Chemistry 222 **Name**____
Spring 2021 **80 Points**
Exam 2: Chapters 6-7

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

You MUST complete problem 1. (16 pts.)

1. When ammonium sulfate dissolves, both the anion and the cation can participate in acid-base equilibria. Considering all the equilibria reflected by the equilibrium constants below, write enough equations so that you could solve for the concentration of each species in ***a solution that is saturated with ammonium sulfate and also contains 0.20 M potassium nitrate.*** You must write the charge balance expression and at least one mass balance. *Identify all unknowns and write enough explicit, independent equations so that only algebra remains to solve for the unknowns. A numerical answer is not necessary. Ignore activities.*

$(NH_4)_2SO_4(s)$	$K_{sp} = 276$
NH_4^+	$K_a = 5.7 \times 10^{-10}$
SO_4^{2-}	$K_b = 9.8 \times 10^{-13}$
H_2O	$K_w = 1.0 \times 10^{-14}$

Reactions (Unknowns are in **Bold**):

$$(NH_4)_2SO_4(s) \rightleftharpoons 2\mathbf{NH_4^+} + \mathbf{SO_4^{2-}}$$

$$NH_4^+ \rightleftharpoons \mathbf{NH_3} + \mathbf{H^+}$$

$$SO_4^{2-} + H_2O \rightleftharpoons \mathbf{HSO_4^-} + \mathbf{OH^-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$KNO_3 \rightarrow \mathbf{K^+} + \mathbf{NO_3^-}$$

So, we need a total of eight equations for our eight unknowns.

Charge Balance (4)

$$[NH_4^+] + [H^+] + [K^+] = 2[SO_4^{2-}] + [HSO_4^-] + [OH^-] + [NO_3^-]$$

Mass Balance: (8)

total concentration of nitrogen from ammonium = 2(total concentration of sulfur from sulfate)

$$[N]_{total} = 2[S]_{total}$$

$$[NH_3] + [NH_4^+] = 2[SO_4^{2-}] + 2[HSO_4^-]$$

Concentrations of Na^+ and NO_3 are constant

$$[K^+] = 0.20\ M$$

$$[NO_3^-] = 0.20\ M$$

Equilibrium constant expressions: (4)

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad K_{sp} = [NH_4^+]^2\,[SO_4^{2-}] \qquad K_w = [H^+]\,[OH^-]$$

$$K_b = \frac{[HSO_4^-][OH^-]}{[SO_4^{2-}]}$$

We now have enough equations to solve for all of the unknowns

Do four of problems 2-6. Clearly mark the problems you do not want graded. (16 pts. ea.)

2. Consider the table of activity coefficients below. As you move from left to right across any row on the table, the values for activity coefficient decrease. As you move down in a given column, the activity coefficient also decreases. Clearly describe the phenomena that cause these trends. **Do not simply point out the trends**; *you must explain why the trends are observed*. No calculations are necessary.

	Ionic Strength		
Species	**0.001 M**	**0.01 M**	**0.1 M**
hydronium ion	0.967	0.914	0.830
nitrate ion	0.964	0.899	0.755
calcium ion	0.870	0.675	0.405
sulfate ion	0.867	0.660	0.355
phosphate ion	0.725	0.395	0.095

The cause for both trends is rooted in electrostatic interactions between the ion of interest and other materials in solution. Moving left to right across a row in the table, the ionic strength of the solution increases. As μ increases, there is a greater probability that the ion of interest will undergo an interaction with a third-party ion in solution, thus decreasing its activity in the reaction of interest. Moving down in the table, the charge on the ion is increasing. This increase in charge provides for stronger electrostatic interactions with all other ions in solution, also reducing activity. For ions of the same charge, the ion with smaller hydrated ion size is more likely to interact with other competing ions in solution, decreasing the activity coefficient.

3. Aziridine (C_2NH_5) is a monobasic weak base with a pK_b of 5.96. Calculate the pH of a solution prepared by mixing 20.0 mL of 0.025 M HCl with 50.0 mL of 0.036 M aziridine and diluting the resulting solution to 100.0 mL. *Do not consider autoprotolysis or activities*.

Whenever you mix a strong acid with a weak base, they will react until one is completely consumed. Whatever remains after the reaction is complete will determine pH.

(6) What's left after HCl and aziridine react? (I'll call the aziridine "B")

	HCl	+	B	→	BH^+	+	Cl^-
Start (mmol)	0.50		1.8		0 mmol		0 mmol
End (mmol)	0.50-0.50 = 0		1.8-0.5 = 1.3		0.50		0.50
Concentration(M)	0		1.3mmol/100mL = 0.013 M		0.50mmol/100 mL = 0.0050M		0.0050 M

(10) Now the equilibrium:

	B	+	H_2O	⇄	BH^+	+	OH^-
I	0.013M		--		0.0050M		0
C	-x		--		+x		+x
E	0.013-x		--		0.0050+x		x

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$K_b = \frac{(0.0050+x)(x)}{0.013-x}$$

After some algebra, $0 = x^2 + (0.0050+K_b)x - 0.013K_b$

Solving for x, we get $x = [OH^-] = \mathbf{2.85\text{x}10^{-6}\ M}$, $[H^+] = K_w/[OH^-] = 2.85_1\text{x}10^{-9}$ M

$$\mathbf{pOH = 5.54_5}$$

$$\mathbf{pH = 14\text{-}pOH = 8.45_5}$$

You can simplify the math a little if your realize this is a buffer solution and that we would not expect the equilibrium concentrations to vary much from their original concentrations, essentially assuming x<<0.0050 M. In doing so, the K_b expression becomes:

$$K_b = \frac{0.0050x}{0.013}$$

Solving for x produces the same result as above since $2.85\text{x}10^{-6} << 0.0050$

A third approach would be to recognize that, after reaction with HCl, a buffer solution is formed, and Henderson Hasslebach equation could be used:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

$$pH = (14\text{-}pK_b) + \log \frac{[B]}{[BH^+]}$$

$$pH = 8.04 + \log \frac{[0.013]}{[0.0050]} = \mathbf{8.45}$$

4. *Using activities*, find the mercury concentration of a solution of 0.025 M K_2SO_4 that is saturated with $Hg(SCN)_2$ (K_{sp} for $Hg(SCN)_2$ is 2.8×10^{-20}). Assume that all other salts are soluble. You may ignore the autoprotolysis of water and any acid-base character of sulfate and thiocyanate. Compare this result to that obtained if you were to ignore activities.

(4) Let's set up the system first:

	$Hg(SCN)_2$ =	Hg^{2+} +	$2\ SCN^{2-}$
i	-	0	0
c	-	+x	+2x
e	-	x	2x

$$Ksp = A_{Hg2+}(A_{SCN-})^2 = \gamma_{Hg2+}[Hg^{2+}](\gamma_{SCN-}[SCN^-])^2 = \gamma_{Hg2+}(x)(\gamma_{SCN-}(2x))^2 = 4(\gamma_{Hg2+})(\gamma_{SCN-})x^3$$

$$x = [Hg^{2+}] = \left[\frac{K_{sp}}{4(\gamma_{Hg2+})(\gamma_{SCN-})^2}\right]^{1/3}$$

(4)To find activity coefficients, we need to calculate ionic strength:

$[SO_4^{2-}] = 0.025$ M

$[Li^+] = 2(0.025M) = 0.050$ M

$\mu = 1/2([Li^+]\,(+1)^2 + [SO_4^{2-}](-2)^2) = 1/2(0.050(1) + 0.025(4)) = 0.075$ M

(4) To find activity coefficients, we can either use the Debye-Huckel equation or interpolate from the tabulated values, since $\mu = 0.075$ M is not explicitly given on the table

After interpolation, for $\mu = 0.075$ M, $\gamma_{Hg2+} = 0.423$, $\gamma_{SCN-} = 0.785$. If you use the D-H equation, you get $\gamma_{Hg2+} = 0.412$, $\gamma_{SCN-} = 0.783$

$$x = [Hg^{2+}] = \left[\frac{K_{sp}}{4(\gamma_{Hg2+})(\gamma_{SCN-})^2}\right]^{1/3} = \left[\frac{K_{sp}}{4(0.423)(0.785)^2}\right]^{1/3}$$

Substituting into the equation above gives $[Hg^{2+}] = 2.99 \times 10^{-7}$ M

(4) Ignoring activities,

$$[Hg^{2+}] = x = \left[\frac{K_{sp}}{4}\right]^{1/3}$$

Which gives $[Hg^{2+}] = 1.91 \times 10^{-7}$ M

5. Complete both parts a and b. (8 points each)
   a. A saturated solution of Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$) that originally had a volume of 1.00 L is allowed to evaporate until the solution volume is 0.500 L. How does the new concentration of Ag^+ compare to the concentration in the original solution? Clearly justify your response. *Do not consider activities*.

Since the solution was initially saturated, a decrease in solution volume will force an increase in the concentrations of Ba^{2+} and SO_4^{2-} in solution, leading to supersaturation. This increase will cause the K_{sp} for barium sulfate to be exceeded, resulting in the precipitation of $BaSO_4$, and a decrease in the concentration of Ba^{2+} and SO_4^{2-} back to their original values. Therefore, the $[Ba^{2+}]$ after evaporation will be the same as its initial concentration.

   b. In determining the pH of a solution that contains and 0.10 M formic acid ($K_a = 1.8 \times 10^{-4}$) and 0.10 M HF ($K_a = 6.8 \times 10^{-4}$), why is the ICE table approach not a valid strategy to employ? What approach should be used instead? *Do not consider activities*.

Since we have two weak acids in solution, we must account for them simultaneously. That is, since H^+ appears in both equilibria and since there can only be one H^+ concentration in solution, that single concentration must satisfy both equilibrium constant expressions simultaneously. The ICE table approach only addresses one equilibrium at a time. Therefore, if you solve the ICE table for HF to determine $[H^+]$, the concentration you arrive at will not correspond to the equilibrium concentration for formic acid. You should use the systematic approaching using mass and charge balance instead.

6. Is it possible to perform a 99.99 % complete separation of barium and silver by precipitation with carbonate if both Ba^{2+} and Ag^{+} are present initially at 0.010 M? Justify your decision. *Do not consider activities*.

$BaCO_3$	$K_{sp} = 5.0 \times 10^{-9}$
Ag_2CO_3	$K_{sp} = 8.1 \times 10^{-12}$

Two equilibria to consider:

$BaCO_3 = Ca^{2+} + CO_3^{2-}$	$K_{sp} = 5.0 \times 10^{-9}$
$Ag_2CO_3 = 2Ag^{+} + CO_3^{2-}$	$K_{sp} = 8.1 \times 10^{-12}$

1. What $[CO_3^{2-}]$ is needed to lower each ion's concentration to 0.01% of its initial value?
Target $[Ba^{2+}] = 0.0001(0.010M) = 1.0 \times 10^{-6}$ M, Target $[Ag^{+}] = 1.0 \times 10^{-6}$ M

$$Ba^{2+}: \quad [CO_3^{2-}] = \frac{K_{sp}}{[Ba^{2+}]} = \frac{5.0 \times 10^{-9}}{1.0 \times 10^{-6}\ M} = \mathbf{0.0050\ M\ CO_3^{2-}}$$

$$Ag^{+}: \quad [CO_3^{2-}] = \frac{K_{sp}}{[Ag^{+}]^2} = \frac{8.1 \times 10^{-12}}{(1.0 \times 10^{-6}\ M)^2} = \mathbf{8.10\ M\ CO_3^{2-}}$$

So, Ba^{2+} will precipitate first.

2. Will Ag^{+} precipitate if $[CO_3^{2-}] = 0.0050$ M?
$Q = [Ag^{+}]^2[CO_3^{2-}] = (0.010\ M)^2(0.0050\ M) = 5.0 \times 10^{-7}$

Since $Q > K_{sp}$ for Ag_2CO_3, Ag^{+} will precipitate before $[Ba^{2+}] = 1.0 \times 10^{-6}$ M.
Separation is not feasible.

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^-, $H_2\text{citrate}^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	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-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $H\text{citrate}^{2-}$	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]

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