

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad 1 \text{ L atm} = 101.3 \text{ J} \quad T(0^\circ\text{C}) = 273.2 \text{ K} \quad s^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_a} \right)$$

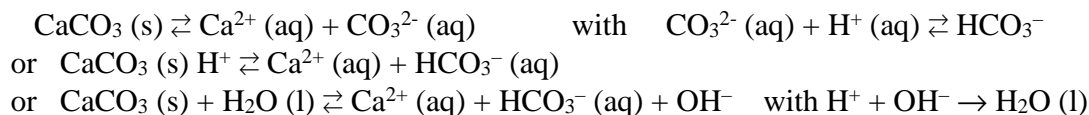
Answer 8 of the following 10 questions. If you answer more than 8 cross out the ones you wish not to be graded, otherwise only the first 8 will be graded. (6 points each)

1. Is  $\text{PbBr}_2$  more soluble in : (a) pure water, (b) 0.10 M NaBr, or (c) 0.10 M  $\text{Pb}(\text{NO}_3)_2$  ?

2. Circle the stronger acid in each pair:

(a) HF, HBr                      (b)  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$                       (c) HClO<sub>3</sub>,  $\text{HBrO}_3$

3. Write the reactions that show why  $\text{CaCO}_3(\text{s})$  has increasing solubility with decreasing pH.



4. Are aqueous solutions of the following acidic, basic, or neutral?

(a)  $\text{NH}_4\text{Cl}$  acidic    (b)  $\text{KNO}_3$  neutral    (c)  $\text{Na}_2\text{SO}_4$  basic

5. Consider the general reagents at 0.1 M concentration: HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$ , NaOH. Which of these four reagents do you add to get the following precipitates to dissolve? You can use each reagent only once (in other words you will use all four choices).

(a). To dissolve  $\text{Cu}(\text{OH})_2(\text{s})$  add HCl or  $\text{H}_2\text{SO}_4$   
(b). To dissolve  $\text{Zn}(\text{OH})_2(\text{s})$  add NaOH  
(c). To dissolve  $\text{AgCl}(\text{s})$  add  $\text{NH}_3$   
(d). To dissolve  $\text{CaF}_2(\text{s})$  add HCl or  $\text{H}_2\text{SO}_4$

6. In the titration of ammonia with strong acid, is the equivalence point acidic, basic, or neutral? Show the reaction that determines the pH.

7. What are the two conjugate acid base pairs in the reaction:  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + \text{OH}^-$   
base ————— acid  
acid ————— base

Make sure to indicate which in each pair is the acid and which the base.

8. For the following reactions, does the equilibrium position lie to the left or right?

(a)  $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$  left

(b)  $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$  left

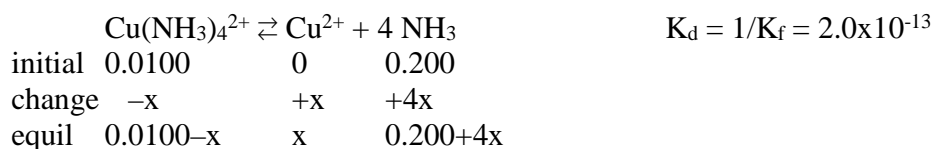
9. The volume of an ideal gas is increased from 1.00 L to 5.00 L at a constant pressure of 2.00 atm. Assume  $q = 0$  and calculate the change in internal energy for this process. Remember to convert to J: (not this year)

10. Name the following compounds:

- (a) HIO           hypoiodous acid            
 (b) H<sub>3</sub>PO<sub>4</sub>           phosphoric acid            
 (c) Na<sub>2</sub>SO<sub>3</sub>           sodium sulfite

### Part II.

11. Calculate the concentration of Cu<sup>2+</sup> in a solution of 0.0100 M Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, with an ammonia concentration of 0.20 M. The formation constant is: Cu<sup>2+</sup> (aq) + 4 NH<sub>3</sub> (aq) ⇌ Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> (aq) K<sub>f</sub> = 5.0 × 10<sup>12</sup>.



$$K_d = 1/K_f = 2.0 \times 10^{-13} = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = \frac{x(0.20+4x)^4}{0.0100-x} \cong \frac{x(0.20)^4}{0.0100}$$

$$x = 1.25 \times 10^{-13} \text{ M}$$

12. Calculate the pH at the equivalence point of a titration of 30.0 mL of 0.100 M HClO with 0.100 M NaOH. For HClO, K<sub>a</sub> = 1.1 × 10<sup>-8</sup> M. Show the reaction that determines the pH.

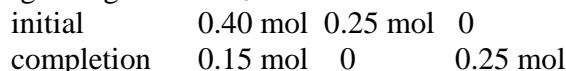
reaction that determines the pH: ClO<sup>-</sup> ⇌ HClO + OH<sup>-</sup>  
 equil: 0.0500-x      x      x

$$K_b = 1 \times 10^{-14} / 1.1 \times 10^{-8} = 9.09 \times 10^{-7} = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{x^2}{0.05-x} \cong \frac{x^2}{0.0500}$$

$$[\text{OH}^-] = x = \sqrt{K_b \times 0.0500} = \sqrt{9.09 \times 10^{-7} \times 0.0500} = 2.13 \times 10^{-4} \quad \text{and} \quad \text{pOH} = 3.671 \quad \text{pH} = 10.33$$

13. What is the pH of a solution prepared by adding 1.00 L of 0.25 M HCl to 1.00 L of 0.40 M ammonia. For ammonium ion K<sub>a</sub> = 5.5 × 10<sup>-10</sup> M.

The reaction with strong acid gives: NH<sub>3</sub> + H<sup>+</sup> → NH<sub>4</sub><sup>+</sup> (assume goes to completion)



$$[\text{H}^+] \cong K_a \frac{C_A}{C_B} = K_a \frac{n_A}{n_B} \quad (\text{mole ratio} - \text{both species are in the same volume})$$

$$[\text{H}^+] \cong 5.5 \times 10^{-10} \frac{0.25 \text{ mol}}{0.15 \text{ mol}} = 9.17 \times 10^{-10} \text{ M} \quad \text{and} \quad \text{pH} = 9.04$$

CH145, 1999

14. Calculate the solubility of  $\text{Mg}(\text{OH})_2$  in a solution buffered to a pH of 12.0.  
 $K_{\text{SP}} = 1.8 \times 10^{-11} \text{ M}^3$ .



giving  $\text{pOH} = 2.0$  and  $[\text{OH}^-] = 0.010 \text{ M}$

$$[\text{Mg}^{2+}] = K_{\text{sp}}/[\text{OH}^-]^2 = 1.8 \times 10^{-11} \text{ M}^3 / (0.010)^2 = 1.8 \times 10^{-7} \text{ M} = 2 \times 10^{-7} \text{ M}$$

15. Calculate the solubility of LiF in a solution buffered at pH 7.00. The  $K_{\text{sp}}$  of LiF is  $1.7 \times 10^{-3} \text{ M}^2$ . The  $K_{\text{a}}$  of hydrofluoric acid is  $6.8 \times 10^{-4}$ .

Since LiF is a 1:1 salt:

$$s^2 = K_{\text{sp}} \left( 1 + \frac{[\text{H}^+]}{K_{\text{a}}} \right) = 1.7 \times 10^{-3} \text{ M}^2 \left( 1 + \frac{1.00 \times 10^{-7}}{6.8 \times 10^{-4}} \right) = 1.7002 \times 10^{-3} \text{ M}$$

$$s = 0.04123 \text{ M}$$

*Note* that  $s = \sqrt{K_{\text{sp}}}$  is fine at this pH. However at  $\text{pH} = 3$ :

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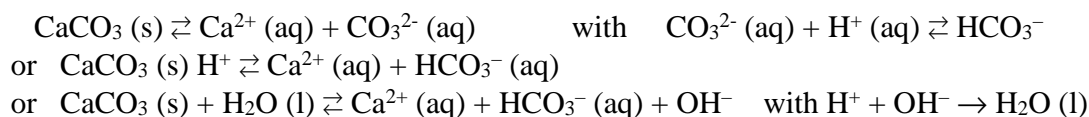
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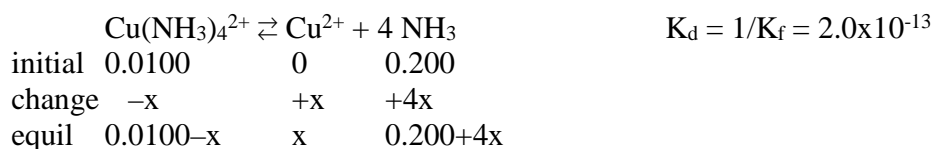
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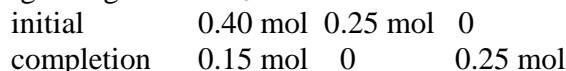
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