Chemistry 192
Problem Set 6
Spring, 2018
Solutions

1. The solubility product of $Al(OH)_3$ 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:

$$Al(OH)_{3(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3OH^-_{(aq)}$$

$$K_{sp} = [Al^{3+}][OH^-]^3 = 1.1 \times 10^{-15}$$

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

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

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

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

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{2.4 \times 10^{-4}} = 4.2 \times 10^{-11}$$

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

$$Ag_2S_{(s)} \rightleftharpoons 2Ag^+_{(aq)} + S^{2-}_{(aq)}$$

	$[Ag^+]$	$[S^{2-}]$
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 $\times 10^{-4}$ g mL^{-1}. Calculate the solubility product of silver arsenate.
Answer:

$$Ag_3AsO_{4(s)} \rightleftharpoons 3Ag^+_{(aq)} + AsO^{3-}_{4(aq)}$$

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

$$[AsO_4^{3-}] = \frac{1.8 \times 10^{-6}\ \text{mol}}{0.00100\ \text{L}} = 1.8 \times 10^{-3}\ \text{M}$$

$$[Ag^+] = 3[AsO_4^{3-}] = 5.5 \times 10^{-3}\ \text{M}$$

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

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:

$$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO^{2-}_{3(aq)}$$

(a)

	$[Ag^+]$	$[CO_3^{2-}]$
initial	0 M	0 M
change	$2s$	s
equilibrium	$2s$ M	s M

$$[Ag^+]^2[CO_3^{2-}] = 4s^3 = 5.0 \times 10^{-12}$$

$$s = \text{solubility} = [CO_3^{2-}] = 1.1 \times 10^{-4}\ \text{M}$$

(b)

	$[Ag^+]$	$[CO_3^{2-}]$
initial	0.20 M	0 M
change	$2s$	s
equilibrium	$(0.20 + 2s)$ M	s 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:

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = 1.1 \times 10^{-10}$$

$$[\mathrm{Ag^+}] = \frac{1.1 \times 10^{-10}}{0.10} = 1.1 \times 10^{-9}\ \mathrm{M}$$

$$(1.1 \times 10^{-9}\ \mathrm{mol\ L^{-1}})(0.010\ \mathrm{L}) = 1.1 \times 10^{-11}\ \mathrm{mol}$$

$$(1.1 \times 10^{-11}\ \mathrm{mol})(170.\ \mathrm{g\ mol^{-1}}) = 1.9 \times 10^{-9}\ \mathrm{g}$$

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:

$$\mathrm{Ag_2SO_{4(s)}} \rightleftharpoons 2\mathrm{Ag^+_{(aq)}} + \mathrm{SO^{2-}_{4(aq)}}$$

$$[\mathrm{Ag^+}] = 0.0050\ \mathrm{M} \qquad [\mathrm{SO_4^{2-}}] = 0.010\ \mathrm{M}$$

$$Q = [\mathrm{Ag^+}]^2[\mathrm{SO_4^{2-}}] = (0.0050)^2(0.010) = 2.5 \times 10^{-7} < K_{sp}$$

No precipitation.

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

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

$$\mathrm{Cu(OH)_{2(s)}} \rightleftharpoons \mathrm{Cu^{2+}_{(aq)}} + 2\mathrm{HO^-_{(aq)}}$$

$$K_{sp} = [\mathrm{Cu^{2+}}][\mathrm{OH^-}]^2$$

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

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

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

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

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

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

i.e. completely soluble.

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

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

$$[Cu^{2+}] = \frac{1.0 \times 1)^{-16}}{(0.10)^2} = 1.0 \times 10^{-14} \text{ M}$$

8. Problem 54, page 814 textbook.
Answer:

$$Cu(NH_3)^{2+}_{4(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 4NH_{3(aq)} \qquad K = \frac{1}{K_f} = \frac{1}{1.1 \times 10^{13}} = 9.1 \times 10^{-14}$$

	$[Cu(NH_3)^{2+}_2]$	$[Cu^{2+}]$	$[NH_3]$
initial	0.10 M	0 M	6.0-0.40 = 5.6 M
change	-x	x	$4x$
equilibrium	$(0.10 - x)$ M	x M	$(5.6 + 4x)$ M

$$\frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)^{2+}_4]} = \frac{x(5.6+x)^4}{0.10-x} \approx \frac{x(5.6)^4}{0.10} = 9.1 \times 10^{-14}$$

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

9. Problem 56, page 814 textbook.
Answer:
As in problem 8

$$Cu(NH_3)^{2+}_{4(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 4NH_{3(aq)} \qquad K = \frac{1}{K_f} = \frac{1}{1.1 \times 10^{13}} = 9.1 \times 10^{-14}$$

$$\frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)^{2+}_4]} = \frac{[Cu^{2+}](0.10)^4}{0.015} = 9.1 \times 10^{-14}$$

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

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)}OH^-_{(aq)}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
initial	0.10 M	0.10 M	0 M
change	-x	x	x
equilibrium	$(0.10 - x)$ M	$(0.10 + x)$ M	x M

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

$$Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)}$$

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

No precipitate.

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

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons Ag(S_2O_3)^{3-}_{2(aq)},$$

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:

$$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)} \qquad K_{sp} = 8.5 \times 10^{-17}$$

$$\underline{Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons Ag(S_2O_3)^{3-}_{2(aq)} \qquad K_f = 1.7 \times 10^{13}}$$

$$AgI_{(s)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons Ag(S_2O_3)^{3-}_{2(aq)} + I^-_{(aq)} \qquad K = K_{sp}K_f = 1.4 \times 10^{-3}$$

	$[S_2O_3^{2-}]$	$[Ag(S_2O_3)_2^{3-}]$	$[I^-]$
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

$$\mathrm{Zn}^{2+}_{(aq)} + 4\mathrm{CN}^{-}_{(aq)} \rightleftharpoons \mathrm{Zn(CN)}^{2-}_{4(aq)}$$

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:

$$\mathrm{ZnSe}_{(s)} + 4\mathrm{CN}^{-}_{(aq)} \rightleftharpoons \mathrm{Zn(CN)}^{2-}_{4(aq)} + \mathrm{Se}^{2-}_{(aq)}$$

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

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

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

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

$$\mathrm{ZnSe}_{(s)} \rightleftharpoons \mathrm{Zn}^{2+}_{(aq)} + \mathrm{Se}^{2-}_{(aq)}$$

	$[\mathrm{Zn}^{2+}]$	$[\mathrm{Se}^{2-}]$
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, $\mathrm{Ag(CN)}_2^-$ forms by the reaction

$$\mathrm{Ag}^{+}_{(aq)} + 2\mathrm{CN}^{-}_{(aq)} \rightleftharpoons \mathrm{Ag(CN)}^{-}_{2(aq)}$$

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 $[\mathrm{CN}^-]$=0.500 M.

Answer:

$$\mathrm{AgI}_{(s)} + 2\mathrm{CN}^{-}_{(aq)} \rightleftharpoons \mathrm{Ag(CN)}^{-}_{2(aq)} + \mathrm{I}^{-}_{(aq)}$$

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

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

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

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

13. Zinc ions form a coordination complex in aqueous ammonia

$$Zn^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons Zn(NH_3)^{2+}_{4(aq)}$$

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:

$$ZnS_{(s)} + 4NH_{3(aq)} \rightleftharpoons Zn(NH_3)^{2+}_{4(aq)} + S^{2-}_{(aq)}$$

$$K = K_f K_{sp} = 8.2 \times 10^{-17} = \frac{[Zn(NH_3)_4^{2+}][S^{2-}]}{[NH_3]^4}$$

	$[NH_3]$	$[Zn(NH_3)_4^{2+}]$	$[S^{2-}]$
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 $Ag(SCN)_4^{3-}$ 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

$$Ag(SCN)^{3-}_{4(aq)} \rightleftharpoons Ag^+_{(aq)} + 4SCN^-_{(aq)}$$

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

Initially

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

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

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

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

15. The formation equilibrium constant for the cobalt ammonia complex $[\mathrm{Co(NH_3)_6^{3+}}]$ is $K_f = 4.5 \times 10^{33}$. Calculate the molar concentration of free $\mathrm{Co^{3+}_{(aq)}}$ in a solution made by mixing 0.100 L of 0.0500 M $\mathrm{Co^{3+}}$ to 0.500 L of 0.250 M aqueous ammonia. Approximations work for this problem.
Answer:

$$\mathrm{Co(NH_3)^{3+}_{6(aq)} \rightleftharpoons Co^{3+}_{(aq)} + 6NH_{3(aq)}} \qquad K = \frac{1}{K_f} = 2.2 \times 10^{-34}$$

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

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

Before complexation

$$n_{NH_3} = (0.250 \text{ mol L}^{-1})(0.500 \text{ L}) = 0.125 \text{ mol}$$

After complexation

$$n_{NH_3} = 0.125 \text{ mol} - 6(5.00 \times 10^{-3} \text{ mol}) = 0.095 \text{ mol}$$

$$[\mathrm{Co(NH_3)_6^{3+}}] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.600 \text{ L}} = 8.33 \times 10^{-3} \text{ M}$$

$$[\mathrm{NH_3}] = \frac{0.095 \text{ mol}}{0.600 \text{ L}} = 0.16 \text{ M}$$

	$[Co(NH_3)_6^{3+}]$	$[Co^{3+}]$	$[NH_3]$
initial	8.33 $\times 10^{-3}$ M	0 M	0.16 M
change	-y	y	$6y$
equilibrium	$(8.33 \times 10^{-3} - y)$ M	y M	$(0.16 + 6y)$ M

$$2.2 \times 10^{-34} = \frac{[Co^{3+}][NH_3]^6}{[Co(NH_3)_6^{3+}]} = \frac{y(0.16+6y)^6}{8.33 \times 10^{-3} - y} \approx \frac{y(0.16)^6}{8.33 \times 10^{-3}}$$

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

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 $[Zn(CN)_4^{2-}]$ is 1.0×10^{18}. Consider a mixture that is formed by combing 0.25 L of a 1.0×10^{-4} M CN^- solution and 0.35 L of a 6.0×10^{-6} 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

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

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

After complex formation

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

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

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

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

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

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

$$[C_2O_4^{2-}] = \frac{0.50 \text{ mol}}{0.60 \text{ L}} = 0.83 \text{ M}$$

$$Q = [Zn^{2+}][C_2O_4^{2-}] = (1.4 \times 10^{-5})(0.83) = 1.2 \times 10^{-5} > K_{sp}$$

Precipitate forms