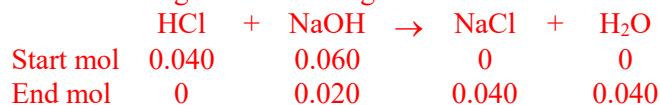


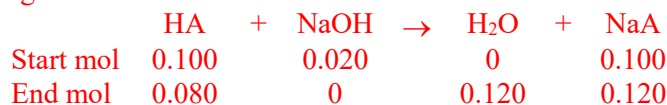
Do five of problems 1-6. Clearly mark the problems you do not want graded. (16 pts. ea.) You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. You may ignore activities in all problems.

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, 0.040 mol HCl, and 0.060 mol NaOH.

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 0.090 mol acetic acid and 0.110 moles acetate:

$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}} = 4.76 + \log \frac{0.120 \text{ mol}}{0.080 \text{ mol}} = 4.94$$

In the end, **pH = 4.94**

2. You are asked to prepare 0.500 L of 0.200 M acetate buffer at pH 4.90 using only pure acetic acid (MW=60.05 g/mol, pKa=4.76), 3.00 M NaOH, and water.
- a. How many grams of acetic acid will be needed to prepare the 0.500 L buffer? Note that the given concentration of acetate refers to the concentration of all acetate species in solution. (6 points)

Regardless of pH, the total concentration of acetate must be 0.200 M. We will start with a 0.200 M acetic acid solution and use NaOH to adjust pH. Therefore, we need to solution initially to be 0.200 M acetic acid.

$$\frac{0.200 \text{ mol HA}}{1 \text{ L}} \times 0.500 \text{ L} \times \frac{60.05 \text{ g HA}}{1 \text{ mol HA}} = 6.005 = \mathbf{6.01 \text{ g acetic acid}}$$

- b. What volume of 3.00 M NaOH, must be added to the acetic acid to achieve a buffer with a pH of 4.90 at a final volume of 0.500 L? Ignore activity coefficients. (10 points)

We need to add enough NaOH to produce the appropriate ratio of A⁻:HA to produce pH 4.90. What ratio do we need?

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

$$4.90 = 4.76 + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$10^{(4.90-4.76)} = 1.38 = \frac{\text{mol A}^-}{\text{mol HA}}$$

So, 1.38(mol HA) = mol A⁻

From mass balance, we know that mol HA + mol A⁻ = (0.500L)(0.200M) = 0.100 mol

Now some algebra to find how many mol A⁻ we need to produce:

$$1.38(\text{mol HA}) = \text{mol A}^- \text{ or } \text{mol HA} = \text{mol A}^-/1.38$$

$$\text{mol HA} + \text{mol A}^- = 0.100$$

$$(\text{mol A}^-/1.38) + \text{mol A}^- = 0.100$$

$$\text{mol A}^-((1/1.38) + 1) = 0.100$$

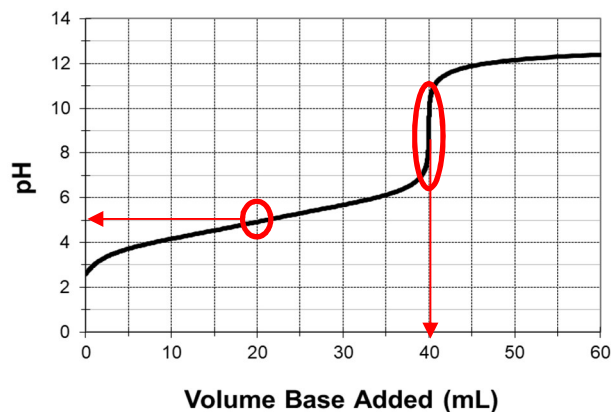
$$\text{mol A}^- = 0.0579_8 \text{ mol}$$

To produce mol A⁻ = 0.0579₈ mol A⁻ we need to add 0.0579₈ mol NaOH. That will require:

$$0.0579_8 \text{ mol NaOH} \times \frac{1000 \text{ mL}}{3.00 \text{ mol NaOH}} = \mathbf{19.3 \text{ mL NaOH}}$$

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 acetic acid	4.76
B: 0.100 M maleic acid	1.83, 6.07
C: 0.100 M nicotinic acid	2.03, 4.08
D: 0.100 M succinic acid	4.21, 5.64



Before examining the candidates, let's take a look at the titration curve and see what it can tell us. (1) we see a single clear equivalence point, indicative of either a monoprotic weak acid or a diprotic weak acid with K_a 's that are "close". The pH midway to the sharp equivalence point is ~ 5 , which would correspond to the pK_a if the acid is monoprotic or to the average of the pK_a values if the acid is diprotic. (2) We see the sharp equivalence point at 40 mL titrant added. We are titrating 20.00 mL of a 0.100 M solution of our acid with 0.100 M NaOH. If the acid were monoprotic, we would expect an equivalence point at 20.00 mL. The fact that the sharp equivalence point occurs at 40 mL indicates a diprotic acid. From this information, we can assess our candidates.

A: 0.100 M acetic acid. While the pK_a does correspond to the pH half way to the equivalence point, if this were the identity, our equivalence point would occur at 20 mL, not 40 mL. So the acid cannot be acetic acid.

B: 0.100 M maleic acid. Maleic acid is diprotic, but the K_a values are far enough apart that we would expect two distinct equivalence points. Maleic cannot be the unknown acid.

C: 0.100 M nicotinic acid. Nicotinic acid is diprotic and the K_a values are close to one another, so the absence of two clear equivalence points makes sense. However, the average of the pK_a values is 3.05, which does not correspond to the value at 20 mL in the titration curve. So nicotinic is not the unknown acid.

D: 0.100 M succinic acid. Succinic is diprotic, with the K_a values close to one another, so the absence of two clear equivalence points is reasonable. Also, the average of the pK_a values is 4.92, which corresponds to the value at 20 mL in the titration curve. **Therefore, succinic is the most likely identity for the unknown acid.**

4. Calculate the pH of 6.6×10^{-7} M nitric acid. What fraction of the total H^+ in this solution is from the nitric acid?

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



Charge Balance: $[H^+] = [NO_3^-] + [OH^-]$

$$[NO_3^-] = 6.6 \times 10^{-7} M, [OH^-] = K_w/[H^+]$$

$$[H^+] = 6.6 \times 10^{-7} M + \frac{K_w}{[H^+]}$$

$$[H^+]^2 = 6.6 \times 10^{-7} M [H^+] + K_w$$

$$0 = [H^+]^2 - 6.6 \times 10^{-7} M [H^+] - K_w$$

Solve for $[H^+]$ using quadratic formula: $[H^+] = 6.7_5 \times 10^{-7} M$, **pH = 6.17**

If total $[H^+] = 6.7_5 \times 10^{-7} M$, and HNO_3 contributes $6.6 \times 10^{-7} M H^+$, then the fraction of H^+ from nitric acid is:

$$\frac{6.6 \times 10^{-7} M}{6.7_5 \times 10^{-7} M} = \mathbf{0.978 \text{ or } 98\%}$$

5. What is the predominant species present in a solution of maleic acid that is buffered at pH 4.00? If the formal concentration of this solution is 0.125 M, what is the concentration of the predominant species at this pH? Maleic acid is $\text{HOOC}(\text{CH})_2\text{COOH}$, but you can call this H_2A . $K_{a1} = 1.20 \times 10^{-2}$ and $K_{a2} = 5.37 \times 10^{-7}$

$$\text{p}K_{a1} = -\log(1.20 \times 10^{-2}) = 1.92$$

$$\text{p}K_{a2} = -\log(5.37 \times 10^{-7}) = 6.27$$

At $\text{pH} = \text{p}K_{a1} = 1.92$, $[\text{H}_2\text{A}] = [\text{HA}^-]$, while at $\text{pH} = \text{p}K_{a2} = 6.27$, $[\text{HA}^-] = [\text{A}^{2-}]$. Therefore, at an intermediate pH (such as 4.00), HA^- will be the predominant species. We can use an α calculation to figure out its concentration.

$$[\text{HA}^-] = (\alpha_{\text{HA}^-})F$$

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

$$\alpha_{\text{HA}^-} = \frac{10^{-4}(1.20 \times 10^{-2})}{(10^{-4})^2 + 10^{-4}(1.20 \times 10^{-2}) + (1.20 \times 10^{-2})(5.37 \times 10^{-7})} = 0.986$$

$$[\text{HA}^-] = (\alpha_{\text{HA}^-})F = 0.986 \times 0.125\text{M} = \mathbf{0.123\text{ M}}$$

6. A weak diprotic acid, H_2A , has acid dissociation constants of $K_{a1} = 1.20 \times 10^{-2}$ and $K_{a2} = 5.37 \times 10^{-7}$. Calculate the pH and molar concentrations of H_2A , HA^- , and A^{2-} at equilibrium for a 0.125F solution of NaHA.

First find the $[H^+]$:

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = \sqrt{\frac{(1.20 \times 10^{-2})(5.37 \times 10^{-7})(0.125M) + (1.20 \times 10^{-2})(10^{-14})}{(1.20 \times 10^{-2}) + 0.125M}} = 7.67 \times 10^{-5}M$$

pH = $-\log(7.67 \times 10^{-5}) = 4.12$ (you could also take the average of the pK_{a} s and get nearly the same result (pH 4.09))

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:

$$\begin{aligned} d &= [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2} \\ &= (7.67 \times 10^{-5})^2 + (1.20 \times 10^{-2})(7.67 \times 10^{-5}) + (1.20 \times 10^{-2})(5.37 \times 10^{-7}) = 9.327 \times 10^{-7} \end{aligned}$$

For H_2A :

$$\alpha_{H_2A} = \frac{[H^+]^2}{d} = \frac{(7.67 \times 10^{-5})^2}{9.327 \times 10^{-7}} = 0.00631$$

$$\text{and } [H_2A] = \alpha_{H_2A}F = 0.00631 \times 0.125M = 7.88 \times 10^{-4}M$$

For HA^- :

$$\alpha_{HA^-} = \frac{K_{a1}[H^+]}{d} = \frac{(1.20 \times 10^{-2})(7.67 \times 10^{-5})}{9.327 \times 10^{-7}} = 0.987$$

$$\text{and } [HA^-] = \alpha_{HA^-}F = 0.987 \times 0.125M = 0.123M$$

For A^{2-} :

$$\alpha_{A^{2-}} = \frac{K_{a1}K_{a2}}{d} = \frac{(1.20 \times 10^{-2})(5.37 \times 10^{-7})}{9.327 \times 10^{-7}} = 0.00691$$

$$\text{and } [A^{2-}] = \alpha_{A^{2-}}F = 0.00691 \times 0.125M = 8.64 \times 10^{-4}M$$

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 Table of the Elements

1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A												
1 H Hydrogen 1.008												5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180												
3 Li Lithium 6.941	4 Be Beryllium 9.012											11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
		3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B																		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798												
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294												
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 Lanthanide Series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine 209.987	86 Rn Radon 222.018												
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Actinide Series	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]												
		57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967													
		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]													

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