Problem 16.10. Ammonium hexachloroplatinate(IV), $(NH_4)_2(PtCl_6)$, is one of the few sparingly soluble ammonium salts. Its K_{sp} at 20°C is 5.6×10^{-6}. Compute its solubility in grams per liter of solution.

Solution: The solubility equilibrium is

$$(NH_4)_2(PtCl_6)(s) \rightleftharpoons 2\,NH_4{}^+(aq) + PtCl_6{}^{2-}(aq)$$

and the expression for the solubility product is

$$K_{sp} = [NH_4^+]^2[PtCl_6^{2-}] = 5.6 \times 10^{-6}$$

Suppose s mol of $(NH_4)_2(PtCl_6)$ is dissolved in 1 L, the equilibrium concentration of $NH_4{}^+$ and $PtCl_6{}^{2-}$ will be $2s$ M and s M, respectively. So we have

$$K_{sp} = [NH_4^+]^2[PtCl_6^{2-}] = (2s)^2 \cdot s = 4s^3 = 5.6 \times 10^{-6} \Longrightarrow s = 0.011$$

Therefore, the solubility in grams per liter of $(NH_4)_2(PtCl_6)$ solution is

$$solubility(g \cdot L^{-1}) = s \cdot M((NH_4)_2(PtCl_6)) = 0.011 mol \cdot L^{-1} \times 443.87 g \cdot mol^{-1} = \underline{4.9 g \cdot L^{-1}}$$

□

Problem 16.15. At 100°C, water dissolves 1.8×10^{-2} g of AgCl per liter. Compute the K_{sp} of AgCl at this temperature.

Solution: The solubility equilibrium is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The concentration of Ag^+ and Cl^- is

$$[Ag^+] = [Cl^-] = \frac{solubility(g \cdot L^{-1}) of AgCl}{M(AgCl)} = \frac{1.8 \times 10^{-2} g \cdot L^{-1}}{143.32 g \cdot mol^{-1}} = 1.26 \times 10^{-4} mol \cdot L^{-1}$$

Therefore, the K_{sp} of AgCl is

$$K_{sp} = [Ag^+][Cl^-] = 1.26 \times 10^{-4} \times 1.26 \times 10^{-4} mol = \underline{1.6 \times 10^{-8}}$$

□

Problem 16.20. Suppose 100.0 mL of a 0.0010 M $CaCl_2$ solution is added to 50.0 mL of a 6.0×10^{-5} M NaF solution at 25°C. Determine whether $CaF_2(s)$ ($K_{sp} = 3.9 \times 10^{-11}$) tends to precipitate from this mixture.

Solution: Suppose the total volume of the mixed solution is the sum of volume of the $CaCl_2$ solution and the NaF solution, which is

$$V = V_1 + V_2 = 100.0mL + 50.0mL = 150.0mL = 0.1500L$$

The concentration of Ca^{2+} and F^- in the solution after mix are

$$[Ca^{2+}] = \frac{c_1(CaCl_2)V_1}{V} = \frac{0.0010mol \cdot L^{-1} \times 0.1000L}{0.1500L} = 6.67 \times 10^{-4} mol \cdot L^{-1}$$
$$[F^-] = \frac{c_2(NaF)V_2}{V} = \frac{6.0 \times 10^{-5} mol \cdot L^{-1} \times 0.0500L}{0.1500L} = 2.0 \times 10^{-5} mol \cdot L^{-1}$$

The solubility equilibrium of CaF_2 is

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

So the reaction quotient is

$$Q_{sp} = [Ca^{2+}][F^-]^2 = 6.67 \times 10^{-4} \times (2.0 \times 10^{-5})^2 = 2.7 \times 10^{-13}$$

Since $Q_{sp} = 2.7 \times 10^{-13} < 3.9 \times 10^{-11} = K_{sp}$, the $CaF_2(s)$ does not tend to precipitate from this mixture. □

Problem 16.27. The solubility product of nickel(II) hydroxide, $Ni(OH)_2$, at 25°C is $K_{sp} = 1.6 \times 10^{-16}$.
(a) Calculate the molar solubility of $Ni(OH)_2$ in pure water at 25°.
(b) Calculate the molar solubility of $Ni(OH)_2$ in 0.100 M NaOH.

Solution:
(a) The solubility equilibrium of $Ni(OH)_2$ is

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2\,OH^-(aq)$$

and the expression for the solubility product is

$$K_{sp} = [Ni^{2+}][OH^-]^2 = 1.6 \times 10^{-16}$$

Suppose the molar solubility of $Ni(OH)_2$ in pure water is s_1 M, then the concentration of Ni^{2+} and OH^- are s_1 M and $2s_1$ M, respectively. So we have

$$K_{sp} = [Ni^{2+}][OH^-]^2 = s_1 \cdot (2s_1)^2 = 4s_1^3 = 1.6 \times 10^{-16} \Longrightarrow s_1 = 3.4 \times 10^{-6}$$

Therefore, the molar solubility of $Ni(OH)_2$ in pure water at 25°C is $\underline{3.4 \times 10^{-6}\ \text{M}}$.
(b) The concentration of OH^- in 0.100 M NaOH is 0.100 M. Suppose the molar solubility of $Ni(OH)_2$ in 0.100 M NaOH is s_2 M, then the concentration of Ni^{2+} is s_2 M. So we have

$$K_{sp} = [Ni^{2+}][OH^-]^2 = s_2 \cdot (0.100)^2 = 1.6 \times 10^{-16} \Longrightarrow s_2 = 1.6 \times 10^{-14}$$

Therefore, the molar solubility of $Ni(OH)_2$ in 0.100 M NaOH at 25°C is $\underline{1.6 \times 10^{-14}\ \text{M}}$. □

Problem 16.32. Compare the molar solubility of $Mg(OH)_2$ in pure water with that in a solution buffered at pH 9.00.

Solution: The solubility equilibrium of $Mg(OH)_2$ is

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

and the expression for the solubility product is

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$$

In pure water, suppose the molar solubility of $Mg(OH)_2$ is s_1 M, then the concentration of Mg^{2+} and OH^- are s_1 M and $2s_1$ M, respectively. So we have

$$K_{sp} = [Mg^{2+}][OH^-]^2 = s_1 \cdot (2s_1)^2 = 4s_1^3 = 1.2 \times 10^{-11} \Longrightarrow s_1 = 1.4 \times 10^{-4}$$

In a solution buffered at pH 9.00, the concentration of OH^- is

$$[OH^-] = 10^{-14.00+pH} mol \cdot L^{-1} = 10^{-5} mol \cdot L^{-1}$$

Suppose the molar solubility of $Mg(OH)_2$ is s_2 M, then the concentration of Mg^{2+} is s_2 M. So we have

$$K_{sp} = [Mg^{2+}][OH^-]^2 = s_2 \cdot (10^{-5})^2 = 1.2 \times 10^{-11}$$
$$\Longrightarrow s_2 = 0.12 > s_1 = 1.4 \times 10^{-4}$$

Therefore, $\underline{\text{the molar solubility of } Mg(OH)_2 \text{ in pure water is less than in a solution buffered at pH 9.00}}$. □

Problem 16.38. The organic compound 18-crown-6 (see preceding problem) also binds strongly with the alkali metal ions in methanol.

$$K^+ + 18\text{-crown}-6 \rightleftharpoons [\text{complex}]^+$$

In methanol solution the equilibrium constant is 1.41×10^6. A similar reaction with Cs 1 has an equilibrium constant of only 2.75×10^4. A solution is made (in methanol) containing $0.020 mol \cdot L^{-1}$ each of K^+ and Cs^+. It also contains $0.30 mol \cdot L^{-1}$ of 18-crown-6. Compute the equilibrium concentrations of both the uncomplexed K^+ and the uncomplexed Cs^+.

Solution: The solubility equilibrium of K^+ with 18-crown-6 is

$$Cs^+(aq) + 18\text{-crown}-6(aq) \rightleftharpoons Cs-\text{crown}^+(aq),\ K_{sp} = 2.75 \times 10^4$$

Because K_{sp} of both two solubility equilibrium is very large, the equilibrium concentration of 18-crown-6 is approximately

$$\begin{aligned}[18 - crown - 6(aq)] =& [18 - crown - 6(aq)]_0 - [K^+]_0 - [Cs^+]_0 \\ =& 0.30 mol \cdot L^{-1} - 0.020 mol \cdot L^{-1} - 0.020 mol \cdot L^{-1} = 0.26 mol \cdot L^{-1}\end{aligned}$$

Suppose the equilibrium concentration of K^+ and Cs^+ are $-x$ M and y M, respectively, then So the expression for the solubility products of the two equilibrium is

	$K^+(aq)$	+	18-crown$-6(aq)$	$\rightleftharpoons$	$K-\text{crown}^+(aq)$
Equilibrium, M	x		0.26		$0.020 - x$

	$Cs^+(aq)$	+	18-crown$-6(aq)$	$\rightleftharpoons$	$Cs-\text{crown}^+(aq)$
Equilibrium, M	y		0.26		$0.020 - y$

$$\begin{aligned}K_{sp1} &= \frac{[K - crown^+]}{[K^+][18 - crown - 6]} = \frac{0.020 - x}{0.26x} = 1.41 \times 10^6 \\ K_{sp2} &= \frac{[Sc - crown^+]}{[Cs^+][18 - crown - 6]} = \frac{0.020 - y}{0.26y} = 2.75 \times 10^4 \\ &\Longrightarrow x = 5.5 \times 10^{-8},\ \ y = 2.8 \times 10^{-6}\end{aligned}$$

Therefore, the equilibrium concentrations of the uncomplexed K^+ and umcomplexed Cs^+ are $\underline{5.5 \times 10^{-8} mol \cdot L^{-1}}$ and $\underline{2.8 \times 10^{-6} mol \cdot L^{-1}}$, respectively. □

Problem 16.47. K_{sp} for $Pb(OH)_2$ is 4.2×10^{-15}, and K_f for $Pb(OH)_3{}^-$ is 4×10^{14}. Suppose a solution whose initial concentration of $Pb^{2+}(aq)$ is 1.00 M is brought to pH 13.0 by addition of solid NaOH. Will solid $Pb(OH)_2$ precipitate, or will the lead be dissolved as $Pb(OH)_3{}^-(aq)$? What will be Pb^{2+} and $[Pb(OH)_3{}^-]$ at equilibrium? Repeat the calculation for an initial $[Pb^{2+}]$ concentration of 0.050 M. (Hint: One way to solve this problem is to assume that

$Pb(OH)_2$(s) is present and calculate Pb^{2+} and [$Pb(OH)_3{}^-$] that would be in equilibrium with the solid. If the sum of these is less than the original Pb^{2+}, the remainder can be assumed to have precipitated. If not, there is a contradiction and we must assume that no $Pb(OH)_2$(s) is present. In this case we can calculate Pb^{2+} and [$Pb(OH)_3{}^-$] directly from K_f.)

Solution: The equilibrium equation and the expression of equilibrium equation of $Pb(OH)_3$ and Pb are

$$Pb(OH)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,OH^-(aq)$$

$$K_{sp} = [Pb^{2+}][OH^-]^2 = 4.2 \times 10^{-15}$$

$$Pb^{2+}(aq) + 3\,OH^-(aq) \rightleftharpoons Pb(OH)_3{}^-(aq)$$

$$K_f = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} = 4 \times 10^{14}$$

In the solution with pH pf 13.0, the concentration of OH^- is

$$[OH^-] = 10^{-14.0+pH} mol \cdot L^{-1} = 10^{-14.0+13.0} mol \cdot L^{-1} = 0.10 mol \cdot L^{-1}$$

When the initial concentration of 1.00 M: assume that $Pb(OH)_2$(s) is present, then we have

$$K_{sp} = [Pb^{2+}][OH^-]^2 = [Pb^{2+}] \times 0.10^2 = 4.2 \times 10^{-15} \Longrightarrow \underline{[Pb^{2+}] = 4.2 \times 10^{-13}}$$

and

$$K_f = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} = \frac{[Pb(OH)_3^-]}{4.2 \times 10^{-13} \times 0.10^3} = 4 \times 10^{14} \Longrightarrow \underline{[Pb(OH)_3^-] = 0.2 mol \cdot L^{-1}}$$

Since $[Pb^{2+}]+[Pb(OH)_3^-] = 4.2\times10^{-13} mol\cdot L^{-1}+0.2 mol\cdot L^{-1} < 1.00 mol\cdot L^{-1} = [Pb^{2+}]_0$, the assumption is correct. Therefore, solid $Pb(OH)_2$ precipitate and some lead will be dissolved as $Pb(OH)_3{}^-$.

When the initial concentration of 0.050 M: the former assumption is not correct any more, since $[Pb^{2+}]+[Pb(OH)_3^-] = 4.2\times10^{-13}+0.2 mol\cdot L^{-1} > 0.050 mol\cdot L^{-1} = [Pb^{2+}]_0$. Therefore, solid $Pb(OH)_2$ will not precipitate, but the lead will be dissolved as $Pb(OH)_3{}^-$. In this way, suppose the concentration of Pb^{2+} and $Pb(OH)_3{}^-$ will have following relationship

$$[Pb^{2+}] + [Pb(OH)_3^-] = [Pb^{2+}]_0 = 0.050 mol \cdot L^{-1}$$

So we have

$$K_f = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} = \frac{(0.050 - [Pb^{2+}])}{[Pb^{2+}] \times 0.10^3} = 4 \times 10^{14}$$

$$\Longrightarrow \underline{[Pb^{2+}] = 1 \times 10^{-13} mol \cdot L^{-1}}, \ \underline{[Pb(OH)_3^-] = 0.050 mol \cdot L^{-1}}$$

□

Problem 16.53. Calculate the $[Zn^{2+}]$ in a solution that is in equilibrium with ZnS(s) and in which $[H_3O^+] = 1.0 \times 10^{-5}$ M and $[H_2S] = 0.10$ M.

Solution: The concentration of OH^- is

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{1.0 \times 10^{-5}} mol \cdot L^{-1} = 1.0 \times 10^{-9} mol \cdot L^{-1}$$

The ionization equilibrium equation of H_2S is

$$\mathrm{H_2S\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)}$$

and the expression of its ionization constant is

$$K_a = \frac{[H_3O^+][HS^-]}{[H_2S]} = \frac{1.0 \times 10^{-5} \times [HS^-]}{0.10} = 9.1 \times 10^{-8} \Longrightarrow [HS^-] = 9.1 \times 10^{-4} mol \cdot L^{-1}$$

The solubility equilibrium of ZnS is

$$\mathrm{ZnS\,(s) + H_2O\,(l) \rightleftharpoons Zn^{2+}(aq) + HS^-(aq) + OH^-(aq)}$$

and the expression of its solubility product is

$$K_{sp} = [Zn^{2+}][HS^-][OH^-] = [Zn^{2+}] \times 9.1 \times 10^{-4} \times 1.0 \times 10^{-9} = 2 \times 10^{-25}$$
$$\Longrightarrow [Zn^{2+}] = \underline{2 \times 10^{-13} mol \cdot L^{-1}}$$

□

Problem 16.56. What is the highest pH at which 0.050 M Mn^{2+} will remain entirely in a solution that is saturated with H_2S at a concentration of $[H_2S] = 0.10$ M? At this pH, what would be the concentration of Cd^{2+} in equilibrium with solid CdS in this solution?

Solution: Suppose the concentration of [H3O+] is x M.Then the concentration of OH^- is

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{x} mol \cdot L^{-1}$$

The ionization equilibrium equation of H_2S is

$$\mathrm{H_2S\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)}$$

and the expression of its ionization constant is

$$K_a = \frac{[H_3O^+][HS^-]}{[H_2S]} = \frac{x[HS^-]}{0.10} = 9.1 \times 10^{-8} \Longrightarrow [HS^-] = \frac{9.1 \times 10^{-9}}{x} mol \cdot L^{-1}$$

The solubility equilibrium of MnS is

$$\mathrm{MnS(s) + H_2O(l) \rightleftharpoons Mn^{2+}(aq) + HS^-(aq) + OH^-(aq)}$$

and the expression of its solubility product is

$$K_{sp} = [Mn^{2+}][HS^-][OH^-] = 0.050 \times \frac{9.1 \times 10^{-9}}{x} \times \frac{10^{-14}}{x} = 3 \times 10^{-14}$$
$$\Longrightarrow \underline{[H_3O^+]} = xmol \cdot L^{-5} = 1.2 \times 10^{-5} mol \cdot L^{-1}$$

Therefore, the highest pH at which 0.050 M Mn^{2+} will remain entirely in a solution that is saturated with H_2S at a concentration of $[H_2S] = 0.10$ M is

$$\underline{pH} = -\log_{10}[H_3O^+] = -\log_{10}(1.2 \times 10^{-5}) = \underline{4.92}$$

At this pH, for the solubility equilibrium of solid CdS, we have

$$K_{sp} = [Cd^{2+}][HS^-][OH^-] = [Cd^{2+}] \times \frac{9.1 \times 10^{-9}}{1.2 \times 10^{-5}} \times \frac{10^{-14}}{1.2 \times 10^{-5}} = 7 \times 10^{-28}$$
$$\Longrightarrow \underline{[Cd^{2+}]} = \underline{1.1 \times 10^{-15} mol \cdot L^{-1}}$$

□