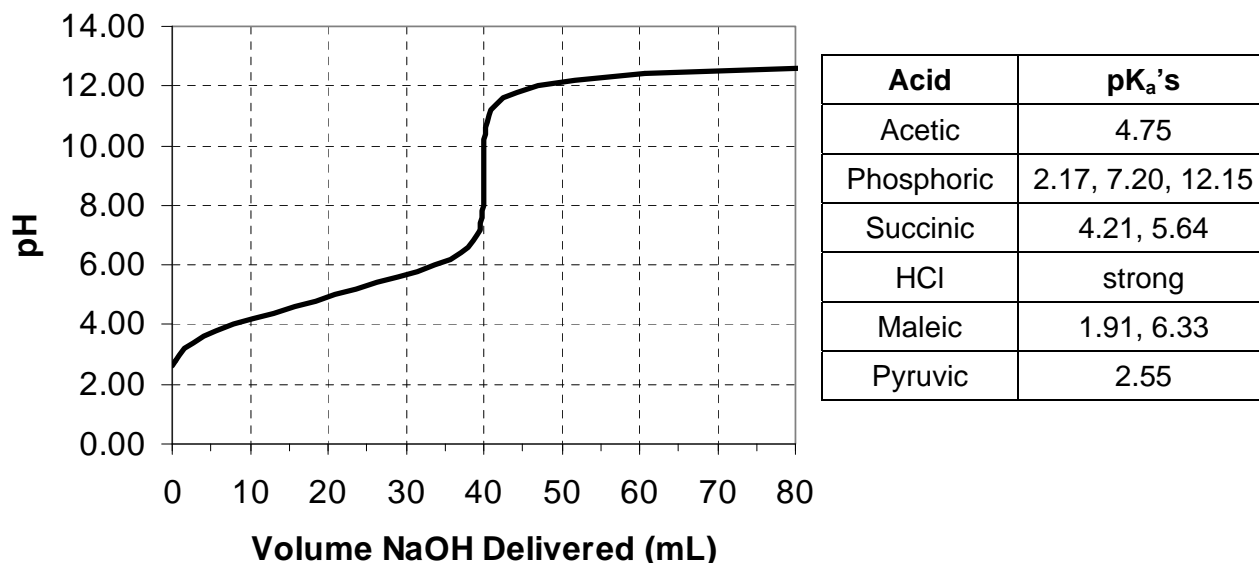


Complete five (5) of the following problems. Each problem is worth 16 points. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. You do not need to account for activities in your calculations.

1. Consider the titration curve below. The curve is the result of the titration of 20.00 mL of a 0.100 M solution of one of the acids below with 0.100 M NaOH. Identify the acid. Clearly justify your decision.



First, let's look at the experimental conditions. Since the concentration of the acid and base are the same, we'd expect to see an equivalence point at 20 mL if the acid is monoprotic, 20 and 40 mL if the acid is diprotic (and the K_a 's are different enough), and at 20, 40, and 60 mL if the acid is triprotic (and the K_a 's are different enough). We see a single clear equivalence point at 40 mL, therefore the acid cannot be monoprotic, ruling out acetic, pyruvic, and HCl. The remaining options are polyprotic acids. What would we expect from each?

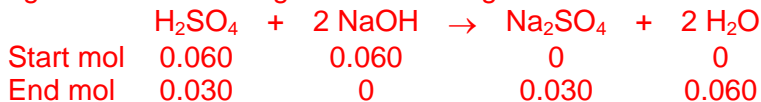
Phosphoric Acid: Since K_{a1} and K_{a2} differ by $\sim 10^5$, we'd expect to see a clear distinction between the two equivalence points (@ 20 and 40 mL). Since we don't observe this, the acid isn't phosphoric.

Maleic Acid: The same argument holds in this case as well. Because the K_a 's are quite different, we'd expect to see both equivalence points, since we do not, the acid can't be maleic.

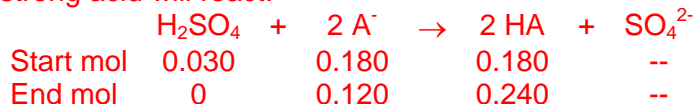
Succinic Acid: The K_a 's are quite similar, therefore we would not expect to see two distinct equivalence points. Instead, we'd expect to see them merge at ~ 40 mL. This is what we observe in the titration curve. Therefore, the acid must be **Succinic**. You could do additional calculations to verify this, but it is unnecessary.

2. Find the pH of a solution prepared by dissolving all of the following compounds in one beaker and diluting to a volume of 1.00 L: 0.180 mol acetic acid ($pK_a = 4.75$), 0.180 mol sodium acetate, 0.060 mol H_2SO_4 , and 0.060 mol NaOH. Assume sulfuric acid dissociates completely (i.e. it is a strong acid).

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



Now, the excess strong acid will react:



So, we now have a buffer with 0.120 mol acetic acid and 0.240 moles acetate:

$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}} = 4.75 + \log \frac{0.120 \text{ mol}}{0.240 \text{ mol}} = \mathbf{4.45}$$

In the end, **pH = 4.45**

3. As part of an undergraduate research project, you have synthesized a new monoprotic organic acid that you have named T-Painic acid (*you suck up!*). In order to determine the strength of this acid, you prepare a 0.111 F aqueous solution of the acid and determine the pH of the solution to be 3.15. What is the pK_a for T-Painic acid?

The equilibrium we are interested in is: $HA = H^+ + A^-$, where HA is our T-Painic acid. We know that, at equilibrium the sum of [HA] and $[A^-]$ must be the formality of our acid (0.111 F). We also know that every time an HA dissociates to produce an H^+ , and A^- is also formed. Therefore:

$$[HA] + [A^-] = 0.111 \text{ M and } [H^+] = [A^-]$$

Given that $pH = 3.15$, $[H^+] = [A^-] = 10^{-3.15} = 7.079 \times 10^{-4} \text{ M}$, so $[HA] = 0.1013 \text{ M}$

Inserting into the K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.079 \times 10^{-4} \text{ M})^2}{0.1013 \text{ M}} = 4.54 \times 10^{-6}$$

$$pK_a = -\log(4.54 \times 10^{-6}) = \mathbf{5.34}$$

An alternate approach is to rearrange the H-H equation:

$$pK_a = pH - \log \frac{[A^-]}{[HA]} = 3.15 - \log \frac{7.079 \times 10^{-4} \text{ M}}{0.1013 \text{ M}} = \mathbf{5.34}$$

4. Complete the following calculations: (8 points each)
 a. Determine the pH of a 5.04×10^{-8} F solution of sodium hydroxide.

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



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

$$[\text{H}^+] + 5.04 \times 10^{-8} \text{ M} = \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^2 + 5.04 \times 10^{-8} \text{ M} [\text{H}^+] = K_w$$

$$0 = [\text{H}^+]^2 + 5.04 \times 10^{-8} \text{ M} [\text{H}^+] - K_w$$

Solve for $[\text{H}^+]$ using quadratic formula: $[\text{H}^+] = 7.79 \times 10^{-8} \text{ M}$, **pH = 7.10₈**.

- b. A 0.020 F solution of succinic acid ($\text{pK}_{a1} = 4.20$, $\text{pK}_{a2} = 5.64$) is buffered at pH 5.00. What fraction of the succinic acid is present as the amphiprotic form at this pH?

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

With $[\text{H}^+] = 1.0 \times 10^{-5} \text{ M}$, $K_{a1} = 10^{-4.20} = 6.31 \times 10^{-5}$, and $K_{a2} = 10^{-5.64} = 2.29 \times 10^{-6}$;
 $\alpha_{\text{HA}^-} = 0.72$, or 72% is present as HA^- .

5. A 50.0 mL sample of 0.100 F freakinacidic acid (H_2A , $\text{pK}_{\text{a}1} = 3.00$, $\text{pK}_{\text{a}2} = 7.00$) is titrated with 0.200 F NaOH. Calculate the pH at any **three** of the following volumes of NaOH added: 0.0 mL, 10.0 mL, 20.0 mL, 30.0 mL, 40.0 mL, 50.0 mL, 60.0 mL, 70.0 mL, 80.0 mL, 90.0 mL, 100.0 mL.

We first need to determine where the equivalence points are. Given that H_2A is diprotic, we expect to see equivalence points at 25 and 50 mL. At volumes between 0 and 25 mL, we have a buffer of H_2A and HA^- , between 25 and 50 mL, we have a buffer of HA^- and A^{2-} . Following the second equivalence point, we need to determine the amount of excess NaOH added to find the $[\text{OH}^-]$ that results.

Volume (mL)	Dominant Species	Approach	pH
0	H_2A	Monoprotic Acid (ICE table with $K_{\text{a}1}$)	2.02
10	H_2A , HA^-	Buffer (ratio = 10/15)	2.85
20	H_2A , HA^-	Buffer (ratio = 20/5)	3.61
30	HA^- , A^{2-}	Buffer (ratio = 5/20)	6.40
40	HA^- , A^{2-}	Buffer (ratio = 15/10)	7.18
50	A^{2-}	Monobasic Base (ICE table with $K_{\text{b}1}$)	10.0
60	NaOH	Excess $[\text{OH}^-]$	12.26
70	NaOH	Excess $[\text{OH}^-]$	12.53
80	NaOH	Excess $[\text{OH}^-]$	12.66
90	NaOH	Excess $[\text{OH}^-]$	12.75
100	NaOH	Excess $[\text{OH}^-]$	12.82

6. Briefly explain how we are able to use initial concentrations in the Henderson-Hasselbalch equation and still get reasonable estimates of the equilibrium pH of a solution? Under what conditions would this not be the case?

In the derivation of the H-H equation, we recognize that, if there is a significant amount of both the acid and conjugate base in solution, Le Chatelier's Principle would suggest that there will be a significant resistance to movement of the equilibrium in either direction. That is, the presence of HA would decrease the tendency to form more HA by consuming A^- and vice versa. As a result, the equilibrium concentrations for HA and A^- should not vary much from the initial conditions.

We begin to run into problems as the concentration of HA or A^- , or both decrease. At these low concentrations, the assumption we made above, may not be good.

7. Your new employer has asked you to prepare 1.00 L of a pH 12.00 buffer with a total phosphate concentration of 0.0500 M. You have at your disposal 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 12.00 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 Na_2HPO_4/Na_3PO_4 combination seems best since the pK_a for HPO_4^{2-} is 12.37.

First, determine the ratio of PO_4^{3-}/HPO_4^{2-} needed for pH 12.00 by rearranging the Henderson Hasselbalch equation.:

$$\frac{\text{mol } PO_4^{3-}}{\text{mol } HPO_4^{2-}} = 10^{pH-pK_a} = 10^{12-12.37} = 0.422$$

We also know that the total moles of PO_4^{3-} and HPO_4^{2-} = 1L x 0.0500M = 0.0500 mol. So:

$$\begin{aligned} \text{mol } PO_4^{3-} + \text{mol } HPO_4^{2-} &= 0.0500 \text{ and} \\ \text{mol } PO_4^{3-} &= 0.422 \text{ mol } HPO_4^{2-} \end{aligned}$$

Solving for each term, we find: mol PO_4^{3-} = 0.0148 mol and mol HPO_4^{2-} = 0.0352 mol

Masses for each salt:

$$0.0148 \text{ mol } Na_3PO_4 \times \frac{163.9407 \text{ g } Na_3PO_4}{1 \text{ mol } Na_3PO_4} = 2.43 \text{ g } Na_3PO_4$$

$$0.0352 \text{ mol } Na_2HPO_4 \times \frac{141.9588 \text{ g } Na_2HPO_4}{1 \text{ mol } Na_2HPO_4} = 4.99 \text{ g } Na_2HPO_4$$

- b. If you did exactly what you calculated in part (a), you would not get a pH of *exactly* 12.00. 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.

Possibly Useful Information

$V_b \cdot 10^{-\text{pH}} = K_a(V_e - V_b)$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$	$\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$
$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$	$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$
$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$	$\text{pH} + \text{pOH} = 14.00$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	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 (265)	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 (256)	103 Lr (257)
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