CH 113 Principles of Chemistry I
Fall 2000
Computer Project I

Names (print) ________________________________

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(200 points + 20 points extra credit)

This is a group project (two people) and only one report will be turned in for the entire group; however, it is important that each individual contribute substantially and equitably to this project.. Complete the following project, applying the graphing and computer skills learned in the Principles of Chemistry courses. Submit a report, constructed with either Word or WordPerfect word processor, with a coversheet that clearly indicates an appropriate title, the date submitted and the co-authors of this report. This handout and attached data must immediately follow the coversheet. The body of the report should be broken down into sections which answer each of the problems noted below. Be sure to clearly show your answer for each problem, and give a concise rationale for your answer. At the end of the report, each student should write a paragraph describing what they contributed to this project and then sign below that paragraph. Each of their partners should then initial below this signature if they agree with their partner's assessment. This assignment is to be turned in at the beginning of your lab on the week of September 17th.

Since we want you to learn how to use data analysis computer software, we decided to use real experimental data that may be affected by noise and experimental inaccuracies. Do not become overly worried with the new chemical and physical terms that are mentioned in the problems. Rather, concentrate on the analysis of the data itself. For this particular project, we will be using data from **nuclear magnetic resonance** (**NMR**), a form of spectroscopy that allows us to determine the chemical environment of different atoms in a molecule. Each atom is associated with a parameter called the **chemical shift**, whose value reports on the characteristics of the environment of the atom. The units of the chemical shift, or δ, are **parts-per-million**, or **ppms** – again, do not worry about what they really mean. For the purpose of the computer project we could call them "apples" or "oranges".

The δ of some of the hydrogen atoms, or **protons**, in a molecule can change with temperature almost linearly (**y = m * x + b**), and their rate of change, or **gradient** (**$\Delta\delta$ / ΔT**), is related to the presence or absence of tight associations of the protons with other atoms in the molecule. Protons whose δ changes considerably with temperature are not associated, and those who do not are more strongly associated. As a rule of thumb, the following relationship is used:

If $\Delta\delta / \Delta T > 0.004$ ppm/K   No association
If $\Delta\delta / \Delta T < 0.004$ ppm/K   Association

We have a molecule that we will call Pepe-1, for which we have measured the temperature gradients for 5 protons, and we want to determine which ones are associated and which ones aren't. After completing the following questions, you will be able to answer this, as well as to determine which data sets were accurately obtained and which ones were not. The following table has all the temperature gradient data you will need:

T (K)	H1 δ (ppm)	H2 δ (ppm)	H3 δ (ppm)	H4 δ (ppm)	H5 δ (ppm)
278	8.51	8.78	7.74	7.85	8.12
283	8.50	8.73	7.73	7.81	8.11
288	8.48	8.67	7.71	7.77	8.09
293	8.47	8.62	7.70	7.73	8.08
298	8.46	8.56	7.68	7.69	8.07
303	8.44	8.51	7.67	7.66	8.05
308	8.43	8.46	7.65	7.62	8.04
313	8.41	8.40	7.64	7.58	8.03
318	8.40	8.35	7.62	7.55	8.02
323	8.38	8.28	7.59	7.51	7.78

A) (60 points) For protons H1, H2, H3, and H4 in Pepe-1 draw a plot of chemical shift (δ) versus temperature (T), and calculate their temperature gradients Δδ / ΔT. The plots for all protons have to be on the same graph, so you will have to distinguish them with different symbols (circles, filled circles, squares, triangles, etc.). Hints: In SigmaPlot ***AND*** Excel, build a table with 5 columns, one for the temperature and the remaining four for the chemical shifts. Label all columns in the spreadsheet appropriately. Then create a graph with temperature as the independent variable (x) and chemical shifts as the dependent variable (y). In order to obtain the Δδ / ΔT gradients, you can assume that the relationship between δ and T is linear (δ = a * T + b), and then a linear regression analysis will provide you all the information you need to complete the question. Be sure to report the equations you obtain from your linear regression analyses. Visually, inspect the quality of the data and compare it with the correlation coefficients ($\boldsymbol{R^2}$) you obtained.

B) (20 points) Using the results obtained from question (A), determine which of the four protons you analyzed in Pepe-1 are tightly associated and which ones aren't. Hint: Compare the gradients you obtained to the rule of thumb described in page 1.

C) (40 points) From the graph, determine which pairs of protons will have the same chemical shift at a certain temperature. For each pair (if any), calculate at which temperatures (up to the third decimal place) the chemical shifts will be equal. Hints: The graphs indicate the chemical shifts at different temperatures, therefore, the intersections of the lines could give you an important piece of information. Since the relationship between δ and T is a simple formula, you can solve when they become equal by combining them and solving the simple equation that you obtain.

For proton H5 of Pepe-1, the experimental conditions were less than optimal, as the graduate student was tired and wanted to go home really bad. Therefore, we left it behind, as some of the data obtained for H5 may not be as good as it was for the other four protons. Our job is evaluate how bad the data is, and what parts of it, if any, we can use in our analyses.

d) (40 points) Create a plot of δ versus T for H5, and note the differences you see with respect to the other protons you plotted earlier. Specifically, what is the main difference? Considering the information you were given (i.e., this was the last data set collected, and the person doing it was in a hurry), do you think there could have been serious experimental errors while the data was being acquired? With this in mind, do you think that certain points in the data set can be left out of our analyses?

e) (40 points) Now you should have an idea as to which points in the data set may be seriously affected by experimental errors. Perform two linear regressions, one using all the data points for H5, and one leaving out the points that you feel are wrong. Are the differences in $\boldsymbol{R^2}$ correlation coefficients in both analyses consistent with the your observations from question (D)? Now consider the two temperature gradients obtained in each analyses. To what conclusion you would have arrived if no analysis of the data had been done? What is the most likely state of H5 in Pepe-1 (i.e., associated or not associated)?

NOTES:

1) In order to obtain full credit, your report has to conform to the following set of 'rules':

- You have to include print-outs of you spread-sheets with all the data.
- In your graphs, you have to label both the X and Y axes correctly and you have to give a title to the plot.
- The mayor and minor ticks in both axes have to make sense.
- The symbols and line formats corresponding to the different data sets have to be clearly labeled.
- Graphs and tables have to be numbered, and when you refer to any graph or table in the text, the correct number has to be included.

2) Additionally, remember that you have to do all calculations using both SigmaPlot 5.0 ***AND*** Excel to obtain full credit.