CHEMISTRY 204   Name _____

Hour Exam II

March 21, 2024   Signature _____

Dr. D. DeCoste

                                                 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, H_3O^+ and H^+ are used interchangeably.

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

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

$pH = -\log[H_3O^+] = -\log[H^+]$

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

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) $HC_2H_3O_2$ c) HF   d) HOCl   e) All concentrations are the same.

3.   Determine the pH of a solution labeled "$3.14 \times 10^{-7}M$ 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 H_2O
      c) CN^- and H_3O^+
      d) F^- and H_3O^+
      e)   HF and H_2O

5.   Which of the following 1.00*M* aqueous solutions has the **highest pH**?

      a) $NaHSO_3$ b) $NaHSO_4$ c) $NaHC_2O_4$ d) $NaHC_6H_6O_6$ e) $NaHCO_3$

6.   Consider the following diprotic acids along with their stepwise dissociation constants:

Acid	K_{a1}	K_{a2}
H_2A	1.0×10^{-3}	1.0×10^{-12}
H_2B	1.0×10^{-4}	1.0×10^{-11}
H_2C	1.0×10^{-5}	1.0×10^{-10}
H_2D	1.0×10^{-6}	1.0×10^{-9}

      You have separate 1.00*M* 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) $D^{2-}(aq)$

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 8.0×10^{-5} M.

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

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

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 $AgNO_3(aq)$ to a solution containing aqueous sodium chromate, $Na_2CrO_4(aq)$, and aqueous sodium chloride, $NaCl(aq)$. The solids silver chromate and silver chloride both formed eventually based on their solubilities. Given that K_{sp} for silver chromate $= 9.0 \times 10^{-12}$ and K_{sp} for silver chloride $= 1.6 \times 10^{-10}$, 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 AgCl(s) is added to an aqueous $1.0M$ NaBr solution. Determine $[Ag^+]$ at equilibrium.

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

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, $Co(OH)_3$, has a K_{sp} value of 2.5×10^{-43}, answer the following questions.
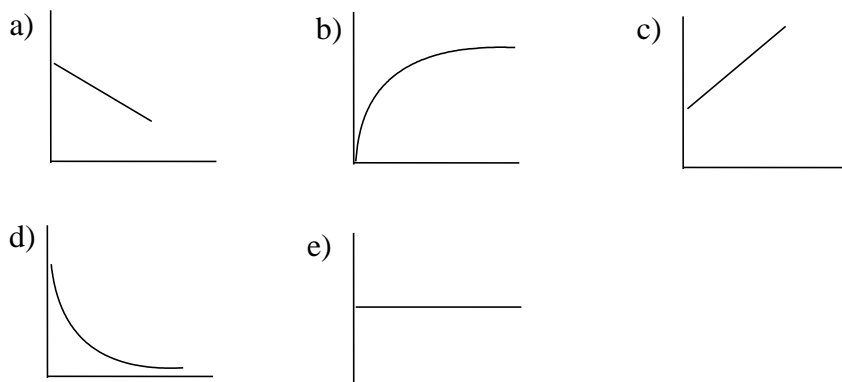
17.   What is the pH of a saturated solution of cobalt(III) hydroxide?

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

18.   What is the $Co^{3+}(aq)$ 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 AgCl(s) (y) vs. $[Cl^-]_{initial}$ (x) when AgCl(s) is added to an aqueous solution of NaCl.

20.   Solubility of AgCl(s) in $HNO_3(aq)$ (y) vs. concentration of $HNO_3(aq)$ (x).

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:

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

- **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 1.00*M* 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]

----

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$_3$PO$_4$, K_{a1} = 7.5 x 10^{-3}, K_{a2} = 6.2 x 10^{-8}, and K_{a3} = 4.8 x 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.

----

22.   b.   Address the following for the titration of 100.0 mL of 0.100M phosphoric acid
           (H_3PO_4, K_{a1} = 7.5 x 10^{-3}, K_{a2} = 6.2 x 10^{-8}, and K_{a3} = 4.8 x 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]**
----

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 0.100$M$ 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]**

----

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]**
----

23.   b.   As it turns out, with a high enough concentration of HCl(*aq*), the answer becomes
           "d". That is, as we add the HCl(*aq*) to 100.0 mL of the saturated NaCl(*aq*) solution,
           the NaCl(s) precipitates until a point, and then as we continue to add the HCl(*aq*), the
           solid begins to dissolve. In fact, the tendency to precipitate increases, reaches a
           maximum, and then decreases until the Na^+(aq), Cl^-(aq) and NaCl(s) are at
           equilibrium again. As we add more HCl(*aq*) to this solution at equilibrium, the solid
           begins to dissolve. Please answer the following:

           i.   Determine the concentration of HCl(*aq*) required so that the system reaches
                equilibrium again when 100.0 mL of HCl(*aq*) is added to 100.0 mL of saturated
                NaCl(*aq*) (recall that K_{sp} for NaCl = 38). **Show and explain all work**. **[7 points]**

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

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 31.4*M* and use volumes of 10.0mL, 20.0mL, and 1.00L of HCl(*aq*) added for this part of the question.

----

23. c.   **Explain why**, with a high enough concentration of HCl(*aq*), the answer becomes "d".
           If the NaCl **starts to precipitate** with the addition of the 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]**

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