

CH302 Spring 2007 Worksheet 5 Answer Key

20 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	$[H^+] = (K_a C_a)^{0.5}$
HgI_2	salt	$[Hg^{++}] = (K_{sp}/4)^{1/3}$
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	$[H^+] = (K_a C_a)^{0.5}$
AgI	salt	$[Ag^+] = K_{sp}^{0.5}$

3-11. For the next eight 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 eight 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 molar solubility of HgI_2 ? The K_{sp} of HgI_2 is 3×10^{-29} . Answer: 1.96×10^{-10}

Comment. You would estimate this was about 10^{-10} by dividing the exponent by 3 and sure enough, that is about right when you do the exact calculation.

6. 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.

7. What is the pH of 0.2 M CH₃NH₂ if the pK_b is 3.8? **Answer: pH = 11.7**
Comment. Straight ahead weak base calculation. Convert the pK_b using the 10^x 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.

8. What is the pH of 0.2 M HClO₄? **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.

9. What is the pH of 0.2 M lithium acetate if the pK_b is 9.3? **Answer: pH = 9.0**
Comment. Straight ahead weak base calculation. Convert the pK_b using the 10^x 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.

10. What is the pH of 0.1 M lactic acid if the K_a is 1.4 x 10⁻⁴? **Answer: pH = 2.4**
Comment. A weak acid with 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.

11. What is the molar solubility of AgI if the K_{sp} is 8.3 x 10⁻¹⁷? **Answer: 9.1 x 10⁻⁹**
Comment. You would estimate this was about 10⁻⁹ by dividing the exponent by 9 and sure enough, that is about right when you do the exact calculation.

12. Dr. Laude walks into class every day during the sections on water equilibria and wastes a lot of tape putting the following simple symbols for acids and bases on the board. Then he rants that no matter how complicated an acid or base is, it can be simplified to one of these six forms.

H⁺ HA BH⁺ B A⁻ OH⁻

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, humor Dr. Laude by learning 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 ⁺	Strong acid	0.2 M HClO ₄	[H ⁺] = C _a
HA	Neutral weak acid	0.1 M tartaric acid	[H ⁺] = (K _a C _a) ^{0.5}
BH ⁺	Charged weak acid	0.1 M NH ₄ Cl	[H ⁺] = (K _a C _a) ^{0.5}
B	Neutral weak base	0.2 M CH ₃ NH ₂	[OH ⁻] = (K _b C _b) ^{0.5}
A ⁻	charged weak base	0.2 M lithium acetate	[OH ⁻] = (K _b C _b) ^{0.5}
OH ⁻	Strong base	0.03 M Ba(OH) ₂	[OH ⁻] = C _b

13. Remember how much fun it was to take IQ tests as a child, back when you thought you were a genius? One type of problem that you no doubt saw was a series of symbols in which you had to figure out the next one in the pattern. Here is one that is relevant to this course:

Answer:

1x² 4x³ 27x⁴ 256x⁵ ← representing AB₄

By the way, as you figure it out, I hope you realize that this is the pattern for the simple relationship between K_{sp} values and molar solubilities you would find from the RICE expression..

14. The mathematically inclined might want to write down the general solution for the pattern in problem 13.

Answer:

$$(n-1)^{n-1}x^n \quad \text{where } n \text{ is the number of ions formed upon dissociation}$$

15. You may notice that there is a nice approximation you can use for finding the molar solubilities for a given salt: the molar solubility is approximately **the root of the number of ions in solution**. For example:

- AgCl puts **two ions** in solution and the molar solubility is approximately the **square root** of the K_{sp} .
- CuCl_2 puts **three ions** in solution and the molar solubility is approximately the **cubed root** of the K_{sp} .
- AuCl_3 puts **four ions** in solution and the molar solubility is approximately the **fourth root** of the K_{sp} .

Given this handy trick, what are the approximate solubilities of the following fake salts and their K_{sp} values. Please don't use a calculator.

Answer:

AB	$K_{sp} = 1 \times 10^{-60}$	Molar solubility is approximately 10^{-30}
AB_2	$K_{sp} = 1 \times 10^{-60}$	Molar solubility is approximately 10^{-20}
AB_3	$K_{sp} = 1 \times 10^{-60}$	Molar solubility is approximately 10^{-15}
A_2B_3	$K_{sp} = 1 \times 10^{-60}$	Molar solubility is approximately 10^{-12}

16. Use the approximation you learned in problem 15 above to solve the following problem in just a few seconds without using a calculator. Rank the solubilities of the following compounds from least soluble to most soluble. (Hint: unlike ranking weak acids and bases, the size of the K is not all you have to consider.)

Answer:

abbreviation	type	Solubility rank
AB	$K_{sp} = 1 \times 10^{-30}$	$[\text{M}] \sim 10^{-15}$ rank 2
AB_2	$K_{sp} = 1 \times 10^{-50}$	$[\text{M}] \sim 10^{-17}$ rank 3
AB_3	$K_{sp} = 1 \times 10^{-90}$	$[\text{M}] \sim 10^{-22}$ rank 4
A_2B_3	$K_{sp} = 1 \times 10^{-60}$	$[\text{M}] \sim 10^{-12}$ rank 1

Enough on equations of simple (single compound) equilibria. Not it is time to think about approximations that make simple equilibrium equations possible.

17. Derive the weak acid equation ($[\text{H}^+] = (\text{K}_a\text{C}_a)^{0.5}$) by placing C_a for the concentration of weak acid into the RICE expression and solving:

R	HA \rightarrow	H^+	+	A^-
I	C_a			
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: $[\text{H}^+] = (\text{K}_a\text{C}_a)^{0.5}$ "

18. During the derivation in problem 17 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 Dr. Laude's notion that 1% error is permissible?

Answer:

R	HA →	H ⁺	+	A ⁻
I	C _a	Initial H⁺ box:		
C				
E	Equilibrium [HA]			

- 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 (>10⁻⁴M) 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 << C_a. The general rule for this to happen is when C_a is a large concentration (>10⁻⁴M) and the K_a is not greater than 10⁻⁴

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

20. What is the pH of 2.4 x 10⁻⁸ M HNO₃? Hint: if you get a pH greater than 7 for a strong acid it will make your professor very sad.

Answer: Assume H⁺ from H₂O is 1 x 10⁻⁷M so total H⁺ is 1.24 x 10⁻⁷M and pH = 6.9