

You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

The take-home problem will account for 15 possible points on this exam.

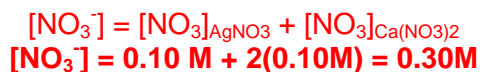
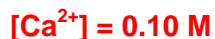
Complete problems 1-5

1. Consider a solution that contains 0.10 M AgNO₃ and 0.10 M Ca(NO₃)₂ and is *saturated* with AgCl.

a. Write the charge balance expression for this system. (4 points)



b. Write three independent mass balance expressions for this system (6 points)



2. Write the letter for the correct answer in the appropriate blank: (3 points each)

a. A buffer solution is most effective at a pH within _____ of the pK_a for the acid used to make the buffer.

- a. ±0.1
- b. ±1
- c. ±10
- d. ±100

Answer _____ **b** _____

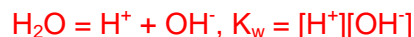
b. While the pH of a buffer is effectively independent of dilution, the capacity of the buffer _____ as it becomes more dilute.

- a. increases
- b. decreases
- c. stays the same
- d. peanut butter

Answer _____ **b** _____

3. Calculate the pH of a 2.2×10^{-7} F solution of KOH (8 points)

You **must** use charge (or mass) balance to solve this problem!



Charge Balance: $[\text{H}^+] + [\text{K}^+] = [\text{OH}^-]$

$$[\text{H}^+] + 2.2 \times 10^{-7} \text{ M} = \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^2 + 2.2 \times 10^{-7} \text{ M} [\text{H}^+] = K_w$$

$$0 = [\text{H}^+]^2 + 2.2 \times 10^{-7} \text{ M} [\text{H}^+] - K_w$$

Solve for $[\text{H}^+]$ using quadratic formula: $[\text{H}^+] = 3.87 \times 10^{-8} \text{ M}$, **pH = 7.41₃**

4. The pH of a 0.10 M solution of acetic acid ($\text{p}K_a = 4.76$) is measured to be 2.88. What fraction of the acetic acid is dissociated (present as acetate ion) at this pH? (6 points)

Consider the equilibrium $\text{HA} = \text{H}^+ + \text{A}^-$. Given that the pH of the solution is 2.88, when 0.10 M HA dissociates, it produces $10^{-2.88} = 1.318 \times 10^{-3} \text{ M}$ H^+ . Since an A^- is produced each time an H^+ is liberated, the $[\text{A}^-] = 1.318 \times 10^{-3} \text{ M}$ as well. Therefore the α_{A^-} can be calculated as:

$$\alpha_{\text{A}^-} = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} = \frac{1.318 \times 10^{-3} \text{ M}}{0.10 \text{ M}} = 0.013_2$$

There are a couple of other approaches as well that are equally valid.

5. Why is a sparingly soluble salt (like AgCl) more soluble in a solution that contains an inert electrolyte (like KNO_3) than in pure water alone? Limit your answer to no more than three sentences. (6 points)

The addition of an inert electrolyte increases the charge in the ion atmosphere around all ions in solution, including the ion of interest. This increased concentration and charge provides opportunities for the ions in our sparingly soluble salt to interact with dissolved ions in solution, thus encouraging more of the salt to dissolve.

Do three of problems 6-9. Clearly mark the problem you do not want graded. (15 pts ea.) I intentionally let LOTS of space for you, I do not expect that you will use all the space.

6. Complete both parts a and b.
- a. A saturated solution of Ag_2CO_3 ($K_{\text{sp}} = 8.1 \times 10^{-12}$) 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.*

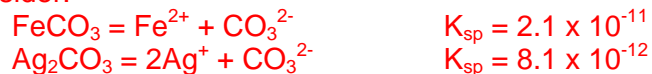
Since the solution was initially saturated, a decrease in solution volume will force an increase in the concentrations of Ba^{2+} and SO_4^{2-} in solution, leading to supersaturation. This increase will cause the K_{sp} for barium sulfate to be exceeded, resulting in the precipitation of BaSO_4 , and a decrease in the concentration of Ba^{2+} and SO_4^{2-} back to their original values. Therefore, the $[\text{Ba}^{2+}]$ 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 ($K_{\text{a}} = 1.8 \times 10^{-4}$) and 0.10 M HF ($K_{\text{a}} = 6.8 \times 10^{-4}$), 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 $[\text{H}^+]$, the concentration you arrive at will not correspond to the equilibrium concentration for formic acid.

7. You have a mixture that contains 0.0010M Ag^+ and 0.0010M Fe^{2+} . To this mixture you slowly add a solution of carbonate ion until a precipitate forms. What cation precipitates first? Justify your answer with appropriate calculations. K_{sp} for silver carbonate is 8.1×10^{-12} , K_{sp} for iron (II) carbonate is 2.1×10^{-11} .

Two equilibria to consider:



What is the minimum $[\text{CO}_3^{2-}]$ needed to reach the K_{sp} and cause precipitation to occur?

$$\text{Fe}^{2+}: [\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Fe}^{2+}]} = \frac{2.1 \times 10^{-11}}{0.0010 \text{ M}} = 2.1 \times 10^{-8} \text{ M CO}_3^{2-}$$

$$\text{Ag}^+: [\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ag}^+]^2} = \frac{8.1 \times 10^{-12}}{(0.0010 \text{ M})^2} = 8.1 \times 10^{-6} \text{ M CO}_3^{2-}$$

Since it requires a lower carbonate concentration to cause the iron carbonate to precipitate, Fe^{2+} will precipitate first, even though silver carbonate has a lower K_{sp} , because of the different stoichiometry of the two salts.

8. Consider a solution of 0.0025 M MgSO_4 that is saturated with $\text{Hg}(\text{SCN})_2$ (K_{sp} for $\text{Hg}(\text{SCN})_2$ is 2.8×10^{-20}).
- a. Determine the activity coefficients for Hg^{2+} and SCN^{2-} in this solution.

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

$$[\text{Mg}^{2+}][\text{SO}_4^{2-}] = 0.0025 \text{ M}$$

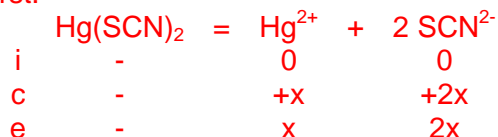
$$\mu = 1/2([\text{Mg}^{2+}] (+2)^2 + [\text{SO}_4^{2-}] (-2)^2) = 1/2(0.0025(+2)^2 + 0.0025(-2)^2) = 0.010 \text{ M}$$

From the table, for $\mu = 0.0050 \text{ M}$, $\gamma_{\text{Hg}^{2+}} = 0.67$, $\gamma_{\text{SCN}^{2-}} = 0.90$

(Using the Debye-Huckel equation would produce similar values)

- b. *Using activities*, find the mercury concentration in this solution. Compare this result to that obtained if you were to ignore activities

Let's set up the system first:



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

$$x = [\text{Hg}^{2+}] = \left[\frac{K_{\text{sp}}}{4(\gamma_{\text{Hg}^{2+}})(\gamma_{\text{SCN}^{2-}})^2} \right]^{1/3} = \left[\frac{K_{\text{sp}}}{4(0.67)(0.90)^2} \right]^{1/3}$$

Substituting into the equation above gives $[\text{Hg}^{2+}] = 2.35 \times 10^{-7} \text{ M}$

Ignoring activities,

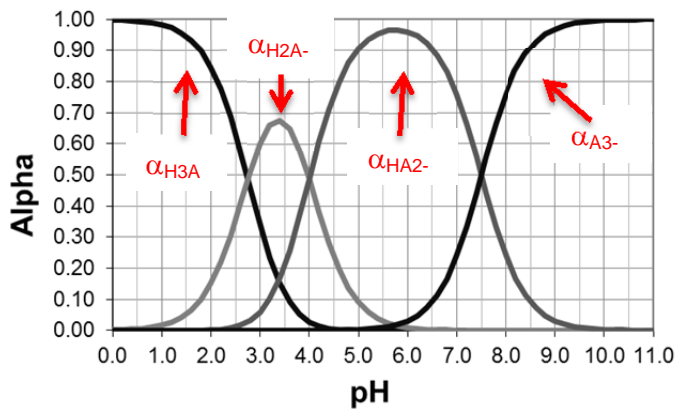
$$[\text{Hg}^{2+}] = x = \left[\frac{K_{\text{sp}}}{4} \right]^{1/3}$$

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

Therefore the salt is more soluble in the higher ionic strength solution, as expected.

9. For this problem consider the newly discovered *kick acid*, a triprotic weak acid of the form H_3A .
- a. The plot below represents the fraction of dissociation for kick acid. Label the four curves with their corresponding alphas (α_{H_3A} , $\alpha_{H_2A^-}$, $\alpha_{HA^{2-}}$, $\alpha_{A^{3-}}$) and determine the values for pK_{a1} , pK_{a2} , and pK_{a3} . (5 points)

The pK 's occur where alpha lines for two protonation states cross at 0.50. Therefore:
 $pK_{a1} = 2.75$
 $pK_{a2} = 4.00$
 $pK_{a3} = 7.50$



- b. Would you be able to make an effective pH 6.00 buffer using any of the forms of kick acid? Justify your response. (the plot above may be useful) (5 points)

Considering the plot above, at pH 6, almost all of the acid is present in a single state (HA^{2-}) and very small amounts are present as either H_2A^- or A^{3-} . Therefore, if you tried to prepare a pH 6 buffer, you would need to use a very large ratio of HA^{2-} to one of the other forms (likely A^{3-}). This large ratio would produce a buffer with incredibly poor capacity, leading to an ineffective buffer.

- c. Estimate is the maximum concentration of H_2A^- that can exist in a 0.200 F kick acid solution? (5 points)

Looking at the alpha plot above, the largest fraction of H_2A^- that can exist in solution is about 0.67, which occurs at about pH 3.4. Therefore in a 0.200 F solution at pH 3.4, the concentration of H_2A^- would be at its maximum at $0.67 \times 0.200F = 0.134$ M. At any other pH, the concentration would be smaller because the alpha would be smaller.

Possibly Useful Information

$-\log \gamma = \frac{0.51z^2\sqrt{\mu}}{1 + \alpha\sqrt{\mu}/305}$	$\mu = \frac{1}{2} \sum_i c_i z_i^2$
$\Delta G = \Delta H - T\Delta S = -RT \ln K$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = 1.00 \times 10^{-14}$	$\text{pH} = -\log[\text{H}^+]$
$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$	$\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$
$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$	$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$
$\alpha_{\text{A}^{2-}} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$	$K_a K_b = K_w$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	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.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic 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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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 ⁺ , 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 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.