Chemistry 222 **Name**_______________________________________
Spring 2020 **80 Points**
Exam 1: Chapters 1-5

Complete three (3) of problems 1-4 and three (3) of problems 5-8. CLEARLY mark the problems you do not want graded. Show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures and with the appropriate units.

Do <u>three</u> of problems 1-4. Clearly mark the problem you do not want graded. (10 pts each)

1. Choose ONE of the following pairs of terms and briefly (but clearly) compare and contrast the two concepts.
   a. TC vs. TD
   b. Systematic Error vs.Random Error

   a. **<u>TC = to contain.</u>** TC glassware is designed to hold a fixed volume of material (within its tolerance) when filled to the mark. The glassware is calibrated for a given temperature (usually 20°C). Complete transfer of all the material from TC glassware requires rinsing.
   <u>TD = to deliver.</u> TD glassware is designed to dispense a fixed volume of solution (within its tolerance) after being filled to the mark. It is also calibrated at a fixed temperature. Care must be taken to use TD glassware properly and not blow out all the liquid unless the glassware was calibrated as "blow out" (etched stripe)

   b. **Systematic** or Determinate error affects accuracy. This error is usually constant and can be identified and corrected.
   Random or Indeterminate error cannot be removed but can be evaluated and minimized with appropriate experiment design and running multiple samples. Random errors impact the precision of a measurement.

2. While preparing for this exam, one of your classmates asks you why a confidence interval is used to describe the "quality" of a result, as opposed to a standard deviation alone. Clearly explain why a confidence interval is used and what types of information we can infer from the confidence interval about the quality of a result.

   When we refer to quality of results, we are typically considering the accuracy and precision of a value. In terms of precision, statistics are a useful tool to evaluate how reproducible our data are, with a standard deviation serving as an estimate of the scatter of the data. The challenge comes in the fact that we typically have a very small data set and are forced to rely on that small set to approximate the standard deviation. The confidence interval helps to account for this by adjusting the size of the confidence interval, depending on how well we have defined the scatter in the data (based on the number of data points). This allows a more realistic estimation of the measurement's precision.

   The confidence interval also allows us to make some inferences about the accuracy of a method, assuming only random errors are impacting our measurement.

3. In producing a calibration curve, raw data is typically subjected to a "linear least squares" analysis. Dissect the phrase "linear least squares" and describe qualitatively what is done in a linear least squares analysis. Why "linear"? "Least squares" of what? No calculations are necessary.

   The goal of a linear least squares analysis is to determine the linear relationship (y = mx+b) that "best" describes the trend in a data set. In this analysis, "best" means that the calculated values for slope (m) and intercept (b) describe a line where the sum of the squares of the residuals (the difference between the actual y-values and those predicted by the line) is minimized. This is accomplished by setting the partial derivatives of the residuals calculation with respect to the slope and intercept to zero and solving for m and b. A key assumption in this analysis is that the x-values are known to a high degree of precision, while the y-values hold the most uncertainty.

4. The sensitivity of an analytical method is often confused with the limit of detection, even though they are not the same. Explain the differences between the sensitivity and limit of detection.

   Your discussion should focus on the fact that sensitivity describes the ability of a method to distinguish between small changes in concentration (or amount) of analyte throughout the range of the measurement. The limit of detection describes the minimum concentration (or amount) of analyte that can be distinguished from the blank with some level of certainty. It is certainly possible for a method to be sensitive and not have a small limit of detection, and vice versa.

Do three of #'s 5-8. Clearly mark the problem you do not want graded. (16 pts each)

5. In the EDTA experiment, we use a solution of zinc ion to standardize a solution of EDTA. The data below was obtained for such a titration. Based on this information, calculate the concentration of EDTA in moles per liter (with its associated uncertainty) in the solution. NOTE: EDTA and zinc react in a one to one stoichiometric ratio.

Concentration of zinc standard	0.01117 ± 0.00001 M
Volume of zinc solution used	20.00 ± 0.03 mL
Initial buret reading	1.46 ± 0.05 mL
Final buret reading	23.54 ± 0.05 mL

Uncertainty in the volume delivered by the buret:

$$(23.54 \pm 0.05\text{ mL}) - (1.46 \pm 0.05\text{ mL}) = 22.08 \pm e_1\text{ mL}$$

$$e_1 = [(0.05)^2 + (0.05)^2]^{1/2} = 0.0707\text{ mL}$$

Concentration calculation:

$$\frac{0.01117 \pm 0.00001\text{ mol Zn}^{2+}}{1\text{L}} \times \underline{20.00 \pm 0.03\text{mL}} \times \frac{1\text{ mol EDTA}}{1\text{ mol Zn}^{2+}} \times \frac{1}{22.08 \pm 0.07\text{mL}} = 0.010118 \pm e_2\text{ M}$$

$$e_2 = 0.010118\text{M}\sqrt{\left(\frac{0.00001}{0.01117}\right)^2 + \left(\frac{0.03}{20.00}\right)^2 + \left(\frac{0.07}{22.08}\right)^2}$$

$e_2 = 0.00003_7 = 0.00004$ M so the **EDTA concentration is 0.01012 ± 0.00004 M**

(if you choose to report relative uncertainty, it is 0.003_9 or 0.4% relative error.)

6. A 5.24 g sample of a solid containing Ni is dissolved in 20.0 mL water. A 5.00 mL aliquot of this solution is diluted to 100.0 mL and analyzed in the lab. The analyzed solution was determined to contain 6.16 ppm Ni.
   a. Determine the molar concentration (molarity) of Ni in the sample.

      One approach is to calculate the molarity of the diluted solution from its concentration in ppm:

$$\frac{6.16\text{g Ni}}{10^6\text{g sol'n}} \times \frac{1\text{ g sol'n}}{1\text{ mL sol'n}} \times \frac{10^3\text{ mL}}{1\text{L}} \times \frac{1\text{ mol Ni}}{58.693\text{ g Ni}} = 1.0495\text{x}10^{-4}\text{ M}$$

      Now account for the dilution from the original solution:

$$1.0495\text{x}10^{-4}\text{ M} \times \frac{100.0\text{ mL}}{5.00\text{ mL}} = 2.099 \times 10^{-3}\text{ M} = \mathbf{2.10 \times 10^{-3}\ M}$$

   b. Determine the weight percent (% w/w) of Ni in the sample.

From the concentration and the initial volume that the sample was dissolved in, we can determine the mass of nickel in the original sample:

$$\frac{2.10 \times 10^{-3}\text{ mol Ni}}{\text{L sol'n}} \times 0.0200\text{ L sol'n} \times \frac{58.693\text{ g Ni}}{1\text{ mol Ni}} = 0.002464\text{g Ni}$$

So, the weight percent is:

$$\frac{0.002464\text{g Ni}}{5.24\text{ g sample}} \times 100\ \% = \mathbf{0.0470\%\ Ni}$$

7. You have run a series of titrations to determine the unknown concentration of KHP in a solid sample. The results of titrations indicate KHP concentrations of 35.69%, 30.03%, 35.55%, 36.07%, 35.98%. The "true" value for KHP in this sample is 36.29%. Evaluate the data and determine if your results differ from the true value at the 95% confidence level.

   Looking at the data, it appears that the value 30.03% is an outlier so try a Q-test or a G-Test:

$$Q_{calc} = \frac{35.55 - 30.03}{36.07 - 30.03} = 0.91 \qquad G_{calc} = \frac{34.66 - 30.03}{2.60} = 1.78$$

   Q_{table} = 0..64 < Q_{calc}, and G_{table} = 1.672 < G_{calc} so the data point should be rejected.

   Based on the remaining data, the mean for the data set is 35.82_3% with a standard deviation of 0.2_4 %. Do a t-test:

$$t_{calculated} = \frac{|36.29-35.82|}{0.24}\sqrt{4} = 3.84$$

   t_{table} for 4 degrees of freedom is 3.182, since $t_{calc} > t_{table}$, the results do differ significantly.

   (NOTE: if you do not do the Q-test, the standard deviation is large enough that is looks like the results do not differ. Always look at the data!)

   Alternatively, you could have calculated the range determined by the confidence limit and shown that 36.29% lies outside this range. The 95% CI is 35.8 ± 0.4 %

8. Nitrite (NO_2^-) was measured in rainwater and unchlorinated drinking water using U by an established spectrophotometric method. Based on the results below, does drinking water sample contain significantly more nitrite than rainwater sample (at the 95% confidence level)?

Replicate	1	2	3	4	5	mean	st. dev.
Rainwater (ppb)	55.1	59.6	63.1	66.4	71.5	63.1	6.28
Drinking Water (ppb)	74.6	81.0	87.3	91.8	93.2	85.6	7.77

Note that the question was worded poorly. I intended for it to read: "Nitrite (NO_2^-) was measured in rainwater and unchlorinated drinking water using an established spectrophotometric method, measuring replicates of a single sample of each water type. Based on the results below, does drinking water sample contain significantly more nitrite than rainwater sample (at the 95% confidence level)?" Even with the poor wording, the use of the term "replicate" in the table was a strong clue to the appropriate approach.

This is a comparison of two methods, using several runs of a single sample to establish the uncertainty on each method. Since we have two means and standard deviations, use s_{pooled} to perform a t-test. Check the standard deviations with an F-test first:

$$F_{calculated} = \frac{(s_1)^2}{(s_2)^2} = \frac{(7.77)^2}{(6.28)^2} = 1.53$$

Since $F_{calculated}$ is less than F_{table} (6.39), our "normal" equations will be fine.

$$s_{pooled} = \sqrt{\frac{(6.28)^2(4)+(7.77)^2(4)}{5+5-2}} = 7.06$$

$$t_{calculated} = \frac{85.2-63.0}{7.06}\sqrt{\frac{25}{5+5}} = 5.02$$

t_{table} for (5+5-2) = 8 degrees of freedom is 2.306

Since $t_{calculated} > t_{table}$, the results **are** significantly different

Possibly Useful Information

$m = \dfrac{m'\left(1-\dfrac{d_a}{d_w}\right)}{\left(1-\dfrac{d_a}{d}\right)}$	Density of air = 0.012 g/ml Density of balance weights = 8.0 g/ml
$\mu = \bar{x} \pm \dfrac{ts}{\sqrt{n}}$	$y = \dfrac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
$e_C = \sqrt{e_A^2 + e_B^2}$	$e_C = C\sqrt{\left(\dfrac{e_A}{A}\right)^2 + \left(\dfrac{e_B}{B}\right)^2}$
$t_{calculated} = \dfrac{\lvert \text{known value} - \bar{x} \rvert}{s}\sqrt{n}$	$s = \sqrt{\dfrac{\sum_i (x_i - \bar{x})^2}{n-1}}$
$t_{calculated} = \dfrac{\lvert \bar{x}_1 - \bar{x}_2 \rvert}{s_{pooled}}\sqrt{\dfrac{n_1 n_2}{n_1 + n_2}}$	$s_{pooled} = \sqrt{\dfrac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$
$t_{calculated} = \dfrac{\bar{d}}{s_d}\sqrt{n}$	$s_d = \sqrt{\dfrac{\sum_i (d_i - \bar{d})^2}{n-1}}$
$s_x = \dfrac{s_y}{\lvert m \rvert}\sqrt{\dfrac{1}{k} + \dfrac{1}{n} + \dfrac{(y - \bar{y})^2}{m^2 \sum (x_i - \bar{x})^2}}$	$s_y = \sqrt{\dfrac{\sum (d_i - \bar{d})^2}{n-2}} = \sqrt{\dfrac{\sum d_i^2}{n-2}}$
$s_m^2 = \dfrac{s_y^2 \times n}{D}$	$s_b^2 = \dfrac{s_y^2 \sum x_i^2}{D}$
$y_{LOD} = y_{blank} + 3s$	$F_{calculated} = \dfrac{(s_1)^2}{(s_2)^2}$
$Q_{calculated} = \dfrac{gap}{range}$	$G_{calculated} = \dfrac{\lvert \text{suspect value} - \bar{x} \rvert}{s}$

Values of Student's t

Degrees of Freedom	Confidence Level (%) 90	95	99.5	99.9
1	6.314	12.706	127.32	636.61
2	2.920	4.303	14.089	31.598
3	2.353	3.182	7.453	12.924
4	2.132	2.776	5.598	8.610
5	2.015	2.571	4.773	6.869
6	1.943	2.447	4.317	5.959
7	1.895	2.365	4.029	5.408
8	1.860	2.306	3.832	5.041
9	1.833	2.262	3.690	4.781
10	1.812	2.228	3.581	4.587
∞	1.645	1.960	2.807	3.291

Values of *Q* for rejection of data

# of Observations	Q (90% Confidence)
4	0.76
5	0.64
6	0.56

Grubbs Test for Outliers

# of Observations	$G_{critical}$ At 95% confidence
4	1.463
5	1.672
6	1.822

Critical Values of F at the 95% Confidence Level

Degrees of freedom for s_2	Degrees of freedom for s_1: 2	3	4	5	6	7	8	9	10
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74