

Chem 332
Analytical Chemistry
Exam I

Name:

Show all work for partial credit

1. (10 points) For my DUSEL project I need to be able to detect a 0.1 ppm N₂ impurity in Ar gas. If the density of Ar gas is 1.78 g/liter and it contains 0.1 ppm N₂, how many grams of N₂ are in a liter of this gas? What is the concentration of the N₂ in moles/liter?

$$\text{ppm} = \frac{\text{g solute}}{\text{g solvent}} \times 10^6$$

$$0.1 = \frac{X(\text{g / liter})}{1.78(\text{g / liter})} \times 10^6$$

$$X = \frac{0.1 \times 1.78(\text{g / liter})}{1 \times 10^6}; = 1.78 \times 10^{-7} \text{ g / l}$$

$$\text{Molar Conc} = \frac{1.78 \times 10^{-7}}{28.02 \text{ g / mol}} = 6.35 \times 10^{-9} \text{ M}$$

Note 1: ppm = mg / l only works for aqueous solutions

Note 2: My DUSEL work actually requires 0.1 ppb

2. (10 points) A class A 250ml volumetric flask has an uncertainty of $\pm .12$ ml, and a 50 ml volumetric pipet has an uncertainty of $\pm .05$ ml. If I fill a 250 ml volumetric flask to the line and remove four 50 ml aliquots with my volumetric pipet, I should have 50 ml of solution remaining in the flask. What is the uncertainty in this remaining volume?

$$\%e_{250\text{ml}} = .12 / 250$$

$$\%e_{\text{pipet}} = .05 / 50$$

$$\%e_{\text{all subtractions}} = \sqrt{\left(\frac{.12}{250}\right)^2 + \left(\frac{.05}{50}\right)^2 + \left(\frac{.05}{50}\right)^2 + \left(\frac{.05}{50}\right)^2 + \left(\frac{.05}{50}\right)^2}$$

$$= 31\% \text{ or } .156\text{ml}$$

3. (10 points) Calcium content of a mineral was analyzed five times by each of two methods. Are the mean values significantly different at the 95% confidence level?

Method	Ca (wt%)				
1	0.0271	0.0282	0.0279	0.0271	0.0275
2	0.0271	0.0268	0.0263	0.0274	0.0269

Average set 1 = .02756 Standard Deviation set 1 = .000562

Average set 2 = .02690 Standard Deviation set 2 = .000406

$$S_{pooled} = \sqrt{\frac{(.000562^2 \times 4) + (.000406^2 \times 4)}{4 + 4}}$$

$$= .00049$$

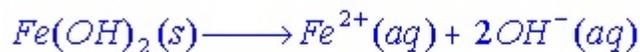
$$t = \frac{|.02756 - .0269|}{.00049} \sqrt{\frac{5 \times 5}{5 + 5}} = 2.177$$

$$t_{table\ 95\% \ d.f. = 8} = 2.302$$

$t < t_{table}$; no significant difference

4. (10 points) $Fe(OH)_2$ has a K_{sp} of 7.9×10^{-16} . What is the molar concentration of Fe^{2+} and OH^- in a saturated solution of $Fe(OH)_2$. What is the pH of this solution? What is the solubility of $Fe(OH)_2$ in g/l?

$$K_{sp} = [Fe^{2+}][OH^-]^2$$



$$\text{if } X = Fe^{2+}, OH^- = 2X$$

$$K_{sp} = X(2X)^2 = 4X^3 = 7.9 \times 10^{-16}$$

$$X = \sqrt[3]{\frac{7.9 \times 10^{-16}}{4}} = 5.82 \times 10^{-6} = [Fe^{2+}]$$

$$[OH^-] = 1.165 \times 10^{-5}; pOH = -\log(1.165 \times 10^{-5}) = 4.934$$

$$pH = 14 - 4.934 = 9.066$$

$$\text{Solubility} = 5.82 \times 10^{-6} \times 89.866 \text{ g/mol} = .000523 \text{ g/l}$$

5.(10 points) What is the pH of a 0.05M solution of Benzylamine? (The K_a of Benzylamine is 4.5×10^{-10})

Benzylamine is a base so this is a weak base problem

$$K_B = K_W/K_A = 1 \times 10^{-14}/4.5 \times 10^{-10} = 2.222 \times 10^{-5}$$

$$K_B = 2.222 \times 10^{-5} = \frac{[BH^+][OH^-]}{[B]} = \frac{X^2}{.05 - X}$$

Assume $.05 - X \approx .05$

$$2.222 \times 10^{-5} = \frac{X^2}{.05}; X = 1.05 \times 10^{-3}$$

Assumption good to 2% error

$$[OH^-] = 1.05 \times 10^{-3}; pOH = -\log(1.05 \times 10^{-3}) = 2.977$$

$$pH = 14 - 2.977 = 11.023$$

6. (10 points) What's the difference-

Between a primary standard and a secondary standard

primary standard - pure enough to weigh out directly

secondary - not pure enough so must be calibrated against a primary

Between an endpoint and an equivalence point

Endpoint - where you observe an physical change like an indicator changing color

Equivalence point- point where moles of analyte are equivalent to moles of titrant

Between a Formal concentration and a Molar concentration

Formal Concentration -Concentration based on moles of solute dissolved in a solution that does not worry about the actual ionic form of the molecules in solution

Molar Concentration -Should only be used for the true concentration of a given ion in solution

Between a Fajans titration and a Volhard titration

Fajan - A silver titration that uses an indicator adsorbed to the surface of a precipitate

Volhard - A silver titration in which an excess of silver is used in the titration, then the excess is titrated with thiocyanate (SCN^-) where the endpoint indicator is Fe^{2+} that has a deep red precipitate when in the presence of excess SCN^-

Between a Lewis base and a Bronsted-Lowry Base

Lewis base electron donor Lewis acid electron acceptor

Bronsted Lowry base proton acceptor B-L acid Proton donor

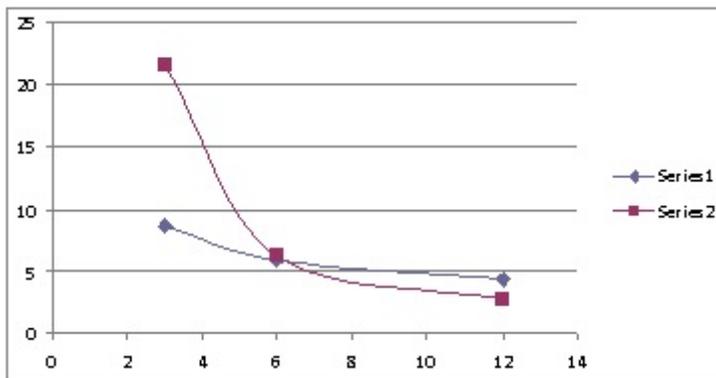
Take home questions (Can be done in excel - if you show work)

7. (10 points) Below is a set of 12 measurements What is the mean, standard deviation and 95% confidence interval for this set of numbers if you use the first 3 numbers, the first 6 numbers or the first 12 numbers. Plot S as a function of N, and Confidence Interval as a function of N. Are these linear functions with N?

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Poor example, I'm not showing equations to get the data below

N	x	sd	t	ci
3	558	8.71	4.303	21.656
6	556.3	5.95	2.571	6.25
12	555.4	4.35	2.228	2.802



8. (10 points) $\text{Fe}(\text{OH})_2$ has a K_{SP} of 7.9×10^{-16} . What is the molar concentration of Fe^{2+} and OH^- in a saturated solution of $\text{Fe}(\text{OH})_2$ made up in 1M NaOH. What is the pH of this solution? What is the solubility of $\text{Fe}(\text{OH})_2$ in g/l?



Table	$\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}^{2+} + 2\text{OH}^-$		
Iron Solution	Solid(1)	x	2x
NaOH	0	0	1
Sum	1	x	2x+1

$$K_{\text{SP}} = 7.9 \times 10^{-16} = x(2x+1)^2$$

However x should be very small, so assume $2x+1 \approx 1$

$$7.9 \times 10^{-16} = x(2x+1)^2 \approx x(1)^2$$

$$x = 7.9 \times 10^{-16} \quad \text{Yes } x \text{ is very small}$$

$$[\text{Fe}^{2+}] = 7.9 \times 10^{-16}$$

$$[\text{OH}^-] = 1, \text{ pOH} = 0, \text{ pH} = 14!$$

$$[\text{Fe}(\text{OH})_2] = 7.9 \times 10^{-16} \times 89.866 \text{ g/mol} = 7.1 \times 10^{-14} \text{ M}$$

9. (10 points) Cyanoacetic acid has a K_a of 3.37×10^{-3} . Determine the pH of a .1M solution of this acid using the method of successive approximation. Show All work

$$K_a = 3.37 \times 10^{-3} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{X^2}{.1 - X}$$

$$\text{Iteration 1: } 3.37 \times 10^{-3} = \frac{X^2}{.1}; X = \sqrt{3.37 \times 10^{-3} \times .1}; X = .018358$$

$$\text{Iteration 2: } 3.37 \times 10^{-3} = \frac{X^2}{(.1 - .018358)}; X = \sqrt{3.37 \times 10^{-3} \times .081642}; X = .016587$$

$$\text{Iteration 3: } 3.37 \times 10^{-3} = \frac{X^2}{(.1 - .016587)}; X = \sqrt{3.37 \times 10^{-3} \times .083413}; X = .016766$$

$$\text{Iteration 4: } 3.37 \times 10^{-3} = \frac{X^2}{(.1 - .016766)}; X = \sqrt{3.37 \times 10^{-3} \times .083234}; X = .016748$$

Good to the first three digits.

10 A (2.5 points) Student A weighs .5112 g of KHP (Molar Mass 204.22) on an analytical balance and places this material in a 250 ml Class A volumetric. What is molarity of this solution and what is the absolute uncertainty in this number?

$$(.5112 \text{ g} / 204.22 \text{ g/mol}) / .250 \text{ l} = \mathbf{.0100 \text{ M}}$$

$$\text{Uncertainty in } .5112 \text{ g} = \sqrt{.0001^2 + .0001^2} = .00014$$

(Uncertainty in .5112 and uncertainty in zero on balance!)

I will ignore uncertainty in molar mass because it is small compared to experimental uncertainties

$$\text{Relative uncertainty in molarity} = \sqrt{(.00014 / .5112)^2 + (.12 / 250)^2} = .000554$$

$$\text{Absolute uncertainty in molarity} = .01 \times .000554 = \mathbf{5.5 \times 10^{-6}}$$

10 B (2.5 points) Student B weighs .511g of KHP (Molar Mass 204.22) on a regular balance and places this material in a 500 ml Class A volumetric. What is the molarity of this solution and what is the absolute uncertainty in this number?

$$(.511 \text{ g} / 204.22 \text{ g/mol}) / .5 \text{ l} = \mathbf{.0050 \text{ M}}$$

$$\text{Uncertainty in } .511 \text{ g} = \sqrt{.001^2 + .001^2} = .0014$$

(Uncertainty in .5112 and uncertainty in zero on balance!)

I will ignore uncertainty in molar mass because it is small compared to experimental uncertainties

$$\text{Relative uncertainty in molarity} = \sqrt{(.00014 / .5112)^2 + (.2 / 500)^2} = .0028$$
$$\text{Absolute uncertainty in molarity} = .005 \times .0028 = \mathbf{1.4 \times 10^{-5}}$$

10 C (2.5 points) Student A now takes a 25 ml aliquot of an unknown using a class A volumetric pipet and titrates it with the KHP solution he made in 10A. During the titration he gets the following data: Initial buret reading: 0.02 ml, final buret reading 36.83 ml. Assuming a 1:1 stoichiometry, what is the molarity of the unknown, and what is the absolute uncertainty in this molarity based on this data?

$$\text{Molarity of unknown} = (36.81 \times .0100) / 25.00 = \mathbf{.01472}$$

$$\text{Absolute error in buret} = \sqrt{.02^2 + .02^2} = .028$$
$$\text{relative uncertainty in molarity} = \sqrt{(.028 / 36.81)^2 + (.03 / 25)^2 + .000554^2}$$
$$= .0015$$
$$\text{absolute uncertainty} = .01472 \times .0015 = \mathbf{2.25 \times 10^{-5}}$$

expressing answer with right sig figs $.01472 \pm .00002$

10 D (2.5 points) Student B now takes a 25 ml aliquot of an unknown using a class A volumetric pipet and titrates it with the KHP solution he made in 10B. Because this solution is more dilute he has to fill his buret twice to finish the titration. During these titrations he gets the following data: Initial reading - first fill: 0.02 ml, final reading - first fill: 49.98 ml, initial reading - second fill: .03, final reading - second fill: 23.69 ml. Assuming a 1:1 stoichiometry, what is the molarity of the unknown, and what is the absolute uncertainty in this molarity based on this data?

$$\text{Molarity of unknown} = (73.59 \times .0050) / 25.00 = \mathbf{.01472}$$

$$\text{Absolute error in buret} = \sqrt{.02^2 + .02^2 + .02^2 + .02^2} = .04$$
$$\text{relative uncertainty in molarity} = \sqrt{(.04 / 73.59)^2 + (.03 / 25)^2 + .0028^2}$$
$$= .003$$
$$\text{absolute uncertainty} = .01472 \times .003 = \mathbf{4.42 \times 10^{-5}}$$

expressing answer with right sig figs $.01472 \pm .00004$

I'm a bit surprised. I thought the two errors here would make a bigger difference!