Chemistry 222 **Name**______________________________
Spring 2020 **80 Points**
Exam 2: Chapters 6-7

Complete problem 1 and four (4) of problems 2-6. CLEARLY mark the problem you do not want graded. Show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures and with the appropriate units.

You <u>MUST</u> do problem 1. (16 points)

1. Consider a 0.010 M silver nitrate solution that is saturated with silver carbonate **AND** silver chloride. Set up the equations necessary to determine the solubility of silver carbonate, considering the equilibria below. You must write the charge balance expression and at least one mass balance. *Identify all unknowns and write enough explicit, independent mass balance, charge balance, and equilibrium expressions so that only algebra remains to solve for the unknowns.* ***<u>A numerical answer is not necessary</u>***.

Ag_2CO_3	$K_{sp} = 8.1 \times 10^{-12}$	H_2CO_3	$K_{a1} = 4.46 \times 10^{-7}$, $K_{a2} = 4.69 \times 10^{-11}$
$AgCl$	$K_{sp} = 1.8 \times 10^{-10}$	H_2O	$K_w = 1.0 \times 10^{-14}$

8 unknowns, need 8 equations (unknowns are in BOLD and UNDERLINED)

$AgNO_3 \rightarrow Ag^+ + \underline{\mathbf{NO_3^-}}$	Completely dissociates
$AgCl\ (s) = \underline{\mathbf{Ag^+}} + \underline{\mathbf{Cl^-}}$	$K_{sp} = [Ag^+][Cl^-]$
$Ag_2CO_3\ (s) = 2\ Ag^+ + \underline{\mathbf{CO_3^{2-}}}$	$K_{sp} = [Ag^+]^2[CO_3^{2-}]$
$\underline{\mathbf{H_2CO_3}} = \underline{\mathbf{HCO_3^-}} + H^+$	$K_{a1} = [HCO_3^-][H^+]/[H_2CO_3]$
$HCO_3^- = CO_3^{2-} + \underline{\mathbf{H^+}}$	$K_{a2} = [CO_3^{2-}][H^+]/[HCO_3^-]$
$H_2O = H^+ + \underline{\mathbf{OH^-}}$	$K_w = [H^+][OH^-]$

Charge Balance:

$$[Ag^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [Cl^-] + [NO_3^-]$$

Mass Balance:

$$[NO_3^-] = 0.010\ M$$

$$[Ag]_{total} = 2[CO_3]_{total} + [Cl]_{total} + [NO_3^-]$$
$$[Ag^+] = 2([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]) + [Cl^-] + 0.010M$$

Complete four (4) of problems 2-6. CLEARLY mark the problem you do not want graded. (16 points each)

2. In determining activity coefficients of ions, there are three primary factors that play a role. Identify these factors and briefly describe the role of these factors on the activity of an ion. Under what combination of these factors are we safest in assuming that activities and concentrations are equal?

   Each affect has an impact on the tendency for an ion to interact with other charged species in solution. Your description should illustrate this.

   1. Ion Size or Hydrated diameter (α): The more strongly solvated the ion is (larger α), the less likely it is to interact with competing ions in solution (larger γ).
   2. Ionic charge (z): The larger the charge, the greater the electrostatic interaction with competing ions (smaller γ).
   3. Ionic strength (μ): The greater the effective concentration of ions in solution, the more opportunities for the ion of interest to interact with competing species (smaller γ).

   So, the combination of larger ion size, smaller charge and lower ionic strength leads to a situation where activity coefficients approach 1 and activities and concentrations become interchangeable.

3. A solution is prepared by mixing 0.175 grams sodium hydroxide, 25.0 mL 0.120 M hydrochloric acid and 20.0 mL 1.00 M acetic acid (pK_a = 4.75) and diluting to 100.0 mL. What is the pH of the resulting solution? *Do not consider activities.*

To deal with this problem, we first must determine what's left after the strong base NaOH, strong acid HCl and weak acid acetic acid (HA) have the opportunity to react,

First the strong acid/strong base will react until the limiting reactant is consumed:

	HCl	+	NaOH	⇄	NaCl	+	H_2O
Start	3.00 mmol		4.375 mmol		0		0
End	0		1.375 mmol		3.00 mmol		3.00 mmol

Now the remaining strong base can react with the weak acid.

	HA	+	OH^-	⇄	A^-	+	H_2O
Start	20.0 mmol		1.375 mmol		0		--
End	18.625 mmol		0		1.375 mmol		--
Concentrations	18.625mmol/100 mL		0		1.375 mmol/100 mL		--
	= 0.1862_5 M		0		= 0.0137_5 M		

Now solve the equilibrium:

	HA	⇄	H^+	+	A^-
I	0.1862_5 M		0		0.0137_5 M
C	-x		+x		+x
E	0.1862_5 -x		x		0.0137_5 +x

$$K_a = (x)(0.0137_5 + x)/(0.1862_5 - x)$$
$$(0.1862_5 - x)K_a = 0.\ 0.0137_5\, x + x^2$$
$$0 = x^2 + (0.0137_5 + K_a)x - 0.1862_5 K_a$$
$$x = 2.365 \times 10^{-4}\text{M}, -1.40\times10^{-2}\text{M}$$

Since a negative value for x makes no chemical sense, the appropriate solution is:

$x = 2.365 \times 10^{-4}$M = $[H^+]$, or pH = $-\log[H^+]$ = 3.63

Note: Making the assumption that $x \ll 0.1862$ M turns out to be reasonable and simplifies the math, while giving the same pH.

4. Given your unnatural passion for solution equilibria, you have been assigned the task of teaching a Quantitative Analysis class about the role of charge and mass balance in equilibrium systems. Briefly *define and illustrate* each term, using a solution containing 0.020 M HNO_3, 0.010 M KNO_3 and 0.10 M oxalic acid ($H_2C_2O_4$, $pK_{a1} = 1.252$, $pK_{a2} = 4.266$) as an example. Your answer must include example mass and charge balance expressions.

Mass Balance illustrates the conservation of mass. (total moles of an atom at any time must be the same as the total moles of the atom introduced)
Charge Balance is a result of the necessity for the solution to be electrically neutral.

Possible Mass Balance:

$0.10\ M = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$

$0.030\ M = [NO_3^-]$

$0.010\ M = [K^+]$

$[H^+] = 0.020M + [HC_2O_4^-] + 2[C_2O_4^{2-}] + [OH^-]$

Charge Balance:

$[H^+] + [K^+] = [NO_3^-] + [HC_2O_4^-] + 2[C_2O_4^{2-}] + [OH^-]$

5. Sodium sulfate is slowly added to a solution containing 0.0500 M $Ca^{2+}(aq)$ and 0.0320 M $Ag^{+}(aq)$. The K_{sp} for calcium sulfate is 4.93×10^{-5} and the K_{sp} for silver sulfate is $1.20 \times 10^{-5.}$
   a. What will be the concentration of $Ca^{2+}(aq)$ when $Ag_2SO_4(s)$ begins to precipitate?

   This is problem 14 from the chapter 6 Sapling assignment.

   First, use K_{sp} find the concentration of sulfate required to precipitate Ag_2SO_4:

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$
$$[SO_4^{2-}] = K_{sp}/[Ag^+]^2 = 1.2\text{x}10^{-5}/(0.0320\text{M})^2 = 0.01172\text{M}$$

   What concentration of Ca^{2+} remains at this $[SO_4^{2-}]$?

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$
$$[Ca^{2+}] = K_{sp}/[SO_4^{2-}] = 4.93 \times 10^{-5}/0.01172\text{M} = 0.004207\text{ M} = \mathbf{4.21 \times 10^{-3}\ M}$$

   b. What percentage of the $Ca^{2+}(aq)$ can be precipitated from the $Ag^{+}(aq)$ by this selective precipitation process??

   The percent removed is calculated by comparing the amount remaining to the initial amount of calcium:

$$\%\text{ precipitated} = \frac{[Ca]_{initial} - [Ca]_{final}}{[Ca]_{initial}} \times 100\% = \frac{0.0500 - 0.00421}{0.0500} \times 100\% = \mathbf{91.6\%}$$

6. *Using activities*, calculate the fluoride concentration in a saturated solution of calcium fluoride in a solution that is 0.010 F magnesium nitrate and 0.020 F sodium chloride. The K_{sp} for calcium fluoride is 3.2 x 10^{-11}, assume that all other salts are soluble. You may ignore the autoprotolysis of water and any acid-base character of fluoride. What fluoride concentration do you calculate if you ignore activities?

	CaF_2 =	Ca^{2+}	+	$2F^-$
I	--	0		0
C	--	+x		+2x
E	--	x		2x

$$K_{sp} = A_{Ca2+}(A_{F-})^2 = \gamma_{Ca2+}[Ca^{2+}](\gamma_{F-}[F^-])^2 = \gamma_{CA2+}x(\gamma_{f-}2x)^2 = \gamma_{Ca2+}(\gamma_{F-})^2 4x^3$$

Since K_{sp} is so small, little dissolution of CaF_2 will occur, and the ionic strength will be determined by the concentrations of $Mg(NO_3)_2$ and NaCl.

$$\mu = ½\{[Mg^{2+}](+2)^2 + [NO_3^-](-1)^2 + [Na^+](+1)^2 + [Cl^-](-1)^2 \} ½$$
$$\mu = ½\,(0.010M(4) + 0.020\ M(1) + 0.020\ M(1) + 0.020\ M(1)) = 0.050\ M$$

Using the table of activity coefficients at this ionic strength, γ_{Ca2+} = 0.485, γ_{F-} = 0.81. (The Debye-Huckel equation gives similar values.)

Therefore, the expression to solve is: $3.2 \times 10^{-11} = (0.485)(0.81)^2 4x^3$

Given these values, and solving for x, x = 2.93 x 10^{-4} M, **$[F^-]$ = 2x = 5.86 x 10^{-4} M**

Ignoring activities, the K_{sp} expression becomes *$3.2 \times 10^{-11} = 4x^3$* and x = 0.0002 and

$[F^-]$ = 2x = 4.00 x 10^{-4} M

Possibly Useful Information

$K_aK_b = K_W = 1.0 \times 10^{-14}$	$pH = -\log [H^+]$
$y = mx + b$	$pH + pOH = 14$
$\log\gamma = \dfrac{-0.51z^2\sqrt{\mu}}{1+\left(\alpha\sqrt{\mu}/305\right)}$ (with α in pm)	$\mu = \dfrac{1}{2}\sum_i c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT\ln K$	$x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, H_2citrate$^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2						
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, Hcitrate^{2-}	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3						
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
citrate^{3-}	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4						
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table. SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675.

Periodic Table of the Elements

IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	VIIIA 8A
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.631	33 **As** Arsenic 74.922	34 **Se** Selenium 78.971	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
37 **Rb** Rubidium 85.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.414	49 **In** Indium 114.818	50 **Sn** Tin 118.711	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.294
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.328	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [278]	110 **Ds** Darmstadtium [281]	111 **Rg** Roentgenium [280]	112 **Cn** Copernicium [285]	113 **Nh** Nihonium [286]	114 **Fl** Flerovium [289]	115 **Mc** Moscovium [289]	116 **Lv** Livermorium [293]	117 **Ts** Tennessine [294]	118 **Og** Oganesson [294]

Lanthanide Series	57 **La** Lanthanum 138.905	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.243	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.055	71 **Lu** Lutetium 174.967
Actinide Series	89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]