

CHEMISTRY 204

Hour Exam II

March 21, 2024

Dr. D. DeCoste

Name **KEY**

Signature _____

T.A. _____

Section _____

This exam contains 23 questions on 11 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	(10 pts.)	_____
22	(25 pts)	_____
23	(25 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, H₃O⁺ and H⁺ are used interchangeably.

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

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

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{H}^+]$$

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

1. Consider two beakers of pure distilled water, one at room temperature (20°C) and one at 75°C. Which of the following is true concerning these samples?
- a) The samples have the same pH values and are both considered neutral.
b) The samples have different pH values but are both considered neutral.
c) The samples have the same pH values but one is more acidic than the other.
d) The samples have different pH values and one is more acidic than the other.
2. Consider separate samples of the following aqueous acids. The relative initial concentrations of each are such that the percent dissociation is the same in all of the samples. Which acid has the **lowest initial concentration**?
- a) HCN b) HC₂H₃O₂ c) HF d) HOCl e) All concentrations are the same.
3. Determine the pH of a solution labeled “3.14 x 10⁻⁷ M HCl(aq)”.
- a) 6.38 b) 6.46 c) 6.50 d) 6.67 e) 7.00
4. In lecture we considered a problem in which “your lab partner” mixed together aqueous solutions of HCl, KCN, and HF. As always, we determined the major species first and used these to rank the reactions by order of dominance. In this ranking, what are the reactants for the **third most dominant** reaction using the major species?
- a) CN⁻ and HF
b) CN⁻ and H₂O
c) CN⁻ and H₃O⁺
d) F⁻ and H₃O⁺
e) HF and H₂O
5. Which of the following 1.00M aqueous solutions has the **highest pH**?
- a) NaHSO₃ b) NaHSO₄ c) NaHC₂O₄ d) NaHC₆H₆O₆ e) NaHCO₃
6. Consider the following diprotic acids along with their stepwise dissociation constants:

Acid	K _{a1}	K _{a2}
H ₂ A	1.0 x 10 ⁻³	1.0 x 10 ⁻¹²
H ₂ B	1.0 x 10 ⁻⁴	1.0 x 10 ⁻¹¹
H ₂ C	1.0 x 10 ⁻⁵	1.0 x 10 ⁻¹⁰
H ₂ D	1.0 x 10 ⁻⁶	1.0 x 10 ⁻⁹

You have separate 1.00M samples of each acid. Which of the following has the highest concentration in terms of molarity?

- a) HA⁻(aq) b) HB⁻(aq) c) HC⁻(aq) d) HD⁻(aq) e) D²⁻(aq)

7. The most common acid-base indicators are complex molecules that are weak acids and change the color of the solution based on the pH. For example, the indicator methyl orange, a weak acid with a pK_a value of 3.4, makes the solution appear red or yellow. For which of the following titrations would the use of methyl orange be **most appropriate**?

- a) 100.0 mL of 1.00M $NH_3(aq)$ titrated with 1.00M $HCl(aq)$
b) 100.0 mL of 1.00M $NaOH(aq)$ titrated with 1.00M $HCl(aq)$
c) 100.0 mL of 1.00M $HNO_3(aq)$ titrated with 1.00M $KOH(aq)$
d) 100.0 mL of 1.00M $HF(aq)$ titrated with 1.00M $NaOH(aq)$
e) It would work well with at least two of the above (a-d) titrations.

8. Aniline, $C_6H_5NH_2$, is a weak base with $K_b = 3.8 \times 10^{-10}$. Determine the pH of an aqueous solution of aniline with a concentration of $8.0 \times 10^{-5} M$.

- a) 7.12 b) 7.24 c) 7.30 e) 7.36 e). 7.44

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- 9-10. Consider a 50.00-mL sample of a buffer solution with a pH of 3.00 made by mixing 0.500M $HF(aq)$ with 0.500M $NaF(aq)$.

9. What volume of 0.500M $HF(aq)$ was used to make this solution?

- a) 14.00 mL b) 20.93 mL c) 25.00 mL d) 29.07 mL e) 36.00 mL

10. What mass of $NaOH(s)$ is required to add to this buffer solution such that $pH = 3.14$? Assume no volume change upon the addition of the base.

- a) 81.4 mg b) 110. mg c) 163 mg d) 220. mg e) 291 mg

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- 11-14. Consider the titration of 50.0 mL of 0.200M H_2A ($K_{a1} = 3.0 \times 10^{-5}$, $K_{a2} = 7.0 \times 10^{-9}$) with 0.100M $NaOH$.

11. Determine the pH when $HA^-(aq)$ and H_2O (and Na^+) are the major species.

- a) 2.61 b) 4.52 c) 6.34 d) 8.15 e) 8.54

12. Determine the pH after a total of 101.0 mL of 0.100M $NaOH$ has been added.

- a) 4.71 b) 6.48 c) 8.10 d) 8.54 e) 10.16

13. Determine the pH after a total of 201.0 mL of 0.100M $NaOH$ has been added.

- a) 10.05 b) 10.16 c) 10.60 d) 10.71 e) 12.51

14. Determine the volume of 0.100M $NaOH$ required to achieve a pH of 5.00.

- a) 31.4 mL b) 54.8 mL c) 75.0 mL d) 91.7 mL e) 116 mL

15. Recall the demonstration from lecture in which we added $\text{AgNO}_3(aq)$ to a solution containing aqueous sodium chromate, $\text{Na}_2\text{CrO}_4(aq)$, and aqueous sodium chloride, $\text{NaCl}(aq)$. The solids silver chromate and silver chloride both formed eventually based on their solubilities. Given that K_{sp} for silver chromate = 9.0×10^{-12} and K_{sp} for silver chloride = 1.6×10^{-10} , which of the following is correct about their relative solubilities in pure water at 25°C ?

- a) Silver chloride is about 18 times more soluble than silver chromate.
- b) Silver chloride is about 10 times more soluble than silver chromate.
- c) Silver chloride is about 4 times more soluble than silver chromate.
- d) Silver chromate is about 18 times more soluble than silver chloride.
- e) Silver chromate is about 10 times more soluble than silver chloride.

16. Excess $\text{AgCl}(s)$ is added to an aqueous $1.0M$ NaBr solution. Determine $[\text{Ag}^+]$ at equilibrium.

$$K_{sp} \text{ for AgCl} = 1.6 \times 10^{-10} \qquad K_{sp} \text{ for AgBr} = 5.0 \times 10^{-13}$$

- a) $1.3 \times 10^{-5} M$
- b) $7.1 \times 10^{-7} M$
- c) $5.1 \times 10^{-8} M$
- d) $1.6 \times 10^{-10} M$
- e) $5.0 \times 10^{-13} M$

17-18. We know from the solubility rules that most hydroxides are not very soluble. We also know from Chemistry 205 that cobalt is our favorite metal. Given that cobalt(III) hydroxide, $\text{Co}(\text{OH})_3$, has a K_{sp} value of 2.5×10^{-43} , answer the following questions.

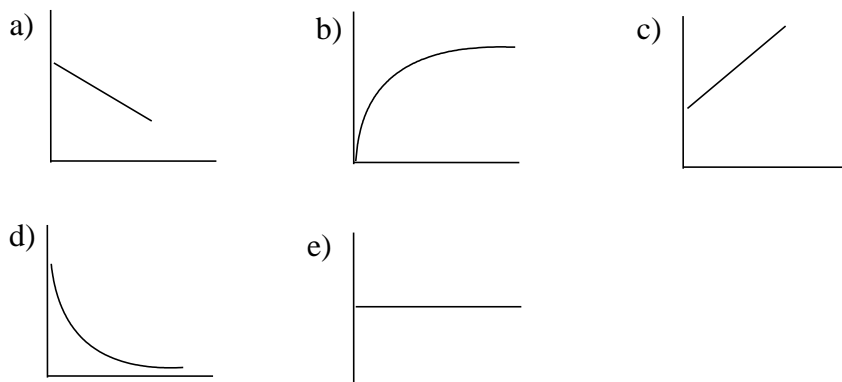
17. What is the pH of a saturated solution of cobalt(III) hydroxide?

- a) 3.00
- b) 7.00
- c) 9.42
- d) 10.50
- e) 11.00

18. What is the $\text{Co}^{3+}(aq)$ concentration in a strong acid solution that is buffered to a pH of 3.14?

- a) $1.8 \times 10^{-4} M$
- b) $1.3 \times 10^{-7} M$
- c) $9.5 \times 10^{-11} M$
- d) $1.3 \times 10^{-21} M$
- e) $1.8 \times 10^{-32} M$

19-20. Indicate which of the graphs below **best** represents each plot described. A graph may be used once, more than once, or not at all.



19. Solubility of $\text{AgCl}(s)$ (y) vs. $[\text{Cl}^-]_{\text{initial}}$ (x) when $\text{AgCl}(s)$ is added to an aqueous solution of NaCl . D

20. Solubility of $\text{AgCl}(s)$ in $\text{HNO}_3(aq)$ (y) vs. concentration of $\text{HNO}_3(aq)$ (x). E

21. Consider three beakers, each with the same “reasonable” volume of an aqueous acid solution of the same “reasonable” concentration (by “reasonable”, we can assume that water does not contribute significantly to $[H_3O^+]$):

- Beaker A contains hydrochloric acid (HCl).
- Beaker B contains acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$).
- Beaker C contains sulfuric acid (H_2SO_4 , $K_{a2} = 1.2 \times 10^{-2}$).

You dilute each of the solutions to 100 times the volume with water. **Consider the following relative ratios** for each beaker:

$$\frac{[H_3O^+] \text{ in the diluted solution}}{[H_3O^+] \text{ in the original solution}}$$

- **Rank the ratios** for each of the beakers from largest to smallest.
- **How do each of the ratios compare to 1/100**, the dilution factor? That is, is the ratio for each greater than, smaller than, or equal to 1/100?
- **Explain** how you are able to determine these answers by considering the **natures of the acids** in the beaker and how they will **respond to dilution**. (Note: If you wish to check your thinking, feel free to make up numbers, like, say 10.0 mL of 1.00M acid solution diluted to 1.00L, but **please do not** include the calculations here. This is about **explaining**.)

Please limit your answer to this side of this page. [10 points]

Ratio in beaker B > ratio in beaker C > ration in beaker A

See lectures, videos, and textbook.

22. Recall that when we discussed the titration of a triprotic acid with a strong base, there are “special points” on the titration curve at which we can estimate pH values based on certain assumptions. In this question we will consider the titration of 100.0 mL of 0.100M phosphoric acid (H_3PO_4 , $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, and $K_{a3} = 4.8 \times 10^{-13}$) with 0.100M NaOH.
- a. The special points on the titration curve are the first two equivalence points, and the three so-called “half-equivalence” points. We can quickly estimate the pH values at these points. Please address the following: **[10 points]**
- **Explain** what is meant by “half-equivalence point” and explain the assumption that is made to estimate the pH values at the half-equivalence points. **Justify** your answer.
 - **Sketch a pH curve** for this titration, filling in the **volumes and pH values** at the first two equivalence points, and the three half-equivalence points. **Justify** your answers.
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See lectures, videos, and textbook.

22. b. Address the following for the titration of 100.0 mL of 0.100M phosphoric acid (H_3PO_4 , $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, and $K_{a3} = 4.8 \times 10^{-13}$) with 0.100M NaOH.

- i. **Determine the pH** at the third equivalence point. **Show all work**, and use this answer to **explain why** the assumption made in part a for the estimate at the third half-equivalence point must be incorrect. **[7 points]**
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pH = 12.17

On the pH plot, the pH at the third half-equivalence point was estimated to be 12.32. But this pH is higher than at the third equivalence point, which cannot be true.

See lectures, videos, and textbook.

22. b. Address the following for the titration of 100.0 mL of 0.100M phosphoric acid (H_3PO_4 , $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, and $K_{a3} = 4.8 \times 10^{-13}$) with 0.100M NaOH.

ii. Determine the pH at the third half-equivalence point. **Explain** why the assumption made in part a is incorrect. **Show all work**, and **explain** why this answer is reasonable. **[8 points]**

pH = 11.85

This value is lower than 12.17, which is the pH at the third equivalence point.

See lectures, videos, and textbook.

23. Recall the following question from the Discussion worksheet this week:

You have 100.0 mL of a saturated solution of aqueous NaCl (contains the maximum concentration of NaCl) and add 0.10M HCl(aq) dropwise. What will happen? The K_{sp} value for NaCl is equal to 38.

- a) The NaCl will precipitate out of solution and continue to do so as more 0.10M HCl is added.
- b) At first NaCl will precipitate out of solution, but it will stop doing so after a while. As more 0.10M HCl is added, the NaCl solid will remain.
- c) At first nothing will seem to happen, but as more 0.10M HCl is added, a precipitate will form.
- d) At first NaCl will precipitate out of solution, and then the NaCl will begin to re-dissolve. After a while there will be no solid left.
- e) No NaCl will ever precipitate out of solution.

The answer to this question, as you determined in Discussion, is “e”.

- a. Without providing calculations, explain why the answer is “e”. That is, if the sodium chloride solution is saturated and we are adding more chloride ions from the hydrochloric acid solution, why doesn't the NaCl ever precipitate? What **needs to be true** about the concentration of the HCl(aq) solution **for precipitation to occur**? **Explain** your answer **completely, yet concisely**. Please **limit your answer to this page**. [4 points]
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See lectures, videos, and textbook.

23. b. As it turns out, with a high enough concentration of $\text{HCl}(aq)$, the answer becomes “d”. That is, as we add the $\text{HCl}(aq)$ to 100.0 mL of the saturated $\text{NaCl}(aq)$ solution, the $\text{NaCl}(s)$ precipitates until a point, and then as we continue to add the $\text{HCl}(aq)$, the solid begins to dissolve. In fact, the tendency to precipitate increases, reaches a maximum, and then decreases until the $\text{Na}^+(aq)$, $\text{Cl}^-(aq)$ and $\text{NaCl}(s)$ are at equilibrium again. As we add more $\text{HCl}(aq)$ to this solution at equilibrium, the solid begins to dissolve. Please answer the following:
- i. Determine the concentration of $\text{HCl}(aq)$ required so that the system reaches equilibrium again when 100.0 mL of $\text{HCl}(aq)$ is added to 100.0 mL of saturated $\text{NaCl}(aq)$ (recall that K_{sp} for $\text{NaCl} = 38$). **Show and explain all work. [7 points]**

[Note: this concentration may be technically higher than the saturation point of HCl in water.]

- **[ACID] = 18.493M $\text{HCl}(aq)$**

See lectures, videos, and textbook.

23. b. ii. Show that NaCl(s) will precipitate when **10.0 mL** of this HCl(aq) solution (at the concentration you determined above) is added to 100.0 mL of saturated NaCl(aq) . Then, show that it has **more of a tendency to precipitate** if **20.0 mL** of the HCl(aq) solution is added. Finally, show that the solid will dissolve when **150.0 mL** of this HCl(aq) solution is added. **Show all work and explain how your answers show precipitation at 10.0 mL and 20.0 mL, and dissolving at 150.0 mL. [10 points]**

Note: If you cannot determine the concentration of HCl(aq) on the previous page, use $31.4M$ and use volumes of 10.0mL, 20.0mL, and 1.00L of HCl(aq) added for this part of the question.

See lectures, videos, and textbook.

23. c. **Explain why**, with a high enough concentration of $\text{HCl}(aq)$, the answer becomes “d”. If the NaCl **starts to precipitate** with the addition of the $\text{HCl}(aq)$, why does it reach a **maximum point**, and then start **redissolving**? Please address this question by **explaining what is happening in the solution**, although you may feel free to add equations/calculation to aid your discussion. **[4 points]**
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See lectures, videos, and textbook.

NOTE: If you've got a bit of time and looking to impress your friends, consider the following:
What volume of the $\text{HCl}(aq)$ solution required for maximum precipitation when added to 100.0 mL of saturated $\text{NaCl}(aq)$? Write your answer below:

[33.3333 mL of 18.493M HCl]