CHEMISTRY 31 FINAL EXAM
May 18, 2015 - 150 points total
Key

Constants:
K_w (autoprotolysis of H_2O) = 1.0×10^{-14} h = Planck's constant = 6.63×10^{-34} J·s
c = speed of light in a vacuum = 3.00×10^{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 point in a titration in which an indicator changes color (in response to a change in reactant concentration) is called:
a) the end point   b) the equivalence point   c) the half way point
d) the equilibrium point

2. Two students, Sue and Joey, both measured the Ca concentration of their tap water using atomic absorption spectroscopy. Sue finds her concentration ± standard deviation to be 8.31±0.02 while Joey finds his to be 6.3±0.1. What can be said of the measurement quality?
a) Sue's measurement is more accurate   **b) Sue's measurement is more precise**
c) Joey's measurement is more sensitive   d) Joey made more measurements

3. A scientist has developed a new test to measure calcium concentration in concrete and wants to check for systematic errors against a standard test or with a concrete standard (of known calcium concentration), the type of test to choose is a:
a) t-test   b) F-test   c) Grubb's test   d) Z test

4. A cation and an anion of a sparingly soluble salt are mixed together. Precipitation is expected to occur if:
a) the cation and anion are in stoichiometric ratios
b) the Gibb's free energy for the precipitation reaction is positive
c) the K_{sp} is less than 1
d) the reaction quotient (Q) is larger than K_{sp}

5. The following salts are dissolved in water. Predict which results in an acidic solution.
a) NaBr   b) $K_2C_2O_4$ **c) $Fe(NO_3)_3$**   d) $Ca(OH)_2$
HBr and HNO_3 are strong acids, $H_2C_2O_4$ is a weak acid, and Na and K are group I metals.

6. How would you expect the aqueous equilibrium reaction, $AgCl(s) + 2NH_3(aq) \Leftrightarrow Ag(NH_3)_2^+ + Cl^-$ to shift following the addition of some $NaNO_3$, assuming the only change is the ionic strength?
a) toward reactants   **b) toward products**   c) no change from addition of NaCl

7. List two components of spectrometers: components:_light source, sample/sample holder, wavelength discriminator, light detector, data processor_

8. In a gas chromatographic separation of a series of compounds of very similar polarity but different boiling point temperatures, the retention factors will depend mostly on:
a) the compound's polarity b) the choice of carrier gas
c) the compound's volatility d) the length of the column

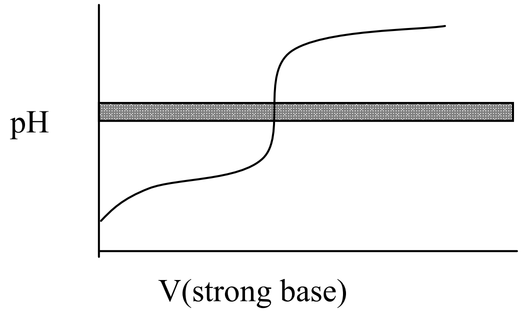
9. A student wants to calculate the pH of a solution containing 1.0×10^{-5} M of a weak base in water using an ICE approach. The student, using the ICE approach correctly, calculates a pH of 8.85. One can conclude,
a) the ICE approach worked because a weakly basic pH is expected
b) the ICE approach failed because a weakly acidic pH was expected
c) the ICE approach failed because a pH of over 12 is expected
d) the ICE approach can never be used for weak base problems

10. 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

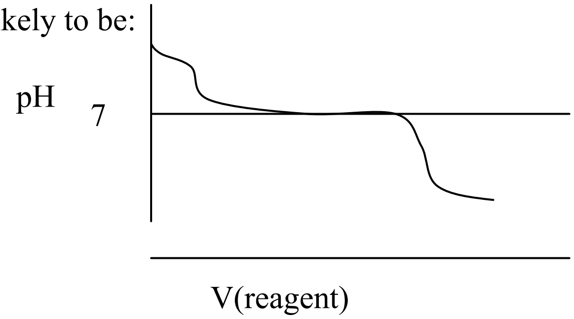
11. 2-aminoethanethiol, $HSCH_2CH_2NH_3^+$ (shown in its acid form), has an acid functional group (HS-R) with pK_{a1} of 8.21 and a base functional group ($R\text{-}NH_2$) with a conjugate acid ($R\text{-}NH_3^+$) pK_{a2} value of 10.73. What is the most prevalent form of this compound at a pH of 9.50?
a) $HSCH_2CH_2NH_3^+$ b) $HSCH_2CH_2NH_2$
c) $^{-}SCH_2CH_2NH_3^+$ d) $^{-}SCH_2CH_2NH_2$

12. In a weak acid – strong base titration with an indicator used to determine the end point, it is important to calculate the pH at the equivalence point to be able to:
a) select a correct indicator b) select the correct strong base
c) calculate the concentration of an unknown weak acid

13. Based on the titration curve shown to the right (with grey box showing where indicator changes color), the titration can be considered to be:
a) precise and accurate
b) precise but not accurate
c) accurate but not precise
d) neither accurate nor precise



14. The titration plot shown to the right is most likely to be:
a) a weak acid by a strong base
b) a base mixture by a strong acid
c) a diprotic weak acid by a strong base
d) a strong base by a strong acid



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.

1. A tap water sample is expected to have an Mg concentration of 13 ppm. A student wants to dilute the tap water to between 0.5 and 0.7 ppm to analyze by atomic absorption spectroscopy. She has 1 and 5 mL volumetric pipets and 100 mL and 250 mL volumetric flasks. **Describe how the student could make the dilution** with the equipment she has and **calculate her expected diluted tap water's Mg concentration**. (10 pts)

The dilution equation is $C_1V_1 = C_2V_2$ (C_1 can be original conc.)
Knowing the original and diluted conc.s we can rearrange the above equation to:
$V_1/V_2 = C_2/C_1 = 0.6/13 = 1/22$ dilution. So this is close to 5/100 or 12/250

The following options are possible: C(diluted) = (13 ppm)V(pipet total)/V(vol. flask)

V(pipet total)	V(vol. flask)	C(diluted)
5	100	0.65
12	250	0.62
11	250	0.57

2. Calcium fluoride is a sparingly soluble salt that dissociates in water as:
CaF_2 (s) ↔ $Ca^{2+} + 2F^-$. The K_{sp} for this reaction is 3.9×10^{-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)

We can start by setting up an ICE table:

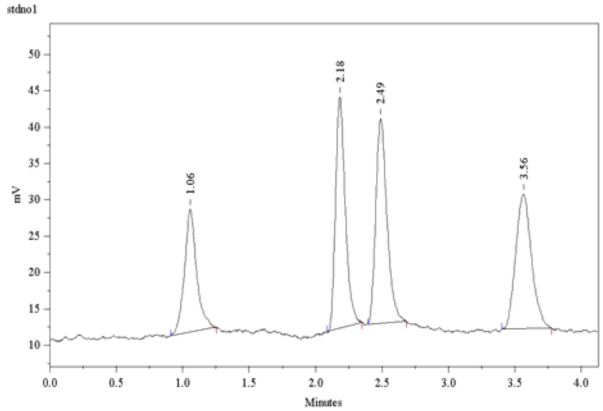
	$CaF_2 (s) \leftrightarrow Ca^{2+}$	$+ \quad 2F^-$
Initial	0	0
Change	$+X$	$+2X$
Equil.	X	$2X$

Next, without considering activity, we would plug these into an equilibrium equation, but because we need to consider activity, we must use an equation modified with activity coefficients:
$K_{sp} = [Ca^{2+}][F^-]^2$ *(low ionic strength) becomes* $K_{sp} = \gamma(Ca^{2+})[Ca^{2+}]\{\gamma(F^-)[F^-]\}^2$
or $K_{sp} = \gamma(Ca^{2+})[Ca^{2+}]\gamma(F^-)^2[F^-]^2$ *or* $3.9 \times 10^{-11} = (0.485)X(0.81)^2(2X)^2 = 1.272X^3$
$X = (3.9 \times 10^{-11}/1.272)^{1/3} = \mathbf{3.1 \times 10^{-4}}$ ***M = solubility***

3. Given the following reverse-phased HPLC chromatogram using 75% water and 25% methanol – also see data table below, determine:

a) the retention factor (k) for adenosine (4 pts)

k = (3.564 – 1.056)/1.056 = **2.375**



Data Table

Peak #	Ret Time (min.)	Name	Area (mV*s)	Peak Width (min.)
1	1.056	Unretained	1074.343	
2	2.182	uracil	1617.349	0.136
3	2.489	sulfanilamide	1645.061	0.155
4	3.564	adenosine	1525.604	0.219

Peak width = peak width at base

b) which compound is the least polar (explain). (4 pts)

Adenosine is the least polar *because it elutes last on a reversed-phase column (non-polar stationary phase).*

c) The plate number (N) of the column (indicate which peak you are using to calculate this). (4 pts)

$N = 16(t_r/w)^2$

Using uracil, sulfanilamide, and adenosine, respectively, we get

$N = 16(2.182/0.136)^2$ = ***4120, 4130, and 4240****, respectively.*

d) the resolution between uracil and sulfanilamide. (4 pts)

$R_S = \Delta t/w_{ave} = (2.489 - 2.182)/[0.5(0.136 + 0.155)] =$ **2.11**

4. 3-nitrophenol, $O_2NC_6H_4OH$, is a monoprotic weak acid with a $pK_a = 8.37$. The salt, sodium 3-nitropenolate, $Na^+O_2NC_6H_4O^-$, is dissolved in water to make a solution with a molarity of 0.024 M. Determine the pH of the solution to 4 sig figs. (12 pts)

Since 3-nitrophenol is a weak acid, its conjugate base 3-nitrophenolate ($O_2NC_6H_4O^-$) is a weak base with $K_b = K_w/K_a = 10^{-14}/10^{-8.37} = 2.344 \times 10^{-6}$
We can label it as A^- and it reacts as a base as follows (with set up as expected for weak base problems by using the ICE method)

	$A^- + H_2O$	$\leftrightarrow HA$	$+ OH^-$
initial	0.024	0	0
change	-x	+x	+x
equil.	0.024 – x	x	x

$2.344 \times 10^{-6} = x^2/(0.024 - x)$ *or assuming* $0.024 >> x$, $x = [(2.344 \times 10^{-6})(0.024)]^{0.5}$
$x = 2.37 \times 10^{-4}$ *M (which is* $<< 0.024$*)*
$[OH^-] = 2.37 \times 10^{-4}$ *M or* $pOH = 3.625$ *and* $pH = 14 - pOH =$ ***10.38***

5. A buffer solution is made by adding 5.00 mL of 2.08 M HCl to 495.0 mL of 0.0621 M aniline ($C_6H_5NH_2$). The conjugate acid of aniline ($C_6H_5NH_3^+$) has $K_a = 2.51 \times 10^{-5}$. Calculate the pH of the solution to 4 significant figures. (12 pts)
This is a strong acid (HCl) + weak base (aniline – we will call B) type buffer requiring a mole table: First, calculate moles HCl and B: n(HCl) = (5.00 mL)(2.08 mmol/mL) = 10.40 mmol and n(B) = (495.0 mL)(0.0621 mmol/mL) = 30.74 mmol
Next, mole table:

	B	$+ H^+$	$\leftrightarrow BH^+$
initial	30.74	10.40	0
change	-10.40	-10.40	+10.40
full right	20.34	0	10.40

Then, we can use the H-H equation:
$pH = pK_a + \log\{[B]/[BH^+]\}$ *or* $pH = pK_a + \log[n(B)/n(BH^+)] = 4.600 + \log(20.34/10.40)$
$\mathbf{pH = 4.891}$

6. Malonic acid, ($HO_2CCH_2CO_2H$), is a diprotic acid ($pK_{a1} = 2.847$ and $pK_{a2} = 5.27$). If 1.0×10^{-4} moles of malonic acid are added to the buffer in problem 5, calculate the concentration of malonic acid present as $HO_2CCH_2CO_2^-$ (HA^- in abbreviated form). Assume that the addition of malonic acid does not change the buffer pH. Hint: Calculate the fraction of the acid in the HA^- form. If you can't solve problem 5, assume the pH = 5. (10 pts)
$\alpha(HA^-) = [H^+]K_{a1}/\{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}\}$
$\alpha(HA^-) = 10^{-4.891}10^{-2.847}/[(10^{-4.891})^2 + 10^{-4.891}10^{-2.847} + 10^{-2.847}10^{-5.27}]$
$= 1.828 \times 10^{-8}/(1.652 \times 10^{-10} + 1.828 \times 10^{-8} + 7.638 \times 10^{-9}) = 1.828 \times 10^{-8}/2.608 \times 10^{-8}$
$\alpha(HA^-) = 0.701$
total $[H_2A] = 1.0 \times 10^{-4}$ *moles/0.5 L =* 2.0×10^{-4} *M and*
$[HA^-] = \alpha(HA^-)(\text{total } [H_2A]) =$ $\mathbf{1.4 \times 10^{-4}\ M}$

7. A 50.0 mL aliquot of an unknown solution containing the weak base, methyl amine (CH_3NH_2, with K_a of conjugate acid = 2.33 x 10^{-11}) is titrated with 0.100 M HCl and found to require 37.3 mL to reach the equivalence point. Calculate: (22 pts)

a) The concentration of methyl amine in the unknown solution.

the moles of the weak base and strong acid will be equal at the equivalence point or

$n(CH_3NH_2) = n(HCl)$ or $[CH_3NH_2](50.0 \text{ mL}) = [0.100 \text{ M}](37.3 \text{ mL})$

$[CH_3NH_2]$ = **0.0746 M**

b) The pH at the equivalence point to 3 sig figs.

At the equivalence point the reaction is complete:

$CH_3NH_2 + H^+ \leftrightarrow CH_3NH_3^+$

, meaning all CH_3NH_2 is converted to the acid form. At this point only the conjugate acid (a weak acid is left), and determination of the pH becomes a “weak acid” problem – the backwards reaction. However, the dilution of the compound from the addition of the HCl must be considered.

Dilution of CH_3NH_2: $[CH_3NH_3^+] = n(CH_3NH_2)/V_{total}$ = 3.73 mmol/87.3 mL = 0.04273 M

Now we can set up an ICE table for the reverse reaction:

	$CH_3NH_3^+$ ↔	$CH_3NH_3^+$ +	H^+
*i*nitial	0.04273	0	0
change	-x	+x	+x
full right	0.04273 - x	x	x

K_a = 2.33 x 10^{-11} = $x^2/(0.04273 - x)$ (can assume x << 0.04273)

x^2 = (2.33 x 10^{-11})(0.04273) or x = (9.96 x 10^{-13})$^{0.5}$ = 1.00 x 10^{-6} M

pH = 6.00

c) The pH after addition of 45.0 mL of HCl.

After the equivalence point (see rxn below), there is excess H^+ and only this determines the pH.

$CH_3NH_2 + H^+ \leftrightarrow CH_3NH_3^+$

$[H^+] = n(H^+)_{excess}/V_{total}$ = [(0.100 M)(45 mL) – (0.100 M)(37.3 mL)]/95 mL = 0.77 mmol/95 mL

$[H^+]$ = 0.00811 M or **pH = 2.09**

bonus) Determine if the above titration, or a titration under the same conditions but of ammonia (conjugate acid K_a = 5.69 x 10^{-10}) would have resulted in a sharper titration. Explain your answer (4 pts)

Ammonium has a greater K_a value so will be a stronger acid. Thus, ammonia will be a weaker base and will give a less sharp titration. ***So the answer is NO.***