Chemistry 222 **Name**_____
Fall 2010 **80 Points**
Exam 1: Chapters 1-4

Complete two (2) of problems 1-3 and four (4) of problems 4-8. CLEARLY mark the problem you do not want graded. You must 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>two</u> of problems 1-3. Clearly mark the problem you do not want graded. (10 pts each)

1. Chose ONE of the following pairs of terms and briefly (but clearly) compare and contrast the two concepts.
   a. TC vs. TD
   b. Determinate Error vs. Indeterminate 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. **Determinate** or systematic error affects accuracy. This error is usually constant and can be identified and corrected.
   Indeterminate or random 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. We ignore the contribution of buoyancy in virtually all of the mass measurements we make in the laboratory. How can we get away with this? Identify one situation where we would be unable to ignore buoyancy-introduced error.

   The buoyancy correction accounts for the varying volume of air displaced when a sample is weighed compared to the volume displaced when the balance was calibrated with calibration weights. When the density of the sample being weighed is similar to the density of the balance weights (8 g/mol), the error due to buoyancy is minimal (remember the plot we discussed in class). In general buoyancy errors are minimal because we have been weighing solid samples and because we do our critical weighing **<u>by difference</u>**. If we were to weigh samples of very low density (like water or organic solvents or especially gases), we should account for buoyancy errors.

3. A statistical analysis is an essential component in the evaluation of experimental results. Early in our discussion of statistics, I mentioned that statistics only tell us about the precision of a measurement, not the accuracy. Why is this so? If this is true, how can we use the confidence interval to predict how close our results are to a "true" or accepted value?

   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 also allows us to make some inferences about the accuracy of a method by taking the fact that we have a small data set into account; **assuming only random errors are impacting our measurement.**

Do four of problems 4-8. Clearly mark the problem you do not want graded. (15 pts each)

4. You need to prepare a 500.0 mL of solution that is 100.0 ppm magnesium. Clearly describe how you would prepare this solution starting from the points below.
   a. starting with solid magnesium chloride
   b. starting with a 0.100 M magnesium chloride solution

   a. Remember, magnesium chloride is $MgCl_2$ (FW = 95.211 g/mol)

$$\frac{100\ \cancel{mg}\ \cancel{Mg^{2+}}}{1\ \cancel{L}} \times \frac{1\ \cancel{mol\ Mg^{2+}}}{24.305\ \cancel{g}} \times \frac{1\ \cancel{mol\ MgCl_2}}{1\ \cancel{mol\ Mg^{2+}}} \times \frac{95.211\cancel{g}\ MgCl_2}{1\ \cancel{mol\ MgCl_2}} \times \frac{1\ g}{1000\ \cancel{mg}} \times 0.500\ \cancel{L} = \mathbf{0.1958\ g\ MgCl_2}$$

   So, dissolve 0.1958 g $MgCl_2$

   b. Since each mole of $MgCl_2$ that dissociates liberates 1 mole of Mg^{2+}, a 0.100 M $MgCl_2$ solution is also 0.100 M Mg^{2+}

$$\frac{100\ mg\ \cancel{Mg^{2+}}}{1\ \cancel{L}} \times \frac{1\ \cancel{mol\ Mg^{2+}}}{24.305\ \cancel{g}} \times 0.500\ \cancel{L} \times \frac{1\ L}{0.100\ \cancel{mol\ Mg^{2+}}} = \mathbf{20.6\ mL}$$

   So, dilute 20.6 mL of 0.100 M $MgCl_2$ solution in a small amount of water in a 500 mL volumetric flask, mix well, dilute to the mark and mix well again. The 20.6 mL could be delivered by pipet or buret.

5. As a highly-paid TA for Quant. Lab, two students approach you with questions regarding the results for their KHP lab. A check of their calculations found no errors. Both students had the same unknown with a "true value" of 44.36% KHP. The expected relative standard deviation 0.15% RSD. Based on your understanding of the importance of both precision and accuracy and knowledge of uncertainties in experimental measurements, **select one student** and briefly describe possible causes for any undesirable characteristics of their results and suggest routes for improvement.

   Stewie Griffin: Average percent KHP: 44.3_2% KHP, absolute standard deviation 0.2% KHP
   Patrick Star: Average percent KHP: 44.66% KHP, absolute standard deviation 0.04% KHP

   The intent here was for you to discuss the accuracy and precision of each student's measurements.

   Stewie Griffin: This student's measurement exhibits reasonable accuracy, but poor precision (>0.4% RSD). This student should work to be more consistent in his experimental measurements. Areas of focus for this experiment would be consistent reading of the buret, taking extra care handling samples (especially solids), and obtaining reproducible endpoints.

   Patric Star: This student's measurement exhibits acceptable precision (0.09% RSD), but poor accuracy. This is likely the result of systematic error, or bias in the measurement, perhaps due to miscalibration of the buret or balance, or by consistently overshooting the endpoint. This student should run a standard sample and/or a blank titration to compensate for systematic error.

6. You have run a series of titrations to determine the unknown concentration of KHP in a solid sample. The results of six titrations indicate KHP concentrations of 46.14%, 45.69%, 40.15%, 45.55%, 46.07%, 45.98%. If the "true" value for KHP in this sample is 46.29%, do your results differ at the 95% confidence level?

   Looking at the data, it appears that the value 40.15% is an outlier so try a Q-test or a G-Test:

$$Q_{calc} = \frac{45.55 - 40.15}{46.14 - 40.15} = 0.90 \qquad G_{calc} = \frac{44.93-40.15}{2.353} = 2.03$$

   $Q_{table} = 0.56 < Q_{calc}$, and $G_{table} = 1.822 < G_{calc}$ so the data point should be rejected.

   Based on the remaining data, the mean for the data set is 45.88_6% with a standard deviation of 0.2_5 %. Do a t-test:

$$\boxed{t_{calculated} = \frac{|46.29 - 45.88_6|}{0.254}\sqrt{5} = 3.553}$$

   t_{table} for 4 degrees of freedom is 2.776, 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 46.29% ;lies outside this range.

7. Given your unnatural passion for solution preparation, you have been asked to instruct a class of green quant students on the proper use of a Class A volumetric pipet and volumetric flask for the preparation of a dilute solution from a more concentrated solution. Clearly outline the proper procedure for using this hardware to obtain high quality quantitative results. Include any pitfalls the students should avoid. It is likely that the terms TD and TC will appear in your discussion.

Your pipet discussion should include all of the following:

1. Procedure for cleaning the pipet
2. Rinsing the pipet with solution prior to dispensing
3. Proper pipetting technique
4. Note that the pipet is a TD piece of glassware; therefore it should not be blown out.

Your volumetric flask discussion should include all of the following:

1. Procedure for cleaning the flask.
2. Mix the solution well before filling to the mark
3. Carefully fill to the mark
4. Note that the flask is a TC piece of glassware; therefore it must be filled properly to contain its calibrated volume.

8. In an experiment, you use a solution of standardized sodium hydroxide ion to determine the concentration of a solution of hydrochloric acid. The data below was obtained for such a titration. Based on this information, calculate the concentration of HCl (with its associated absolute uncertainty) in the solution.

Concentration of NaOH standard	0.1117 ± 0.0005 M
Volume of NaOH solution used	20.00 ± 0.03 mL
Initial buret reading	1.46 ± 0.05 mL
Final buret reading	33.54 ± 0.05 mL

Uncertainty in the volume delivered by the buret:

$$(33.54 \pm 0.05\ \text{mL}) - (1.46 \pm 0.05\ \text{mL}) = 32.08 \pm e_1\ \text{mL}$$

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

Concentration calculation:

$$\frac{0.1117 \pm 0.0005\ \text{mol NaOH}^+}{1\text{L}} \times \frac{20.00 \pm 0.03\text{mL}}{} \times \frac{1\ \text{mol HCl}}{1\ \text{mol MaOH}} \times \frac{1}{32.08 \pm 0.07\text{mL}} = 0.06963_8 \pm e_2\ \text{M}$$

$$\boxed{e_2 = 0.069638\text{M}\sqrt{\left(\frac{0.0005}{0.1117}\right)^2 + \left(\frac{0.03}{20.00}\right)^2 + \left(\frac{0.07}{32.08}\right)^2} = 0.000361}$$

$e_2 = 0.0003_6 = 0.0004$ M so the **HCl concentration is 0.0696 ± 0.0004 M**

Blank Space if You Need Extra Room

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.907	144.24	(147)	150.35	151.96	157.25	158.924	162.50	164.930	167.26	168.934	173.04	174.97

† Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	(231)	238.03	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(253)	(256)	(256)	(257)

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
$\mu = \bar{x} \pm \dfrac{ts}{\sqrt{n}}$	$y = \dfrac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
$t_{calculated} = \dfrac{\lvert \text{known value} - \bar{x} \rvert}{s}\sqrt{n}$	$s = \sqrt{\dfrac{\sum_i (x_i - \bar{x})^2}{n-1}}$
$t_{calculated} = \dfrac{\lvert \bar{x}_1 - \bar{x}_2 \rvert}{s_{pooled}}\sqrt{\dfrac{n_1 n_2}{n_1 + n_2}}$	$s_{pooled} = \sqrt{\dfrac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$
$t_{calculated} = \dfrac{\bar{d}}{s_d}\sqrt{n}$	$s_d = \sqrt{\dfrac{\sum_i (d_i - \bar{d})^2}{n-1}}$
$Q_{calculated} = \dfrac{\text{gap}}{\text{range}}$	$G_{calculated} = \dfrac{\lvert \text{suspect value} - \bar{x} \rvert}{s}$
$F_{calculated} = \dfrac{(s_1)^2}{(s_2)^2}$	Don't eat the yellow snow

Values of Student's t

Degrees of Freedom	Confidence Level (%) 90	95	99.5	99.9
1	6.314	12.706	127.32	636.619
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
20	1.752	2.086	3.153	3.850
30	1.697	2.042	3.030	3.646
40	1.684	2.021	2.971	3.551
60	1.671	2.000	2.915	3.460
120	1.658	1.980	2.860	3.373
∞	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
7	0.51
8	0.47
9	0.44
10	0.41

Grubbs Test for Outliers

# of Observations	$G_{critical}$ At 95% confidence
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176

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
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98