

EA04 Analytical Chemistry  
Week 3 Workshop/Homework solutions

- 9-2. Write a charge balance for a solution containing  $H^+$ ,  $OH^-$ ,  $Ca^{2+}$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $Ca(HCO_3)^+$ ,  $Ca(OH)^+$ ,  $K^+$ , and  $ClO_4^-$ .**

For charge balance we want the sum of the positive charges in the solution equal to the sum of the negative charges. An ion with a charge of 2 has its concentration multiplied by 2, etc. So

$$[H^+] + 2[Ca^{2+}] + [Ca(HCO_3)^+] + [Ca(OH)^+] + [K^+] = [OH^-] + [HCO_3^-] + [CO_3^{2-}] + [ClO_4^-]$$

- 9-5. (a) Suppose that  $MgBr_2$  dissolves to give  $Mg^{2+}$  and  $Br^-$ . Write a charge balance equation for this aqueous solution.**

We will have  $Mg^{2+}$ ,  $Br^-$ ,  $OH^-$  and  $H^+$  ions in solution. So the charge balance is

$$2[Mg^{2+}] + [H^+] = [Br^-] + [OH^-]$$

- (b) What is the charge balance if, in addition to  $Mg^{2+}$  and  $Br^-$ ,  $MgBr^+$  is formed?**

This adds another cation to the equation

$$2[Mg^{2+}] + [H^+] + [MgBr^+] = [Br^-] + [OH^-]$$

- 9-8. Suppose that  $MgBr_2$  dissolves to give  $Mg^{2+}$  and  $Br^-$ .**

- (a) Write the mass balance for  $Mg^{2+}$  for 0.20 M  $MgBr_2$ .**  
**(b) Write the mass balance for  $Br^-$  for 0.20 M  $MgBr_2$ .**

The chemical reaction is



- (a) Thus one mole of magnesium ion goes into solution for each mole of magnesium bromide dissolved. Thus  $[Mg^{2+}]$  is equal to the concentration of dissolved solid, i.e. 0.20 M.

$$[Mg^{2+}] = 0.20 \text{ M}$$

- (b) The concentration of the bromide ion is twice the concentration of dissolved salt.

$$[Br^-] = 0.40 \text{ M}$$

Now suppose that  $\text{MgBr}^+$  is formed in addition to  $\text{Mg}^{2+}$  and  $\text{Br}^-$ .

(c) Write the mass balance for  $\text{Mg}^{2+}$  for 0.20 M  $\text{MgBr}_2$ .

(d) Write the mass balance for  $\text{Br}^-$  for 0.20 M  $\text{MgBr}_2$ .

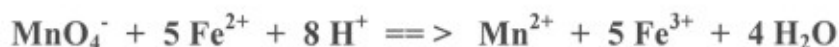
c) Some of the  $\text{Mg}^{2+}$  has become  $\text{MgBr}^+$ , but the total of all the magnesium species is still 0.20 M

$$[\text{Mg}^{2+}] + [\text{MgBr}^+] = 0.20 \text{ M}$$

d) The same is true, all bromine species still equals the total amount in solution which is 0.40M.

$$[\text{Br}^-] + [\text{MgBr}^+] = 0.40 \text{ M}$$

**W3-1) A 0.8040-g sample of iron ore is dissolved and the iron converted to the Iron(II) ( $\text{Fe}^{2+}$ ) ion. The solution is titrated with a 0.02242 M  $\text{KMnO}_4$  solution. The initial buret reading is 0.30 mL and the reading at the end point is 47.52 mL. The balanced equation for the reaction is**



a) What is the percent iron in the ore?

b) If we have the following uncertainty in the measured quantities:

mass  $\pm 0.0001 \text{ g}$

volume  $\pm 0.02 \text{ mL}$

molarity  $\pm 0.00003 \text{ M}$ .

What is the uncertainty in the percent iron in the ore?

The first part of the problem is a stoichiometry problem. Let's look at the volume first.

$$47.52 - 0.30 \text{ mL} = 47.22 \text{ mL}$$

The uncertainty in an added or subtracted reading is found from the absolute uncertainties:

$$\text{Uncertainty in answer} = \sqrt{(\pm 0.02)^2 + (\pm 0.02)^2} = \pm 0.0283 \text{ mL}$$

$$47.22 \text{ mL MnO}_4^- \times \frac{0.02242 \text{ mmol MnO}_4^-}{\text{mL MnO}_4^-} \times \frac{5 \text{ mmol iron}}{1 \text{ mmol MnO}_4^-} \times \frac{55.845 \text{ mg iron}}{\text{mmol iron}} =$$

$$295.608 \text{ mg Fe in sample or } 0.295608 \text{ g Fe}$$

$$\frac{0.295608 \text{ g iron}}{0.8040 \text{ g sample}} \times 100\% = 36.77\% \text{ iron in the ore sample}$$

The uncertainty in multiplication and/or division is found from percent relative errors:

Volume	$\pm 0.0283/47.22 \times 100\%$	$= \pm 0.06\%$
Concentration	$\pm 0.00003/0.02242 \times 100\%$	$= \pm 0.134\%$
Mass	$\pm 0.0001/0.8040 \times 100\%$	$= \pm 0.012\%$
Atomic Weight	$\pm 0.002/55.845 \times 100\%$	$= \pm 0.004\%$

$$\text{Uncertainty in answer} = \sqrt{(\pm 0.06)^2 + (0.134)^2 + (0.012)^2 + (0.004)^2} = \pm 0.1474\%$$

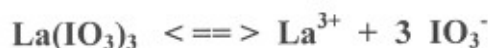
$$= 0.001474$$

$$36.77 \times \pm 0.1474\% = 36.77 \pm 0.05\% \text{ Fe in ore}$$

There is a very important utility to this exercise. Which measurement contributes the most uncertainty to the answer? If you want to decrease the uncertainty, which measurement needs to be improved?

Got to here

**W3-2) The  $pK_{sp}$  at 25°C and zero ionic strength of lanthanum iodate,  $\text{La}(\text{IO}_3)_3$  is 10.99.**



**Assume that La(III) and iodate are the only ions formed when the salt dissolves. What is the solubility of lanthanum iodate (FM 663.63) under these conditions?**

$$K_{sp} = 10^{-10.99} = 1.02 \times 10^{-11}$$

The molar solubility of lanthanum iodate equals the concentration of lanthanum ion since one lanthanum ion results for each formula unit dissolved.

	$\text{La}(\text{IO}_3)_3$	$\rightleftharpoons$	$\text{La}^{3+}$	$+$	$3 \text{IO}_3^-$
Before	solid		0		0
After	solid		x		3x

$$K_{sp} = [\text{La}^{3+}][\text{IO}_3^-]^3 = 1.02 \times 10^{-11} = x(3x)^3 = 27x^4 \rightarrow x^4 = (1.02 \times 10^{-11})/27$$

$$x = 7.85 \times 10^{-4} \text{ M} \times 663.63 \text{ g/mol} = 0.52 \text{ g La}(\text{IO}_3)_3 / \text{L}$$

name \_\_\_\_\_

Environmental Analysis  
Analytical Chemistry Exam I: Practice

The actual exam will be open textbook (and calculator) only. No notes, homework, workshop answers or this practice exam are to be used during the test. Remember to show all work for full credit, and to express all answers with the correct number of significant figures. **Please circle your final answer.**

1. An analysis was to be carried out on a sample of bauxite to determine the aluminum content as weight percent  $\text{Al}_2\text{O}_3$  (Aluminum oxide, FW 101.961) in the ore. A truckload of ore was sampled at evenly spaced intervals by taking a one-foot-long portion as it passed by during unloading onto a conveyor belt. Each portion was bagged and transported to the central laboratory, where it was crushed and mixed thoroughly before four samples (with weights given below) were taken.

Each sample was dissolved and the aluminum content determined by gravimetric analysis. The reaction involved is the formation of  $\text{Al}(\text{8-hydroxyquinolate})_3$  precipitate (abbreviated  $\text{AlQ}_3$ ). [structure and FW on page (690)]. The precipitates were dried and weighed giving the following results.

Sample #	Sample weight (g)	$\text{AlQ}_3$ weight (g)
1	0.6500	2.2769
2	0.6450	2.2920
3	0.6623	2.3266
4	0.6557	2.3170

- Calculate the number of moles of  $\text{AlQ}_3$  in each of the four precipitates.
- How many moles of  $\text{AlQ}_3$  contain the same number of moles of Al as 1 mole of  $\text{Al}_2\text{O}_3$ ?
- Calculate the mass of Aluminum oxide in each of the original small solid samples.
- Calculate the average weight percent  $\text{Al}_2\text{O}_3$  in the ore and its standard deviation.
- Calculate the 95% Confidence Interval of  $\text{Al}_2\text{O}_3$  (%w/w) in the ore.

$$\begin{aligned} \text{(a)} \quad 2.2769 \text{ g AlQ}_3 \times \frac{1 \text{ mol AlQ}_3}{459.43 \text{ g AlQ}_3} &= 4.9559 \times 10^{-3} \text{ moles AlQ}_3 \text{ in Sample \#1} \\ &4.9888 \times 10^{-3} \text{ moles AlQ}_3 \text{ in Sample \#2} \\ &5.0641 \times 10^{-3} \text{ moles AlQ}_3 \text{ in Sample \#3} \\ &5.0432 \times 10^{-3} \text{ moles AlQ}_3 \text{ in Sample \#4} \end{aligned}$$

(b) Two moles of  $\text{AlQ}_3$  contains the same number of moles of Al as 1 mole of  $\text{Al}_2\text{O}_3$ .

$$\begin{aligned} \text{(c)} \quad 4.9559 \times 10^{-3} \text{ mol AlQ}_3 \times \frac{1 \text{ mol Al}_2\text{O}_3}{2 \text{ mol AlQ}_3} \times \frac{101.961 \text{ g Al}_2\text{O}_3}{1 \text{ mol Al}_2\text{O}_3} &= 0.25266 \text{ g Al}_2\text{O}_3 \\ &\text{in Sample \#1} \\ &0.25433 \text{ g Al}_2\text{O}_3 \text{ in Sample \#2} \\ &0.25817 \text{ g Al}_2\text{O}_3 \text{ in Sample \#3} \\ &0.25711 \text{ g Al}_2\text{O}_3 \text{ in Sample \#4} \end{aligned}$$

$$\begin{aligned} \text{d)} \quad \text{sample 1} &= 0.25266 \text{ g Al}_2\text{O}_3 / 0.6500 \times 100\% = 38.87\% \\ \text{sample 2} &= 0.25433 \text{ g} / 0.6450 \text{ g} = 39.43\% \\ \text{sample 3} &= 0.25817 \text{ g} / 0.6623 \text{ g} = 38.98\% \\ \text{sample 4} &= 0.25711 \text{ g} / 0.6557 \text{ g} = 39.21\% \end{aligned}$$

$$\bar{x} = 39.12 \pm 0.25\% \text{ (standard deviation)}$$

(e) Confidence intervals are described on pages 66-67. The 95% confidence t value for 3 degrees of freedom (4-1) is 3.182 from page 67.

$$\mu = \bar{x} \pm t s / \sqrt{n} = 39.12 \pm 3.182 * 0.25 / \sqrt{4} = 39.12 \pm 0.40 \%$$

2. The arsenic in a 9.131 g sample of pesticide (slug bait) was converted to arsenate ( $\text{AsO}_4^{3-}$ ) and the arsenate precipitated in a titration as  $\text{Ag}_3\text{AsO}_4$  with a solution containing 0.02105 M  $\text{Ag}^+$  ion. The reading of the buret before the titration was 0.23 mL and the reading at the end point was 45.88 mL.

(a) Write a balanced chemical equation for the precipitation reaction, i.e. the formation of the solid  $\text{Ag}_3\text{AsO}_4$ .

(b) Calculate the percent arsenic in the sample from this one titration.

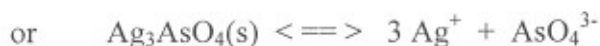
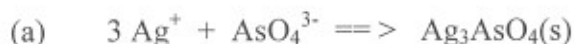
(c) Assume the error in the weight is  $\pm 0.0001$  g; the error in the standard silver solution is  $\pm 0.00002$  M and the error in each of the readings of the buret is  $\pm 0.02$  mL.

i) Determine the absolute uncertainty in the volume reading.

ii) Determine the relative uncertainties in the volume, mass and concentration.

iii) What is the experimental error in the percent arsenic? [Assume the error in the atomic mass of As is negligible.]

(d) What measured quantity contributes the most experimental error?



$$(b) \quad (45.88 - 0.23) \text{ mL Ag}^+ \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.02105 \text{ mol Ag}^+}{1 \text{ L Ag}^+} \times \frac{1 \text{ mol As}}{3 \text{ mol Ag}^+} \times \frac{74.9216 \text{ g As}}{1 \text{ mol As}} =$$

$$\frac{0.023998 \text{ g As}}{9.1310 \text{ g sample}} \times 100\% = 0.2628 \% \text{ As}$$

(c) The buret readings were subtracted from each other. To propagate a subtraction error we need absolute uncertainty so that we can combine the error of both readings

$$i) \text{ buret reading absolute uncertainty (p. 52)} \quad e = \sqrt{[(0.02)^2 + (0.02)^2]} = 0.028$$

ii) for multiplication and division we need to convert the errors to percent relative uncertainty

$$\text{volume: } .028 / 45.65 \times 100\% = 0.0613 \%$$

$$\text{concent: } .00002 / .02105 \times 100\% = 0.0950 \%$$

$$\text{mass: } .0002 / 9.1310 \times 100\% = 0.0022 \%$$

iii) experimental uncertainty in percent arsenic

$$\% e = \sqrt{[(0.0613)^2 + (0.0950)^2 + (.0022)^2]} = 0.113 \% \text{ error or } 0.00113$$

$$\text{If we convert this back to \% Arsenic we get } 0.2628 \times 0.0011 = .0003 \% \text{ As}$$

$$\text{so answer is } 0.2628 \pm 0.0003 \% \text{ As}$$

The standardized solution contributes the most error. Notice that the error from the buret readings is small because the total volume is large. If the buret volume delivered were 5 mL instead of 45 mL, the buret error would be much larger.

- 3) (a) Calculate the equilibrium concentration of  $\text{Ba}^{2+}$  in a saturated solution of  $\text{BaSO}_4$  that also contains 0.025 M  $\text{Na}_2\text{SO}_4$ . The  $K_{sp}$  for  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ . [Assume activity coefficients are 1. Assume that only sulfate ion is formed.]  
 (b) Calculate  $\text{pBa}^{2+}$  for the saturated solution in part (a).  
 (c) Calculate the ionic strength of the saturated solution from part (a).

(a) This is a common ion problem. The chemical equation for barium sulfate solubility is:



Concentration table:

before dissolving	solid	0	0.025	Let $x = [\text{Ba}^{2+}]$ at equilibrium
at equilibrium	solid	$x$	$0.025 + x$	

$$K_{sp} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x(0.025 + x) \quad \text{assume } x \text{ small compared to } 0.025$$

$$x(0.025) = 1.1 \times 10^{-10} \rightarrow x = 1.1 \times 10^{-10} / 0.025 = 4.4 \times 10^{-9} \text{ M}$$

This is the solubility for barium sulfate when the common ion sulfate is present at 0.025 M. Our assumption is substantiated as 0.0000000044 is small compared to 0.025.

$$(b) \text{pBa}^{2+} = -\log [\text{Ba}^{2+}] = -\log (4.4 \times 10^{-9}) = 8.36$$

(c) ionic strength (p. 151)

the concentration of ions in solution are:

$$[\text{Ba}^{2+}] = 4.4 \times 10^{-9} \text{ M (should be negligible)}$$

$$[\text{SO}_4^{2-}] = 0.025 \text{ M}$$

$$[\text{Na}^+] = 2 \times 0.025 \text{ M} = 0.050 \text{ M}$$

likewise the concentrations of hydrogen and hydroxide ions should be small and insignificant, compared with the sodium and sulfate ion concentrations.

$$\mu = \frac{1}{2} \{ [\text{Na}^+] (1)^2 + [\text{SO}_4^{2-}] (2)^2 \} = \frac{1}{2} \{ (0.050)(1)^2 + (0.025)(2)^2 \} = 0.075$$

4. Two independent analytical testing labs [Shaky Hands Testing and High Accuracy, Inc.] were competing for a large contract with several municipal water plants to determine the concentration of nitrate in drinking water samples. Both labs were given a National Institute of Standards and Technology (NIST) standard to analyze and results of 5 measurements by each lab are shown below.

Shaky Hands Testing: 3.50, 3.57, 3.38, 3.47, 3.41 ppm

High Accuracy, Inc.: 3.23, 3.21, 3.29, 3.30, 3.24 ppm

(a) Calculate the mean, standard deviation, and percent relative standard deviation for each laboratory. You do not need to show all your work, but may want to identify the appropriate equations for partial credit in case you enter values incorrectly on your calculator.

(b) Calculate a confidence interval for each laboratory at the 95% confidence level. The NIST standard was known to have a concentration of 3.40 ppm. Based on your 95% confidence intervals from each lab, which laboratory would you hire? Why?

(c) Which laboratory gave results that:

were more accurate? \_\_\_\_\_ were more precise? \_\_\_\_\_  
had more random error? \_\_\_\_\_ had more systematic error? \_\_\_\_\_

(a) Shaky Hands Testing:  $\bar{x} = 3.46_6$ ;  $s = 0.075$ ;  $\%RSD = 0.075/3.466 \times 100\% = 2.2\%$   
High Accuracy, Inc.:  $\bar{x} = 3.25_4$ ;  $s = 0.039$ ;  $\%RSD = 0.039/3.254 \times 100\% = 1.2\%$

(b) 95% confidence t value for 4 degrees of freedom (5-1) is 2.776 from page 74.

Shaky Hands

$$\mu = \bar{x} \pm t s / \sqrt{n} = 3.466 \pm 2.776 * 0.075 / \sqrt{5} = 3.466 \pm 0.093 \text{ at 95\% confidence}$$

High Accuracy

$$\mu = \bar{x} \pm t s / \sqrt{n} = 3.254 \pm 2.776 * 0.039 / \sqrt{5} = 3.254 \pm 0.048 \text{ at 95\% confidence}$$

Hire Shaky Hands Testing. Their 95% confidence interval  $3.37_3$  to  $3.55_9$  includes the NIST value of 3.40. This is not true for High Accuracy  $3.20_6$  to  $3.30_2$ . High Accuracy had a precise analysis, but you should not be confident in the numbers they report as their analysis seems to have a large systematic error.

(c)

were more accurate? Shaky Hands were more precise? High Accuracy

had more random error? Shaky Hands had more systematic error? High Accuracy