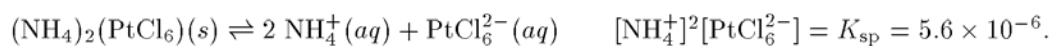


- 10.** Ammonium hexachloroplatinate(IV),  $(\text{NH}_4)_2(\text{PtCl}_6)$ , is one of the few sparingly soluble ammonium salts. Its  $K_{\text{sp}}$  at  $20^\circ\text{C}$  is  $5.6 \times 10^{-6}$ . Compute its solubility in grams per liter of solution.



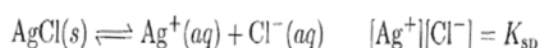
Let  $S = [\text{PtCl}_6^{2-}]$  at equilibrium at  $20^\circ\text{C}$ . If neither of the product ions reacts significantly with the solvent or with each other, then at equilibrium  $[\text{NH}_4^+] = 2S$ . Substitution gives

$$(2S)^2 S = 5.6 \times 10^{-6} \quad \text{which is easily solved: } S = 0.011 \text{ mol L}^{-1}$$

The gram solubility is  $(0.011 \text{ mol L}^{-1})(443.87 \text{ g mol}^{-1}) = 5.0 \text{ g L}^{-1}$ .

- 15.** At  $100^\circ\text{C}$ , water dissolves  $1.8 \times 10^{-2} \text{ g}$  of  $\text{AgCl}$  per liter. Compute the  $K_{\text{sp}}$  of  $\text{AgCl}$  at this temperature.

The dissolution reaction and its  $K_{\text{sp}}$ -expression are



At equilibrium in 1.00 L of the solution at  $100^\circ\text{C}$

$$n_{\text{Ag}^+} = 0.018 \text{ g} \times \left( \frac{1 \text{ mol AgCl}}{143.3 \text{ g AgCl}} \right) \left( \frac{1 \text{ mol Ag}^+}{1 \text{ mol AgCl}} \right) = 1.26 \times 10^{-4} \text{ mol}$$

Since the volume of the solution is 1.00 L, the concentration of  $\text{Ag}^+$  ion is  $1.26 \times 10^{-4} \text{ M}$ . The concentration of  $\text{Cl}^-$  ion is the same—one mole per liter of chloride ion is produced in solution for every mole per liter of silver ion. Substitute the concentrations into the mass-action expression

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (1.26 \times 10^{-4})(1.26 \times 10^{-4}) = \boxed{1.6 \times 10^{-8}} \text{ at } 100^\circ\text{C}$$

**Tip.** This  $K_{\text{sp}}$  exceeds the  $K_{\text{sp}}$  in text Table 16.2 (by a factor of 100!) because the temperature is higher.

- 20.** Suppose 100.0 mL of a  $0.0010 \text{ M}$   $\text{CaCl}_2$  solution is added to 50.0 mL of a  $6.0 \times 10^{-5} \text{ M}$   $\text{NaF}$  solution at  $25^\circ\text{C}$ . Determine whether  $\text{CaF}_2(s)$  ( $K_{\text{sp}} = 3.9 \times 10^{-11}$ ) tends to precipitate from this mixture.

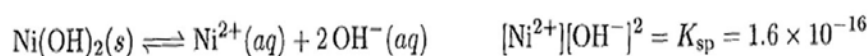
The calcium chloride and sodium fluoride solutions dilute each other as they are mixed. The concentration of  $\text{Ca}^{2+}$  is  $2/3$  of  $0.0010 \text{ M}$  immediately after mixing, and the concentration of  $\text{F}^-$  is  $1/3$  of  $6.0 \times 10^{-5} \text{ M}$ . Substituting these concentrations in the  $K_{\text{sp}}$  expression for  $\text{CaF}_2$  gives a  $Q$  of about  $2.7 \times 10^{-13}$ . Because this is less than  $K_{\text{sp}}$ , no precipitate forms.

**27.** The solubility product of nickel(II) hydroxide,  $\text{Ni}(\text{OH})_2$ , at  $25^\circ\text{C}$  is  $K_{\text{sp}} = 1.6 \times 10^{-16}$ .

(a) Calculate the molar solubility of  $\text{Ni}(\text{OH})_2$  in pure water at  $25^\circ\text{C}$ .

(b) Calculate the molar solubility of  $\text{Ni}(\text{OH})_2$  in  $0.100 \text{ M}$   $\text{NaOH}$ .

a) For every  $y \text{ mol L}^{-1}$  of  $\text{Ni}(\text{OH})_2$  that is dissolved at equilibrium,  $y \text{ mol L}^{-1}$  of  $\text{Ni}^{2+}$  and  $2y \text{ mol L}^{-1}$  of  $\text{OH}^-$  have formed according to the equation



Substituting into the  $K_{\text{sp}}$  expression gives the equation  $(y)(2y)^2 = 1.6 \times 10^{-16}$ . Solving gives  $y = 3.4 \times 10^{-6}$ . The solubility of  $\text{Ni}(\text{OH})_2$  is  $3.4 \times 10^{-6} \text{ mol L}^{-1}$  at  $25^\circ\text{C}$ .

b) The presence of a common ion (the  $\text{OH}^-$  ion) reduces the solubility of the nickel(II) hydroxide. Set up the usual three-line table:

	$\text{Ni}(\text{OH})_2(s)$	$\rightleftharpoons$	$\text{Ni}^{2+}(aq)$	$+$	$2\text{OH}^-(aq)$
Init. Conc. ( $\text{mol L}^{-1}$ )	—		0		0.100
Change in Conc. ( $\text{mol L}^{-1}$ )	—		$+z$		$+2z$
Equil. Conc. ( $\text{mol L}^{-1}$ )	—		$z$		$0.100 + 2z$

Substitute the equilibrium concentrations into the  $K_{\text{sp}}$  expression

$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = z(0.100 + 2z)^2 = 1.6 \times 10^{-16}$$

Assume that  $2z$  is much smaller than  $0.100 \text{ mol L}^{-1}$ . Then

$$(0.100)^2(z) = 1.6 \times 10^{-16} \quad \text{so that} \quad z = 1.6 \times 10^{-14} \text{ mol L}^{-1}$$

The assumption is obviously justified. The solubility is  $1.6 \times 10^{-14} \text{ mol L}^{-1}$  at  $25^\circ\text{C}$ .

**32.** Compare the molar solubility of  $\text{Mg}(\text{OH})_2$  in pure water with that in a solution buffered at  $\text{pH } 9.00$ .

a) Assume that neither the  $\text{Mg}^{2+}$  ion nor the  $\text{OH}^-$  ion from the dissolution of the  $\text{Mg}(\text{OH})_2$  interacts further in the solution. Then, if  $S$  is the solubility of the  $\text{Mg}(\text{OH})_2$ , the concentration of  $\text{Mg}^{2+}$  ion is  $S$  and the concentration of  $\text{OH}^-$  ion is  $2S$ . At equilibrium,

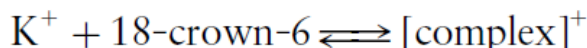
$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(2S)^2 \quad \text{from which} \quad S = 1.4 \times 10^{-4} \text{ mol L}^{-1}$$

b) If the solution is buffered at  $\text{pH} = 9$ , then the  $[\text{OH}^-]$  is being held at  $10^{-5} \text{ M}$ . This concentration is *less* than what forms from the dissolution of the  $\text{Mg}(\text{OH})_2$  in pure water. After the dissolution of  $\text{Mg}(\text{OH})_2$  comes to equilibrium, the concentration of  $\text{OH}^-$  ion remains at  $10^{-5} \text{ M}$  because of the action of the buffer. Let  $S$  again represent the solubility of the salt. Then:

$$K_{\text{sp}} = 1.2 \times 10^{-11} = S(10^{-5})^2$$

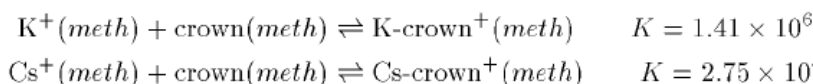
and the solubility is  $0.12 \text{ mol L}^{-1}$ .

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



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

The two equilibria are



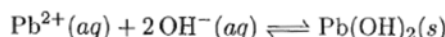
The equilibrium constants are fairly large, so both equilibria lie far to the right. The 18-crown-6 compound is in excess in the solution. Thus, effectively all of the  $\text{K}^+$  and  $\text{Cs}^+$  ion are consumed leaving  $0.30 - 0.020 - 0.020 = 0.26 \text{ mol L}^{-1}$  of crown and forming  $0.020 \text{ mol L}^{-1}$  of  $\text{K-crown}^+$  and  $0.020 \text{ mol L}^{-1}$  of  $\text{Cs-crown}^+$ .

$$1.41 \times 10^6 = \frac{[\text{K-crown}^+]}{[\text{K}^+][\text{crown}]} = \frac{0.020}{[\text{K}^+]0.26} \quad \text{from which} \quad [\text{K}^+] = 5.5 \times 10^{-8} \text{ mol L}^{-1}$$

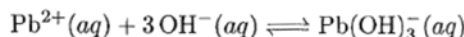
A similar computation on the  $\text{Cs}^+$  equilibrium gives  $[\text{Cs}^+] = 2.8 \times 10^{-6} \text{ mol L}^{-1}$ .

- 47.**  $K_{sp}$  for  $\text{Pb}(\text{OH})_2$  is  $4.2 \times 10^{-15}$ , and  $K_f$  for  $\text{Pb}(\text{OH})_3^-$  is  $4 \times 10^{14}$ . Suppose a solution whose initial concentration of  $\text{Pb}^{2+}(\text{aq})$  is 1.00 M is brought to pH 13.0 by addition of solid NaOH. Will solid  $\text{Pb}(\text{OH})_2$  precipitate, or will the lead be dissolved as  $\text{Pb}(\text{OH})_3^-(\text{aq})$ ? What will be  $[\text{Pb}^{2+}]$  and  $[\text{Pb}(\text{OH})_3^-]$  at equilibrium? Repeat the calculation for an initial  $\text{Pb}^{2+}$  concentration of 0.050 M. (*Hint:* One way to solve this problem is to *assume* that  $\text{Pb}(\text{OH})_2(\text{s})$  is present and calculate  $[\text{Pb}^{2+}]$  and  $[\text{Pb}(\text{OH})_3^-]$  that would be in equilibrium with the solid. If the sum of these is less than the original  $[\text{Pb}^{2+}]$ , the remainder can be assumed to have precipitated. If not, there is a contradiction and we must assume that *no*  $\text{Pb}(\text{OH})_2(\text{s})$  is present. In this case we can calculate  $[\text{Pb}^{2+}]$  and  $[\text{Pb}(\text{OH})_3^-]$  directly from  $K_f$ .)

The problem concerns the fate of  $\text{Pb}^{2+}(\text{aq})$  in a solution adjusted to pH 13.0 by the addition of NaOH. The precipitation reaction



tends to reduce the concentration of  $\text{Pb}^{2+}(\text{aq})$ . The  $K$  for this reaction is the reciprocal of the  $K_{sp}$  of  $\text{Pb}(\text{OH})_2(\text{s})$ . It is quite large ( $K_{sp}$  is  $4.2 \times 10^{-15}$  so  $1/K_{sp}$  is  $2.38 \times 10^{14}$ ). This seems to mean that 1.00 M  $\text{Pb}^{2+}$  ion gives a precipitate of  $\text{Pb}(\text{OH})_2(\text{s})$  at pH 13.0. But there is a complication. The equilibrium



ties up  $\text{Pb}^{2+}$  ion in a *soluble* form, thereby opposing the precipitation of  $\text{Pb}(\text{OH})_2(\text{s})$ . The  $K$  for this reaction is the  $K_f$  for  $\text{Pb}(\text{OH})_3^-(\text{aq})$  and is large (given as  $4 \times 10^{14}$  in the problem). Whether  $\text{Pb}(\text{OH})_2$  precipitates depends how the competition between these reactions plays out.

Suppose  $\text{Pb}(\text{OH})_2(\text{s})$  *does* precipitate. Then, at pH 13.0, where  $[\text{OH}^-] = 0.10$  M, the concentration of  $\text{Pb}^{2+}$  must fulfill the equation

$$K_{sp} = 4.2 \times 10^{-15} = [\text{Pb}^{2+}][\text{OH}^-]^2 = [\text{Pb}^{2+}](0.10)^2$$

This means  $[\text{Pb}^{2+}]$  is locked at  $4.2 \times 10^{-13}$  M if solid  $\text{Pb}(\text{OH})_2$  is present. The mass-action expression for the complexation equilibrium is

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

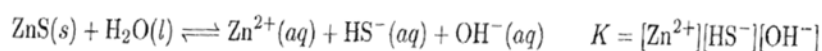
Substitute  $[\text{OH}^-] = 0.10$  and  $[\text{Pb}^{2+}] = 4.2 \times 10^{-13}$  M, and solve for  $[\text{Pb}(\text{OH})_3^-]$ . The answer is 0.17 M. Any concentration of  $\text{Pb}^{2+}$  ion that exceeds this threshold value causes precipitation. Because 1.00 M exceeds 0.17 M,  $\text{Pb}(\text{OH})_2(\text{s})$  precipitates in the case defined in this problem. At equilibrium,  $[\text{Pb}^{2+}]$  equals  $4.2 \times 10^{-13}$  M, and the concentration of  $\text{Pb}(\text{OH})_3^-$  equals 0.17 M.

The problem also asks whether  $\text{Pb}(\text{OH})_2(s)$  precipitates if the initial concentration of  $\text{Pb}^{2+}$  is 0.050 M. This value is less than the precipitation threshold of 0.17 M so no precipitate of  $\text{Pb}(\text{OH})_2(s)$  can form. The  $K_{\text{sp}}$  equilibrium is *not* in effect. Essentially all of the  $\text{Pb}^{2+}$  ion is tied up in the complex, making the concentration of  $\text{Pb}(\text{OH})_3^-$  equal  $\boxed{0.050 \text{ M}}$ . Put this value into the  $K_f$  mass-action expression

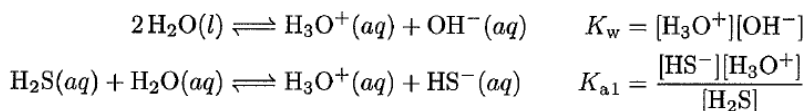
$$K_f = 4 \times 10^{14} = \frac{[\text{Pb}(\text{OH})_3^-]}{[\text{Pb}^{2+}][\text{OH}^-]^3} = \frac{0.050}{[\text{Pb}^{2+}](0.10)^3}$$

Solving gives the concentration of  $\text{Pb}^{2+}(aq)$  (also called “free”  $\text{Pb}^{2+}$  ion) as  $\boxed{1 \times 10^{-13} \text{ M}}$ .

- 53.** Calculate the  $[\text{Zn}^{2+}]$  in a solution that is in equilibrium with  $\text{ZnS}(s)$  and in which  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-5} \text{ M}$  and  $[\text{H}_2\text{S}] = 0.10 \text{ M}$ .



The equilibrium expression is a triple product, but is otherwise not exceptional. Both the  $\text{OH}^-$  and  $\text{HS}^-$  concentrations depend strongly on the concentration of  $\text{H}_3\text{O}^+$  according to the equations



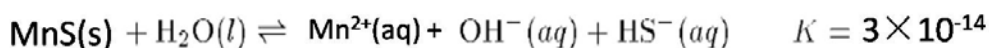
Solve these equations for  $[\text{OH}^-]$  and  $[\text{HS}^-]$ , and substitute into the triple-product  $K$  expression

$$[\text{Zn}^{2+}] \left( \frac{K_{a1}[\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]} \right) \left( \frac{K_w}{[\text{H}_3\text{O}^+]} \right) = K$$

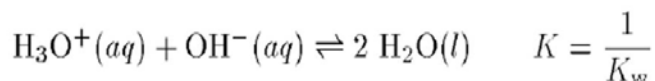
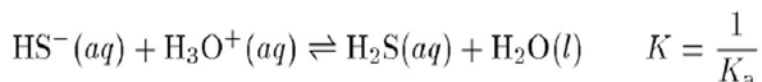
Assume that the temperature is 25°C. Then  $K_{a1}$  of  $\text{H}_2\text{S}$  equals  $9.1 \times 10^{-8}$ ,  $K_w$  equals  $1.0 \times 10^{-14}$ , and  $K$  equals  $2 \times 10^{-25}$ .<sup>6</sup> Also, the concentration of  $\text{H}_2\text{S}$  equals 0.10 M, and the concentration of  $\text{H}_3\text{O}^+$  equals  $1.0 \times 10^{-5} \text{ M}$ . Solve the preceding equation for the concentration of  $\text{Zn}^{2+}$ , and insert the three equilibrium constants and two concentrations

$$\begin{aligned} [\text{Zn}^{2+}] &= K \left( \frac{[\text{H}_3\text{O}^+]}{K_{a1}[\text{H}_2\text{S}]} \right) \left( \frac{[\text{H}_3\text{O}^+]}{K_w} \right) \\ &= 2 \times 10^{-25} \left( \frac{1.0 \times 10^{-5}}{(9.1 \times 10^{-8})(0.10)} \right) \left( \frac{1.0 \times 10^{-5}}{1.0 \times 10^{-14}} \right) = \boxed{2 \times 10^{-13} \text{ M}} \end{aligned}$$

- 56.** What is the highest pH at which 0.050 M  $\text{Mn}^{2+}$  will remain entirely in a solution that is saturated with  $\text{H}_2\text{S}$  at a concentration of  $[\text{H}_2\text{S}] = 0.10 \text{ M}$ ? At this pH, what would be the concentration of  $\text{Cd}^{2+}$  in equilibrium with solid  $\text{CdS}$  in this solution?



Add to this the equilibria



This gives



The condition for  $\text{Mn}^{2+}$  to remain in solution is

$$\frac{[\text{Mn}^{2+}][\text{H}_2\text{S}]}{[\text{H}_3\text{O}^{+}]^2} < \frac{K}{K_{\text{a}}K_{\text{w}}} = \frac{3 \times 10^{-14}}{(9.1 \times 10^{-8})(1.0 \times 10^{-14})} = 3.3 \times 10^7$$

Inserting  $[\text{Mn}^{2+}] = 0.050 \text{ M}$  and  $[\text{H}_2\text{S}] = 0.10 \text{ M}$  gives

$$[\text{H}_3\text{O}^{+}]^2 > \frac{[\text{Mn}^{2+}][\text{H}_2\text{S}]}{3.3 \times 10^7} = \frac{(0.050)(0.10)}{3.3 \times 10^7} = 1.5 \times 10^{-10}$$

$$[\text{H}_3\text{O}^{+}] > 1.2 \times 10^{-5}; \quad \text{pH} < 4.9$$

$$[\text{Cd}^{2+}] = \frac{[\text{H}_3\text{O}^{+}]^2}{[\text{H}_2\text{S}]}(7.7 \times 10^{-7}) = \frac{(1.2 \times 10^{-5})^2}{0.10}(7.7 \times 10^{-7}) = 1 \times 10^{-15} \text{ M}$$