

Chem 112 Experiment in Solution Density Measurements and Statistical Data Analysis

I. Introduction

All branches of science are grounded on repetitive measurements and statistical data analysis. This first Chem112 experiment will re-visit density measurements of the type performed in Chem 111 and take the analysis a few steps further.

As is well known, laboratory measurements are rife with errors. The word "error" is used here not in any derogatory sense. Rather an error quantifies the difference between an experimentally measured value of a physical quantity of interest (density, temperature, pressure, etc.) and nature's true value.

Errors arise for all sorts of reasons, yet they basically fall into two camps: random and systematic. In this experiment we will perform mass density measurements for an aqueous salt solution. Our first purpose will be to assess the nature of our errors: are they random, systematic, or some combination of the two? Random errors permeate virtually all measurements, including those of today's lab; they derive from many sources, for example, temperature and pressure fluctuations of the sample and the room environment. Systematic errors also have many parents, and these typically point to faulty equipment, design, and procedure execution.

We will examine the nature of errors in solution density measurements via the distribution function $F(z)$. It turns out that $F(z)$ can be predicted extremely accurately for random experimental errors. $F(z)$ is thus a time-honored tool for quantifying the random errors in an experimental design, in addition to exposing systematic errors in the equipment, design, and procedure execution.

The second purpose of the experiment concerns significance testing. If Chemist A and Chemist B each measure a physical quantity repeatedly, two different averages are always obtained given a mix of random and systematic errors. An important question is: at what level of confidence can the differences in the averages be interpreted as significant?

There are quite a few ways to address the above question, some better than others. In today's experiment, however, we will hope that the Chemists' errors are primarily random. We will then use "t-test" statistics to answer the \$64 question concerning significance.

II. Experimental

A. Equipment

Please assemble the following:

- 1 10.0 mL graduated cylinder
- 1 250 mL Erlenmeyer flask
- 1 1.00 mL calibrated transfer buret

B. Chemicals

There are four aqueous solutions that have been prepared prior to this lab. All of them feature ammonium chloride as the solute. The solutions have the following concentrations:

0.756 Molar
0.947 Molar
1.140 Molar
1.334 Molar

The lab assistant will assign one of the above concentrations to each chem112 team.

C. Procedure

Goggles are required at all times during this experiment.

1. Begin by pouring 50 - 60 mL of the assigned ammonium chloride solution into a thoroughly cleaned and dry Erlenmeyer flask. Please wear latex gloves when carrying out this procedure
2. Transfer the solution to a thoroughly cleaned and dry buret. If necessary, allow ten - fifteen minutes for the solution and buret temperatures to equilibrate.
3. Carefully and very thoroughly clean and dry three-five glass test tubes. Using a beaker as a tare, weigh each test tube carefully according to methods discussed in Chem 111. *Accuracy and consistency are of utmost importance here.*
4. Use the buret to transfer a measured volume of the ammonium chloride solution to a test tube. The volume should be 3 - 5 ml and should be measured as accurately as possible.
5. Using the same beaker as a tare, weigh the test tube-plus-solution. Compute the mass density of the solution.
6. Perform the mass density measurement twelve - fifteen times. Fifteen is better than twelve. Each measurement must be performed as independently as possible of all the previous measurements. The test tubes will have to be used more than once. Make sure that prior to each solution transfer, the receiving tube is cleaned, dried, and weighed. The volume and mass of the solution in each tube must be measured as accurately as possible. Please cover the solution during the experiment to minimize evaporation. Please note any temperature changes should they arise during the experiment.

III. Data Tabulation

1. Let each density measurement be denoted by x_1, x_2, \dots, x_n . Compute the **average**

value $\langle x \rangle$ of the n measurements using units of grams per cubic centimeter. The " $\langle \rangle$ " brackets mean "average value of quantity enclosed by the brackets".

2. Let the square each density measurement be denoted by $x_1^2, x_2^2, \dots, x_n^2$. Compute the **average value** $\langle x^2 \rangle$ of the squares of the n density measurements. This quantity will be in units of $\text{grams}^2 / \text{cm}^6$

3. Compute an estimate for the variance $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$.

4. Then compute an estimate for the standard deviation σ (Greek letter sigma). For a large number of samples, this is simply the square root of the variance. For a limited number of samples, the standard deviation follows from a more complicated calculation. Many calculators have this function internally programmed. Feel free to use such a calculator program to arrive at the standard deviation.

5. Compute n values of the variable z defined as follows:

$$z_i = \frac{x_i - \langle x \rangle}{\sigma}$$

Note that roughly half of the z -values will be positive, e.g. +1.68, +0.723, +2.22, etc.. Roughly half will be negative: -0.826, -0.112, -1.83, etc. .

6. Using one of the attached sheets, construct a quality well-labeled and executed graph of the function $F(z)$.

$F(z)$ quantifies the fraction of the number of measurements with value less than or equal to z . For example, if three out of the twelve density measurements demonstrated z -values ≤ -2.18 , then $F(z = -2.18) = 3/12 = 0.250$.

Note that $F(z)$ evaluated at the maximum value of z equals 1. Mark only the data points on the graph; use no interconnecting lines. The vertical scale should cover only the range zero to one. When constructed correctly, a sigmoidal or "S"-like plot should be evident.

7. Consider the literature value ρ (Greek letter rho) of the density of ammonium chloride solution--the teaching assistant will have this information as supplied by the *Handbook of Chemistry and Physics*. Compute a value for the t -test statistic as follows:

$$t = \frac{(\langle x \rangle - \rho) n^{1/2}}{\sigma}$$

8. Now consider only the absolute value of t . Use this value and the table included with this handout to assign a level of confidence comparing your density measurement results with the literature value. The number of degrees of freedom in your experiment equals $p = n - 1$. For example, if $t = 1.363$ for $p = 12 - 1 = 11$ degrees of freedom, this corresponds to the 0.90 quantile, or the 90% level of confidence. One then claims that the differences between the measured and literature values of the density are significant at

the 90% level of confidence. In other words, there is only a 10% chance that the differences are simply due to random errors in experimental performance.

Larger t-values correspond to greater degrees of significance in the differences between the measured average value of the solution density and the literature value. Smaller t-values correspond to smaller degrees of significance attached to the differences. Smaller t-values correspond to situations where the observed differences between the literature and experimental values are due primarily to random errors.

9. Now consider the results obtained by two different Chem 112 Chemists, A and B, for identical ammonium chloride solutions. One will have to consider two different average values $\langle x \rangle^{(A)}$ and $\langle x \rangle^{(B)}$ with variances σ_A^2 and σ_B^2 , based on n_A and n_B number of measurements by the chemists.

(i) First compute the **pooled variance** S_{AB}^2 :

$$S_{AB}^2 = \frac{(n_A - 1) \sigma_A^2 + (n_B - 1) \sigma_B^2}{n_A + n_B - 2}$$

(ii) Then compute the estimated standard deviation S_D between the two average values:

$$S_D = S_{AB} \left[(1/n_A) + (1/n_B) \right]^{1/2}$$

(iii) Then compute the difference D between the two averages:

$$D = \langle x \rangle^{(A)} - \langle x \rangle^{(B)}$$

(iv) Now compute the ever-informative **t-test statistic**:

$$t = D / S_D$$

10. Consider only the absolute value of t . Use this value and the attached table to assign a level of confidence comparing the density measurements of Chemists A and B. The number of degrees of freedom will equal $n_A + n_B - 2$.

Larger t-values will again correspond to greater degrees of significance in the differences between the two average values measured by the chemists.

For measurements performed on identical solutions, larger t-values indicate systematic differences in the procedures carried out by the chemists. Smaller t-values correspond to smaller degrees of significance in the differences. Smaller t-values indicate consistency and uniformity in the procedures carried out by the chemists.

IV. Preliminary Report

Refer to the final page of this handout. Please report the values for \bar{x} , σ^2 , and the t-statistics based on your assigned solution. Please show all the calculations which lead to these values.

V. Final Report

Each final report should be based on data acquired by the team. Every individual should submit his/her own final typewritten report.

A. Introduction

Please state the purpose of the experiment in your own words.
Briefly summarize the concepts relevant to the experiment.

B. Experimental

Describe the procedure briefly. State any deviations from the procedure described in the handout.

C. Results and Data Analysis

Please report all data and calculations in a clearly-labeled table format. Include the graphs for $F(z)$. Please label horizontal and vertical axes of the lab.

The specific calculations to include are the following:

- (i) the average density of the aqueous ammonium chloride solutions.
- (ii) the variance and standard deviation of the density measurements.
- (iii) the function $F(z)$ in numerical and graphical form.
- (iv) The t-test statistic comparing your data with the appropriate density value provided by the lab assistant (and listed in the Handbook of Chemistry and Physics).
- (v) The t-test statistic comparing your data with those of a Chem 112 team performing the same density measurements.

D. Discussion.

Please discuss the significance of the results. In particular, please address the questions:

- (1) At what confidence level can one claim that the difference between the measured average density and the literature value is significant?
- (2) At what confidence level can one state claim that the difference between the measured average density and the average density obtained by another Chem 112 team is significant?
- (3) Does the $F(z)$ plot indicate the experimental errors to be primarily random or primarily systematic? Does the plot indicate that some combination of random and systematic errors have transpired?

Pre-Lab Assignment

1. A chemist prepares fifteen independent solutions of 0.291 molar sodium carbonate in water at temperature 20 C. The chemist measures the density of each sample and records the results as follows.

Measurement #	Density (g/cc)
1	1.0330
2	1.0179
3	1.0302
4	1.0187
5	1.0198
6	1.0342
7	1.0357
8	1.0217
9	1.0322
10	1.0199
11	1.0426
12	1.0299
13	1.0294
14	1.0174
15	1.0202

- (a) What is the average density from the solution density measurements?
- (b) What is the variance and standard deviation?
- (c) *The Handbook of Chemistry and Physics* reports the density of 0.291 molar sodium carbonate at 20 C to be 1.0294 grams per cubic centimeter. What is the value of the t-test statistic comparing the above data with the CRC value?
- (d) Please construct a plot of $F(z)$ for the above data. Does the plot indicate the experimental errors to be random or systematic? Some combination of the two?

Ye Olde Chem 112 Lab Quiz for Experiment One, July 1,2 2008

1. A chemist prepares six independent solutions of 1.145 Molar sodium acetate in water at temperature 20 C. The chemist measures the density of each sample and records the results as follows.

Measurement #	Density (g/cc)
1	1.1401
2	1.2379
3	1.1537
4	1.1113
5	1.2534
6	1.1025

(a) What is the average density from the solution density measurements?

(b) What is the variance and standard deviation?

(c) Literature tables report the density of 1.145 molar sodium acetate at 20 C to be 1.0440 grams per cubic centimeter. Qualitatively speaking, what comparison does the t-test enable between the literature value and that calculated via the (a)-measurements?

Preliminary Report for Chem 112 Experiment Number One:

Name:

Date:

Lab Assistant:

(1) Measured Average Density of Ammonium Chloride Solution:

(2) Density Variance:

(3) t-statistic from comparing measured value to literature value:

(4)) t-statistic from comparing measured value to the value obtained by another Chem 112 team:

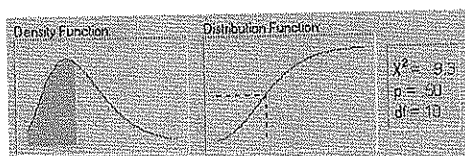
t table with right tail probabilities



df \ p	0.40	0.25	0.10	0.05	0.025	0.01	0.005	0.0005
1	0.324920	1.000000	3.077684	6.313752	12.70620	31.82052	63.65674	636.6192
2	0.288675	0.816497	1.885618	2.919986	4.30265	6.96456	9.92484	31.5991
3	0.276671	0.764892	1.637744	2.353363	3.18245	4.54070	5.84091	12.9240
4	0.270722	0.740697	1.533206	2.131847	2.77645	3.74695	4.60409	8.6103
5	0.267181	0.726687	1.475884	2.015048	2.57058	3.36493	4.03214	6.8688
6	0.264835	0.717558	1.439756	1.943180	2.44691	3.14267	3.70743	5.9588
7	0.263167	0.711142	1.414924	1.894579	2.36462	2.99795	3.49948	5.4079
8	0.261921	0.706387	1.396815	1.859548	2.30600	2.89646	3.35539	5.0413
9	0.260955	0.702722	1.383029	1.833113	2.26216	2.82144	3.24984	4.7809
10	0.260185	0.699812	1.372184	1.812461	2.22814	2.76377	3.16927	4.5869
11	0.259556	0.697445	1.363430	1.795885	2.20099	2.71808	3.10581	4.4370
12	0.259033	0.695483	1.356217	1.782288	2.17881	2.68100	3.05454	4.3178
13	0.258591	0.693829	1.350171	1.770933	2.16037	2.65031	3.01228	4.2208
14	0.258213	0.692417	1.345030	1.761310	2.14479	2.62449	2.97684	4.1405
15	0.257885	0.691197	1.340606	1.753050	2.13145	2.60248	2.94671	4.0728
16	0.257599	0.690132	1.336757	1.745884	2.11991	2.58349	2.92078	4.0150
17	0.257347	0.689195	1.333379	1.739607	2.10982	2.56693	2.89823	3.9651
18	0.257123	0.688364	1.330391	1.734064	2.10092	2.55238	2.87844	3.9216
19	0.256923	0.687621	1.327728	1.729133	2.09302	2.53948	2.86093	3.8834
20	0.256743	0.686954	1.325341	1.724718	2.08596	2.52798	2.84534	3.8495
21	0.256580	0.686352	1.323188	1.720743	2.07961	2.51765	2.83136	3.8193
22	0.256432	0.685805	1.321237	1.717144	2.07387	2.50832	2.81876	3.7921
23	0.256297	0.685306	1.319460	1.713872	2.06866	2.49987	2.80734	3.7676
24	0.256173	0.684850	1.317836	1.710882	2.06390	2.49216	2.79694	3.7454
25	0.256060	0.684430	1.316345	1.708141	2.05954	2.48511	2.78744	3.7251
26	0.255955	0.684043	1.314972	1.705618	2.05553	2.47863	2.77871	3.7066
27	0.255858	0.683685	1.313703	1.703288	2.05183	2.47266	2.77068	3.6896
28	0.255768	0.683353	1.312527	1.701131	2.04841	2.46714	2.76326	3.6739
29	0.255684	0.683044	1.311434	1.699127	2.04523	2.46202	2.75639	3.6594
30	0.255605	0.682756	1.310415	1.697261	2.04227	2.45726	2.75000	3.6460
inf	0.253347	0.674490	1.281552	1.644854	1.95996	2.32635	2.57583	3.2905

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Chi-Square Table



Like the Student's *t*-Distribution, the *Chi-square* distribution's shape is determined by its degrees of freedom. The animation above shows the shape of the *Chi-square* distribution as the degrees of freedom increase (1, 2, 5, 10, 25 and 50). For examples of tests of hypothesis which use the *Chi-square* distribution, see [Statistics in crosstabulation tables](#) in the [Basic Statistics and Tables](#) chapter as well as the [Nonlinear Estimation](#) chapter. See also, [Chi-square Distribution](#). As shown in the illustration below, the values inside this table are critical values of the Chi-square distribution with the corresponding degrees of freedom. To determine the value from a Chi-square

Ye Olde Chem 112 Plot

