

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.

Bonus (4 points):

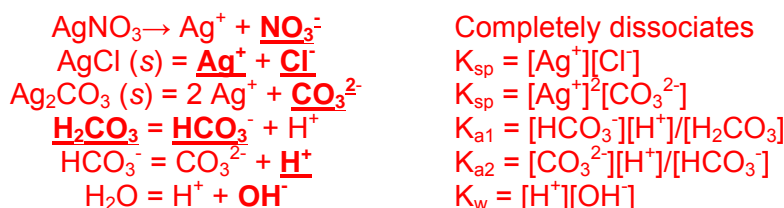
One day last week, Dr. Lamp told those in class a pH at 8:30 AM as he started class and said that the pH would be an answer to one of the exam 2 questions. What was that pH? 3.63

You MUST 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. A numerical answer is not necessary.*

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

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



Charge Balance:

$$[\text{Ag}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-]$$

Mass Balance:

$$[\text{NO}_3^-] = 0.010 \text{ M}$$

$$[\text{Ag}]_{\text{total}} = 2[\text{CO}_3]_{\text{total}} + [\text{Cl}]_{\text{total}} + [\text{NO}_3^-]$$

$$[\text{Ag}^+] = 2([\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]) + [\text{Cl}^-] + 0.010 \text{ M}$$

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.

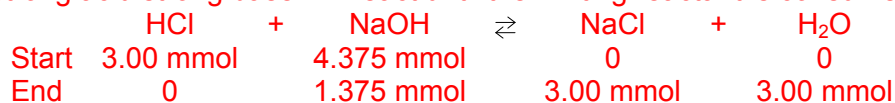
1. Ion Size or Hydrated diameter (α): The more strongly solvated the ion is (larger α), the less likely it is to interact with competing ions in solution (larger γ).
2. Ionic charge (z): The larger the charge, the greater the electrostatic interaction with competing ions (smaller γ).
3. Ionic strength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

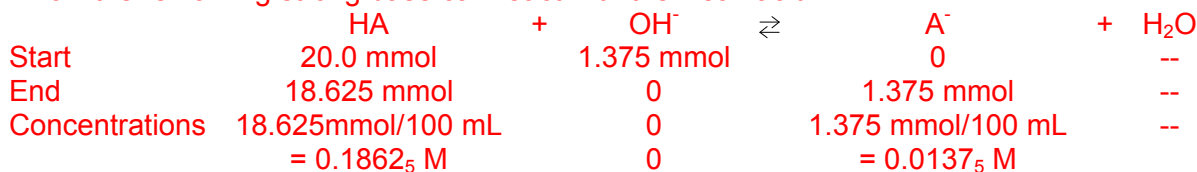
3. A solution is prepared by mixing 0.175 grams sodium hydroxide, 25.0 mL 0.120 M hydrochloric acid and 20.0 mL 1.00 M acetic acid ($pK_a = 4.75$) and diluting to 100.0 mL. What is the pH of the resulting solution? *Do not consider activities.*

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:



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



Now solve the equilibrium:



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

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

Note: Making the assumption that $x \ll 0.1862 \text{ M}$ 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 HNO₃, 0.010 M KNO₃ and 0.10 M oxalic acid (H₂C₂O₄, 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:

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

$$0.030 \text{ M} = [\text{NO}_3^-]$$

$$0.010 \text{ M} = [\text{K}^+]$$

$$[\text{H}^+] = 0.020\text{M} + [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-]$$

Charge Balance:

$$[\text{H}^+] + [\text{K}^+] = [\text{NO}_3^-] + [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{OH}^-]$$

5. 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 in the measured solution corresponds to the value at the x-intercept.
6. Account for dilutions to back-calculate the original composition of the unknown solution.

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

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 3.2×10^{-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?

	$\text{CaF}_2 =$	Ca^{2+}	+	2F^-
I	--	0		0
C	--	+x		+2x
E	--	x		2x

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

Since K_{sp} is so small, little dissolution of CaF_2 will occur, and the ionic strength will be determined by the concentrations of $\text{Mg}(\text{NO}_3)_2$ and NaCl .

$$\begin{aligned} \mu &= \frac{1}{2}\{[\text{Mg}^{2+}](+2)^2 + [\text{NO}_3^-](-1)^2 + [\text{Na}^+](+1)^2 + [\text{Cl}^-](-1)^2\} \frac{1}{2} \\ \mu &= \frac{1}{2}(0.010\text{M}(4) + 0.020\text{M}(1) + 0.020\text{M}(1) + 0.020\text{M}(1)) = 0.050\text{M} \end{aligned}$$

Using the table of activity coefficients at this ionic strength, $\gamma_{\text{Ca}^{2+}} = 0.485$, $\gamma_{\text{F}^-} = 0.81$. (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, $x = 2.93 \times 10^{-4}\text{M}$, **$[\text{F}^-] = 2x = 5.86 \times 10^{-4}\text{M}$**

Ignoring activities, the K_{sp} expression becomes $3.2 \times 10^{-11} = 4x^3$ and $x = 0.0002$ and **$[\text{F}^-] = 2x = 4.00 \times 10^{-4}\text{M}$**

Possibly Useful Information

$K_a K_b = K_w = 1.0 \times 10^{-14}$	$\text{pH} = -\log [\text{H}^+]$
$y = mx + b$	$S_{\text{LOD}} = S_{\text{blank}} + 3s_{\text{blank}}$
$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)}$ (with α in pm)	$\mu = \frac{1}{2} \sum_i c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT \ln K$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\frac{I_x}{I_{s+x}} = \frac{k[x]_i}{k([s]_f + [x]_f)} = \frac{[x]_i}{[s]_f + [x]_f}$	$\frac{\text{Analyte Signal}}{\text{Analyte Concentration}} = F \left(\frac{\text{Standard Signal}}{\text{Standard Concentration}} \right)$

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.

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES	
1 H 1.00797															1 H 1.00797	2 He 4.0026	
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atonic weights corrected to conform to the 1963 values of the Commission on Atonic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (258)	102 No (258)	103 Lr (257)
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