

Chemistry 192

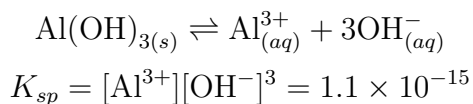
Problem Set 6

Spring, 2018

Solutions

1. The solubility product of $\text{Al}(\text{OH})_3$ is 1.1×10^{-15} . Calculate the concentrations of aluminum ions, hydroxide ions and hydronium ions in a saturated aqueous solution of aluminum hydroxide.

Answer:



	$[\text{Al}^{3+}]$	$[\text{OH}^{-}]$
initial	0 M	0 M
change	s	$3s$
equilibrium	s M	$3s$ M

$$27s^4 = 1.1 \times 10^{-15}$$

$$s = [\text{Al}^{3+}] = 8.0 \times 10^{-5} \text{ M}$$

$$[\text{OH}^{-}] = 3s = 2.4 \times 10^{-4} \text{ M}$$

$$[\text{H}_3\text{O}^{+}] = \frac{1.00 \times 10^{-14}}{2.4 \times 10^{-4}} = 4.2 \times 10^{-11}$$

2. The solubility product of Ag_2S is 1.6×10^{-49} . Calculate the molar solubility of silver sulfide in water.

Answer:



	$[\text{Ag}^{+}]$	$[\text{S}^{2-}]$
initial	0 M	0 M
change	$2s$	s
equilibrium	$2s$ M	s M

$$(2s)^2 s = 4s^3 = 1.6 \times 10^{-49}$$

$$s = \text{molar solubility} = 3.4 \times 10^{-17} \text{ M}$$

3. The solubility of Ag_3AsO_4 in water is $8.5 \times 10^{-4} \text{ g mL}^{-1}$. Calculate the solubility product of silver arsenate.

Answer:



$$\text{moles dissolved of silver arsenate} = \frac{8.5 \times 10^{-4} \text{ g}}{463 \text{ g mol}^{-1}} = 1.8 \times 10^{-6} \text{ mol}$$

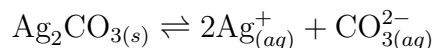
$$[\text{AsO}_4^{3-}] = \frac{1.8 \times 10^{-6} \text{ mol}}{0.00100 \text{ L}} = 1.8 \times 10^{-3} \text{ M}$$

$$[\text{Ag}^+] = 3[\text{AsO}_4^{3-}] = 5.5 \times 10^{-3} \text{ M}$$

$$K_{sp} = (5.5 \times 10^{-3})^3 (1.8 \times 10^{-3}) = 3.1 \times 10^{-10}$$

4. The solubility product of Ag_2CO_3 is $K_{sp} = 5.0 \times 10^{-12}$. Calculate the molar solubility of silver carbonate in a) water and b) a 0.20 M aqueous AgNO_3 solution (silver nitrate is 100% ionized).

Answer:



(a)

	$[\text{Ag}^+]$	$[\text{CO}_3^{2-}]$
initial	0 M	0 M
change	$2s$	s
equilibrium	$2s \text{ M}$	$s \text{ M}$

$$[\text{Ag}^+]^2 [\text{CO}_3^{2-}] = 4s^3 = 5.0 \times 10^{-12}$$

$$s = \text{solubility} = [\text{CO}_3^{2-}] = 1.1 \times 10^{-4} \text{ M}$$

(b)

	$[\text{Ag}^+]$	$[\text{CO}_3^{2-}]$
initial	0.20 M	0 M
change	$2s$	s
equilibrium	$(0.20 + 2s) \text{ M}$	$s \text{ M}$

$$s(0.20 + 2s)^2 \approx s(0.20)^2 = 5.0 \times 10^{-12}$$

$$\text{solubility} = s = 1.3 \times 10^{-10} \text{ M}$$

5. The solubility product of AgCl is $K_{sp} = 1.1 \times 10^{-10}$. Calculate the weight of silver nitrate that must be added to 10. mL of a 0.10 M sodium chloride solution to initiate the silver chloride precipitation reaction.

Answer:

$$\begin{aligned}
 [\text{Ag}^+][\text{Cl}^-] &= 1.1 \times 10^{-10} \\
 [\text{Ag}^+] &= \frac{1.1 \times 10^{-10}}{0.10} = 1.1 \times 10^{-9} \text{ M} \\
 (1.1 \times 10^{-9} \text{ mol L}^{-1})(0.010 \text{ L}) &= 1.1 \times 10^{-11} \text{ mol} \\
 (1.1 \times 10^{-11} \text{ mol})(170. \text{ g mol}^{-1}) &= 1.9 \times 10^{-9} \text{ g}
 \end{aligned}$$

6. The solubility product of Ag_2SO_4 is 7.0×10^{-5} . A laboratory student mixes 10. mL of a 0.010 M silver nitrate solution with 10. mL of a 0.020 M sodium sulfate (Na_2SO_4) solution. Calculate a suitable reaction quotient to determine if silver sulfate precipitate should form when the two solutions are mixed.

Answer:

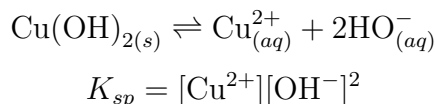
$$\begin{aligned}
 \text{Ag}_2\text{SO}_{4(s)} &\rightleftharpoons 2\text{Ag}_{(aq)}^+ + \text{SO}_{4(aq)}^{2-} \\
 [\text{Ag}^+] &= 0.0050 \text{ M} \quad [\text{SO}_4^{2-}] = 0.010 \text{ M} \\
 Q &= [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (0.0050)^2(0.010) = 2.5 \times 10^{-7} < K_{sp}
 \end{aligned}$$

No precipitation.

7. The solubility product of $\text{Cu}(\text{OH})_2$ is 1.0×10^{-16} . Calculate

- (a) the pH of a saturated solution of copper (II) hydroxide in water;

Answer:



	$[\text{Cu}^{2+}]$	$[\text{OH}^-]$
initial	0 M	0 M
change	s	$2s$
equilibrium	$s \text{ M}$	$2s \text{ M}$

$$4s^3 = 1.0 \times 10^{-16} \quad s = 2.9 \times 10^{-6} \quad [\text{OH}^-] = 2s = 5.8 \times 10^{-6}$$

$$\text{pOH} = -\log_{10}(5.8 \times 10^{-6}) = 5.23 \quad \text{pH} = 14.00 - \text{pOH} = 8.77$$

- (b) the molar solubility of copper (II) hydroxide in a solution having pH=1.00;

Answer:

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-1}} = 1.00 \times 10^{-13}$$

$$[\text{Cu}^{2+}] = \frac{1.0 \times 10^{-16}}{(1.00 \times 10^{-13})^2} = 1.0 \times 10^{10}$$

i.e. completely soluble.

(c) the molar solubility of copper (II) hydroxide in a solution having pH=13.00.

Answer:

$$[\text{OH}^-] = 0.10 \text{ M}$$

$$[\text{Cu}^{2+}] = \frac{1.0 \times 10^{-16}}{(0.10)^2} = 1.0 \times 10^{-14} \text{ M}$$

8. Problem 54, page 814 textbook.

Answer:

$$\text{Cu}(\text{NH}_3)_4^{2+} \rightleftharpoons \text{Cu}^{2+} + 4\text{NH}_3(aq) \quad K = \frac{1}{K_f} = \frac{1}{1.1 \times 10^{13}} = 9.1 \times 10^{-14}$$

	$[\text{Cu}(\text{NH}_3)_4^{2+}]$	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$
initial	0.10 M	0 M	6.0-0.40 = 5.6 M
change	$-x$	x	$4x$
equilibrium	$(0.10 - x) \text{ M}$	$x \text{ M}$	$(5.6 + 4x) \text{ M}$

$$\frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = \frac{x(5.6 + x)^4}{0.10 - x} \approx \frac{x(5.6)^4}{0.10} = 9.1 \times 10^{-14}$$

$$x = [\text{Cu}^{2+}] = 9.2 \times 10^{-18} \text{ M}$$

9. Problem 56, page 814 textbook.

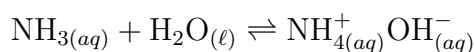
Answer:

As in problem 8

$$\text{Cu}(\text{NH}_3)_4^{2+} \rightleftharpoons \text{Cu}^{2+} + 4\text{NH}_3(aq) \quad K = \frac{1}{K_f} = \frac{1}{1.1 \times 10^{13}} = 9.1 \times 10^{-14}$$

$$\frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = \frac{[\text{Cu}^{2+}](0.10)^4}{0.015} = 9.1 \times 10^{-14}$$

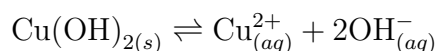
$$[\text{Cu}^{2+}] = 1.4 \times 10^{-11} \text{ M}$$



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
initial	0.10 M	0.10 M	0 M
change	$-x$	x	x
equilibrium	$(0.10 - x)$ M	$(0.10 + x)$ M	x M

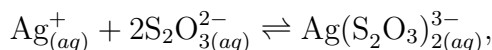
$$\frac{(0.10 + x)x}{0.10 - x} \approx x = 1.8 \times 10^{-5} = [\text{OH}^-]$$



$$Q = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.4 \times 10^{-11})(1.8 \times 10^{-5})^2 \\ = 4.5 \times 10^{-21} < K_{sp}$$

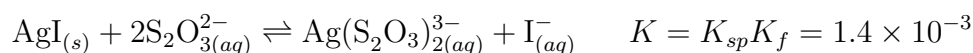
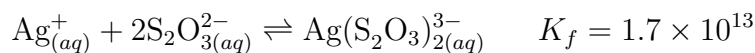
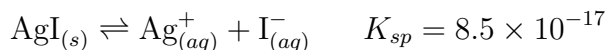
No precipitate.

10. Aqueous silver ions form a coordination complex with thiosulfate anions according to the reaction



where the formation equilibrium constant for the complex is $K_f = 1.7 \times 10^{13}$. Given the solubility product of silver iodide, AgI, is $K_{sp} = 8.5 \times 10^{-17}$, calculate the molar solubility of silver iodide in a solution that is 0.100 M in thiosulfate.

Answer:



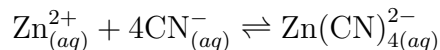
	$[\text{S}_2\text{O}_3^{2-}]$	$[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]$	$[\text{I}^-]$
initial	0.100 M	0 M	0 M
change	$-2y$	y	y
equilibrium	$(0.100 - 2y)$ M	y M	y M

$$\frac{y^2}{(0.100 - 2y)^2} = 1.4 \times 10^{-3}$$

$$\frac{y}{0.100 - 2y} = 3.7 \times 10^{-3}$$

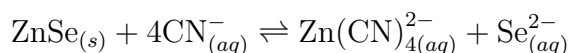
$$y = 3.4 \times 10^{-3} \text{ M}$$

11. Zinc ions form a complex in cyanide solutions according to the reaction



with a formation constant $K_f = 1.0 \times 10^{18}$. It is found that the solubility of solid zinc selenide (ZnSe) in a 0.100 M cyanide solution is 6.0×10^{-5} M. Calculate the solubility of zinc selenide in water.

Answer:

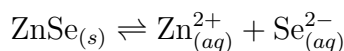


	$[\text{CN}^{-}]$	$[\text{Zn}(\text{CN})_4^{2-}]$	$[\text{Se}^{2-}]$
initial	0.100 M	0 M	0 M
change	$-4(6.0 \times 10^{-5})$ M	6.0×10^{-5} M	6.0×10^{-5} M
equilibrium	0.100 M	6.0×10^{-5} M	6.0×10^{-5} M

$$K = \frac{(6.0 \times 10^{-5})^2}{(0.100)^4} = 3.6 \times 10^{-5}$$

$$= K_{sp}K_f = 1.0 \times 10^{18}K_{sp}$$

$$K_{sp} = 3.6 \times 10^{-23}$$

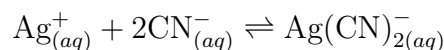


	$[\text{Zn}^{2+}]$	$[\text{Se}^{2-}]$
initial	0 M	0 M
change	s M	s M
equilibrium	s M	s M

$$s^2 = 3.6 \times 10^{-23}$$

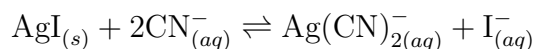
$$s = 6.0 \times 10^{-12} \text{ M}$$

12. The silver cyanide coordination complex, $\text{Ag}(\text{CN})_2^{-}$ forms by the reaction



with associated equilibrium constant $K_f = 5.6 \times 10^{18}$. Given the solubility product of silver iodide (AgI) is $K_{sp} = 8.5 \times 10^{-17}$, calculate the solubility of silver iodide in a solution having $[\text{CN}^{-}] = 0.500$ M.

Answer:



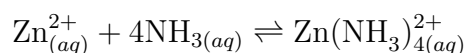
$$K = K_fK_{sp} = 5.6 \times 10^{18} \times 8.5 \times 10^{-17} = 4.8 \times 10^2$$

	$[\text{CN}^-]$	$[\text{Ag}(\text{CN})_2^-]$	$[\text{I}^-]$
initial	0.500 M	0 M	0 M
change	$-2s$	s	s
equilibrium	$(0.500 - 2s)$ M	s M	s M

$$4.8 \times 10^2 = \frac{[\text{Ag}(\text{CN})_2^-][\text{I}^-]}{[\text{CN}^-]^2} = \frac{s^2}{(0.500 - 2s)^2}$$

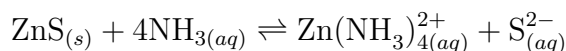
$$\frac{s}{0.500 - 2s} = 22. \quad s = 11. - 44.s \quad s = 0.24 \text{ M}$$

13. Zinc ions form a coordination complex in aqueous ammonia



having formation equilibrium constant $K_f = 4.1 \times 10^8$. Zinc sulfide (ZnS) is only sparingly soluble in water with solubility product constant $K_{sp} = 2.0 \times 10^{-25}$. Calculate the molar solubility of zinc sulfide in a 0.10 M aqueous ammonia solution. Approximations work for this system.

Answer:



$$K = K_f K_{sp} = 8.2 \times 10^{-17} = \frac{[\text{Zn}(\text{NH}_3)_4^{2+}][\text{S}^{2-}]}{[\text{NH}_3]^4}$$

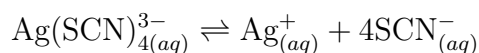
	$[\text{NH}_3]$	$[\text{Zn}(\text{NH}_3)_4^{2+}]$	$[\text{S}^{2-}]$
initial	0.10 M	0 M	0 M
change	$-4s$	s	s
equilibrium	$(0.10 - 4s)$ M	s M	s M

$$8.2 \times 10^{-17} = \frac{s^2}{(0.10 - 4s)^4} \approx \frac{s^2}{1.0 \times 10^{-4}}$$

$$s = 9.1 \times 10^{-11} \text{ M}$$

14. Silver ions (Ag^+) react with thiocyanate ions (SCN^-) in aqueous solution to form the coordination complex $\text{Ag}(\text{SCN})_4^{3-}$ with associated formation constant $K_f = 1.2 \times 10^{10}$. Consider a solution that is made by adding 0.050 moles of silver ions to 0.250 L of a 2.50 M thiocyanate solution. Calculate the concentration of free silver ions (Ag^+) when equilibrium is reached. Approximations work for this problem.

Answer



$$K = \frac{1}{K_f} = 8.3 \times 10^{-11}$$

Initially

$$[\text{Ag}(\text{SCN})_4^{3-}] = \frac{0.050 \text{ mol}}{0.250 \text{ L}} = 0.20 \text{ M}$$

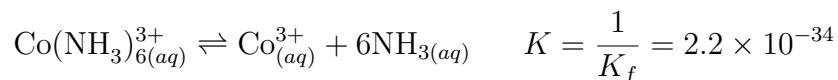
	$[\text{Ag}(\text{SCN})_4^{3-}]$	$[\text{Ag}^+]$	$[\text{SCN}^-]$
initial	0.20 M	0 M	$(2.50 - 4(0.20)) = 1.70 \text{ M}$
change	$-y$	y	$4y$
equilibrium	$(0.20 - y) \text{ M}$	$y \text{ M}$	$(1.70 + 4y) \text{ M}$

$$8.3 \times 10^{-11} = \frac{[\text{Ag}^+][\text{SCN}^-]^4}{[\text{Ag}(\text{SCN})_4^{3-}]} = \frac{y(1.70 + 4y)^4}{(0.20 - y)} \approx \frac{y(1.70)^4}{0.20}$$

$$y = [\text{Ag}^+] = 2.0 \times 10^{-12} \text{ M}$$

15. The formation equilibrium constant for the cobalt ammonia complex $[\text{Co}(\text{NH}_3)_6^{3+}]$ is $K_f = 4.5 \times 10^{33}$. Calculate the molar concentration of free $\text{Co}_{(aq)}^{3+}$ in a solution made by mixing 0.100 L of 0.0500 M Co^{3+} to 0.500 L of 0.250 M aqueous ammonia. Approximations work for this problem.

Answer:



We assume initially all the cobalt ions are in the form of the complex. The initial concentrations are found using

$$n_{\text{Co}^{3+}} = (0.0500 \text{ mol L}^{-1})(0.100 \text{ L}) = 5.00 \times 10^{-3} \text{ mol}$$

Before complexation

$$n_{\text{NH}_3} = (0.250 \text{ mol L}^{-1})(0.500 \text{ L}) = 0.125 \text{ mol}$$

After complexation

$$n_{\text{NH}_3} = 0.125 \text{ mol} - 6(5.00 \times 10^{-3} \text{ mol}) = 0.095 \text{ mol}$$

$$[\text{Co}(\text{NH}_3)_6^{3+}] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.600 \text{ L}} = 8.33 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3] = \frac{0.095 \text{ mol}}{0.600 \text{ L}} = 0.16 \text{ M}$$

	$[\text{Co}(\text{NH}_3)_6^{3+}]$	$[\text{Co}^{3+}]$	$[\text{NH}_3]$
initial	$8.33 \times 10^{-3} \text{ M}$	0 M	0.16 M
change	$-y$	y	$6y$
equilibrium	$(8.33 \times 10^{-3} - y) \text{ M}$	$y \text{ M}$	$(0.16 + 6y) \text{ M}$

$$2.2 \times 10^{-34} = \frac{[\text{Co}^{3+}][\text{NH}_3]^6}{[\text{Co}(\text{NH}_3)_6^{3+}]} = \frac{y(0.16 + 6y)^6}{8.33 \times 10^{-3} - y} \approx \frac{y(0.16)^6}{8.33 \times 10^{-3}}$$

$$y = [\text{Co}^{3+}] = 1.2 \times 10^{-31} \text{ M}$$

16. The solubility product constant for zinc oxalate (ZnC_2O_4) is 2.7×10^{-8} and the formation constant for the zinc cyanide coordination complex $[\text{Zn}(\text{CN})_4^{2-}]$ is 1.0×10^{18} . Consider a mixture that is formed by combining 0.25 L of a $1.0 \times 10^{-4} \text{ M}$ CN^- solution and 0.35 L of a $6.0 \times 10^{-6} \text{ M}$ Zn^{2+} solution. After the solutions are mixed 0.50 moles of oxalate ions are added to the solution. Assuming the added oxalate does not change the total volume of the solution, determine if a zinc oxalate precipitate will form. Approximations work for this problem.

Answer: Before complex formation

$$n_{\text{CN}^-} = (1.0 \times 10^{-4} \text{ mol L}^{-1})(0.25 \text{ L}) = 2.5 \times 10^{-5} \text{ mol}$$

$$n_{\text{Zn}^{2+}} = (6.0 \times 10^{-6} \text{ mol L}^{-1})(0.35 \text{ L}) = 2.1 \times 10^{-6} \text{ mol}$$

After complex formation

$$n_{\text{CN}^-} = 2.5 \times 10^{-5} \text{ mol} - 4(2.1 \times 10^{-6} \text{ mol}) = 1.7 \times 10^{-5} \text{ mol}$$

$$[\text{CN}^-] = \frac{1.7 \times 10^{-5} \text{ mol}}{0.60 \text{ L}} = 2.8 \times 10^{-5} \text{ M} \quad [\text{Zn}(\text{CN})_4^{2-}] = \frac{2.1 \times 10^{-6} \text{ mol}}{0.60 \text{ L}} = 3.5 \times 10^{-6} \text{ M}$$

$$\text{Zn}(\text{CN})_{4(aq)}^{2-} \rightleftharpoons \text{Zn}_{(aq)}^{2+} + 4\text{CN}_{(aq)}^- \quad K = \frac{1}{K_f} = 1.0 \times 10^{-18} = \frac{[\text{Zn}^{2+}][\text{CN}^-]^4}{[\text{Zn}(\text{CN})_4^{2-}]}$$

	$[\text{Zn}(\text{CN})_4^{2-}]$	$[\text{Zn}^{2+}]$	$[\text{CN}^-]$
initial	$3.5 \times 10^{-6} \text{ M}$	0 M	$2.8 \times 10^{-5} \text{ M}$
change	$-y$	y	$4y$
equilibrium	$(3.5 \times 10^{-6} - y) \text{ M}$	$y \text{ M}$	$(2.8 \times 10^{-5} + 4y) \text{ M}$

$$1.0 \times 10^{-18} = \frac{y(2.8 \times 10^{-5} + 4y)^4}{2.5 \times 10^{-6} - y} \approx \frac{y(2.8 \times 10^{-5})^4}{3.5 \times 10^{-6}}$$

$$y = [\text{Zn}^{2+}] = 1.4 \times 10^{-5} \text{ M}$$

$$[\text{C}_2\text{O}_4^{2-}] = \frac{0.50 \text{ mol}}{0.60 \text{ L}} = 0.83 \text{ M}$$

$$Q = [\text{Zn}^{2+}][\text{C}_2\text{O}_4^{2-}] = (1.4 \times 10^{-5})(0.83) = 1.2 \times 10^{-5} > K_{sp}$$

Precipitate forms