

NAME: _____

Instructions: The exam is open book and open notes. You may use a laptop to do the computations. Write your name on the exam. Work both problems. You have two hours. Hand in your exam as well as your solution at the end. When you are finished, also email your m-files to rawlings@engr.wisc.edu.

Exercise 1. Who has the error? 50 points.

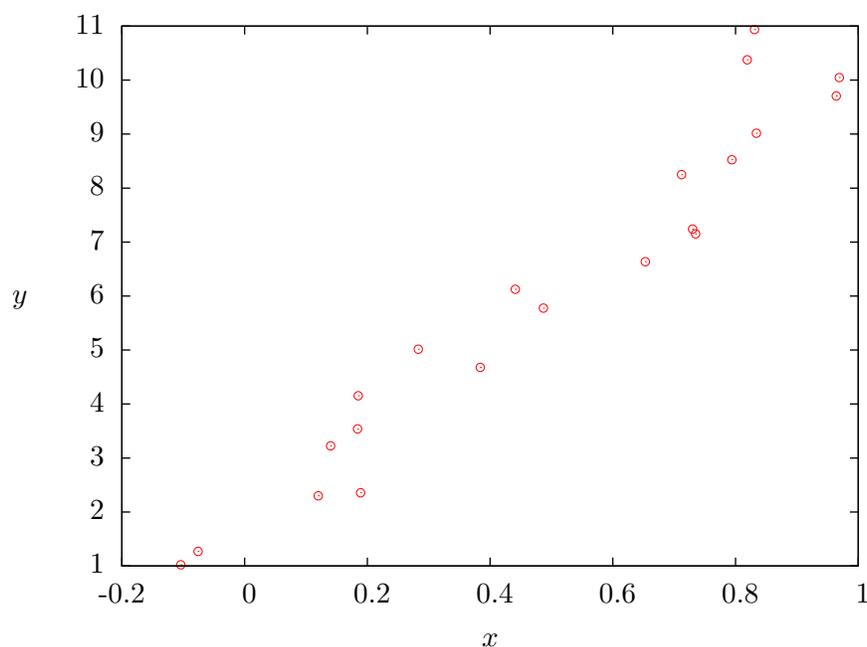


Figure 1: Plot of y versus x from data file `errvbls.dat` on the website www.che.wisc.edu/~jbrow/.

You are fitting some n laboratory measurements to a linear model

$$y_i = mx_i + b + e_{yi} \quad i = 1, 2, \dots, n$$

in which you have been told that the x variable is known with high accuracy and the y variable has measurement error e_y distributed as

$$e_y \sim N(0, 0.03)$$

The data are shown in Figure 1 and are given in file `errvbls.dat` on the website www.che.wisc.edu/~jbraw/.

- (a) Given these assumptions, write the model as

$$\mathbf{y} = \mathbf{X}\theta + \mathbf{e}_y$$

find the best estimate of the slope and intercept

$$\hat{\theta} = \begin{bmatrix} \hat{m} \\ \hat{b} \end{bmatrix}$$

and the 95% probability confidence ellipse, and also the plus/minus bounds on the parameter estimates.

- (b) Plot the data, and the line of best fit to these data.
- (c) Due to some confusion in the lab, you are told later that actually y is known with high accuracy and the x variable has measurement error e_x distributed as

$$e_x \sim N(0, 0.01)$$

Transform the model so that it is linear in a transformed parameter vector ϕ

$$x_i = f(y_i, \phi_1, \phi_2) + e_{xi} \quad i = 1, 2, \dots, n$$

What are f and ϕ for the transformed model?

- (d) Given these assumptions, write the model as

$$\mathbf{x} = \mathbf{Y}\phi + \mathbf{e}_x$$

find the best estimate $\hat{\phi}$ for this model. Add this line of best fit to the plot of the data and the line of best fit from the previous model. Clearly label which line corresponds to which model.

- (e) Compute the 95% confidence ellipse and plus/minus bounds for $\hat{\phi}$.
- (f) Can you tell from the estimates and the fitted lines which of these two proposed models is more appropriate for these data? Discuss why or why not.

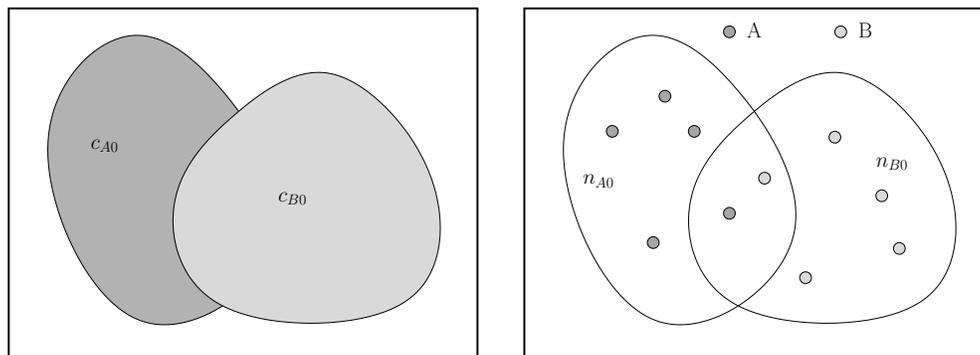
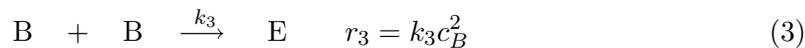
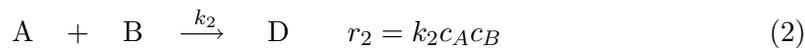
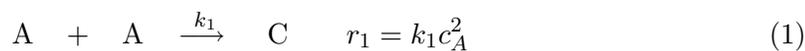
Exercise 2. What happened to my rate? 50 points.

Figure 2: Species A and B in a well-mixed volume element. Continuum and molecular settings.

Consider a well-mixed continuum setting in which we have positive, real-valued concentrations of reacting molecules of two types, A and B, as depicted in Figure 2. Let the concentration of A and B molecules in the volume of interest be denoted c_{A0} , c_{B0} . Consider the three possible irreversible reactions between these species using the elementary rate expressions



Consider also the total rate of reaction

$$r = r_1 + r_2 + r_3$$

- (a) If the A and B species are chemically similar so the different reactions' rate constants are all similar, $k_1 = k_2 = k_3 = k$, and the concentrations of A and B are initially equal, the total rate is given by

$$r = 3k c_{A0}^2$$

But if we erase the distinctions between A and B completely and relabel the B molecules in Figure 2 as A molecules, we obtain the new concentrations of A and

B as $c_A = 2c_{A0}$, $c_B = 0$ and the total rate is then

$$r = r_1 + r_2 + r_3$$

$$r = k_1 c_A^2 + k_2 c_A c_B + k_3 c_B^2$$

$$r = k(2c_{A0})^2 + k(2c_{A0} \cdot 0) + k(0)^2$$

$$r = 4kc_{A0}^2$$

Why are these two total rates different and which one is correct?

- (b) Repeat your analysis of the reaction rates if we reduce the length scale and consider the molecular kinetic setting in which we have integer-valued n_{A0} , n_{B0} molecules of A and B in the volume of interest.
- (c) Perform a stochastic simulation of the molecular setting using the following parameters

$$n_{A0} = 50 \quad n_{B0} = 60 \quad n_{C0} = n_{D0} = n_{E0} = 0$$
$$k_1 = k_2 = k_3 = k = 10\text{sec}^{-1}$$

Make a plot of all species versus time. Print the plot and the simulation code and hand them in with your exam solution.