

Chemistry 222
Spring 2011
Exam 2: Chapters 5-7
80 Points

Name _____

Complete two (2) of problems 1-3, problem 4, and three (3) of problems 5-8. 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.

Do two of problems 1-3. Clearly mark the problem you do not want graded. (10 pts each)

1. A saturated solution of BaSO_4 ($K_{\text{sp}} = 1.1 \times 10^{-10}$) that originally held a volume of 1.00 L is allowed to evaporate until the solution volume is 0.500 L. How does the new concentration of Ba^{2+} compare to the concentration in the original solution? Justify your response.

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 $[\text{Ba}^{2+}]$ after evaporation will be the same as its initial concentration.

2. Consider the table of activity coefficients on the last page of this exam. 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. No calculations are necessary.

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.

3. Given your unnatural passion for simultaneous 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 0.0010 M HCl and 0.10 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, $\text{pK}_{\text{a}1} = 1.252$, $\text{pK}_{\text{a}2} = 4.266$) as an example. Your answer should 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:

$$0.10 \text{ M} = [\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$$

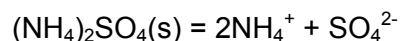
$$0.0010 \text{ M} = [\text{Cl}^-]$$

Charge Balance:

$$[\text{H}^+] = [\text{Cl}^-] + [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-]$$

Do problem 4. (15 pts)

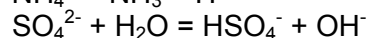
4. When ammonium sulfate dissolves, both the anion and the cation can participate in acid-base equilibria. Considering the equilibria below, write enough equations so that you could solve for the concentration of each species in solution. You must write the charge balance expression and at least one mass balance. A numerical result isn't necessary.



$$K_{\text{sp}} = 276$$



$$K_{\text{a}} = 5.7 \times 10^{-10}$$



$$K_{\text{b}} = 9.8 \times 10^{-13}$$

Charge Balance:

$$[\text{NH}_4^+] + [\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{OH}^-]$$

Mass Balance:

total concentration of nitrogen (ammonia) = 2(total concentration of sulfur (sulfate))

$$[\text{NH}_3] + [\text{NH}_4^+] = 2[\text{SO}_4^{2-}] + 2[\text{HSO}_4^-]$$

One approach to solve for $[\text{NH}_3]$:

1. Get everything in terms of $[\text{H}^+]$ and one variable (such as $[\text{NH}_3]$ or $[\text{NH}_4^+]$)

$$[\text{NH}_3] = \frac{K_{\text{a}}[\text{NH}_4^+]}{[\text{H}^+]}, \quad [\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{NH}_4^+]^2}, \quad [\text{OH}^-] = \frac{K_{\text{w}}}{[\text{H}^+]}$$

$$[\text{HSO}_4^-] = \frac{K_{\text{b}}[\text{SO}_4^{2-}]}{[\text{OH}^-]} = \frac{K_{\text{b}}[\text{H}^+][\text{SO}_4^{2-}]}{K_{\text{w}}} = \frac{K_{\text{b}}K_{\text{sp}}[\text{H}^+]}{K_{\text{w}}[\text{NH}_4^+]^2}$$

2. Substitute these expressions into the charge balance equation:

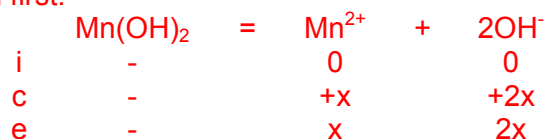
$$\frac{K_{\text{a}}[\text{NH}_4^+]}{[\text{H}^+]} + [\text{NH}_4^+] = \frac{2K_{\text{sp}}}{[\text{NH}_4^+]^2} + \frac{K_{\text{b}}K_{\text{sp}}[\text{H}^+]}{K_{\text{w}}[\text{NH}_4^+]^2} + \frac{K_{\text{w}}}{[\text{H}^+]}$$

3. Solve the charge balance for $[\text{NH}_4^+]$, use this concentration and $[\text{H}^+]$ to get $[\text{NH}_3]$ from the K_{a} expression

Do three of probs 5-8. Clearly mark the problem you do not want graded. (15 pts each)

5. Using activities, show how to find the pH of a solution of 0.0167 M Na₂SO₄ saturated with Mn(OH)₂ (K_{sp} for Mn(OH)₂ is 2.0 x 10⁻¹³). You do not need a numerical solution, just determine the value for the activity coefficients and generate an expression that could be solved for [OH⁻]. Would the pH be larger or smaller if you ignore activities?

Let's set up the system first:



$$K_{sp} = A_{Mn^{2+}}(A_{OH^-})^2 = \gamma_{Mn^{2+}}[Mn^{2+}](\gamma_{OH^-}[OH^-])^2 = \gamma_{Mn^{2+}}(x)(\gamma_{OH^-}(2x))^2 = 4\gamma_{Mn^{2+}}(\gamma_{OH^-})^2x^3$$

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

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

$$[Na^{2+}] = 2(0.0167M) = 0.0334 M; [SO_4^{2-}] = 0.0167 M$$

$$\mu = 1/2([Na^+](+1)^2 + [SO_4^{2-}](-2)^2) = 1/2(0.0334(1) + 0.0167(4)) = 0.050 M$$

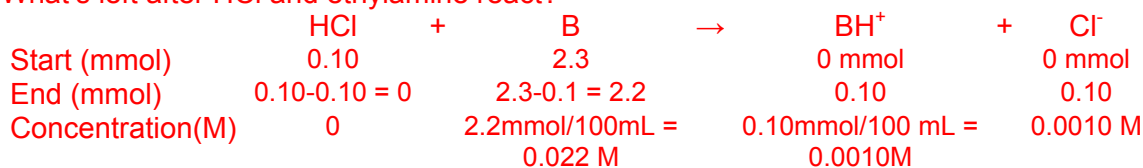
$$\text{For } \mu = 0.050 M, \gamma_{Mn^{2+}} = 0.48, \gamma_{OH^-} = 0.81$$

Substituting into the equation above gives [OH⁻] = 1.08 x 10⁻⁴ M, pH = 10.03

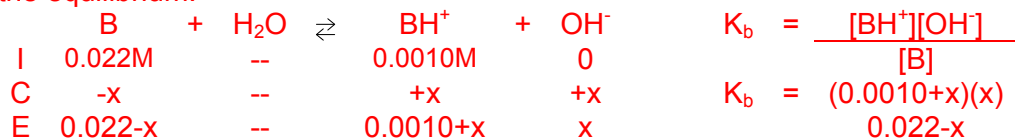
Ignoring activities, [OH⁻] = 7.4 x 10⁻⁵ M, pH = 9.87

6. Ethylamine (CH₃CH₂NH₂) is a monobasic weak base with a pK_b of 3.33. Calculate the pH of a solution prepared by mixing 10.0 mL of 0.010 M HCl with 50.0 mL of 0.046 M ethylamine (CH₃CH₂NH₂) and diluting the resulting solution to 100.0 mL. Do not consider activities.

What's left after HCl and ethylamine react?



Now the equilibrium:



After some algebra, $0 = x^2 + (0.0010+K_b)x - 0.022K_b$

Solving for x, we get $x = [OH^-] = 0.002557M$, $[H^+] = K_w/[OH^-] = 3.91_1 \times 10^{-12} M$

pH = 11.41.

7. Clearly describe the case when it is preferable to use calibration by standard additions, rather than a traditional calibration curve for an analysis. Include an example of how you would run the experiment and extract an unknown concentration from your data.

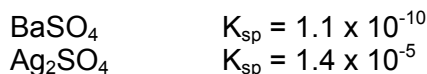
Calibration by standard additions is appropriate when the sample composition is unknown or complex and affects the analytical signal. This matrix effect makes it difficult to prepare reliable standards.

Here is one procedure for using standard additions:

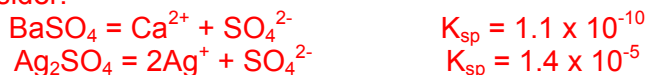
1. Prepare several solutions, each "spiked" with a different (and known) concentration of analyte (including "0")
2. Perform analysis using each solution
3. Plot signal vs. added analyte concentration
4. Calculate least-squares line
5. Extrapolate the line to the x-intercept. The unknown concentration corresponds to the value at the x-intercept.

It is also possible to run standard additions with only two samples, an adequate description if this alternate procedure was also acceptable.

8. Is it possible to perform a 99.9 % complete separation of barium and silver by precipitation with sulfate if both Ba^{2+} and Ag^+ are present initially at 0.020 M? Justify your decision.



Two equilibria to consider:



1. What $[\text{SO}_4^{2-}]$ is needed to lower each ion's concentration to 1% of its initial value? Target $[\text{Ba}^{2+}] = 0.001(0.020\text{M}) = 2.0 \times 10^{-5}\text{M}$, Target $[\text{Ag}^+] = 2.0 \times 10^{-5}\text{M}$

$$\text{Ba}^{2+}: [\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ba}^{2+}]} = \frac{1.1 \times 10^{-10}}{2.0 \times 10^{-5}\text{M}} = 5.5 \times 10^{-6}\text{M SO}_4^{2-}$$

$$\text{Ag}^+: [\text{SO}_4^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{1.4 \times 10^{-5}}{(2.0 \times 10^{-5}\text{M})^2} = 3.5 \times 10^4\text{M SO}_4^{2-} \text{ (wow!)}$$

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

2. Will Ag^+ precipitate if $[\text{SO}_4^{2-}] = 5.5 \times 10^{-6}\text{M}$?
 $Q = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (0.020\text{M})^2(5.5 \times 10^{-6}\text{M}) = 2.2 \times 10^{-9}$

Since $Q < K_{\text{sp}}$ for Ag_2SO_4 , Ag^+ will not precipitate before $[\text{Ba}^{2+}] = 2.0 \times 10^{-5}\text{M}$.
Separation is feasible.

Possibly Useful Information

$K_a K_b = K_w = 1.0 \times 10^{-14}$	Don't eat the yellow snow.
$-\log \gamma = \frac{0.51z^2 \sqrt{\mu}}{1 + \alpha \sqrt{\mu}/305}$	$\mu = \frac{1}{2} \sum c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT \ln K$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\frac{I_x}{I_{s+x}} = \frac{k[X]_i}{k([S]_f + [X]_f)} = \frac{[X]_i}{[S]_f + [X]_f}$	$\frac{\text{Analyte Signal}}{\text{Analyte Concentration}} = F \left(\frac{\text{Standard Signal}}{\text{Standard Concentration}} \right)$

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 ₆ H ₅) ₂ CHCO ₂ ⁻ , (C ₃ H ₇) ₄ N ⁺	800	0.966	0.931	0.912	0.85	0.82
(O ₂ N) ₃ C ₆ H ₂ O ⁻ , (C ₃ H ₇) ₃ NH ⁺ , CH ₃ OC ₆ H ₄ CO ₂ ⁻	700	0.965	0.930	0.909	0.845	0.81
Li ⁺ , C ₆ H ₅ CO ₂ ⁻ , HOC ₆ H ₄ CO ₂ ⁻ , ClC ₆ H ₄ CO ₂ ⁻ , C ₆ H ₅ CH ₂ CO ₂ ⁻ , CH ₂ =CHCH ₂ CO ₂ ⁻ , (CH ₃) ₂ CHCH ₂ CO ₂ ⁻ , (CH ₃ CH ₂) ₄ N ⁺ , (C ₃ H ₇) ₂ NH ₂ ⁺	600	0.965	0.929	0.907	0.835	0.80
Cl ₂ CHCO ₂ ⁻ , Cl ₃ CCO ₂ ⁻ , (CH ₃ CH ₂) ₃ NH ⁺ , (C ₃ H ₇)NH ₃ ⁺	500	0.964	0.928	0.904	0.83	0.79
Na ⁺ , CdCl ⁺ , ClO ₂ ⁻ , IO ₃ ⁻ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , H ₂ AsO ₄ ⁻ , Co(NH ₃) ₄ (NO ₂) ₂ ⁺ , CH ₃ CO ₂ ⁻ , ClCH ₂ CO ₂ ⁻ , (CH ₃) ₄ N ⁺ , (CH ₃ CH ₂) ₂ NH ₂ ⁺ , H ₂ NCH ₂ CO ₂ ⁻	450	0.964	0.928	0.902	0.82	0.775
⁺ H ₃ NCH ₂ CO ₂ H, (CH ₃) ₃ NH ⁺ , CH ₃ CH ₂ NH 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 citrate ⁻ , CH ₃ NH ₃ ⁺ , (CH ₃) ₂ NH 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 ⁺ , TI ⁺ , 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 ₂ CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CH ₂ CO 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 ₆ H ₄ (CO ₂ ⁻) ₂ , H ₂ C(CH ₂ CO ₂ ⁻) ₂ , (CH ₂ CH ₂ CO ₂ ⁻) ₂	600	0.870	0.749	0.675	0.485	0.405
Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , S ₂ O ₄ ²⁻ , WO ₄ ²⁻ , H ₂ C(CO ₂ ⁻) ₂ , (CH ₂ CO 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) ₅ Cl ²⁺ , Fe(CN) ₅ NO ²⁻ , C ₂ O ₄ ²⁻ , Hcitrate ²⁻	450	0.867	0.742	0.665	0.455	0.37
Hg ₂ ²⁺ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₆ ²⁻ , S ₂ O 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) ₅ H ₂ O 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.