Name _____

CHM 3120
Summer 2011
June 2

EXAMINATION ONE

I _____ II _____ III _____ IV _____ V _____ Total _____

This exam consists of five questions generously spread out over five pages. Please glance over the entire exam, and then attempt the questions in the order of your choice. ***You must show your work to receive any credit for a calculated answer.*** Draw a box around your final answer given to the correct number of ***significant figures***, and ***be sure to include the correct units***. An information packet was passed out before the exam. Good luck!

I. (12 points) You were asked the following question in one of the early WebAssign assignments:

How many grams of methanol (CH_3OH, FM 32.04) are contained in 0.290 L of 1.37 M aqueous methanol (i.e., 1.37 mol CH_3OH/L solution)?

It's a pretty straightforward calculation of the type covered early in your first general chemistry course. One approach is shown below.

$$\frac{0.290\ \text{L} \mid 1.37\ \text{mol CH}_3\text{OH} \mid 32.04\ \text{g}}{\qquad\quad \mid \quad \text{L} \quad \mid \quad \text{mol}} = 12.7_3\ \text{g CH}_3\text{OH}$$

But of course in the stark reality of an analytical chemist's world, all of those values have errors. The molar mass has an error of ±0.002 g/mol. The error in the concentration was determined to be ±0.04 mol/L. Worst of all, the volume was measured with a 1 L graduated cylinder, giving an error of ±0.01 L.

Based on this new information, calculate the absolute error in the mass of methanol contained in the solution.

$$\left(\frac{0.01\ \text{L}}{0.290\ \text{L}}\right)100\% = 3.4\%$$

$$\left(\frac{0.04\ \text{M}}{1.37\ \text{M}}\right)100\% = 2.9\%$$

$$\left(\frac{0.002\ \text{g/mol}}{32.04\ \text{g/mol}}\right)100\% = 6.2\times10^{-3}\%$$

$$\%_e = \sqrt{(3.4\%)^2 + (2.9\%)^2 + (6.2\times10^{-3}\%)^2}$$

$$= \sqrt{19.97\ldots} = 4.5\%$$

$$12.7_3\ \text{g} \times \frac{4.5}{100} = 0.5_7\ \text{g}$$

$$\Rightarrow \boxed{12.7 \pm 0.6\ \text{g}}$$

II. (20 points) Lead is a neurotoxin, especially for young children whose brains are rapidly developing. Current federal standards limit the allowed amount of lead in toys to 300 ppm. (The legal limit will be lowered to 100 ppm in August 2011.)

A. A new toy ("Factory Barbie" by Mattel®) was tested by HealthyStuff.org in the following manner. A 102 g doll was dissolved in concentrated nitric acid. The pH was increased to 9, and the solution was titrated with EDTA revealing that the doll contained 2.38×10^{-4} mol of lead.

Calculate the amount of lead in the doll in ppm.

$$\frac{2.38\times10^{-4}\ \text{mol Pb}\left(\frac{207.2\ \text{g Pb}}{\text{mol Pb}}\right)}{102\ \text{g "doll"}} = 4.83_5\times10^{-4}\ \frac{\text{g Pb}}{\text{g doll}}$$

$$4.83_5\times10^{-4}\ \frac{\text{g Pb}}{\text{g doll}} \times \frac{10^6\ \text{g doll}}{\text{million g doll}} =$$

483.5 ppm

B. Okay, I made up "Factory Barbie," but the consumer group HealthyStuff.org is a real organization. They test toys for toxic materials and report the results to the public.

Suppose that a new toy is on the market. Five of these toys were purchased and tested for lead, giving the results in the table.

Toy #	Pb concentration (ppm)
1	294
2	289
3	297
4	301
5	295

The mean for this data set is $295._2$ ppm and the standard deviation is $4._4$ ppm.

What is the 95% confidence interval for the concentration of lead in this toy?

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 295._2 \pm \frac{2.776\,(4._4)}{\sqrt{5}}$$

$$= 295._2 \pm 5.5$$

$$\Rightarrow \quad \boxed{295 \pm 5\ \text{ppm}}$$

Can we say with 95% confidence that the concentration is less than 300 ppm (assume 3 sig figs for this number), the federal legal standard?

Oops... borderline $\Rightarrow$ did not mark

III. (34 points) Determine the pH of the following solutions.

A. 0.057 M $HClO_4(aq)$

$pH = -\log[H^+] = -\log(0.057) =$ **1.24**

B. 0.057 M HClO(*aq*) (K_a for HClO is 3.0×10^{-8})

$HClO \rightleftharpoons H^+ + ClO^-$ $\qquad K_a = \dfrac{[H^+][ClO^-]}{[HClO]}$

	HClO	H^+	ClO^-
init	0.057	–	–
eq	0.057 − x	x	x

$3.0\times10^{-8} = \dfrac{x^2}{0.057 - x} \approx \dfrac{x^2}{0.057}$

$\Rightarrow x = 4.1_4 \times 10^{-5} = [H^+] \Rightarrow$ **pH = 4.38**

C. 0.20 M NaBr(*aq*)

Br^- negl. conj base of strong acid; Na^+ spectator $\Rightarrow$ **pH ≈ 7**

D. 0.20 M NaF(*aq*) (K_a for HF is 3.8×10^{-4})

Before doing the calculation for the last solution, please answer a few questions.

Do you expect the solution to be acidic or basic? Briefly explain how you arrived at your answer.

basic F^- is the conj week base of the week acid $HF(aq)$

Please write a balanced chemical equation for the reaction showing the acid/base chemistry, if any, exhibited by this solution.

$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

Okay, now determine the pH.

init	0.20	–	–
eq	0.20 − x	x	x

$K_b = \dfrac{K_w}{K_a} = \dfrac{[HF][OH^-]}{[F^-]}$

$\dfrac{1.0\times10^{-14}}{3.8\times10^{-4}} = \dfrac{x^2}{0.20 - x} \approx \dfrac{x^2}{0.20}$

$\Rightarrow x = 2.2_9 \times 10^{-6} = [OH^-] \Rightarrow pOH = 5.64$

$\Rightarrow$ **pH = 8.36**

IV. (20 points) The methoxide anion, OCH_3^-, is a very strong base used in organic syntheses. It can be generated by adding freshly-cut sodium to dry methanol, but synthetic groups often order it in bulk from Aldrich (a major supplier of reagents for synthesis) as a 25 wt% solution in methanol. However, as the solution absorbs water from the atmosphere, some of the methoxide is leveled to hydroxide, reducing the concentration of methoxide.

A. A bottle of 25 wt% $NaOCH_3$ was ordered from Aldrich. Immediately after it was opened, the concentration of $NaOCH_3$ was measured four (4) times giving a mean of 24.6_1 wt% with a standard deviation of 0.7_4 wt%. Two weeks later, the measurement was repeated six (6) times giving a mean of 22.8_8 wt% with a standard deviation of 0.7_3 wt%.

Show the necessary work in the space provided, and then answer the question below.

$$t_{calc} = \frac{|\bar{x}_1 - \bar{x}_2|}{S_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$= \frac{|24.6_1 - 22.8_8|}{0.7_{35}} \sqrt{\frac{4 \cdot 6}{4+6}}$$

$S_1 = S_2 = S_{pooled}$
$(0.7_4) \quad (0.7_3)$
I used 7.35;
answers vary somewhat depending on value used.

$$= 3.646$$

t_{table} (95%, 10−2 = 8 df) $= 2.306$

$t_{calc} > t_{table} \Rightarrow$ Concentration did change

Did the concentration of sodium methoxide change at the 95% confidence level?

B. Assuming the label value of 25 wt% $NaOCH_3$, what volume of this solution would be required to deliver 65 moles of $NaOCH_3$? The molar mass of $NaOCH_3$ is 54.02 g/mol, and the density of the solution is 0.945 g/mL.

$$\frac{65 \text{ mol}}{1} \left| \frac{54.02 \text{ g}}{\text{mol}} \right| \frac{100 \text{ g solution}}{25 \text{ g } NaOCH_3} \left| \frac{1 \text{ mL solution}}{0.945 \text{ g solution}} \right.$$

$$= 14862.64\ldots \text{ mL}$$

$\Rightarrow$ 15,000 mL or 15 L

V. (14 points) Questions that do not require a calculator…

A. It was later determined that one source of error in the concentration of the methanol solution from Question I on the first page of the exam was cause by a poor seal on the lid of container, allowing the methanol to evaporate. Is that a random error or a systematic error?

systemetic

How might that error have been identified?

evaporation ⇒ (for example) notice odor of methanol, decrease in volume over time, etc ...

B. Suppose the solution in Question III.D was changed from 0.20 M NaF(aq) to 0.20 M LaF_3(aq). Would the pH increase, remain the same, or decrease?

depends

Explain the reasoning behind your answer.

0.20 M LaF_3 ⇒
0.60 M F^- ⇒
more basic, pH inc

Na^+ spectator, but higher positive charge of La^{3+} ⇒ acidic ⇒ pH dec

The experimentally determined pH of 0.20 M LaF_3(aq) turns out to be considerably different from the calculated value based on the molar concentrations of $La^{3+}(aq)$ and $F^-(aq)$, even though no math mistakes were made in the calculation. Explain why the experimental pH is different than the calculated pH.

higher charge and greater conc of ions ⇒ inc ionic strength ⇒ conc (mol/L) a poorer approximation of activity

C. Why is the pH of 1×10^{-8} M HNO_3 not equal to 8? Do not simply say that it is because a solution of nitric acid cannot be basic. Why does $pH = -\log(1 \times 10^{-8})$ not give you the correct pH?

must also include the concentration of H^+ from ionization of water $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

D. A small data set contains a value you believe to be significantly off from the other measurements. Name three things you can do to address your concern.

1. acquire more data / repeat the measurements
2. use the median instead of the mean
3. Q test