

CHEMISTRY 31 FINAL EXAM  
May 15, 2017 - 150 points total

KEY

$K_w$  (autoprotolysis of  $H_2O$ ) =  $1.0 \times 10^{-14}$      $h$  = Planck's constant =  $6.63 \times 10^{-34}$  J·s  
 $c$  = speed of light in a vacuum =  $3.00 \times 10^8$  m/s

**A. Multiple Choice and Short answer Section.** Circle the letter corresponding to the best answer (only one) or fill in the blank (4 points for each question).

1. The number 0.030020 has how many significant figures?

- a) 2                      b) 4                      **c) 5**                      d) 6

*only left two most 0s are not significant*

2. A test sample is analyzed for testosterone using a new method. The measured value is  $38.11 \pm 0.02$  mg/L ( $\pm$ standard deviation) vs. a true value of 27.1 mg/L. It is desired to have % errors under 5% and % relative standard deviations under 2%. Thus, the measurement is:

- a) precise but not accurate**                      b) precise and accurate  
c) accurate but not precise                      d) neither precise nor accurate

*%SD  $\ll$  2% but error  $\gg$  5%*

3. An instrument is expected to give a linear calibration. When a set of standards have been analyzed (responses measured), a linear least squares analysis is performed. What quantities are determined by the least squares analysis that define the calibration line? Quantities:

slope (m) and intercept (b). (Give names or equation symbols)

4. Which of the following combination produces a "traditional" buffer?

- a) 0.0100 M  $NH_4Cl$  + 0.0050 M  $HCl$                       **b) 0.0100 M  $NH_4Cl$  + 0.0050 M  $NaOH$**   
c) 0.0100 M  $NaCH_3CO_2$  + 0.0070 M  $NaOH$     d) 0.0100 M  $NaCH_3CO_2$  + 0.0200 M  $HCl$

$NH_3$  is a weak base and  $CH_3CO_2H$  is a weak acid

- a) WA + SA    c) WB + SB    d) excess SA + limiting WB

5. In a precipitation titration,  $Ba^{2+}$  is added out of a buret to a flask containing  $SO_4^{2-}$  forming solid  $BaSO_4$ . The concentration of initial ions and volume of  $SO_4^{2-}$  solution is known. In order to determine  $[Ba^{2+}]$  at a point before the equivalence point where the volume of  $Ba^{2+}$  added is measured, you want to first calculate:

- a) the initial  $[Ba^{2+}]$  in the buret                      b) the excess  $[Ba^{2+}]$  in the flask  
c) the mass of solid  $BaSO_4$  in the flask                      **d) the excess  $[SO_4^{2-}]$  in the flask**

*[not covered F17]*

6. Which of the following salts is acidic?

- a)  $Mg(OH)_2$                       **b)  $CrCl_3$**                       c)  $KClO$                       d)  $NaNO_2$

$K_a$  values for related weak acids:  $HClO$  ( $K_a = 3.0 \times 10^{-8}$ );  $HNO_2$  ( $K_a = 7.1 \times 10^{-4}$ )

*Bases of WA or strong bases are basic.  $Cr^{3+}$  is not a group I metal and is acidic*

7. Infrared radiation is typically given in wavenumbers. A wavenumber of  $1830\text{ cm}^{-1}$  corresponds to a wavelength of:

- a) 1830 nm                      b)  $1.83 \times 10^{10}$  nm                      c)  $5.46 \times 10^7$  nm                      d) 5460 nm

$$1/1830\text{ cm}^{-1} = (0.000546\text{ cm})(1\text{ m}/100\text{ cm})(10^9\text{ nm}/\text{m}) =$$

8. A separation is occurring in normal phase liquid chromatography with a 85% hexane 15% 2-propanol (more polar solvent) and is taking too long. What is normally done to decrease the retention time of an analyte:

- a) Increase the column temperature                      b) Increase the % hexane  
c) Increase the % 2-propanol                      d) Use a longer column

*propanol is more polar (like SP) will decrease retention*

9. In chromatography, the sample is introduced into the chromatograph using the:

- a) injector                      b) mobile phase reservoir                      c) fraction collector                      d) detector

10. Lead iodide,  $\text{PbI}_2$ , is a sparingly soluble salt. Following dissolution through a secondary reaction,  $\text{Pb}^{2+}$  can react with  $\text{OH}^-$  to form  $\text{PbOH}^+$  in significant quantities.  $\text{HI}$  is a strong acid, and ignore any other Pb complexes. This secondary reaction results in:

- a) increased solubility and a basic solution                      b) decreased solubility and a basic solution  
c) increased solubility and a neutral solution                      d) increased solubility and an acidic solution

*complex forming reaction decreases  $[\text{Pb}^{2+}]$  and splits water giving  $\text{H}^+$  as the other product*

11. A strong base is prepared from NaOH in which prepared concentration is known. The equilibrium concentration of  $\text{OH}^-$ ,  $[\text{OH}^-] = [\text{NaOH}]_0$  (initial prepared concentration) is valid in all cases **except when**:

- a)  $[\text{Na}^+] < [\text{H}^+]$                       b)  $[\text{OH}^-]$  from water is negligible  
c)  $[\text{Na}^+] = [\text{OH}^-]$                       d) activity is considered

12. A student is solving a problem to determine the pH of a  $2.0 \times 10^{-6}\text{ M}$   $\text{NH}_4\text{Cl}$  solution and correctly using the ICE method determines that the pH is 7.47. This result indicates:

- a) the ICE method is NOT valid because a strongly basic solution is expected  
b) the ICE method is NOT valid because a strongly acidic solution is expected  
c) the ICE method is valid because a weakly basic solution is expected  
d) the ICE method is NOT valid because a weakly acidic solution is expected

13. Given are the following 4 compounds shown in their most basic (basic pH) form. All of these compounds exist in an acidic, an intermediate, and a basic form. Which of these compounds forms a plus 2 cation in the most acidic form?

- a)  $\text{CO}_3^{2-}$                       b)  $\text{NH}_2\text{CH}_2\text{CO}_2^-$                       c)  $\text{NH}_2\text{CH}_2\text{NH}_2$                       d)  $\text{NH}_2\text{C}_6\text{H}_4\text{O}^-$

14. It is desired to use the amino acid phenylalanine,  $^+\text{NH}_3\text{CHR}\text{CO}_2^-$ , where  $\text{R} = -\text{CH}_2\text{C}_6\text{H}_5$ , to make a pH = 8.80 buffer. Phenylalanine has  $\text{pK}_{a1} = 2.20$  and  $\text{pK}_{a2} = 9.31$ . What can be added to make the buffer?

- a) HCl                      b) NaOH                      c)  $^+\text{NH}_3\text{CHR}\text{CO}_2\text{HCl}^-$                       d) none of the above

*pH is close to  $\text{pK}_{a2}$  so solution needs to become more basic*

15. Cysteine,  $^+\text{NH}_3\text{CHR}\text{CO}_2^-$ , where  $\text{R} = -\text{CH}_2\text{SH}$ , has two acidic functional groups and one base functional group. How many forms can it be present in (if the pH is varied from 1 to 13)?

- a) 1                      b) 2                      c) 3                      **d) 4**

[could write cysteine as  $\text{H}_3\text{L}^+$  in most acidic form and can lose 3  $\text{H}^+$ s]

**Problem Section.** Show all needed calculations to receive full credit. The number of points are shown in parentheses. Use the back side of the page if needed. Activity only needs to be considered for the parts of problem 2 where it is mentioned and the systematic method only needs to be used for problem 3.

1. A tap water sample is analyzed for Mg by atomic absorption spectroscopy. Using calibration standards between 0.2 and 1.0 ppm, a student finds the equation for the calibration line as:  $A = 0.431C - 0.011$  where  $A$  = absorbance and  $C$  = concentration (in ppm). The tap water is prepared by transferring 5.00 mL of tap water to a 100.0 mL volumetric flask and diluting to the line.

- a) If the diluted tap water sample is found to give an absorbance of 0.107, calculate the concentration of Mg in the diluted tap water. (6 pts)

$$C = (0.107 + 0.011)/0.431 = \mathbf{0.274 \text{ ppm}}$$

- b) What was the concentration of Mg in the original tap water sample (in ppm)? (6 pts)

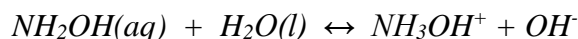
$$C_1V_1 = C_2V_2 \text{ or } C_1 = C_2V_2/V_1 = 0.274 \text{ ppm}(100 \text{ mL})/(5 \text{ mL}) = \mathbf{5.48 \text{ ppm}}$$

Bonus 1) Was the diluted tap water in the best range for determining its concentration? If not suggest a better dilution ratio (2 pts)

*No. It was in the lowest third of the concentration range so was over diluted. A 10:100 dilution would have been better (0.55 ppm diluted conc.)*

2. What is the pH of a  $2.0 \times 10^{-3} \text{ M}$   $\text{NH}_2\text{OH}$  solution?  $\text{NH}_2\text{OH}$  is a weak base with a conjugate acid  $K_a = 1.10 \times 10^{-6}$  (activity can be ignored) (10 pts)

Set up ICE table for base reaction



Initial	$2.0 \times 10^{-3} \text{ M}$	0	0
Change	-x	+x	+x
Equil.	$2.0 \times 10^{-3} - x$	x	x

$$K_b = K_w/K_a = 9.09 \times 10^{-9} = [\text{NH}_3\text{OH}^+][\text{OH}^-]/[\text{NH}_2\text{OH}] = x^2/(2.0 \times 10^{-3} - x)$$

$$\text{Assuming } x \ll 2.0 \times 10^{-3}, x = [(9.09 \times 10^{-9})(2.0 \times 10^{-3})]^{0.5} = 4.26 \times 10^{-6} \text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log(4.26 \times 10^{-6}) = \mathbf{8.63}$$

3. A standard of MTBE (methyl tertiary butyl ether) in gasoline, was analyzed 4 times to test a method. The measured values were: 0.81 wt %, 0.68 wt %, 0.73 wt %, and 0.79 %.

a) Using the table below, give the 95% confidence value about the mean using the correct number of significant figures. (8 pts)

Degrees of freedom	3	4	5
t-value (at 95% level)	3.18	2.776	2.571

$Deg\ of\ free = n - 1 = 3$

Calculate mean and standard deviation: mean = 0.7525; SD = 0.0591

95% CI = mean  $\pm$  tS/(n)<sup>0.5</sup> = 0.7525  $\pm$  (3.18)(0.0591)/4<sup>0.5</sup> = 0.7525  $\pm$  0.0940%

Answer = 0.75  $\pm$  0.09% (1 sig fig in unc. + same place in value)

b) If the true percent of MTBE in the gasoline standard is known, what specific type of statistical test should be used to check for systematic errors? (3 pts)

**Case 1 t-test**

4. Calcium fluoride is a sparingly soluble salt that dissociates in water as:

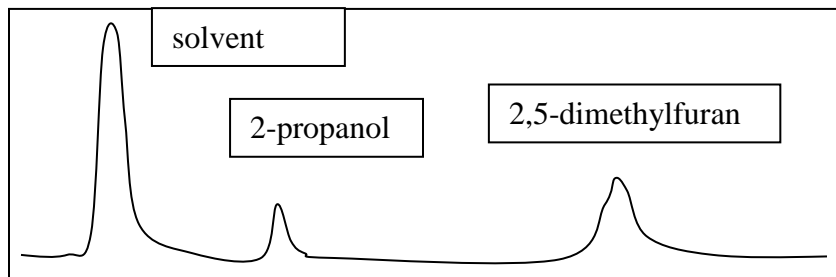
$CaF_2(s) \leftrightarrow Ca^{2+} + 2F^-$ . The  $K_{sp}$  for this reaction is  $3.9 \times 10^{-11}$ . Assume  $F^-$  and  $Ca^{2+}$  do NOT significantly react with water or form an ion pair. Determine the solubility of calcium fluoride in 0.050 M  $KNO_3$  if the activity coefficients,  $\gamma(Ca^{2+})$  and  $\gamma(F^-)$ , are 0.485 and 0.81, respectively, in the  $KNO_3$  solution. Assume the only effect of the  $KNO_3$  solution is through an ionic strength change. (12 pts)

ICE table will give:  $CaF_2(s) \leftrightarrow Ca^{2+} + 2F^-$

Equil  $x \quad 2x$  and  $K_{sp} = 3.9 \times 10^{-11} = \gamma(Ca^{2+})[Ca^{2+}]\{\gamma(F^-)[F^-]\}^2$

$3.9 \times 10^{-11} = (0.485)x[0.81(2x)]^2 = (0.485)(2.62)x^3$  or  $x = (3.9 \times 10^{-11}/1.27)^{0.333} = 3.13 \times 10^{-4} M$

5. The following chromatogram and table shows the separation of 2-propanol from 2, 5-dimethylfuran. The separation was by gas chromatography with a 2 m x 2 mm packed at 95°C.



Compound	Retention time (min)	Peak Area	Peak width* (min)
solvent (unretained)	0.99	63,102	NA
2-propanol	2.31	5,771	0.198
2, 5-dimethylfuran	5.92	10,039	0.481

\* baseline width

a) Calculate the retention factor of 2-propanol. (5 pts)

$k = (2.31 - 0.99)/0.99 = 1.33$

b) Calculate the column plate number (N). (5 pts)

$$N = 16(t_r/w)^2 = 16(5.92/0.481)^2 = \mathbf{2420}$$

Using 2-propanol,  $N = \mathbf{2180}$

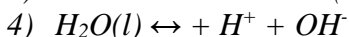
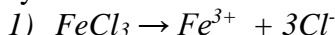
c) Which quantity from the table should be used for quantifying the concentration of 2, 5-dimethylfuran (assuming you also have data from standards). (4 pts)

**10,039 (the peak area)**

bonus #2) What is non-optimal about the separation? and what change could improve it? (2 pts)  
*It wasted time because the resolution was too good. It should be run hotter.*

6. A solution is prepared in which 0.0020 moles of  $\text{FeCl}_3$  is dissolved completely in water making a 1.000 L solution. The  $\text{Fe}^{3+}$  ion is known to form the following complexes (and assume no other complexes form):  $\text{FeOH}^{2+}$  and  $\text{Fe}(\text{OH})_2^+$ . (15 pts)

a) Write out all of the relevant reactions needed if one is solving this problem using the systematic method



b) Give a charge balance equation.

$$3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

c) Give two mass balance equations based on the listed reactions and the initial concentration of the dissolved ionic compound.

$$[\text{FeCl}_3]_o / [\text{Cl}^-] = 1/3 \text{ or } [\text{Cl}^-] = 3[\text{FeCl}_3]_o = \mathbf{0.0060 \text{ M}} = [\text{Cl}^-]$$

$$[\text{FeCl}_3]_o = \mathbf{0.0020 \text{ M}} = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+]$$

7. Phthalic acid,  $\text{HO}_2\text{CC}_6\text{H}_4\text{CO}_2\text{H}$ , is an acid readily available in its intermediate form as KHP (potassium hydrogen phthalate or  $\text{K}^+\text{HO}_2\text{CC}_6\text{H}_4\text{CO}_2^-$ ). If phthalic acid's  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  are 2.95 and 5.41, respectively, calculate the mass of NaOH (FW = 40.00 g/mol) should be added to 500.0 mL of 0.0080 M KHP to get a pH = 6.00 buffer solution. (activity can be ignored) (10 pts)  
*The 6.00 pH is closest to the  $\text{pK}_{a2}$ , which tells us we want the  $\text{HP}^-$  and  $\text{P}^{2-}$  species present. KHP will dissociate in water to give  $\text{HP}^-$ , with addition of  $\text{OH}^-$  converting some of the  $\text{HP}^-$  to  $\text{P}^{2-}$ . We need a mole table with  $n(\text{HP}^-) = (0.5000 \text{ L})(0.0080 \text{ mol/L}) = 0.0040 \text{ moles}$*

	$\text{HP}^-$	+	$\text{OH}^-$	$\leftrightarrow$	$\text{P}^{2-}$	+	$\text{H}_2\text{O}(l)$	
Init.	0.0040		X		0			
Change	-X		-X		+X			$\text{pH} = \text{pK}_{a2} + \log[n(\text{P}^{2-})/n(\text{HP}^-)]$
Full Right	$0.0040 - X$		0		X			$6.00 = 5.41 + \log[X/(0.0040 - X)]$
	$X/(0.0040 - X) = 10^{0.59} = 3.89 \text{ or } X = 0.0156 - 3.89X \text{ or } X = 0.0032 \text{ M or mass} = \mathbf{0.127 \text{ g}}$							

8. Hydrogen cyanide gas can be generated when the  $\text{CN}^-$  ion is placed in an acidic solution because HCN is a weak acid ( $\text{pK}_a = 9.21$ ). Calculate the fraction of  $\text{CN}^-$  that is in the HCN form in a  $\text{pH} = 7.00$  buffer solution. (activity can be ignored) (6 pts)

$$\alpha(\text{HCN}) = [\text{H}^+]/\{[\text{H}^+] + K_a\} = 10^{-7}/(10^{-7} + 10^{-9.21}) = \mathbf{0.994}$$