**Chem 4581, Error Analysis Problem Set**

This problem set is worth one lab report (100 points). As in your lab reports, correct answers without work will be given no credit, whereas incorrect answers with work will be given partial credit. Units must be given. Handwritten problem sets are fine, but you are required to print out the computer data in problem 4.

An Excel tutorial is available on the course webpage (http://www.colorado.edu/chemistry/chem4581_91/) that explains how to perform a linear regression with error analysis. If you are not already familiar with Excel or another spreadsheet program, you are strongly encouraged to work through this tutorial in its entirety.

1. (15 points) You are interested in determining the heat of isomerization of two isomers (A and B), so you measure their heats of combustion. The difference between the heats of combustion is equal to the heat of isomerization. You are given two separate samples of 1.5 ± 0.1 mol each of isomers A and B, and they are burned in a constant-pressure calorimeter. The heat capacity of the calorimeter is 8.44 ± 0.05 kJ/K. Combustion of isomer A causes the temperature to rise by 2.9 ± 0.1 K, and isomer B causes the temperature to rise by 3.5 ± 0.1 K.

(a) Calculate the molar heat of isomerization ($\Delta H_i = \Delta H_B - \Delta H_A$).

(b) Calculate the uncertainty in the molar heat of isomerization. You can assume small uncertainties in your independent variables.

2. (25 points) Now that you have determined the heat of isomerization, you are interested in calculating the equilibrium constant at 300 K. The entropy change is negligible for this reaction, so $\Delta H \approx \Delta G$. The equilibrium constant is given by

$$K_{eq} = \exp\left(-\frac{\Delta G}{RT}\right) \tag{1}$$

(a) Calculate the equilibrium constant using the results of your heat of combustion experiment.

(b) Using your estimated uncertainties in the heat of combustion experiment, give upper and lower bounds for the equilibrium constant using the basic equation

$$f(x_0 - \sigma_-) < f(x_0) < f(x_0 + \sigma_+) \tag{2}$$

(c) Calculate the uncertainty in the equilibrium constant using the approximate rules which assume small uncertainties.

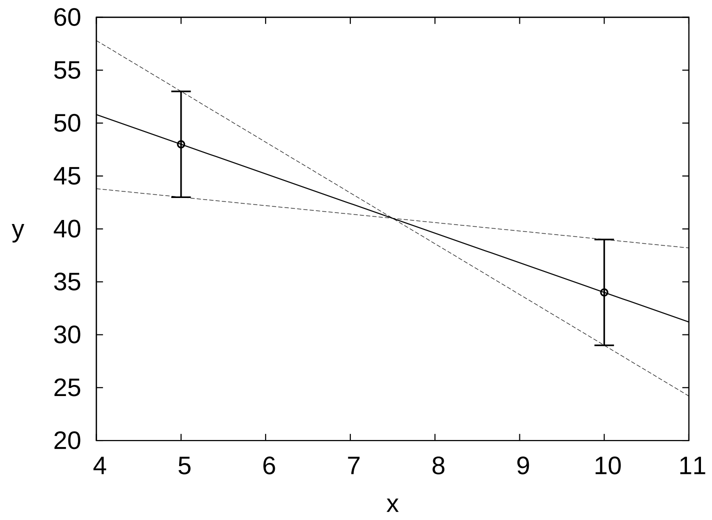


Figure 1: How to determine the uncertainty in the slope and intercept of two data points. The bars indicate the uncertainty in the $y$ variable, and the dashed lines give upper and lower bounds for the line.

3. (30 points) For gas phase reaction with unequal stoichiometry in the products and reactants, it is possible to determine the equilibrium constant by measuring the total pressure. The equilibrium constant as a function of temperature can then be used to determine the heat of reaction and entropy change of reaction:

$$\ln K_{eq} = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

Setting your $x$ variable to be $1/T$ and your $y$ variable to be $\ln K_{eq}$ this equation takes the familiar form $y = mx + b$, with slope $m = -\frac{\Delta H}{R}$ and intercept $b = \frac{\Delta S}{R}$.

You take pressure readings of a gaseous sample at two different temperatures and determine the equilibrium constant ($K_{eq}$):

| T [K] | $K_{eq}$ |
|---|---|
| 100.0 ± 0.01 | $1.6 \pm 0.1 \times 10^4$ |
| 200.0 ± 0.01 | $5.7 \pm 0.1 \times 10^4$ |

(a) Setting $y = \ln K_{eq}$ and $x = 1/T$, calculate the slope and intercept of equation 3 by hand (you can use a calculator, or spreadsheet, but not a linear regression program). Use the slope and intercept to calculate $\Delta H$ and $\Delta S$.

(b) If you define a function $y = \ln K_{eq}$, you can calculate the uncertainty in $y$ from the uncertainty in $K_{eq}$. Calculate the uncertainty in your $y$ variable ($\ln K_{eq}$) for both data points. You can assume small uncertainties in $K_{eq}$.

(c) You can now calculate the uncertainty in the slope and intercept as illustrated in figure 1. Neglect the uncertainty in $1/T$, and calculate upper and lower bounds for the slope and intercept. Use these results to calculate upper and lower bounds for $\Delta H$ and $\Delta S$.

4. (30 points) You proceed to measure the equilibrium constant at three more temperatures, and now have the following results:

| T [K] | $K_{eq}$ |
|---|---|
| $100.0 \pm 0.01$ | $1.6 \pm 0.1 \times 10^4$ |
| $150.0 \pm 0.01$ | $3.3 \pm 0.1 \times 10^4$ |
| $200.0 \pm 0.01$ | $5.7 \pm 0.1 \times 10^4$ |
| $250.0 \pm 0.01$ | $6.2 \pm 0.1 \times 10^4$ |
| $300.0 \pm 0.01$ | $7.8 \pm 0.1 \times 10^4$ |

(a) Linearize your data and perform a linear regression, using Excel or another computer program. Use the program to find the slope, intercept, and uncertainties in the slope and intercept. (You are required to turn in a printout of your spreadsheet.)

(b) Make a publication quality figure of your data points and best fit line. This means that the axes should be labeled, with units, the scale should be appropriate, and the figure should be clear and legible.

(c) Calculate $\Delta H$ and $\Delta S$ for this reaction, and estimate their uncertainties.