order rate coefficient using the differential method of analysis and each of the estimates of $\frac{dn_A}{dt}$ from parts (a) and (b). Comment upon the results.

Problem Solution

(a) In order to perform the polynomial fitting, the value of n_A must be calculated for each experimental data point. The problem provides the reaction volume, V, and the concentration of A for each data point. With this information, the moles of A can be calculated using equation (1).

$$n_A = VC_A \qquad (1)$$

Once that is done, a 2nd, 3rd, 4th and 5th order polynomial can be separately fit to the n_A vs. t data. Figures 1 through 4 show the results. The fifth order polynomial shows the effect of using a polynomial of too high order. The large number of adjustable parameters can result in excess curvature as the parameters are adjusted to bring the model line as close as possible to the experimental data point. In other words, Figure 4 illustrates how using a polynomial of too high order places too much emphasis on the individual data points.

This is an irreversible, isothermal reaction, and it is the only reaction taking place. Therefore, we expect the moles of A to continually decrease. This does not happen in the experimental data due to a high level of experimental noise. Still, we should look for a polynomial that presents this expected behavior. The cubic polynomial, Figure 2, shows a clear minimum in n_A; for this reason, it, too, is rejected. The second and fourth order polynomials also show a very slight minimum, but not as severe as the cubic polynomial. Otherwise, they appear to be essentially equivalent. Either could be used to estimate $\frac{dn_A}{dt}$, but since the quadratic is simpler, I chose to use it.

The fitting process returned equation (2) as the best second order polynomial to represent the n_A vs. t data. Thus, its derivative, equation (3), can be used to estimate the value of $\frac{dn_A}{dt}$ at each experimental data point.

$$n_A \simeq 1.83t^2 - 68.1t + 758.3 \qquad (2)$$

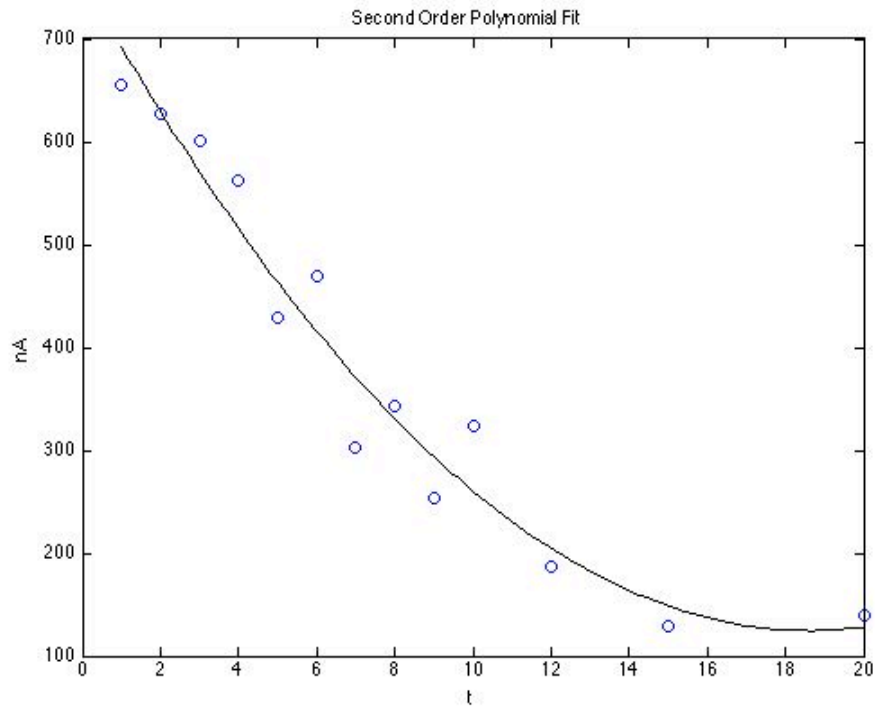$$\frac{dn_A}{dt} \simeq (2)1.83t - 68.1 \qquad (3)$$

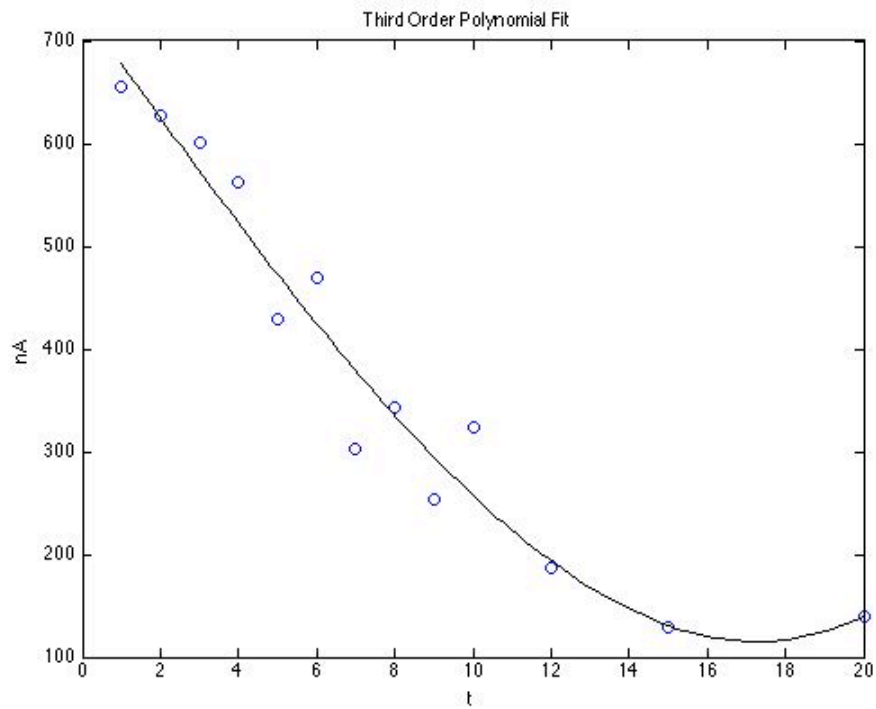*Figure 1. Second order polynomial fit to the experimental data.*

Figure 2. Third order polynomial fit to the experimental data.
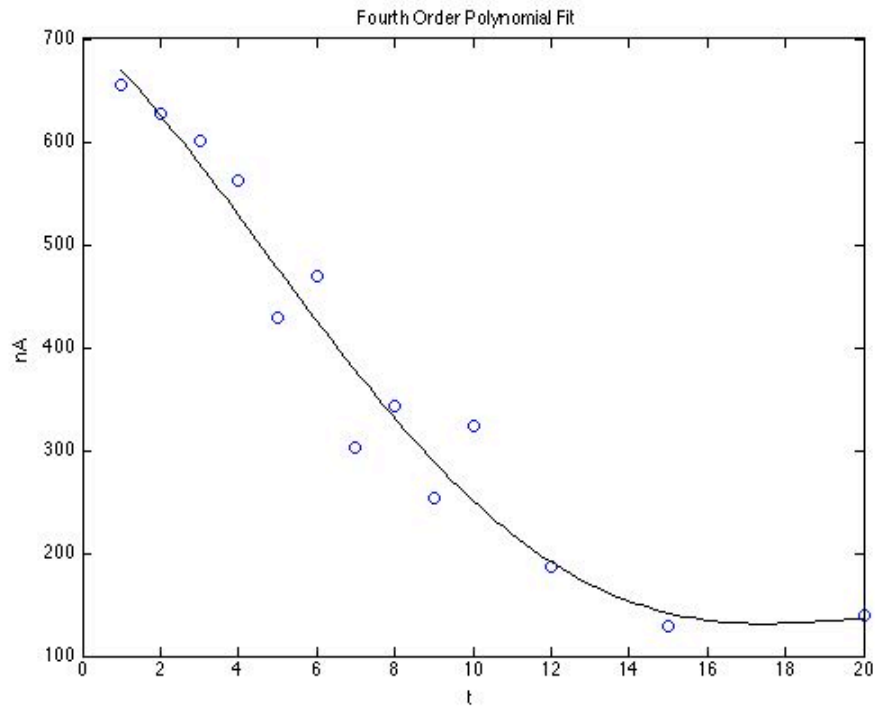
Figure 3. Fourth order polynomial fit to the experimental data.
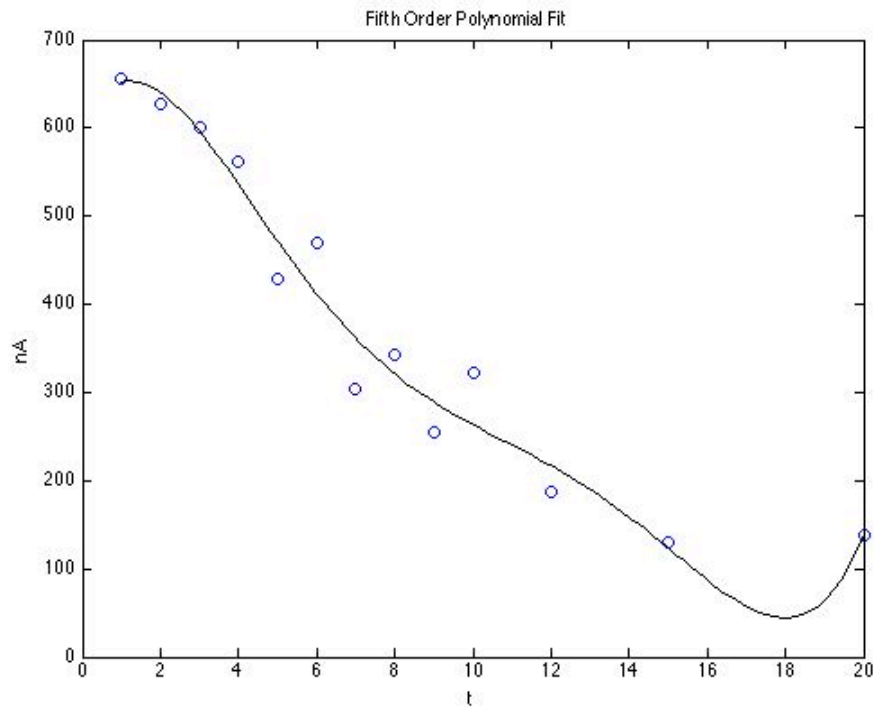

Figure 4. Fifth order polynomial fit to the experimental data.

(b) To approximate the derivative using finite differences, the data points are connected by straight line segments, Figure 5, and the derivative is taken to equal the slope of these segments. For forward differences, equation (4) is used so that the derivative associated with a point is the slope of the line segment following the point. As such, there is not derivative for the final point. For backward differences, equation (5) is used, associating the derivative with the slope of the line segment before the point, meaning there is no derivative for the first point. With central differences, the average of the forward and backward differences are used, equation (6). This would give no derivative at the first or last points, but here the forward and backward differences, respectively, will be used for those points.

$$\frac{dn_i}{dt}\bigg|_k \approx \frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k} \tag{4}$$

$$\frac{dn_i}{dt}\bigg|_k \approx \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}} \tag{5}$$

$$\frac{dn_i}{dt}\bigg|_k \approx \left(\frac{1}{2}\right)\left(\frac{(n_i)_{k+1} - (n_i)_k}{(t)_{k+1} - (t)_k} + \frac{(n_i)_k - (n_i)_{k-1}}{(t)_k - (t)_{k-1}}\right) \tag{6}$$
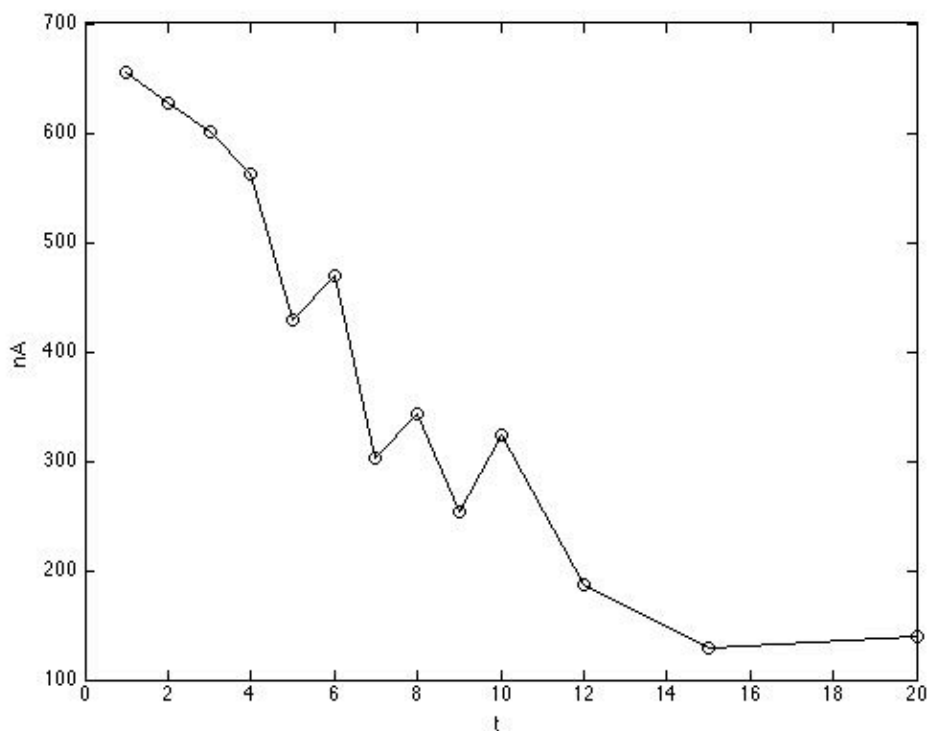

Figure 5. Finite differences approximations to the derivative

Looking at Figure 5, we can see that the finite differences approximations are not going to be very accurate for the data points in the middle of the plot. In that region, due to the noise in the data, the slopes jump back and forth between large positive and negative values. As already noted, we expect the data to decrease monotonically, that is, with a slope that is always negative.

(c) We are asked to test a first order rate expression. If we substitute a first order rate expression into a mole balance design equation for A, equation (7) results. If we are treating the derivative as if it is an experimentally measured quantity, then this equation has the linear form of equation (8) if y, x and m are defined as in equations (9) through (11).

$$\frac{dn_A}{dt} = -kVC_A \tag{7}$$

$$y = mx \tag{8}$$

$$y = \frac{dn_A}{dt} \tag{9}$$

$$x = -VC_A = -V\left(\frac{n_A}{V}\right) = -n_A \tag{10}$$

$$m = k \tag{11}$$

We have already calculated y four different ways (polynomial, forward differences, backward differences and central differences) for each data point. The calculation of x for each data point using equation (10) is trivial. Once it is accomplished, equation (8) can be fit to each of the four (y,x) data sets using linear least squares. The resulting model plots are shown in Figures 6 through 9. As expected, the finite differences data sets give a very poor fit, with large deviations of the data from the line representing the model. One might have expected the averaging used with central differences to improve the situation, but Figure 8 shows that is not the case. Given the figures, it really isn't necessary to even consider the correlation coefficient; these fits are not acceptable.

The polynomial approximation gave a better fit, as seen in Figure 9. Still, the deviations are relatively large, and furthermore, there appears to be a systematic deviation above the model line at low x and below the model line at high x. The correlation coefficient for this fit is only 0.85. If a highly preliminary estimation is all that is needed, this fit might be accepted (that's a judgement call). The best course of action would probably be to run additional experiments, but before doing so, find a better method or instrument to measure the concentration of A at each time. The current data are clearly too noisy to provide a good test of first order kinetics, let alone to estimate the value of the rate coefficient.
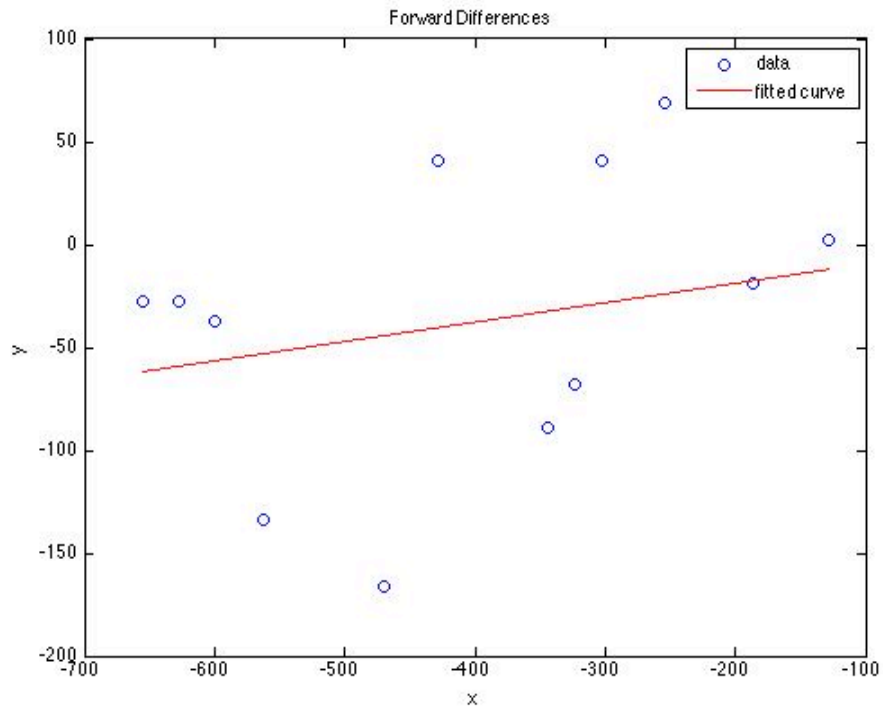
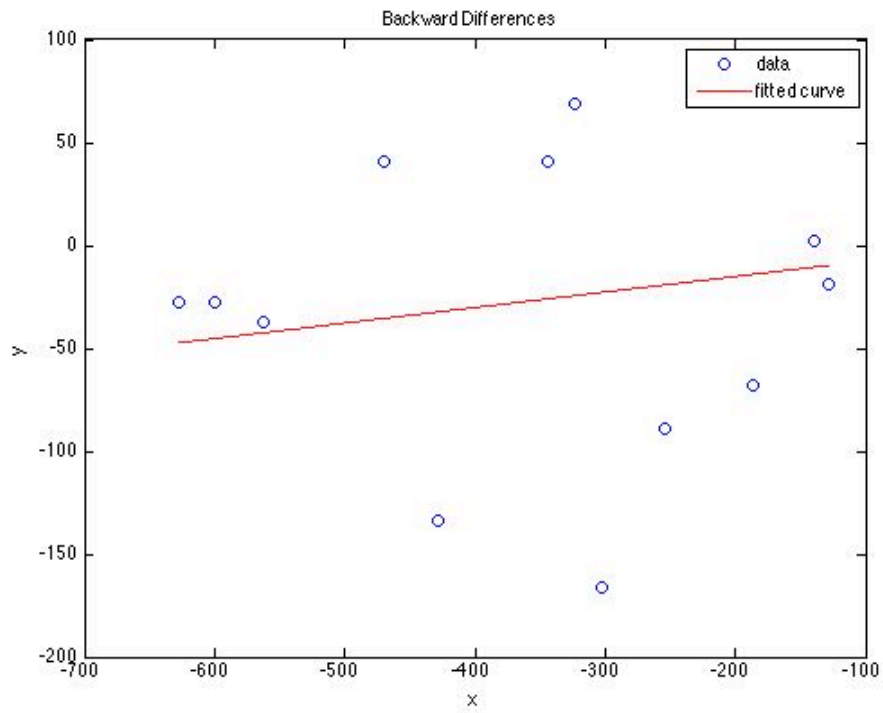*Figure 6. Model plot for the forward differences data.*

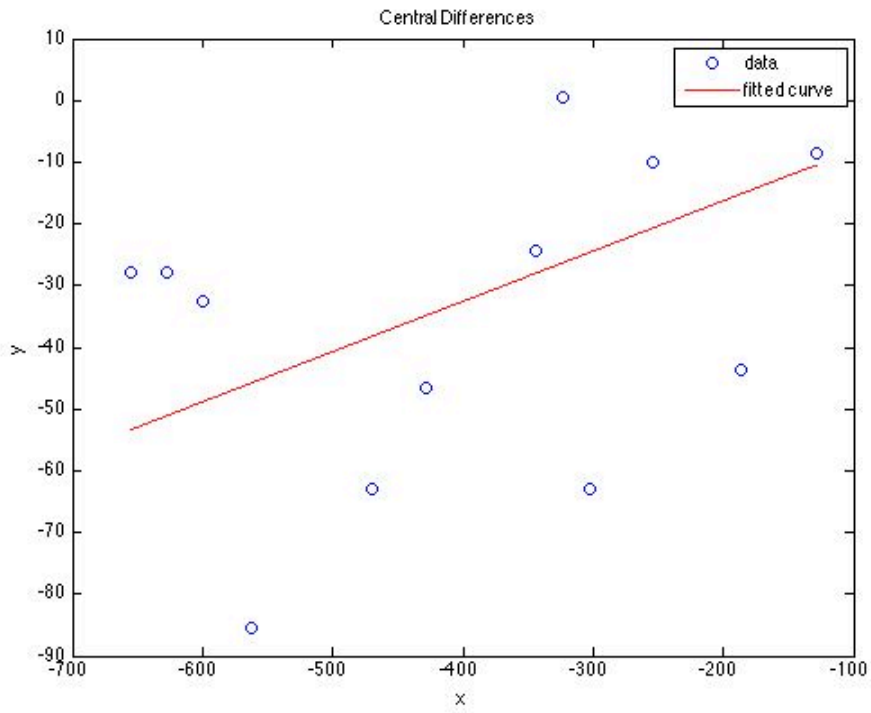*Figure 7. Model plot for the backward differences data.*
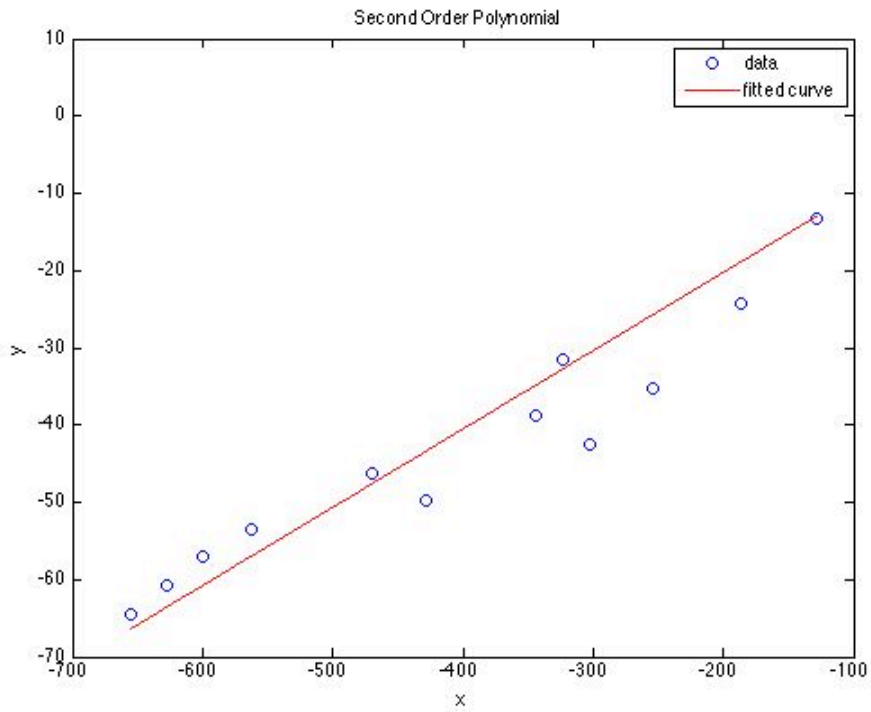
Figure 8. Model plot for the central differences data.

Figure 9. Model plot for the polynomial data.

Calculation Details Using MATLAB

The calculations for this solution were performed using MATLAB. Two files, 14_Activity_1_polyfit.m and 14_Activity_1.m, were used to do so. These files are completely analogous to the files used in the solution of Example 14.2. As a consequence, they are included with this solution, but they will not be discussed or described here.