CHEMISTRY 204
Hour Exam II
March 14, 2019
Dr. D. DeCoste

Name **KEY**

Signature ____________________

T.A. ____________________

Section ____________________

This exam contains 23 questions on 10 numbered pages. Check now to make sure you have a complete exam. You have two hours to complete the exam. Determine the **best** answer to the first 20 questions and enter these on the special answer sheet. Also, circle your responses in this exam booklet. **Show all of your work and provide complete answers to questions 21, 22 and 23.**

1-20	(60 pts.)	______
21	(20 pts.)	______
22	(20 pts)	______
23	(20 pts.)	______
Total	(120 pts)	______

Useful Information:

- Unless otherwise noted, all solutions referred to on this exam are aqueous solutions at 25°C.
- On this exam, H_3O^+ and H^+ are used interchangeably.

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C.

For $ax^2 + bx + c = 0$, $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$pH = -\log[H^+]$

$$K_a = \frac{[H^+]^2 - K_w}{[HA]_o - \dfrac{[H^+]^2 - K_w}{[H^+]}}$$

1. The pH of a 0.50*M* solution of a weak base is 9.87. Calculate the value of K_b for this base.

a) 1.5×10^{-4}
b) 7.4×10^{-5}
[✓ c) 1.1×10^{-8}]
d) 2.7×10^{-10}
e) 3.6×10^{-20}

2. The autoionization of water, as represented by the equation below, is known to be endothermic. Which of the following correctly states what occurs as the temperature of water is **lowered**?

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

a) The pH of the water does not change, and the water remains neutral.
b) The pH of the water decreases, and the water becomes more acidic.
c) The pH of the water decreases, and the water remains neutral.
d) The pH of the water increases, and the water becomes more basic.
[✓ e) The pH of the water increases and the water remains neutral.]

3. You are tutoring students about acid-base chemistry and tell them to visualize what the solution looks like and perhaps draw pictures of the solutions. For example, if you wanted to show a neutral solution with hydrogen ions (H^+, small circles) and hydroxide ions (OH^-, larger circles), you could draw something like this:

This is neutral because the $[H^+] = [OH^-]$. What about for a solution with a pH of 3.14? For every one hydroxide ion you would draw, ***about*** how many hydrogen ions would you have to draw?

a) ~3
b) ~1380
c) ~2900
[✓ d) ~52 million]
e) $\sim 7.2 \times 10^{10}$

4. Hydrogen cyanide (HCN), while extremely poisonous, is found in apple seeds. If you isolate the HCN from about a pound of apple seeds and dissolve it in water, you can get a 0.10*M* solution of hydrocyanic acid [HCN(*aq*), $K_a = 6.2 \times 10^{-10}$]. Suppose you add 0.0001 moles of HCl to 1.0L of a 0.10*M* aqueous solution of HCN. Determine the pH of the resulting solution. Assume no volume change upon addition of HCl.

a) 3.96
[✓ b) 4.00]
c) 5.10
d) 6.21
e) 9.40

5. In lecture demonstrations we often used 3.00*M* acetic acid solution ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$). What initial concentration of HF ($K_a = 7.2 \times 10^{-4}$) has the same pH as 3.00*M* acetic acid?

a) 0.025*M*
b) 0.075*M*
[✓ c) 0.082*M*]
d) 3.00*M*
e) 4.17*M*

6. For which 0.010 *M* diprotic acid would the second dissociation affect the pH significantly?

[✓ a) H_2A; $K_{a1} = 1.8 \times 10^{-3}$, $K_{a2} = 9.3 \times 10^{-4}$]
b) H_2B; $K_{a1} = 2.4 \times 10^{-4}$, $K_{a2} = 6.1 \times 10^{-8}$
c) H_2C; $K_{a1} = 1.3 \times 10^{-4}$, $K_{a2} = 5.2 \times 10^{-9}$
d) H_2D; $K_{a1} = 4.2 \times 10^{-2}$, $K_{a2} = 1.8 \times 10^{-7}$
e) The second dissociation **never** affects the pH significantly.

7. How many of the following mixtures would result in a buffered solution?

I. Mixing 100.0 mL of 0.100 *M* HCl with 100.0 mL of 0.100 *M* NaOH.
II. Mixing 100.0 mL of 0.100 *M* NH_3 ($K_b = 1.8 \times 10^{-5}$) with 100.0 mL of 0.100 *M* NaOH.
III. Mixing 100.0 mL of 0.100 *M* HCl with 100.0 mL of 0.100 *M* NH_3 ($K_b = 1.8 \times 10^{-5}$).
[✓ IV. Mixing 50.0 mL of 0.100 *M* HCl with 100.0 mL of 0.100 *M* NH_3 ($K_b = 1.8 \times 10^{-5}$).]

a) 0 [✓ b) 1] c) 2 d) 3 e) 4

8. Consider a 1.00 L aqueous solution to which has been added 1.00 mole of each of the following: HCl, HF($K_a = 7.2 \times 10^{-4}$), LiCl, NaF, and KOH. How many of the following statements are true about the solution at equilibrium?

[✓ I. $[H^+] > [OH^-]$]
[✓ II. The species with the highest concentration is Cl^-.]
III. $[HF] > [F^-]$
[✓ IV. $[HF] > [H^+]$]

a) 0 b) 1 c) 2 [✓ d) 3] e) 4

9-11. A 0.250-g sample of a weak diprotic acid is dissolved in 10.0 mL of water and titrated with 0.100*M* NaOH. The following data are collected:

- After 3.00 mL of 0.100*M* NaOH are added, the pH is 4.99.
- The first equivalence point is reached after a total of 20.00 mL of 0.100*M* NaOH are added.
- After a total of 30.00 mL of 0.100*M* NaOH are added, the pH is 9.64.

9. Determine the molar mass of the acid.

a) 62.5 g/mol b) 83.3 g/mol c) 109 g/mol [✓ d) 125 g/mol] e) 833 g/mol

10. Determine the value of K_{a1} for the acid.

a) 1.0×10^{-5} [✓ b) 1.8×10^{-6}] c) 6.2×10^{-8} d) 6.2×10^{-10} e) 8.0×10^{-10}

11. Determine the value of K_{a2} for the acid.

[✓ a) 2.3×10^{-10}] b) 8.0×10^{-10} c) 6.6×10^{-11} d) 8.5×10^{-11} e) 2.9×10^{-14}

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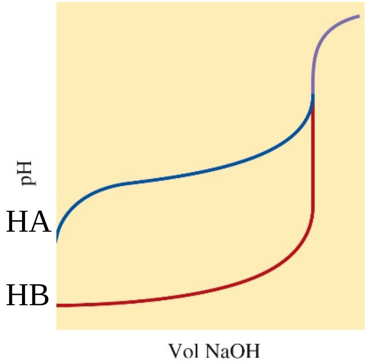
12. A 3.0×10^{-4}-mol sample of Na_2SO_4 is added to 1.0 L of each of two solutions. One solution contains 2.5×10^{-6}*M* $Ba(NO_3)_2$; the other contains 2.5×10^{-3}*M* $Ca(NO_3)_2$. Given that K_{sp} for $BaSO_4 = 1.5 \times 10^{-9}$ and K_{sp} for $CaSO_4 = 6.1 \times 10^{-5}$:

[✓ a) Neither $BaSO_4$ nor $CaSO_4$ would precipitate.]
b) Both $BaSO_4$ and $CaSO_4$ would precipitate.
c) $BaSO_4$ would precipitate but $CaSO_4$ would not.
d) $CaSO_4$ would precipitate but $BaSO_4$ would not.
e) Not enough information is given to determine if precipitation would occur.

13, 14. You have 100.0-mL samples of two acids, HA and HB, in separate beakers. You titrate each of these with 0.10*M* NaOH and generate the following two pH curves:



13. Which of the following best describes the acids?

[✓ a) HA is a weak acid and HB is a strong acid.]
b) HA is a strong acid and HB is a weak acid.
c) HA and HB are both strong acids.
d) HA and HB are both weak acids.
e) We do not get any information about the relative strengths of the acids from these curves.

14. How many of the following statements can we say are true given the pH curves above?

[✓ I. The initial concentrations of the acids (before the titration) were the same.]
[✓ II. The equivalence points of the titrations are at the same volume of NaOH added.]
III. The pH values of the solutions at the equivalence points are the same.
IV. Both beakers contain a buffered solution at some point in the titration.

a) 0 b) 1 [✓ c) 2] d) 3 e) 4

15, 16. Consider the ionic solid AgCl, for which $K_{sp} = 1.6 \times 10^{-10}$.

15. Calculate the solubility of AgCl(*s*) in pure water.

a) $5.4 \times 10^{-4}\ M$ b) $7.4 \times 10^{-4}\ M$ [✓ c) $1.3 \times 10^{-5}\ M$] d) $6.3 \times 10^{-5}\ M$ e) $1.6 \times 10^{-10}\ M$

16. Silver ions in solution can react with NH(aq) as follows:

$$Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq) \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = 8.2 \times 10^3$$

Calculate the solubility of AgCl(*s*) in 10.0 *M* $NH_3(aq)$.

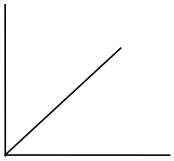
a) $1.6 \times 10^{-10}\ M$ b) $1.3 \times 10^{-5}\ M$ c) $6.3 \times 10^{-5}\ M$ d) $2.8 \times 10^{-3}\ M$ [✓ e) 0.48*M*]

17. The salts AgX, AgY, and AgZ are all essentially equally soluble in water (and none are very soluble at all). When each salt is added to separate beakers of 100 mL of 1.0 *M* HNO_3, you notice that AgY and AgZ are more soluble in acid than in water, and AgY is much more soluble than AgZ in acid. The salt AgX is no more soluble in strong acid than it is in water. Which of the following best lists the respective K_a values for the acids HX, HY, and HZ?

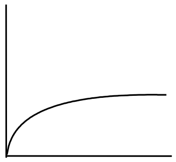
	K_a for HX	K_a for HY	K_a for HZ
a)	1.0×10^{-4}	1.0×10^{-8}	1.0×10^{-11}
b)	1.0×10^{-11}	1.0×10^{-8}	1.0×10^{-4}
c)	v. large	1.0×10^{-4}	1.0×10^{-8}
d)	1.0×10^{-8}	1.0×10^{-4}	v. large
e)	v. large	1.0×10^{-8}	1.0×10^{-4}

18-20. Indicate which of the graphs below best represents each plot described. **Note: a particular graph may NOT be used more than once.**

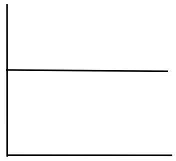
a)



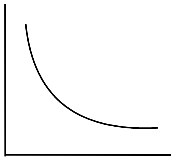
b)



c)



d)



e)

18. Percent dissociation (y) vs. $[HA]_o$ (initial concentration) (x) for an aqueous weak acid at constant temperature. $\boxed{E}$

19. K_a (y) vs. K_b (x) for a series of aqueous conjugate acid-base pairs (constant T). $\boxed{D}$

20. Solubility (y) vs. K_{sp} (x) for a series of ionic solids with the formula MX in pure water at constant temperature. $\boxed{B}$

21. We discussed in class that the best approach to solving acid-base problems is to think about major species, dominant equilibrium, etc. instead of labeling problems by type and forcing a memorized solution to each. Let's put this idea to practice. Consider mixing the following aqueous solutions together in one beaker:

- H_2A ($K_{a1} = 1.5 \times 10^{-4}$, $K_{a2} = 2.5 \times 10^{-7}$)
- KOH
- HCN ($K_a = 6.2 \times 10^{-10}$)

a. What are the initial **major species**? **Explain** your answer. **[5 points]**

MS: $H_2A(aq)$, $K^+(aq)$, $OH^-(aq)$, $HCN(aq)$, $H_2O(l)$

See textbook and lectures.

b. **List all possible reactions** that can occur between the major species and determine the values of the equilibrium constant, K, for all of these reactions. **Show all work. [12 points]**

See textbook and lectures.

21. (con't)

c. What is the **dominant reaction** that will take place given your answers to part b? **Why?** Could we consider the dominant reaction to go essentially to completion, or must we treat it as an equilibrium reaction? **Explain**. **[3 points]**

$$H_2A(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + HA^-(aq)$$

See textbook and lectures.

22. Now let's start mixing! In this problem, you will be given different volumes of the aqueous solutions you were given in Problem 21 and asked to determine the pH of each of the mixtures at equilibrium. In both of the cases:

- **label major species** as/if they change
- **determine *K* values** for all reactions between new major species for which you did not determine *K* in Problem 21.
- **determine the pH** of the solution at equilibrium.

Full credit is reserved for coherent, systematic work that we can follow. Show all work,

a. 100.0 mL of 1.0M H_2A ($K_{a1} = 1.5 \times 10^{-4}$, $K_{a2} = 2.5 \times 10^{-7}$), 50.0 mL of 1.0$M$ KOH, and 100.0 mL of 2.0M HCN ($K_a = 6.2 \times 10^{-10}$) **[10 points]**

See textbook and lectures.

pH = 3.82

22. b. 100.0 mL of 1.0*M* H_2A ($K_{a1} = 1.5 \times 10^{-4}$, $K_{a2} = 2.5 \times 10^{-7}$), 200.00 mL of 1.0*M* KOH, and 50.0 mL of 2.0*M* HCN ($K_a = 6.2 \times 10^{-10}$) **[10 points]**

See textbook and lectures.

pH = 7.91

23. Ionic solids (salts) are soluble in water, but their solubility varies. Some salts are more soluble in acidic solutions, and some are equally soluble in pure water and acidic aqueous solutions.

a. Consider the generic calcium salt: CaX_2. Given that $K_{sp} = 4.0 \times 10^{-11}$ for this salt, **determine the solubility of CaX_2** in pure water (ignore any potential basic properties of X^-). **Show all work. [3 points]**

See textbook and lectures.

Solubility in pure water = 2.15×10^{-4} *M*.

b. Knowing that HX is actually a weak acid, is the solubility of CaX_2 in pure water higher or lower than you determined in part a? Do not do any calculations here, but **explain your answer** conceptually, using chemical equations as appropriate. **[4 points]**

See textbook and lectures.

23. c. It turns out that the calcium salt with $K_{sp} = 4.0 \times 10^{-11}$ is CaF_2. Knowing that for HF $K_a = 7.2 \times 10^{-4}$, show that while the solubility of CaF_2 in pure water is different from what you determined in part a, it is not significantly different. You do not necessarily need to determine the solubility of CaF_2 in pure water, but you do need to **support your answer with numbers/calculations and an explanation**. **[5 points]**

See textbook and lectures.

d. **Determine the solubility** of CaF_2 in an aqueous solution buffered at a pH of 2.00. **Show all work**. **Is the solubility higher or lower** than you determined in part a? **Explain** conceptually why that answer makes sense. **[8 points]**

See textbook and lectures.

Solubility = $\mathbf{1.30 \times 10^{-3}}\,\boldsymbol{M}$