

## CH302 Spring 2008 Worksheet 5 Answer Key

### 14 questions involving simple water equilibria and the approximations that make them simple.

1. The only water equilibrium for which we make no approximations is the case of pure water (amazing how simple something is when you don't add anything to it.) What is the most common approximation made when we add acids or bases to water?

Answer: The most common assumption is that the  $H^+$  or  $OH^-$  contribution from water dissociation isn't significant. You know this assumption has occurred because you rarely see a calculation of pH for an acid or base that includes a  $K_w$  term.

2. For each of the compounds and concentrations shown below, tell what kind of compound it is (strong acid, weak acid, strong base, weak base, salt) and write down the equation you would use to solve the problem.

Answer:

compound	type	equation
0.2 M $HClO_4$	strong acid	$[H^+] = C_a$
0.1 M $NH_4Cl$	weak acid	$[H^+] = (K_a C_a)^{0.5}$
0.03 M $Ba(OH)_2$	strong base	$[OH^-] = C_b$
0.2 M $CH_3NH_2$	weak base	$[OH^-] = (K_b C_b)^{0.5}$
0.2 M lithium acetate	weak base	$[OH^-] = (K_b C_b)^{0.5}$
0.1 M lactic acid	weak acid	$[H^+] = (K_a C_a)^{0.5}$

3-9. For the next six problems, find either the pH or the molar solubility of the compound for the compounds in Table 2. Assume a simple equilibrium in each case. You will note that the total time and uncertainty involved in solving these six problems will probably be less than the time and doubt involved in completing Table 2. This should be a heads up to you that the biggest reason people struggle in this section of material is that they don't know what kind of problem they are working—and we haven't even started dumping multiple compounds into solution!!

3. What is the pH of 0.2 M  $HClO_4$ ? Answer: pH = 0.69

Comment: Straight ahead strong acid calculation. The answer makes sense, a really low pH.

4. What is the pH of 0.1 M  $NH_4Cl$ ? The  $pK_b$  of  $NH_3$  is 4.75. Answer: pH = 5.1

Comment: Tricky one. First you have to convert from  $pK_b$  to  $pK_a$  by subtracting from 14 so that you are working in acid terrain. Then use the 10x function on your calculator and perform a simple weak acid calculation. The answer makes sense, a little acidic as weak acids should be.

5. What is the pH of 0.03 M  $Ba(OH)_2$ ? (Hint, there are 2  $OH^-$  dumped into solution for each  $Ba(OH)_2$ .) Answer: pH = 12.8  
Comment. Classic trick question. There are two hydroxides so you need to have double the 0.03 concentration (kind of like that van't Hoff concept in colligative properties.) Otherwise, aside from converting from pOH to pH, this is pretty easy and a guarantee to be the kind of problem you will see on exam 2.

6. What is the pH of 0.2 M  $CH_3NH_2$  if the  $pK_b$  is 3.8? Answer: pH = 11.7

Comment. Straight ahead weak base calculation. Convert the  $pK_b$  using the 10<sup>x</sup> function, solve for the weak base case for  $OH^-$ , convert to pOH and subtract from 14 to get a pH about where weak bases should be.

7. What is the pH of 0.2 M HClO<sub>4</sub>? Answer: pH = 0.69

Comment: I did this one before. The solace you should take is that there are actually only 19 questions on this worksheet.

8. What is the pH of 0.2 M lithium acetate if the pK<sub>b</sub> is 9.3? Answer: pH = 9.0

Comment. Straight ahead weak base calculation. Convert the pK<sub>b</sub> using the 10<sup>x</sup> function, solve for the weak base case for OH<sup>-</sup>, convert to pOH and subtract from 14 to get a pH about where weak bases should be.

9. What is the pH of 0.1 M lactic acid if the K<sub>a</sub> is 1.4 x 10<sup>-4</sup>? Answer: pH = 2.4

Comment. A weak acid with a a pretty large K value so it should be a pH in the lower range of weak acids around 2 or 3. Otherwise, a straight ahead weak acid calculation.

10. Chemical species in acid and base reactions can all be simplified into the following six forms.



Many of you will not think it is necessary to learn this simple notation, but that is because we haven't dealt with buffers and neutralizations yet. So for the mean time, learn what the symbols mean and finding an example of each of these symbols in question 2.

One example is provided to get you started.

Answer:

abbreviation	type	example	equation
H <sup>+</sup>	Strong acid	0.2 M HClO <sub>4</sub>	[H <sup>+</sup> ] = C <sub>a</sub>
HA	Neutral weak acid	0.1 M tartaric acid	[H <sup>+</sup> ] = (K <sub>a</sub> C <sub>a</sub> ) <sup>0.5</sup>
BH <sup>+</sup>	Charged weak acid	0.1 M NH <sub>4</sub> Cl	[H <sup>+</sup> ] = (K <sub>a</sub> C <sub>a</sub> ) <sup>0.5</sup>
B	Neutral weak base	0.2 M CH <sub>3</sub> NH <sub>2</sub>	[OH <sup>-</sup> ] = (K <sub>b</sub> C <sub>b</sub> ) <sup>0.5</sup>
A <sup>-</sup>	charged weak base	0.2 M lithium acetate	[OH <sup>-</sup> ] = (K <sub>b</sub> C <sub>b</sub> ) <sup>0.5</sup>
OH <sup>-</sup>	Strong base	0.03 M Ba(OH) <sub>2</sub>	[OH <sup>-</sup> ] = C <sub>b</sub>

**Enough on equations of simple (single compound) equilibria. Not it is time to think about approximations that make simple equilibrium equations possible. This isn't on Exam 1 but it is worth thinking through to really understand what we are trying to do with the calculations.**

11. Derive the weak acid equation ( [H<sup>+</sup>] = (K<sub>a</sub>C<sub>a</sub>)<sup>0.5</sup> ) by placing C<sub>a</sub> for the concentration of weak acid into the RICE expression and solving:

R	HA →	H <sup>+</sup>	+	A <sup>-</sup>
I	C <sub>a</sub>			
C				
E				

Answer: The derivation for the weak acid equation is found in the notes on dumping weak acids into water and starts on page 3 under the heading "Time for the weak acid derivation using RICE to yield the weak acid expression: [H+] = (KaCa)<sup>0.5</sup>"

12. During the derivation in problem 11 you made two approximations. In which boxes of the RICE expression did these approximations occur and what were the approximations? Can you suggest a general rule for when the approximations will hold based upon the notion that 1% error is permissible?

Answer:

R	HA →	H <sup>+</sup>	+	A <sup>-</sup>
I	C <sub>a</sub>	<b>Initial H<sup>+</sup> box:</b>		

C			
E	<b>Equilibrium [A]</b>		

- Initial  $H^+$  box: this box is set to 0 and assumes that  $H^+$  from water is negligible. The general rule for this to happen is that  $C_a$  is large ( $>10^{-4}M$ ) and  $K_a$  is not close to  $K_w$ , i.e.  $K_a > 10^{-10}$
- Equilibrium [A] box: This box assumes  $[A] = C_a$  because  $x \ll C_a$ . The general rule for this to happen is when  $C_a$  is a large concentration ( $>10^{-4}M$ ) and the  $K_a$  is not greater than  $10^{-4}$

13. For the various combinations of weak acid  $K_a$  values and concentrations shown below, indicate the ones that can be solved using the equation  $[H^+] = (K_a C_a)^{0.5}$  because the approximations we made in the derivation hold. If you can't use the approximation, explain why. (Note, get to answer  $[H^+] = (K_a C_a)^{0.5}$  very often, which tells you how careful we have to be teaching general chemistry to make sure our questions are just right.)

Answers:

acid	$K_a$	concentration	Reason $[H^+] = (K_a C_a)^{0.5}$ doesn't work
chlorous acid	$1.2 \times 10^{-2}$	1 M	Doesn't work, K is too large
chlorous acid	$1.2 \times 10^{-2}$	$1 \times 10^{-2}M$	Doesn't work, K is too large
chlorous acid	$1.2 \times 10^{-2}$	$1 \times 10^{-7}M$	Doesn't work, K is too large and [ ] is too dilute
formic acid	$1.8 \times 10^{-4}$	1 M	Can be solved with $[H^+] = (K_a C_a)^{0.5}$
formic acid	$1.8 \times 10^{-4}$	$1 \times 10^{-2}M$	Can be solved with $[H^+] = (K_a C_a)^{0.5}$
formic acid	$1.8 \times 10^{-4}$	$1 \times 10^{-7}M$	Doesn't work, [ ] is too dilute
Hydrocyanic acid	$5 \times 10^{-10}$	1 M	Can be solved with $[H^+] = (K_a C_a)^{0.5}$
Hydrocyanic acid	$5 \times 10^{-10}$	$1 \times 10^{-7}M$	Doesn't work, [ ] is too dilute
hydrogen peroxide	$2.4 \times 10^{-12}$	1M	Doesn't work, K is too small

14. What is the pH of  $2.4 \times 10^{-8} M HNO_3$ ? Hint: if you get a pH greater than 7 for a strong acid it will make your professor very sad.

Answer: Assume  $H^+$  from  $H_2O$  is  $1 \times 10^{-7}M$  so total  $H^+$  going to be something just a little more than  $1 \times 10^{-7} M$  and thus the pH is a little under 7. A more exact solution will come soon.