# CHEMISTRY 31 FINAL EXAM - KEY
Dec. 12, 2016 - 150 points total

NAME ___________________

Equations:
Debye-Hückel Equation:

$$\log\gamma = \frac{-0.51\cdot z^2\sqrt{\mu}}{1+(\alpha\sqrt{\mu}/305)}$$

Where: $\gamma$ = activity coefficient, $\mu$ = ionic strength, $\alpha$ = hydrated ion radius, and z = ion charge

Quadratic Equation: for $ax^2 + bx + c = 0$, $x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$

Constants:
$K_w$ (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 Mg standard used in the AA lab was 0.996% by mass. The concentration of Mg in ppm is:
Mg (atomic weight = 24.3 g $mol^{-1}$ and density of solution = 1.04 g $mL^{-1}$)
a) 9.96 b) 9960 c) 415 d) 426
*ppm = (mass fraction)·*$10^6$ *and mass fraction = 0.996/100 = 0.00996*

2. A researcher has invented a cheaper method to measure glucose in blood. She is interested in comparing the precision of her method compared to a standard method. She measures one blood sample 6 times by her method and the standard method to compare the standard deviations from the two methods. Which test is best to use to compare precision?
a) case 1 t-test b) case 2 t-test c) F-test d) Grubb's test

3. A student is analyzing a tap water sample for Mg by atomic absorption spectroscopy and has the following table of standards data:

| Conc. (ppm) | 0.20 | 0.40 | 0.70 | 1.0 |
|---|---|---|---|---|
| Absorbance | 0.131 | 0.255 | 0.498 | 0.641 |

She prepared 3 dilutions of her tap water (see below). Which dilution is the best to use?

| Tap Dilution ratio | 1:4 | 1:20 | 1:50 |
|---|---|---|---|
| Absorbance | 1.321 | 0.330 | 0.130 |

a) any value could be used with equal precision c) the 1:20 dilution is best
b) the 1:4 dilution is best d) the 1:50 dilution is best
*1:4 is off scale (too high – A > 0.641) and 1:50 is just off scale (near lowest std). 1:20 comes out in upper 2/3rds of range*

4. Given that for $Hg^{2+} + 2CH_3CO_2^- \leftrightarrow Hg(CH_3CO_2)_2(aq)$, K = $2.8 \times 10^8$ and for $CH_3CO_2H(aq) \leftrightarrow H^+ + CH_3CO_2^-$, K = $1.8 \times 10^{-5}$, K for $Hg^{2+} + 2CH_3CO_2H(aq) \leftrightarrow Hg(CH_3CO_2)_2(aq) + 2H^+$, is:
a) $9.1 \times 10^{-2}$ b) $1.0 \times 10^4$ c) $2.8 \times 10^8$ d) $8.6 \times 10^{17}$
*$K_3 = K_1 \cdot K_2^2$ =*

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, and $H_2C_2O_4$ is a weak acid.
*$Fe^{3+}$ is weakly acidic, $Br^-$ and $NO_3^-$ are neutral, $C_2O_4^{2-}$ is weakly basic and $OH^-$ is strongly basic.*

6. In gas chromatography, what is normally done to decrease the retention factor of an analyte:
a) Increase the column temperature b) Use a longer column
c) Use a more polar column d) Use a larger diameter column
*Increasing T increases volatility which decreases retention*

7. The concentration of $Ag^+$ in an unknown solution can be determined through a precipitation titration with $Cl^-$, $Br^-$, or $I^-$. Given the $K_{sp}$ values, which titration gives the sharpest equivalence point?

| Salt | AgCl | AgBr | AgI |
|---|---|---|---|
| $K_{sp}$ | $1.8 \times 10^{-10}$ | $5.0 \times 10^{-13}$ | $8.3 \times 10^{-17}$ |

a) $K_{sp}$ doesn't affect titration sharpness b) $Cl^-$ titration
c) $Br^-$ titration d) $I^-$ titration
*Sharpest titration has largest $K_{sp}$ value. Precipitation reaction is reverse of dissolution so K = $1/K_{sp}$*

8. The purpose of a monochromator is to:
a) detect light transmitted through the sample in a spectrometer
b) select a single ion in an ion chromatograph
c) to detect gases leaving a gas chromatograph
d) to select a single wavelength of light in a spectrometer

9. How would the aqueous equilibrium reaction, $Mg^{2+} + HIn^{2-} \Leftrightarrow MgIn^- + H^+$ shift following the addition of some NaCl, assuming the main change is the ionic strength? (In = indicator)
a) toward reactants b) toward products c) no change from addition of NaCl
*Reactants are both doubly charged vs. single charge in products*

10. In step 5 of the systematic method, everything checks out if:
a) the number of unknown species is greater than the number of equations
b) the number of unknown species is equal to or less than the number of equations
c) there are no redundant equations
d) the number of unknown species is equal to the number of equilibrium equations
*Should have the same # of unknowns as equations, but with redundant equations can have more equations.*

11. Which of the following equal volume mixtures will make a traditional buffer solution:

a) 0.010 M HCl + 0.010 M NaOH b) 0.010 M HCl + 0.0050 M $NH_4Cl$
c) 0.030 M HCl + 0.008 M $NaCH_3CO_2$ d) 0.0080 M HCl + 0.0180 M $NH_3$
($NH_4^+$ and $CH_3CO_2H$ are weak acids)
*a) strong acid + strong base, b) strong acid + weak acid, and c) has excess strong acid*
*d) strong acid converts some of $NH_3$ to $NH_4^+$ giving weak base + conjugate acid*

12. $H_2C_2O_4$ is a weak diprotic acid with $K_{a1} >> K_{a2}$. 0.020 moles of $H_2C_2O_4$ is dissolved in water to prepare 1.00 L of solution. To determine which of the following concentrations must the second $K_a$ reaction be considered (as opposed to just the first reaction)?

a) $[H^+]$ b) $[H_2C_2O_4]$ c) $[HC_2O^-_4]$ d) $[C_2O_4^{2-}]$
*d) is only species that only is in 2nd reaction*

13. Which of the following affects the sharpness of a strong acid – strong base titration?

a) the type of strong acid used b) the type of strong base used
*c) the concentration of the acid and base* d) the indicator chosen for the titration

14. In which of the following salts, is a diprotic acid being given in its most acidic form?

a) $NaHSO_3$ b) $NaNH_2CH_2CO_2$ c) $NH_3CH_2CO_2HCl$ d) $NH_2CH_2NH_3Cl$
$H_2SO_3$ is a weak acid, $NH_3CH_2CO_2$ is a zwitterion at pH = 7, and $NH_2CH_2NH_2$ has two base functional groups.
*To be a "most acidic form" and a salt, it must have base functional groups (this eliminates a)).*
*c) is of the $H_2L^+$ form – max # Hs, b) is of the $L^-$ form and d) is of the $HL^+$ form.*

15. Citric acid is a triprotic acid (e.g. $H_3A$) with $pK_a$ values given in the table below. Which two species should be present to make a buffer at a pH of 6.2?

| $pK_{a1}$ | $pK_{a2}$ | $pK_{a3}$ |
|---|---|---|
| 3.13 | 4.76 | 6.40 |

a) $H_3A + H_2A^-$ b) $H_2A^- + HA^{2-}$ c) $HA^{2-} + A^{3-}$ d) $H_3A + HA^{2-}$
*pH is closest to $pK_{a3}$ so species in $K_{a3}$ reaction are needed.*

**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 student performed the water hardness titration four times on a tap water sample, and got the following results (ppm $CaCO_3$ equivalent calculated each time):

| Trial 1 | Trial 2 | Trial 3 | Trial 4 |
|---|---|---|---|
| 533 | 541 | 525 | 538 |

Calculate the 95% confidence interval for her values using the table below for student t values. Be sure to express your answer with the correct number of significant figures. (8 pts)

| Degrees of freedom | 3 | 4 | 5 |
|---|---|---|---|
| t-value (at 95% level) | 3.182 | 2.776 | 2.571 |

Mean = 534.25 and standard deviation = 6.99 deg of freedom = n – 1 = 3

*95% CI = mean* $\underline{+}$ *tS/(n)*$^{0.5}$

*95% CI = 534.25 + (3.182)(6.99)/(4)*$^{0.5}$ *= 534.25 + 11.12*

*95% CI =* ***530*** $\underline{+}$ ***10*** *(correct sig fig)*

2. The $K_{sp}$ for $Mg(OH)_2$ is 7.1 x $10^{-12}$.

a) Without considering activity and ignoring any post-dissolution reactions (e.g. those that would require the use of the systematic method), determine the solubility of $Mg(OH)_2$ in 5.0 x $10^{-3}$ M NaOH. (7 pts)

*This can be solved using ICE method. First, we need see that* $[OH^-] = [NaOH]_o = 0.0050$ *M*

| | $Mg(OH)_2(s) \leftrightarrow$ | $Mg^{2+}$ + | $2OH^-$ |
|---|---|---|---|
| *Init* | | 0 | 0.0050 |
| *Change* | | +x | +2x |
| *Equil* | | x | 0.0050 + 2x |

$K_{sp} = 7.1 \times 10^{-12} = [Mg^{2+}][OH^-]^2 = x(0.0050 + 2x)^2 \sim x(0.0050)^2$ *(assuming x << 0.0050)*

$7.1 \times 10^{-12} = x(2.5 \times 10^{-5})$

$\mathbf{x = 2.8 \times 10^{-7}}$ **M = solubility** *(assumption o.k.)*

b) Calculate the ionic strength of the saturated $Mg(OH)_2$ in 5.0 x $10^{-3}$ M NaOH solution described in a). (4 pts)

*Since x << 0.0050, we can ignore* $Mg(OH)_2(s)$ *dissolution in calculating* $\mu$

*Main ions are just* $[Na^+]$ *and* $[OH^-]$ *from NaOH*

$\mu = 0.5[(0.0050\ M)(+1)^2 + (0.0050\ M)(-1)^2] = \mathbf{0.0050\ M}$

c) From the ionic strength in b), determine the activity coefficients for $Mg^{2+}$ and $OH^-$ given that $\alpha(Mg^{2+})$ = 800 pm and $\alpha(OH^-)$ = 350 pm. (If you couldn't determine the ionic strength assume it is 0.010 M) (8 pts)

*for* $Mg^{2+}$, $\log\gamma(Mg^{2+}) = -(0.51)(+2)^2(0.0050)^{0.5}/[1+(800)(0.0050)^{0.5}/305] = -0.144/1.185 = -0.121$

$\boldsymbol{\gamma(Mg^{2+}) = 0.756}$, *for* $OH^-$, $\boldsymbol{\gamma(OH^-) = 0.926}$

d) Using the activity coefficients in c), recalculate the solubility of $Mg(OH)_2$, now accounting for activity. (You do not need to recalculate the ionic strength though. If you couldn't solve c) assume $\gamma(Mg^{2+}) = \gamma(OH^-) = 0.8$). (6 pts)

*We can modify our solution from part a) (no need to redo ICE table)*

$K_{sp} = 7.1 \times 10^{-12} = \{\gamma(Mg^{2+})[Mg^{2+}]\}\{\gamma(OH^-)[OH^-]\}^2 = 0.756 \cdot x(0.926 \cdot 0.0050)^2$

$x = 7.1 \times 10^{-12}/[0.756(0.926 \cdot 0.0050)^2] = \mathbf{4.4 \times 10^{-7}\ M}$

BONUS – 2pts) Give the pH of the solution (using the true definition and to 4 sig figs).

$pH = 14 - pOH = 14 + \log\{\gamma(OH^-)[OH^-]\} = \mathbf{11.67}$

3. A solution is prepared that is 0.0050 M $CdCl_2$. Assuming $Cd^{2+}$ can react to form the complexes $CdCl^+$ and $CdOH^+$ but no other complexes, complete the following steps in determining the concentrations of all species using the systematic method. Note that you are only asked to do specific steps. Ignore activity for this problem

a) List all of the relevant reactions for the above problem: (8 pts)

1) $CdCl_2(aq) \rightarrow Cd^{2+} + 2Cl^-$ *(one way arrow because no solid or $CdCl_2$ complex)*
2) $Cd^{2+} + OH^- \leftrightarrow CdOH^+$
3) $Cd^{2+} + Cl^- \leftrightarrow CdCl^+$
4) $H_2O(l) \leftrightarrow H^+ + OH^-$

b) Give the charge balance equation for the above problem: (4 pts)

$2[Cd^{2+}] + [CdOH^+] + [CdCl^+] + [H^+] = [OH^-] + [Cl^-]$

c) Give mass balance equations relating concentrations of species to the initial concentration of $CdCl_2$. (6 pts)

*Source = $CdCl_2$ (totally dissolved ionic compounds – so 2 mass balance equations)*

1) $[Cd]_{total} = [CdCl_2]_o = \mathbf{0.0050\ M = [Cd^{2+}] + [CdOH^+] + [CdCl^+]}$
2) $[Cl]_{total} = 2[CdCl_2]_o = 0.010\ M$ *(due to $[Cl^-]/[CdCl_2]_o = 2/1$)*
   $\mathbf{0.010\ M = [CdCl^+] + [Cl^-]}$

d) Give the equilibrium equations. (3 pts)

rxn 1 is not equil. – no equation $\quad K_2 = [CdOH^+]/[Cd^{2+}][OH^-]$

$K_3 = [CdCl^+]/[Cd^{2+}][Cl^-] \quad K_4 = [H^+][OH^-]$

4. A solution of 0.050 M NaBrO is made by dissolving NaBrO into 1.00 L of solution. The $K_a$ of HBrO (the conjugate acid of $BrO^-$) = $2.3 \times 10^{-9}$ and $K_w = 1.0 \times 10^{-14}$. Using the ICE method, determine the pH of the solution to 4 sig figs. (9 pts)

NaBrO is an ionic scompound and dissociates to give $BrO^-$. $[BrO^-]_o = 0.050$ M

Next we make an ICE table

| | $BrO^- + H_2O(l)$ | $\leftrightarrow HBrO(aq)$ | $+ 2OH^-$ |
|---|---|---|---|
| *Init* | 0.050 | 0 | 0.0050 |
| *Change* | -x | +x | +x |
| *Equil* | 0.050 – x | x | x |

$K_b = K_w/K_a = 4.35 \times 10^{-6} = x^2/(0.050 - x)$ *and* $x = 4.66 \times 10^{-4}$ M *(can assume x << 0.050)*

$pH = 14 + \log[OH^-] = \mathbf{10.67}$

5. How many moles of $NaCH_3CO_2$ should be added to 100.0 mL of 0.150 M $CH_3CO_2H$ to make a pH = 5.00 buffer. $pK_a$ ($CH_3CO_2H$) = 4.76. (8 pts)

*$pH = pK_a + \log[CH_3CO_2^-]/[CH_3CO_2H]$ or $= pK_a + \log[n(CH_3CO_2^-)/n(CH_3CO_2H)]$*
*$5.00 = 4.76 + \log[n(CH_3CO_2^-)/(0.100\ L)(0.150\ mol/L]$*
*$10^{0.24} = n(CH_3CO_2^-)/(0.0150\ mol)$ and $n(CH_3CO_2^-) = 1.738 \cdot 0.0150\ mol$ = **0.026 mol***

6. Aminobenzene is a weak base ($pK_a$ for conjugate acid is 4.601). It is desired to analyze for it in a complex sample by reversed phase HPLC, which requires the main form of it to be in an uncharged form (not as an ion).
a) A scientist tries to analyze it using a mobile phase of methanol and water buffered with acetic acid/sodium acetate to a pH of 5.20. Calculate the fraction of aminobenzene in the uncharged form (assuming that aminobenzene does not change the pH and that the fraction in the uncharged form is not affected by methanol). (8 pts)
*The uncharged form is the base form (B vs. $BH^+$ for the charged form)*
*Can calculate $\alpha(B) = K_a/([H^+] + K_a) = 10^{-4.601}/(10^{-5.20} + 10^{-4.601})$ = **0.80***

b) How will an increase in the % of methanol in the HPLC mobile phase affect retention of aminobenzene? (3 pts)
*Methanol is less polar and is the strong eluent, so increasing the % methanol will decrease retention.*

BONUS 2) In the intial analysis it turns out that aminobenzene elutes at almost the same time as another compound (call it compound X) in the sample so the resolution is very bad (<1). It is known that compound X has no acid or base functional groups. Suggest a change in the eluent that will allow better separation of aminobenzene and compound X and describe the expected effect of the change. (3 pts)
*Since compound X is not an acid or a base, its retention should be independent of pH. For the base, **decreasing pH** will decrease $\alpha(B)$ and **decrease retention** (ion is not retained). **This would result in resolution by having B elute before X**. Could also **increase pH which would cause B to elute later than X**.*

7. A 25.0 mL aliquot of 0.0340 M NaOH is being titrated by 0.0250 M HCl. What is the pH after 30.0 mL of HCl has been added? (8 pts)

*n(NaOH) = [NaOH]V(NaOH) = 0.850 mmol   n(HCl) = [HCl]V(HCl) = 0.750 mmol*
*so excess NaOH at this point.*
*$[OH^-] = (0.85 - 0.75\ mmol)/(25.0 + 30.0\ mL) = 0.00182\ M$*
*$pH = 14 + \log[OH^-]$ = **11.260***