Name ____ CHM 1046
Spring 2017
April 7

EXAMINATION THREE

I _______ II _______ III _______ IV _______ V _______ Total __________

Glance over the entire exam, and then attempt the problems in the order of your choice. Rough point values are given for each problem. The total will be scaled to ***150 points*** after the exams are marked. For questions with multiple parts, you do not necessarily need the answer to part A in order to work part B, etc. For calculations, give your answer to the correct number of ***significant figures***, and be sure to include the ***correct units*** for your answer. ***You must show your work to receive any credit for a calculated answer.*** Additional information is provided in a separate information packet; you can use the back for scratch work. Good luck!

I. (1 point) The marked exams will be returned in recitation. Please circle the recitation section that you attend.

Tate Engstrand	2:00-2:50 pm in HTL 213	3:00-3:50 pm in HTL 214	4:00-4:50 pm in HTL 213
Zhicheng Jin	2:00-2:50 pm in HTL 214	3:00-3:50 pm in HTL 219	4:00-4:50 pm in HTL 219
Okten Ungor	4:00-4:50 pm in HTL 520	5:00-5:50 pm in HTL 219	6:00-6:50 pm in HTL 219

II. (17 points) In 2010 it was reported in *Science*, the gold standard of peer-reviewed journals, that an organism discovered in the arsenic-rich sediments of California's Mono Lake thrived in that environment. The researchers concluded that the organism must be incorporating arsenic into its DNA in place of phosphorous. The result was simultaneous exhilarating and controversial, and ultimately shown to be wrong.

https://blogs.scientificamerican.com/the-curious-wavefunction/arsenic-dna-chemistry-and-the-problem-of-differing-standards-of-proof-in-cross-disciplinary-science/

So how did this work get into *Science*? Some aspects of phosphorous and arsenic chemistry are very similar. Let's explore this similarity, starting with the acidity of H_3PO_4 versus H_3AsO_4. Both are triprotic acids, and the K_a values are similar.

Formula	K_{a1}	K_{a2}	K_{a3}
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_3AsO_4.	5×10^{-3}	8×10^{-8}	6×10^{-10}

http://chem-net.blogspot.com/2015/02/polyprotic-acids-ph-calculation.html

Suppose you prepared an aqueous solution of Na_2HAsO_4.

A. Write a chemical equation showing $HAsO_4^{2-}$ acting as an acid in water.

What is the value of K_a for $HAsO_4^{2-}$?

B. Write a chemical equation showing $HAsO_4^{2-}$ acting as a base in water.

What is the value of K_b for $HAsO_4^{2-}$?

C. Is $Na_2HAsO_4(aq)$ expected to be acidic, basic, or essentially neutral? ______________________

Explain your reasoning.

III. (15 points) We waited until we got to Chapter 16 before we covered polyprotic acids because they are often used in buffers. Phosphate buffers are very common, so why not arsenate buffers? (Arsenate buffers were probably used in the study cited on the previous page.)

Three conjugate acid/base pairs can be generated based on the arsenate ion:

H_3AsO_4/ $H_2AsO_4^-$ $H_2AsO_4^-$/ $HAsO_4^{2-}$ $HAsO_4^{2-}$/ AsO_4^{3-}

And here is the table of K_a values from the previous page.

Formula	K_{a1}	K_{a2}	K_{a3}
H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_3AsO_4.	5×10^{-3}	8×10^{-8}	6×10^{-10}

A. Suppose you wanted to prepare a solution buffered at pH 11.00. Which of the ion pairs above would you use?

Why?

B. Now determine the ratio of ions that would give you a pH 11.00 buffer. In other words, what is the value of

$$\frac{[\text{conj base}]}{[\text{conj acid}]} = \underline{\qquad\qquad}$$

C. Suppose the concentration of the conjugate acid in your buffer solution is 0.20 M. What should the concentration of the conjugate be?

D. (2 points) Before we leave the acid/base chemistry of these compounds, anything bother you about the K_a data in table? If so, please state briefly what does not seem right and why? (Your answers to the earlier questions will not be affected by anything you write here.)

VI. (25 points) Many phosphate salts are fairly insoluble in water. For example, the value of K_{sp} for cadmium phosphate, $Cd_3(PO_4)_2$, is 2.5×10^{-33}. The solubility of cadmium arsenate in water is very similar to that of the phosphate analog. The value of K_{sp} for $Cd_3(AsO_4)_2$ is 2.2×10^{-33}.

A. Determine the solubility of $Cd_3(AsO_4)_2(s)$ in water.

1. First, write a chemical equation showing how $Cd_3(AsO_4)_2(s)$ is ionized when it dissolves in water.

2. Now calculate the solubility of $Cd_3(AsO_4)_2(s)$ in mol/L.

B. What would be the solubility of $Cd_3(AsO_4)_2(s)$ in a solution that was already 0.10 *M* in cadmium ion?

C. Solubility is usually reported in units of mass per volume; for example, g/100 mL of solvent. Which compound is more soluble in units of mass per volume, $Cd_3(PO_4)_2$ or $Cd_3(AsO_4)_2$?

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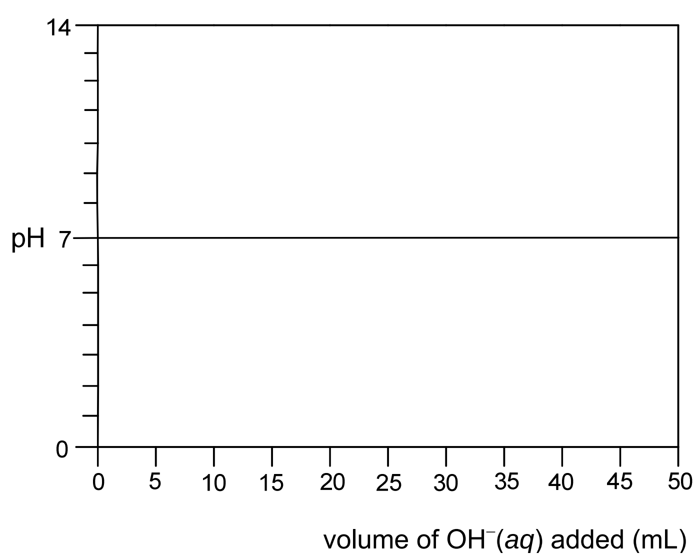
Explain your reasoning using either words or math.

V. (40 points) High blood concentrations of uric acid can lead to gout and are associated with other medical conditions. Only one of the four hydrogen atoms in uric acid is significantly acidic, so we can write the formula as $HC_5H_3N_4O_3$. A 30.0 mL sample of 0.20 *M* $HC_5H_3N_4O_3(aq)$ was titrated with 0.20 *M* $NaOH(aq)$. The K_a of uric acid is 4.1×10^{-3}.

A. Sketch the shape of the curve that you expect to result from this titration from 0 to 50 mL, using reasonable estimates for the initial and final pH values. Label the half-equivalence and equivalence points, and be sure to place these points at the correct volumes and a reasonable pH value.

B. Write a chemical equation corresponding to the reaction that occurs during the titration.



IV. (continued) A 30.0 mL sample of 0.20 *M* $HC_5H_3N_4O_3(aq)$ was titrated with 0.20 *M* NaOH(*aq*). The K_a of uric acid is 4.1×10^{-3}.

C. Calculate the pH after the following volumes of 0.20 M NaOH(*aq*) are added:

1. 15 mL

   What kind of problem are you solving?

   Now solve it.

2. 30 mL

   What kind of problem are you solving?

   Now solve it.

3. 45 mL

   What kind of problem are you solving?

   Now solve it.