

Complete problem 1 and four of problems 2-6. CLEARLY mark the problem 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 may ignore activity coefficients in all problems.

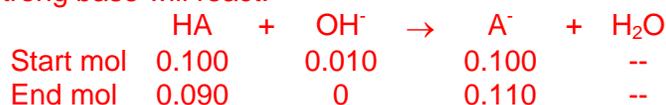
You MUST complete problem 1. (16 pts.)

1. Find the pH of a solution prepared by dissolving all of the following compounds in water in one beaker and diluting to a volume of 0.500 L: 0.100 mol acetic acid ($pK_a = 4.76$), 0.100 mol sodium acetate, 0.030 mol HNO_3 , and 0.040 mol NaOH.

We need to recognize that the strong acid and strong base will react until one is consumed:



Now, the excess strong base will react:



So, we now have a buffer with 0.090 mol acetic acid and 0.110 moles acetate:

$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}} = 4.76 + \log \frac{0.110 \text{ mol}}{0.090 \text{ mol}} = \mathbf{4.85}$$

In the end, **pH = 4.85**

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

2. Your new employer has asked you to prepare 1.00 L of a pH 7.00 buffer with a total phosphate concentration of 0.0500 M. You have at your disposal only the following compounds

Compound	K_a	Molar Mass (g/mol)
H_3PO_4	7.11×10^{-3}	97.9950
NaH_2PO_4	6.34×10^{-8}	119.9769
Na_2HPO_4	4.22×10^{-13}	141.9588
Na_3PO_4	--	163.9407

- a. Which two compounds would you use to prepare a buffer of pH 7.00 and how many grams of each of the two selected compounds would you need? (12 points)

When preparing a buffer, it is best to choose an acid/base pair whose pK_a is as close to the target pH as possible. This optimizes buffer capacity. In the case of the items at our disposal, the NaH_2PO_4/Na_2HPO_4 combination seems best since the pK_a for $H_2PO_4^-$ is 7.20.

First, determine the ratio of $HPO_4^{2-}/H_2PO_4^-$ needed for pH 7.00 by rearranging the Henderson Hasselbalch equation.:

$$\frac{\text{mol } HPO_4^{2-}}{\text{mol } H_2PO_4^-} = 10^{\text{pH}-\text{p}K_a} = 10^{7-7.20} = 0.6309$$

We also know that the total moles of $H_2PO_4^-$ and $HPO_4^{2-} = 1\text{L} \times 0.0500\text{M} = 0.0500$ mol.
So:

$$\begin{aligned} \text{mol } H_2PO_4^- + \text{mol } HPO_4^{2-} &= 0.0500 \text{ and} \\ \text{mol } HPO_4^{2-} &= 0.6309 \text{ mol } H_2PO_4^- \end{aligned}$$

Solving for each term, we find: $\text{mol } H_2PO_4^- = 0.0307$ mol and $\text{mol } HPO_4^{2-} = 0.0193$ mol

Masses for each salt:

$$0.0307 \text{ mol } NaH_2PO_4 \times \frac{119.9769 \text{ g } NaH_2PO_4}{1 \text{ mol } NaH_2PO_4} = 3.68 \text{ g } NaH_2PO_4$$

$$0.0193 \text{ mol } Na_2HPO_4 \times \frac{141.9588 \text{ g } Na_2HPO_4}{1 \text{ mol } Na_2HPO_4} = 2.74 \text{ g } Na_2HPO_4$$

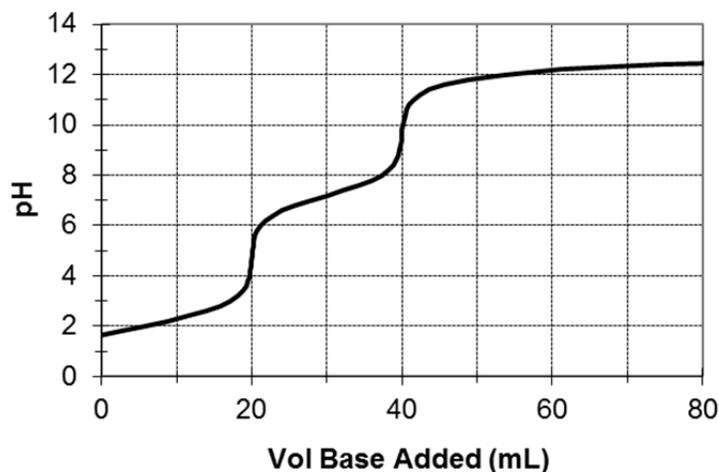
- b. If you did exactly what you calculated in part (a), you would not get a pH of *exactly* 7.00. Why? Explain how you would really prepare this buffer in lab. (4 points)

There are two considerations/assumptions we have made that will introduce some uncertainty in our result: (1) we have ignored the contribution of activities and (2) we have assumed that our initial concentrations of HA and A^- are reasonable approximations of the equilibrium concentrations. While these assumptions may be reasonable, they do introduce some error.

In practice, we could prepare the buffer as above and add small amounts of strong acid or base to fine tune the pH.

3. I've asked you to go into the lab and help me prepare some unknowns for a new acid/base titration experiment we are considering. Unfortunately, I have neglected to label one solution and am nowhere to be found. To identify the solution, you construct the titration curve below by titrating 20.00 mL of the acid solution with standard 0.100 M NaOH. From the titration curve and the list of possible solution compositions below, identify the composition of the solution. Justify your reasoning by explaining how you were able to rule out each of the imposters and choose the appropriate identity.

Solution	pK _a
A: 0.100 M maleic acid	1.83, 6.07
B: 0.100 M succinic acid	4.21, 5.64
C: 0.100 M phosphoric acid	2.15, 7.20, 12.35
D: 0.030 M HCl and 0.070 M acetic acid	strong, 4.76

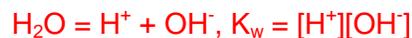


The presence of clearly-resolved breaks in the titration curve indicates the presence of at least two acidic protons with substantially different K_a 's. Also, the fact that the two equivalence points occur exactly at 20.00 mL increments indicates that the solution contains either a polyprotic acid, or two monoprotic acids present at identical concentrations. This rules out D, since this solution will result in a titration curve with one equivalence point at 6 mL and the second at 20 mL. Solution B can also be ruled out because the relative pK_as are close enough that the first equivalence point would be washed out, resulting in a curve showing only a single discrete equivalence point. This leaves solutions A and C, both of which have pK_as which are substantially different. How do we rule one out and arrive at an identity?

For a polyprotic acid, we would expect the pH halfway to the first equivalence point to equal pK_{a1} and the pH halfway to the second equivalence point to equal pK_{a2}. From the plot, we find these values to be ~2.2 and ~7.2, respectively corresponding well to solution C and confirming our assignment. The third proton for phosphoric acid is too basic to be titrated with 0.1 M NaOH, so we do not see a third equivalence point. If solution A were the unknown, we would expect the pH values at the two midpoints to be 1.83 and 6.07, which does not match the data.

4. Calculate the pH of 1.6×10^{-7} M calcium hydroxide (a strong base). What fraction of the total OH^- in this solution is from the calcium hydroxide?

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



$$\text{Charge Balance: } [\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-]$$

$$[\text{Ca}^{2+}] = 1.6 \times 10^{-7} \text{M}, [\text{OH}^-] = K_w/[\text{H}^+]$$

$$[\text{H}^+] + 3.2 \times 10^{-7} \text{M} = \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^2 + 3.2 \times 10^{-7} \text{M} [\text{H}^+] = K_w$$

$$0 = [\text{H}^+]^2 + 3.2 \times 10^{-7} \text{M} [\text{H}^+] - K_w$$

Solve for $[\text{H}^+]$ using quadratic formula: $[\text{H}^+] = 2.87 \times 10^{-8}$ M, **pH = 7.54₂**

If $[\text{H}^+] = 2.87 \times 10^{-8}$ M, the $[\text{OH}^-] = K_w/2.87 \times 10^{-8} = 3.49 \times 10^{-7}$ M. The calcium hydroxide contributes 3.2×10^{-7} M to this or a fraction of:

$$\frac{3.2 \times 10^{-7} \text{M}}{3.49 \times 10^{-7} \text{M}} = \mathbf{0.918 \text{ or } 91.8\%}$$

5. You are asked to prepare 200.0 mL of a 0.150 F benzoate buffer at pH 4.50 using only pure benzoic acid (MW= 122.125 g/mol, $pK_a=4.20$), 3.00 M NaOH, and water. What mass of benzoic acid (in grams) and what volume of 3.00 M NaOH (in mL) will you need to prepare this buffer?

First, determine the ratio of A^-/HA needed for pH 4.50 by rearranging the Henderson Hasslebach equation:

$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}}$$

So,

$$\frac{\text{mol } A^-}{\text{mol HA}} = 10^{pH-pK_a} = 10^{4.50-4.20} = 1.9952$$

We also know that the total moles of HA and $A^- = 0.200 \text{ L} \times 0.150\text{M} = 0.0300 \text{ mol}$.

So:

$$\begin{aligned} \text{mol } A^- + \text{mol HA} &= 0.0300 \text{ and} \\ \text{mol } A^- &= 1.9952 \text{ mol HA} \end{aligned}$$

Solving for each term, we find: $\text{mol HA} = 0.0100_2 \text{ mol}$ and $\text{mol } A^- = 0.0199_8 \text{ mol}$

Quantities for each:

We need a total of 0.0300 moles of benzoic acid (really 0.0300 total moles):

$$0.0300 \text{ mol HA} \times \frac{122.125 \text{ g HA}}{1 \text{ mol HA}} = \mathbf{3.66 \text{ g benzoic acid}}$$

We need to convert 0.0199₈ moles of the benzoic acid to benzoate by adding NaOH

$$0.0199_8 \text{ mol HA} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HA}} \times \frac{1000 \text{ mL}}{3 \text{ mol NaOH}} = \mathbf{6.66 \text{ mL } 3.00 \text{ M NaOH}}$$

6. A weak diprotic acid, H_2A , has acid dissociation constants of $K_{a1} = 3.06 \times 10^{-4}$ and $K_{a2} = 3.37 \times 10^{-11}$. Calculate the pH and molar concentrations of H_2A , HA^- , and A^{2-} at equilibrium for a 0.140F solution of NaHA.

First find the $[H^+]$:

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = \sqrt{\frac{(3.06 \times 10^{-4})(3.37 \times 10^{-11})(0.140M) + (3.06 \times 10^{-4})(10^{-14})}{3.06 \times 10^{-4} + 0.140M}} = 1.01 \times 10^{-7}M$$

pH = $-\log(1.01 \times 10^{-7}) = 6.99$ (you could also take the average of the pK_a s and get the same result)

Once we have $[H^+]$, we can find the concentrations by determining the fraction of each species present. $[X] = \alpha_x F$.

$$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

In all cases, the denominator of the alpha expression is the same:

$$d = [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2} \\ = (1.01 \times 10^{-7})^2 + (3.06 \times 10^{-4})(1.01 \times 10^{-7}) + (3.06 \times 10^{-4})(3.37 \times 10^{-11}) = 3.109 \times 10^{-11}$$

For H_2A :

$$\alpha_{H_2A} = \frac{[H^+]^2}{d} = \frac{(1.01 \times 10^{-7})^2}{3.109 \times 10^{-11}} = 0.000332$$

and **$[H_2A] = \alpha_{H_2A}F = 0.000332 \times 0.140M = 4.64 \times 10^{-5} M$**

For HA^- :

$$\alpha_{HA^-} = \frac{K_{a1}[H^+]}{d} = \frac{(3.06 \times 10^{-4})(1.01 \times 10^{-7})}{3.109 \times 10^{-11}} = 0.999$$

and **$[HA^-] = \alpha_{HA^-}F = 0.999 \times 0.140M = 0.1399M = 0.140 M$**

For A^{2-} :

$$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{d} = \frac{(3.06 \times 10^{-4})(3.37 \times 10^{-11})}{3.109 \times 10^{-11}} = 0.000332$$

and **$[A^{2-}] = \alpha_{A^{2-}}F = 0.000332 \times 0.140M = 4.64 \times 10^{-5} M$**

Possibly Useful Information

$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$	$pH = \frac{1}{2}(pK_{a1} + pK_{a2})$
$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$	$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$
$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$	$K_aK_b = K_w$
$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES				
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 (256)	102 No (256)	103 Lr (257)
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