

Complete five (5) of the following problems. Each problem is worth 16 points. 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.

1. Concisely discuss the validity of the following statements: (8 points each)
 - a. A buffer solution is most effective at a pH within ± 1 unit of the pK_a for the acid used to make the buffer.

The key here is that the buffer capacity for a buffer solution is best when the ratio of A^- to HA is close to 1. This occurs when the $pH = pK_a$. Within ± 1 of the pK_a the ratio is still reasonable, between 0.1 and 10. Outside this range, there is too little of either A^- or HA to allow for reasonable buffer capacity.

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

The key points for discussion here are:

- the ratio of weak acid to conjugate base stays essentially constant with dilution
- the buffer capacity suffers as the buffer is diluted because the addition of strong acid or base will cause a larger shift in the weak acid:conjugate base ratio.

2. Why is every titration where an indicator is used to determine the endpoint subject to titration error? Describe the appropriate choice and use of an indicator help minimize titration error.

In order for an indicator to undergo its physical property (color) change in a titration, it must react with some titrant. Therefore, we must add additional titrant after the equivalence point is reached in order for the indicator to react. This difference between the volume required to reach the equivalence point and the volume required to cause a change in the indicator is our titration error. The goal in any indicator-based titration is to minimize titration error so that the volume at the endpoint (indicator change) is as close to the equivalence point as possible. To help achieve this goal you should:

1. Choose an indicator whose transition range occurs near the equivalence point of the titration.
2. Avoid adding excessive quantities of indicator so that only a minimal amount of titrant is required to consume the indicator and produce the color change.

3. Calculate the pH of the following solutions: (8 points each)
 a. A 3.6×10^{-8} F solution of HNO_3 .

Although HNO_3 is a strong acid, the concentration is low enough that we need to consider the contribution of water as a source of H^+ . Start by writing mass and charge balance equations:

$$\begin{aligned} \text{Charge Balance: } [\text{H}^+] &= [\text{NO}_3^-] + [\text{OH}^-] \\ \text{Mass Balance: } [\text{NO}_3^-] &= 3.6 \times 10^{-8} \text{ M} \end{aligned}$$

Substituting the mass balance expression in to the charge balance and using K_w , we can get everything in terms of $[\text{H}^+]$:

$$[\text{H}^+] = 3.6 \times 10^{-8} + K_w/[\text{H}^+] \rightarrow [\text{H}^+]^2 - 3.6 \times 10^{-8}[\text{H}^+] - K_w = 0$$

Solving the quadratic gives $[\text{H}^+] = 1.196 \times 10^{-7}$ M or **pH = 6.92**

- b. A solution prepared by adding 7.21 mL of 2.14 M NaOH to 1.00 g of hypochlorous acid (HOCl , molar mass 52.46 g/mol, $\text{p}K_a = 7.53$), 1.00 g sodium hypochlorite (NaOCl , molar mass 74.44 g/mol) and diluting to 100.0 mL.

As NaOH is added to the solution, the hypochlorous acid (HOCl) will be converted to hypochlorite (OCl^-). The final ratio of A^- to HA will determine the pH.

$$1.00 \text{ g NaOCl} \times \frac{1 \text{ mol NaOCl}}{74.44 \text{ g}} \times \frac{1 \text{ mol OCl}^-}{1 \text{ mol NaOCl}} \times \frac{1000 \text{ mmol}}{1 \text{ mol}} = 13.434 \text{ mmol OCl}^-$$

$$1.00 \text{ g HOCl} \times \frac{1 \text{ mol HOCl}}{52.46 \text{ g}} \times \frac{1000 \text{ mmol}}{1 \text{ mol}} = 19.062 \text{ mmol HOCl}$$

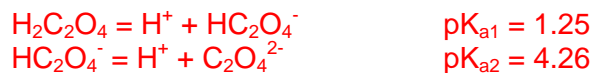
$$7.21 \text{ mL NaOH} \times \frac{2.14 \text{ mol}}{\text{L}} = 15.429 \text{ mmol OH}^-$$

	HOCl	+	OH^-	\rightarrow	OCl^-	+	H_2O
Start (mmol)	19.062		15.429		13.434		0
End (mmol)	$19.062 - 15.429$		0		$13.434 + 15.429$		14.429

$$\text{pH} = \text{p}K_a + \log \frac{\text{mol OCl}^-}{\text{mol HOCl}} = 7.53 + \log \frac{13.434 + 15.429}{19.062 - 15.429} = \mathbf{8.43}$$

4. You need to prepare a pH 4.50 buffer by adjusting the pH of 200.0 mL of a 0.200 M solution of monosodium oxalate (NaHC_2O_4). The only acid and base solutions you have available are 100 mL of 0.100 M NaOH, and 100 mL of 0.100 M HCl. Given these solutions, can you make your buffer? Justify your answer with appropriate calculations. (For oxalic acid, $\text{pK}_{\text{a}1} = 1.252$, $\text{pK}_{\text{a}2} = 4.266$.)

There are two equilibria here to consider:



Since the desired pH of our buffer is closest to $\text{pK}_{\text{a}2}$, we should focus on the $\text{C}_2\text{O}_4^{2-}/\text{HC}_2\text{O}_4^-$ conjugate acid/base pair for our buffer. This will require the addition of NaOH to convert some of the HC_2O_4^- to $\text{C}_2\text{O}_4^{2-}$. What ratio of $\text{C}_2\text{O}_4^{2-}/\text{HC}_2\text{O}_4^-$ is needed?

$$\text{pH} = \text{pK}_{\text{a}2} + \log \frac{\text{mol C}_2\text{O}_4^{2-}}{\text{mol HC}_2\text{O}_4^-}$$

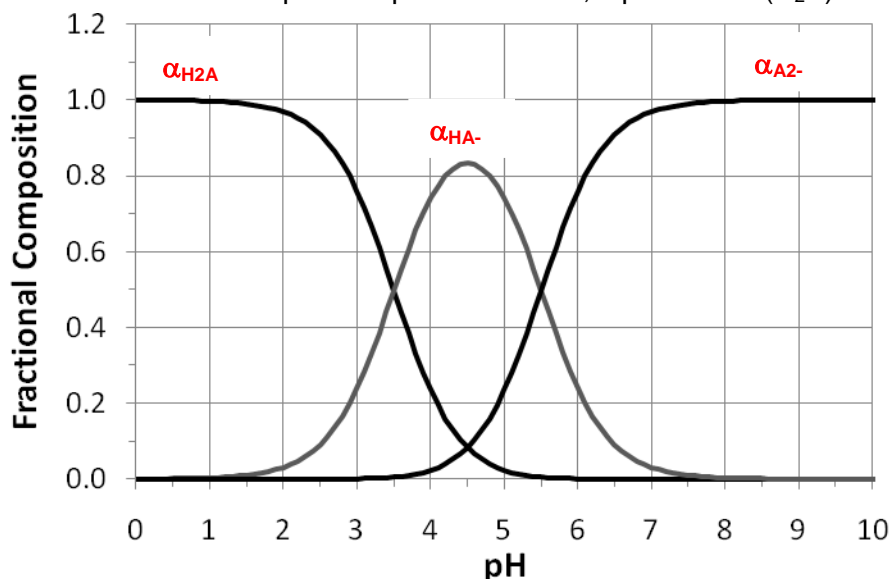
$$4.50 = 4.26 + \log \frac{\text{mol C}_2\text{O}_4^{2-}}{\text{mol HC}_2\text{O}_4^-}$$

Rearranging shows us that the ratio of $\text{mol C}_2\text{O}_4^{2-}/\text{mol HC}_2\text{O}_4^-$ must be 1.714. Do we have enough NaOH to do this? How many mol NaOH are needed? Initially, we have $200 \text{ mL} \times 0.200 \text{ M} = 40.0 \text{ mmol mol HC}_2\text{O}_4^-$

$$1.7140 = \frac{\text{mol C}_2\text{O}_4^{2-}}{\text{mol HC}_2\text{O}_4^-} = \frac{x}{40.0 - x}$$

Solving for x tells us that we need 25.26 mmol NaOH to get to our desired ratio. This requires $25.26 \text{ mmol} \times 1\text{L}/0.100\text{mol} = 252.6 \text{ mL NaOH}$, but we only have 100, therefore, we can't make the buffer!

5. Consider the fractional composition plot for a weak, diprotic acid (H_2A) below.



- On the plot, clearly label the lines that correspond to α_{H_2A} , α_{HA^-} , $\alpha_{A_2^-}$.
- Estimate pK_{a1} and pK_{a2} and explain how you arrived at your estimates.

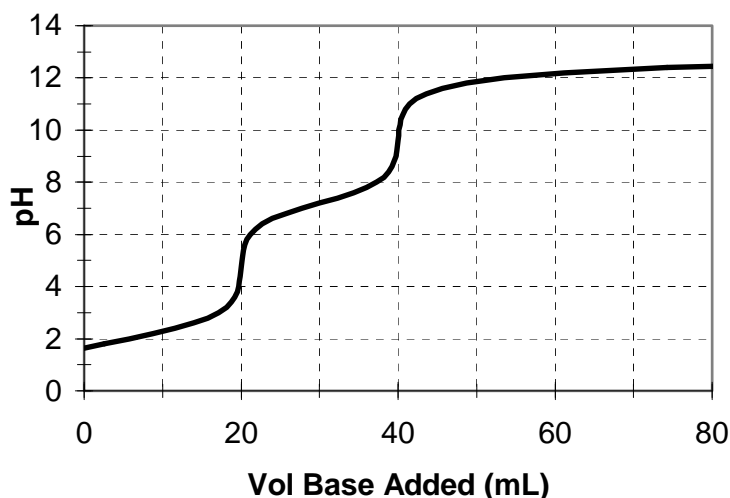
For any acid/conjugate base pair, the Henderson-Hasselbalch equation tells us that the pH will equal the pK_a if the ratio of acid to conjugate base is 1. Using this information, we can estimate pK_{a1} by looking at the pH when α_{H_2A} and α_{HA^-} are equal (both are 0.5). This occurs at pH 3.5. The same analysis for K_{a2} requires us to look for the pH when $\alpha_{A_2^-}$ and α_{HA^-} are equal (0.5). This occurs at pH 5.5. Therefore, our estimates are $pK_{a1} = 3.5$ and $pK_{a2} = 5.5$

- For this acid, is it possible to prepare a solution where 99% of the acid is present as HA^- ? Justify your answer in terms of the tendencies of the equilibria occurring in solution.

An examination of the line corresponding to α_{HA^-} shows that the maximum α_{HA^-} possible is ~ 0.85 . This means that, at best, we could hope for a solution where 85% of the acid is HA^- . Even if we prepare a solution by weighing out "pure" $NaHA$, the HA^- has strong enough acid and base character that $\sim 15\%$ of the HA^- will be converted to H_2A and A^{2-} .

6. 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 why how you were able to rule out the imposters and choose the appropriate identity.

Solution	pK _a
A: 0.100 M H ₂ SO ₄	strong, 2.00
B: 0.100 M phosphoric acid	2.15, 7.20, 12.35
C: 0.100 M succinic acid	4.21, 5.64
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 A can also be ruled out because the relative strengths of the first and second proton on H₂SO₄ are so close that the curve would appear monoprotic, showing only a single discrete equivalence point. Comparing what one would expect from solutions B and C, you would also expect that the equivalence points for solution C to be washed out because the two K_a 's are so close. Therefore, solution B seems likely. How can we confirm this?

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 B 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.

Possibly Useful Information

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

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	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 (256)	102 No (256)	103 Lr (257)
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