CHEM 222 Exam 3

- You may access the exam between 8:00 and 9:30 AM Friday, April 3.
- You may use your book, notes, or online resources, but you MAY NOT receive assistance from anyone other than Dr. Lamp.
- Complete five (5) of the six problems on separate paper. There is no need to print out the exam. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. For discussion problems, be concise in your answers.
- Once you have completed the exam, scan your work as pdf and upload it to Blackboard.
- Submission of your work is your pledge that the exam was completed in an ethical manner! Any unethical work will result in a grade of zero on the exam and the Student Affairs office will be notified.
- Your exam materials must be uploaded by 9:30 AM. You may turn the exam in earlier if you wish.

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$	$K_a K_b = K_w$						
$\alpha_{A^{2^{-}}} = \frac{K_{a1}K_{a2}}{\left[H^{+}\right]^{2} + \left[H^{+}\right]K_{a1} + K_{a1}K_{a2}}$	$\alpha_{H_{2}A} = \frac{\left[H^{+}\right]^{2}}{\left[H^{+}\right]^{2} + \left[H^{+}\right]K_{a1} + K_{a1}K_{a2}}$						
pH = pK _a + log [conjugate base] [weak acid]	$pH = \frac{1}{2} \left(pK_{a1} + pK_{a2} \right)$						
$\left[H^{+}\right] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_{w}}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$						

Possibly Useful Information

IA 1A Hydrogen 1.008 3 Lithium 6.941	2 IIA 2A 4 Beyflium 9,012					Peri	odic 1	[able	of the	e Elerr	nents	13 IIIA 3A 5 Boron 10.811	14 IVA 4A 6 Carbon 12011	15 VA SA 7 Nitrogen 14.007	16 VIA 6A 8 0 0ygen 15,999	17 VIIA 7A 9 Fluorine 13,998	VIIIA 8A 2 He Helium 4.003 10 Ne Neon 20.180
Na Sodium 22.990	Mg Magnesium 24.305	3 111B 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	*	— уш – 8	10	11 IB 1B	12 IIB 2B	Aluminum 26.982	Silicon 28.086	P Phosphorus 30.974	S Sulfur 32.066	Cl Chlorine 35.453	Argon 39.948
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	Chromium 51.996	n 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	Gallium 69.723	32 Germanium 72.631	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 Molybdenu 95.95	m 43 TC Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag 58/ver 107.868	48 Cd Cadmium 112,414	49 In Indium 114.818	50 Sn 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	56 Ba Barium	57-71	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten 183.84	75 Re Rhenium	76 Os Osmium 190.23	77 Ir Irdium 192 217	78 Pt Platinum	79 Au Gold	80 Hg Mercury 200 592	81 TI Thallium	B2 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordius [261]	m 105 Dubnium [262]	106 Sg Seaborgiur [266]	m 107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Darmstadtium [281]	111 Rg Roentgenium [280]	112 Copernicium [285]	113 Nhonium [286]	114 Fl Flerovium (289)	115 Mc Moscovium [289]	116 LV Livermorium [293]	117 TS Tennessine [294]	118 Oganesson [294]
	Lanth Ser	anide ies	La	Ce erium 40.116	Pr rodymium 40.908	Nd eodymium 144.243 61 P Prom 144	62 San 1913	63 barium 50.36	Eu 151.964 64 Gad 12	65 65 7 15 17 15 17 15 17 15 15 15 15 15 15 15 15 15 15	b bium 8.925	Dy 67	Ho tolmium 164.930	Er 69 This 67.259	Tim 102	71 b b b b b b b b	LU tetium 4.967
	Acti Ser	nide ies	Actinium T	Th horium 32.038	Pa tactinium 31.036	U Uranium 238.029	Ip unium 2048	Pu Ar	Am C mericium 243.061	rium 7.070	kelium 7.070	Cf ifornium 51.080	ES Insteinium [254]	mium 57.095	Ad Addelevium 25	JO I belium 9.101 [Lr rencium 262)

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If you have questions email <u>blamp@truman.edu</u>, call 660-785-7251 or click on <u>https://zoom.us/j/101470362</u> to Zoom.

Complete five (5) of the following problems. 16 points each

 Solution A was prepared by dissolving 0.0134 grams potassium hydroxide (molar mass 56.10 g/mol) in water and diluting to a total volume of 1000.0 mL. Next, 1.00 mL of solution A was transferred into a 3.000 L volumetric flask and diluted to the mark to prepare solution B. Calculate the pH of solution A and calculate the pH of solution B.

For solution A: KOH \rightarrow K⁺ + OH⁻ 0.0134 g KOH x <u>1 mol KOH</u> x <u>1 mol OH⁻</u> x <u>1</u> = 2.389x10⁻⁴ M OH⁻ 56.10 g <u>1 mol KOH</u> x <u>1 mol OH⁻</u> x <u>1</u> pOH = -log(2.389x10⁻⁴) = 3.622 pH = 14 - pOH = 10.378 = **10.38**

For solution B: We need to find the [KOH] in this solution: $2.389 \times 10^{-4} \text{ M KOH } \times \frac{1 \text{ mL}}{3000. \text{ mL}} = 7.962 \times 10^{-8} \text{ M OH}^{-1}$ Since the second se

Since this concentration is so small, we cannot ignore the contribution of autoprotolysis of water to the pH.

 $\begin{array}{l} \mbox{Mass balance: } [K^+] = 7.962 \times 10^{-8} \mbox{M} \\ \mbox{Charge balance: } [K^+] + [H^+] = [OH^-] \\ & K_w = [H^+][OH^-] \\ & So, [OH^-] = K_w/[H^+] \\ & So, [OH^-] = K_w/[H^+] \\ & Then [K^+] + [H^+] = K_w/[H^+] \\ & [H^+]([K^+] + [H^+]) = K_w \\ & [H^+][(K^+] + [H^+]) = K_w \\ & [H^+][K^+] + [H^+]^2 = K_w \\ & [H^+]^2 + [K^+][H^+] - K_w = 0 \\ \mbox{Solving quadratic, we get } [H^+] = 6.782 \times 10^{-8}, -1.474 \times 10^{-7} \\ \mbox{Since a negative concentration doesn't make chemical sense, the } [H^+] = 6.782 \times 10^{-8}. \\ & pH = 7.169 = 7.17 \end{array}$

- 2. You need to prepare a pH 3.50 buffer with a total concentration of 100.0 mM. Any of the following monoprotic acid/conjugate base combinations could be used to prepare the buffer.
 - a. Choose which of the three combinations you feel is the best option,
 - b. justify your choice in a sentence or two, and,

di dalcalate the masses of acia and conjugate sase necaca to prepare the sanen						
Acid, HA (molar mass)	Conjugate Base, NaA (molar mass)	Ka	рК _а			
Butanoic acid (88.106 g/mol)	Sodium butanoate (110.088 g/mol)	1.52 x 10 ⁻⁵	4.82			
Formic acid (46.025 g/mol)	Sodium formate (68.007 g/mol)	1.80 x 10 ⁻⁴	3.74			
Pyruvic acid (88.06 g/mol)	Sodium Pyruvate (110.044 g/mol)	3.30 x 10 ⁻³	2.48			

c. calculate the masses of acid and conjugate base needed to prepare the buffer.

In order to optimize buffer capacity, we choose a acid/base combination with pK_a closest to the target pH. This minimizes the chance that the absolute amount of either the acid or conjugate base will be very small and in danger of being completely consumed, thus destroying the solution's buffering ability.

A first step is to convert the K_a values to pK_a (see the added column in the table). Since the formic acid pK_a is closest to 3.50, this would be our acid/base pair of choice (for the reasons above). Now we can calculate the quantities of acid and conjugate base we need.

First, determine the ratio of A⁻/HA needed for pH 3.50 by rearranging the Henderson Hasslebach equation.:

$$\frac{\text{mol } A^{-}}{\text{mol } HA} = 10^{\text{pH-pKa}} = 10^{3.50-3.74} = 0.5754$$

We also know that the total moles of A⁻ and HA will depend on the volume, so let's assume 1L. Then mol A⁻ + mol HA = 1L x 0.1000 M = 0.1000 mol. So:

Now we can convert each of these moles to a mass using the molar mass:

0.06348 mol HA x 46.025 g HA = 2.92 g HA (formic acid) 1 mol HA

0.03652 mol A⁻ x <u>68.007 g A⁻</u> = 2.48 g A⁻ (sodium formate) 1 mol A⁻

Note that you could have chosen any volume. As long as the ratio of moles A⁻ to moles HA is correct (0.5754) and as long as you converted to mass correctly, your answer would be correct.

3. Malonic acid is a weak, diprotic acid of the form H_2A with $K_{a1} = 1.42 \times 10^{-3}$ and $K_{a2} = 2.01 \times 10^{-6}$. What volume, in milliliters, of 0.489 M hydrochloric acid must be added to 250.0 mL of a 0.105 M solution of disodium malonate (Na₂A) to prepare a solution with pH 2.50?

Looking at malonic acid, we see that $pK_{a1} = 2.85$, and $pK_{a2} = 5.70$. So, in order to prepare this solution, we will need to get a molar ratio of HA⁻ to H₂A of: $\frac{\text{mol HA}^{-}}{\text{mol H}_{2}A} = 10^{\text{pH-pKa}} = 10^{2.50-2.85} = 0.4467$

We are starting with Na_2A (or A^{2-}), so we will need to add enough acid to convert all of the A^{2-} to HA^{-} and then add some more to get the appropriate HA^{-}/H_2A ratio.

Our initial moles of Na₂A (or A²⁻): 0.2500 L x 0.105 mol Na₂A x 1 mol A²⁻ = 0.02625 mol A²⁻ 1 L 1 mol Na₂A = 0.02625 mol A²⁻

So, in order to convert all of the A²⁻ to HA⁻, we will need to add 0.02625 mol HCl (since the reaction is 1:1 stoichiometry). When we have done so, we will have 0.02625 mol HA⁻. Adding more HCl will allow us to reach the correct ratio.

mol H₂A + mol HA⁻ = 0.02625 mol HA⁻ = 0.4467 mol H₂A mol H₂A + 0.4467 mol H₂A = 0.02625 mol H₂A = 0.02625/1.4467 = 0.01815 mol H₂A

So, we will need to add enough HCl to create 0.01815 mol H_2A . This will require 0.01815 mol HCl. The total moles HCl needed is the sum of the two steps: 0.02625 + 0.01815 = 0.04440 mol HCl. What volume of 0.489M is this?

0.04440 mol HCl x <u>1 L</u> x <u>1000 mL</u> = **90.8 mL** 0.489 mol HCl 1 L 4. Consider arsenic acid (H₃AsO₄, represented as H₃A), a triprotic acid with acid dissociation constants of 5.8×10^{-3} , 1.1×10^{-7} , and 3.2×10^{-12} . Describe the process you would use to determine the pH where the concentration of H₂A⁻ is at its maximum. You <u>do not need to calculate the pH</u>, but explain the relationship(s) that would be useful and how they could be used to find the pH.

This problem is best addressed by using the alpha expressions. It would be easiest to plot the alpha expression of H_2A^- as a function of $[H^+]$ and see where the alpha is largest.

For a triprotic acid, the alpha for H_2A^- is:



Plotting the alpha expression (which you did not need to do), gives the result below. For this acid, the alpha is maximized at about pH 4.5



Alternatively you could explain how, since the H_2A^- is an amphiprotic form, it will be maximized at the pH described by the combination of the two Ka equilibria that contain the form. Ultimately, the pH is determined by the equation below. In order to employ this relationship, your explanation needed to be clear.

$$\left[H^{+}\right] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_{w}}{K_{a1} + F}} \approx \sqrt{K_{a1}K_{a2}}$$

 Consider the titration below. Calculate the pH at any <u>three</u> of the following points along the titration, 0.00 mL, 10.00 mL, 20.00 mL, 40.00, 60.00 mL titrant added. Sketch the titration curve you would expect. Clearly label your graph.

Analyte in flask	Titrant in buret		
20.0 mL 0.100 M oxalic acid (pK _{a1} = 1.25, pK _{a2} = 4.27)	0.100 M KOH		

It is useful to first determine where the equivalence points occur in the titration. Since the concentration of the acid and base are the same, and since the acid is diprotic, we would expect equivalence points at 20.00 mL and 40.00 mL. This knowledge can streamline the pH calculation. At volumes between 0 and 20 mL, we have a buffer of H₂A and HA⁻. At 10 mL, exactly half of the H₂A has been converted to HA⁻. At 20 mL, we have converted all of the weak acid to its amphiprotic form, HA⁻. At 40 mL we have reached the second equivalence point and have converted all of the weak acid into A²⁻, a weak base. Following the second equivalence point, we need to determine the amount of excess NaOH added to find the [OH⁻] that results.

Volume (mL)	Dominant Species	Approach	рН
0	H ₂ A	Monoprotic Acid (ICE table with K _{a1})	1.29
10	H_2A , HA^-	Buffer (ratio = 10 mmol HA ⁻ /10 mmol H ₂ A)	1.25 (1.76)
20	HA	Amphiprotic form	2.76 (2.92)
40	A ²⁻	A ²⁻ Monobasic Base (ICE table with K _{b1})	
60	NaOH	Excess [OH]	12.40

Note that for 10 mL and 20 mL, I show two values. The value not in parantheses is what we would predict using simplified approximations (pH = pK_{a1} at the 10 mL (1/2 way to the eq.pt.) and pH = $1/2(pK_{a1}+pK_{a2})$ for the amphiprotic form). The values in parentheses are calculated without the approximations. My choice of weak acid made the approximations less good, because pK_{a1} is small. I gave full credit for either approach in this case.

The titration curve should look something like this, with equivalence points appearing at 20 and 40 mL.



6. You are attempting to determine the identity of a <u>dibasic</u> weak base by titrating with standardized hydrochloric acid. You believe the base is either hydrazine (C₂N₂H₄), ethylendiamine (C₂N₂H₈), or piperazine (C₄N₂H₁₀). You weigh out 0.145 grams of the weak base, dissolve it in 50.00 mL water and titrate with 0.105 M HCl. If it requires 32.06 mL of titrant to reach the endpoint, what is the identity of the weak base? (*hint: dibasic is analogous to diprotic when describing an acid*)

There are multiple approaches to solving this problem. Here is one.

Using the titration information, we can determine the molar mass of the weak base. The general reaction for a dibasic base with a strong acid is:

$$B + 2HCI \rightarrow BH_2^{2+} + 2CI$$

With the given information:

 $0.03206 \text{ L HCl} \times 0.105 \text{ mol HCl} \times 1 \text{ mol } B^{-} = 0.001683 \text{ mol B}$ $1 \text{ L HCl} \times 2 \text{ mol HCl}$

The molar mass must be:

0.145 g B⁻ = 86.15 g/mol 0.001683 mol B

Comparing this result to the molar masses of the potential bases:

Base	Molar Mass
hydrazine (C ₂ N ₂ H ₄)	56 g/mol
ethylendiamine (C ₂ N ₂ H ₈)	60 g/mol
piperazine (C ₄ N ₂ H ₁₀)	86 g/mol

Since the molar mass of piperazine matches that from our stoichiometry calculation, the weak base must be piperazine.