

1. **SHOW ALL WORK.** *Include balanced chemical equations for any equilibrium reactions and clearly state any assumptions where appropriate.* The  $K_{sp}$  value for cobalt(II) hydroxide,  $\text{Co}(\text{OH})_2$ , is  $1.0 \times 10^{-15}$ . The formation constant ( $K_f$ ) for the cobalt(II)-ammonia complex ion,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ , is  $5.0 \times 10^4$ .

- (a) (10 points) Calculate the pH of a **saturated solution** of  $\text{Co}(\text{OH})_2$  in water.



$$K_{sp} = [\text{Co}^{2+}][\text{OH}^{-}]^2 \quad \text{let } x = \text{molar solubility}$$

$$K_{sp} = 1.0 \times 10^{-15} = (x)(2x)^2 = 4x^3$$

$$x = 6,30 \times 10^{-6} \text{ M}$$

$$[\text{OH}^{-}] = 2x = 1.26 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log(1.26 \times 10^{-5}) = 4.90 \quad \text{pH} = 9.10$$

- (b) (8 points) Calculate the **molar solubility** of  $\text{Co}(\text{OH})_2$  in a 0.50 M NaOH solution.

$$K_{sp} = [\text{Co}^{2+}][\text{OH}^{-}]^2 \quad \text{let } x = \text{molar solubility}$$

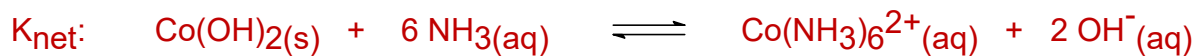
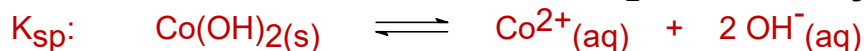
$$[\text{Co}^{2+}] = x \quad [\text{OH}^{-}] = 0.50 + 2x \quad (\text{OH}^{-} \text{ is the common ion})$$

$$1.0 \times 10^{-15} = (x)(0.50 + 2x)^2 \quad (\text{assume } 2x \ll 0.50 \text{ because } K \text{ is very small})$$

$$1.0 \times 10^{-15} \approx (x)(0.50)^2$$

$$x \approx 4.0 \times 10^{-15} \text{ M} \quad (\text{assumption is OK!})$$

- (b) (10 points) Calculate the **molar solubility** of  $\text{Co}(\text{OH})_2$  in a 0.50 M  $\text{NH}_3$  solution.



	I	0	0
	C	- 6x	+ 2x
	E	0.50 - 6x	x

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$$K_{net} = K_{sp} K_f = (1.0 \times 10^{-15})(5.0 \times 10^4) = 5.0 \times 10^{-11} \quad \text{let } x = \text{molar solubility}$$

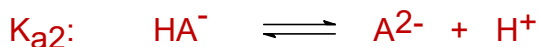
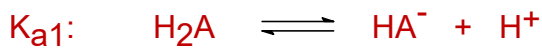
$$5.0 \times 10^{-11} = [\text{Co}(\text{NH}_3)_6]^{2+}[\text{OH}^{-}]^2 / [\text{NH}_3]^6 = (x)(2x)^2 / (0.50 - 6x)^6$$

(assume  $6x \ll 0.50$  because  $K_{net}$  is small)

$$5.0 \times 10^{-11} \approx 4x^3 / (0.50)^6$$

$$x \approx 5.8 \times 10^{-5} \text{ M} \quad (\text{assumption is OK!})$$

2. (8 points) **SHOW ALL WORK.** In a 1.00 M solution of a certain diprotic acid  $\text{H}_2\text{A}$ , the pH was found to be 1.91 and the equilibrium molar concentration of  $\text{A}^{2-}$  was measured as  $5.0 \times 10^{-7}$  M. Determine both the  $\text{pK}_{\text{a}1}$  and  $\text{pK}_{\text{a}2}$  values for this acid.



$$\text{From } K_{\text{a}1}: \quad [\text{H}^+] \approx [\text{HA}^-] = 10^{-1.91} = 1.23 \times 10^{-2} \text{ M}$$

$$K_{\text{a}1} = [\text{H}^+][\text{HA}^-] / [\text{H}_2\text{A}] \approx (1.23 \times 10^{-2})^2 / 1.00 \approx 1.51 \times 10^{-4} \quad \text{pK}_{\text{a}1} = 3.82$$

$$K_{\text{a}2} = [\text{H}^+][\text{A}^{2-}] / [\text{HA}^-] \approx [\text{A}^{2-}] \approx 5.0 \times 10^{-7} \quad \text{pK}_{\text{a}2} = 6.30$$

3. (8 points) **SHOW ALL WORK.** Silver phosphate,  $\text{Ag}_3\text{PO}_4$  (molar mass = 418.6), is a sparingly soluble salt. A saturated aqueous solution of this salt contains only 7.50 mg of  $\text{Ag}_3\text{PO}_4$  per liter of solution. Calculate the solubility product constant ( $K_{\text{sp}}$ ) of  $\text{Ag}_3\text{PO}_4$ .

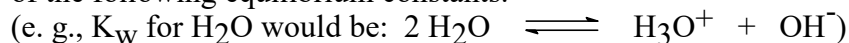


$$K_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = (3x)^3(x) = 27x^4 \quad (\text{where } x = \text{molar solubility})$$

$$x = (7.50 \text{ mg/L}) (10^{-3} \text{ g/mg}) (1 \text{ mole} / 418.6 \text{ g}) = 1.79 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = 27x^4 = 27(1.79 \times 10^{-5})^4 = 2.8 \times 10^{-18}$$

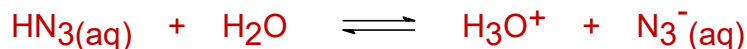
4. (12 points) Write a **balanced chemical equation** for the equilibrium reaction that corresponds to each of the following equilibrium constants.



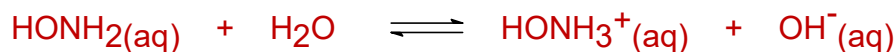
- (a)  $K_{\text{sp}}$  for  $\text{Fe}_2(\text{CO}_3)_3$



- (b)  $K_{\text{a}}$  for  $\text{HN}_3$



- (c)  $K_{\text{b}}$  for  $\text{HONH}_2$



- (d)  $K_{\text{f}}$  for  $\text{Cu}(\text{CN})_4^{2-}$



5. **SHOW ALL WORK.** Calculate the pH of each of the following solutions. *Include balanced net-ionic equations for any equilibrium reactions and clearly state any assumptions where appropriate.*

(a) (7 points) Solution A: 0.15 M HNO<sub>3</sub>

HNO<sub>3</sub> is a strong acid ~ 100 % ionized

$$[\text{H}^+] = 0.15 \text{ M}$$

$$\text{pH} = -\log(0.15) = 0.82$$

(b) (7 points) Solution B: 0.15 M Ba(OH)<sub>2</sub>

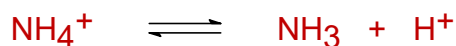
Ba(OH)<sub>2</sub> is a strong base ~ 100 % ionized

$$[\text{OH}^-] = 2(0.15) = 0.30 \text{ M}$$

$$\text{pOH} = -\log(0.30) = 0.52 \quad \text{pH} = 14.00 - \text{pOH} = 13.48$$

(c) (12 points) Solution C: 0.500 M NH<sub>4</sub>NO<sub>3</sub> (The pK<sub>b</sub> value of NH<sub>3</sub> is 4.74)

NH<sub>4</sub>NO<sub>3</sub> is the salt of a weak base (NH<sub>3</sub>), so the cation NH<sub>4</sub><sup>+</sup> acts as a weak acid.



$$K_a = K_w / K_b = 10^{-14} / (10^{-4.74}) = 5.50 \times 10^{-10}$$

$$K_a = 5.50 \times 10^{-10} = [\text{NH}_3][\text{H}^+] / [\text{NH}_4^+] = x^2 / (0.50 - x)$$

(assume  $x \ll 0.50$  because  $K_{\text{net}}$  is small)

$$5.50 \times 10^{-10} \approx x^2 / 0.50$$

$$x = [\text{H}^+] \approx 1.66 \times 10^{-5} \text{ M} \quad (\text{assumption is OK!})$$

$$\text{pH} = -\log(1.66 \times 10^{-5}) = 4.78$$

6. Suppose you had 100.0 mL of each of the same three solutions in problem 5 above:

Solution A: 100.0 mL of 0.15 M HNO<sub>3</sub>

Solution B: 100.0 mL of 0.15 M Ba(OH)<sub>2</sub>

Solution C: 100.0 mL of 0.500 M NH<sub>4</sub>NO<sub>3</sub> (The pK<sub>b</sub> value of NH<sub>3</sub> is 4.74)

(a) (8 points) It is possible to prepare a **buffer solution** by mixing together the complete volumes of two of these solutions. Which two are they? Circle your answer.

A and B

A and C

**B and C**

Briefly explain your answer (50 words max!). Include the **balanced net-ionic equation** for the **reaction that occurs upon mixing** the solutions.

Solution B is 0.30 M OH<sup>-</sup> so it will neutralize some of the weak acid (0.50 M NH<sub>4</sub><sup>+</sup>) in solution C to form some of the conjugate base (NH<sub>3</sub>).

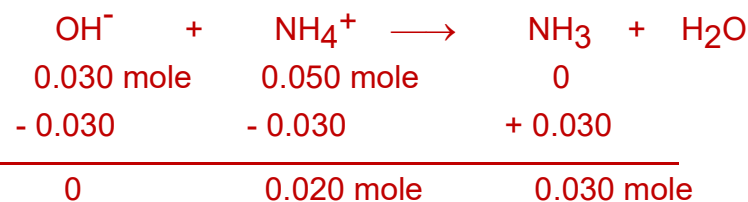


Thus, mixing Solutions B and C will yield an NH<sub>4</sub><sup>+</sup> / NH<sub>3</sub> buffer system.

(b) (10 points) **SHOW ALL WORK.** Calculate the pH of this buffer solution. **Include a balanced chemical equation for the main equilibrium reaction in this solution.**

Solution B: (0.100 L) (0.30 mole OH<sup>-</sup> / L) = 0.030 mole OH<sup>-</sup>

Solution C: (0.100 L) (0.50 mole NH<sub>4</sub><sup>+</sup>) = 0.050 mole NH<sub>4</sub><sup>+</sup>



buffer solution equilibrium: NH<sub>4</sub><sup>+</sup> ⇌ NH<sub>3</sub> + H<sup>+</sup>

$$K_a = K_w / K_b = 10^{-14} / 10^{-4.74} = 5.50 \times 10^{-10}$$

$$[\text{H}^+] = K_a (\text{acid}) / (\text{base}) = K_a (\text{mole NH}_4^+) / (\text{mole NH}_3)$$

$$[\text{H}^+] = (5.50 \times 10^{-10}) (0.020) / (0.030) = 3.67 \times 10^{-10} \quad \text{pH} = 9.44$$

7. **EXTRA CREDIT.** (5 points) **SHOW ALL WORK.** Now suppose that the **complete volumes of all three** of the above solutions (i.e., A, B, and C) are mixed together. Calculate the pH of the final solution.

**Note:** The order in which these solutions are mixed doesn't matter. After all of the acid-base neutralization reactions are finished, the final pH will be the same. Two simple methods are (1) add solution A (0.015 mole H<sup>+</sup>) to the buffer solution already prepared in part 6(b) above, or (2) first mix solutions A (0.015 mole H<sup>+</sup>) and B (0.030 mole OH<sup>-</sup>), followed by the addition of solution C (0.050 mole NH<sub>4</sub><sup>+</sup>), as shown below.



Next, adding this 0.015 mole OH<sup>-</sup> to 0.050 mole NH<sub>4</sub><sup>+</sup> (soln C) will yield a buffer solution similar to that in part 6(b) but with a different NH<sub>4</sub><sup>+</sup> (0.035 mole) / NH<sub>3</sub> (0.015 mole) ratio.

$$[\text{H}^+] = (5.50 \times 10^{-10}) (0.035) / (0.015) = 1.28 \times 10^{-9} \quad \text{pH} = 8.89$$

(Separately, try doing this problem by method 1 as described above. The final pH should be the same!)