Chemistry 2e
15: Equilibria of Other Reaction Classes
15.1: Precipitation and Dissolution

1. Complete the changes in concentrations for each of the following reactions:

(a) $\underset{}{AgI(s)} \longrightarrow \underset{x}{Ag^{+}(aq)} + \underset{\_\_\_\_\_}{I^{-}(aq)}$

(b) $CaCO_3(s) \longrightarrow \underset{\_\_\_\_\_}{Ca^{2+}(aq)} + \underset{x}{CO_3^{2-}(aq)}$

(c) $Mg(OH)_2(s) \longrightarrow \underset{x}{Mg^{2+}(aq)} + \underset{\_\_\_\_\_}{2OH^{-}(aq)}$

(d) $Mg_3(PO_4)_2(s) \longrightarrow \underset{x}{3Mg^{2+}(aq)} + \underset{\_\_\_\_\_}{2PO_4^{3-}(aq)}$

(e) $Ca_5(PO_4)_3OH(s) \longrightarrow \underset{\_\_\_\_\_}{5Ca^{2+}(aq)} + \underset{\_\_\_\_\_}{3PO_4^{3-}(aq)} + \underset{x}{OH^{-}(aq)}$

Solution

In dissolution, one unit of substance produces a quantity of discrete ions or polyatomic ions that equals the number of times that the subunit appears in the formula.

(a) $AgI(s) \rightleftharpoons \underset{x}{Ag^{+}(aq)} + \underset{\underline{x}}{I^{-}(aq)}$

Dissolving AgI(s) must produce the same amount of I^{-} ion as it does Ag^{+} ion.

(b) $CaCO_3(s) \rightleftharpoons \underset{\underline{x}}{Ca^{2+}(aq)} + \underset{x}{CO_3^{2-}(aq)}$

Dissolving $CaCO_3(s)$ must produce the same amount of Ca^{2+} ion as it does CO_3^{2-} ion.

(c) $Mg(OH)_2(s) \rightleftharpoons \underset{x}{Mg^{2+}(aq)} + \underset{\underline{2x}}{2OH^{-}(aq)}$

When one unit of $Mg(OH)_2$ dissolves, two ions of OH^{-} are formed for each Mg^{2+} ion.

(d) $Mg_3(PO_4)_2(s) \rightleftharpoons \underset{\underline{x}}{3Mg^{2+}(aq)} + \underset{\frac{2}{3}x}{2PO_4^{3-}(aq)}$

One unit of $Mg_3(PO_4)_2$ provides two units of PO_4^{3-} ion and three units of Mg^{2+} ion.

(e) $Ca_5(PO_4)_3OH(s) \rightleftharpoons \underset{\underline{5x}}{5Ca^{2+}(aq)} + \underset{\underline{3x}}{3PO_4^{3-}(aq)} + \underset{x}{OH^{-}(aq)}$

One unit of $Ca_5(PO_4)_3OH$ dissolves into five units of Ca^{2+} ion, three units of PO_4^{3-} ion, and one unit of OH^{-} ion.

3. How do the concentrations of Ag^{+} and CrO_4^{2-} in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

Solution

There is no change. A solid has an activity of 1 whether there is a little or a lot.

5. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

Solution

The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

7. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS?

Solution

CaF_2, $MnCO_3$, and ZnS; each is a salt of a weak acid and the hydronium ion from water reacts with the anion, causing more solid to dissolve to maintain the equilibrium concentration of the anion

9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

(a) LaF_3
(b) $CaCO_3$
(c) Ag_2SO_4
(d) $Pb(OH)_2$

Solution

(a) $LaF_3(s) \rightleftharpoons La^{3+}(aq) + 3F^-(aq) \qquad K_{sp} = [La^{3+}][F^-]^3;$

(b) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3{}^{2-}];$

(c) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[SO_4{}^{2-}];$

(d) $Pb(OH)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Pb^{2+}][OH^-]^2$

11. The *Handbook of Chemistry and Physics* (http://hbcponline.com/faces/contents/ContentsSearch.xhtml) gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSeO_4$, 0.0118 g/100 mL
(b) $Ba(BrO_3)_2{\cdot}H_2O$, 0.30 g/100 mL
(c) $NH_4MgAsO_4{\cdot}6H_2O$, 0.038 g/100 mL
(d) $La_2(MoO_4)_3$, 0.00179 g/100 mL

Solution

Convert each concentration into molar units. Multiply each concentration by 10 to determine the mass in 1 L, and then divide the molar mass.

(a) $BaSeO_4$: $\dfrac{0.118\text{ g L}^{-1}}{280.28\text{ g mol}^{-1}} = 4.21 \times 10^{-4}\ M$,

$K = [Ba^{2+}][SeO_4{}^{2-}] = (4.21 \times 10^{-4})(4.21 \times 10^{-4}) = 1.77 \times 10^{-7};$

(b) $Ba(BrO_3)_2{\cdot}H_2O$: $\dfrac{3.0\text{ g L}^{-1}}{411.147\text{ g mol}^{-1}} = 7.3 \times 10^{-3}\ M$,

$K = [Ba^{2+}][BrO_3^{-}]^2 = (7.3 \times 10^{-3})(2 \times 7.3 \times 10^{-3})^2 = 1.6 \times 10^{-6}$;

(c) $NH_4MgAsO_4 \cdot 6H_2O$: $\dfrac{0.38\text{ g L}^{-1}}{289.3544\text{ g mol}^{-1}} = 1.3 \times 10^{-3}\ M$,

$K = [NH_4^{+}][Mg^{2+}][AsO_4^{3-}] = (1.3 \times 10^{-3})^3 = 2.2 \times 10^{-9}$;

(d) $La_2(MoO_4)_3$: $\dfrac{0.0179\text{ g L}^{-1}}{757.62\text{ g mol}^{-1}} = 2.36 \times 10^{-5}\ M$,

$K = [La^{3+}]^2[MoO_4^{2-}]^3 = (2 \times 2.36 \times 10^{-5})^2(3 \times 2.36 \times 10^{-5})^3 = 2.228 \times 10^{-9} \times 3.549 \times 10^{-13} =$ 7.91×10^{-22}

13. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:
(a) $KHC_4H_4O_6$
(b) PbI_2
(c) $Ag_4[Fe(CN)_6]$, a salt containing the $Fe(CN)_6^{4-}$ ion
(d) Hg_2I_2

Solution
Let x be the molar solubility.
(a) $K_{sp} = [K^{+}][HC_4H_4O_6^{-}] = 3 \times 10^{-4} = x^2$, $x = 2 \times 10^{-2} M$;
(b) $K_{sp} = [Pb^{2+}][I^{-}]^2 = 1.4 \times 10^{-8} = x(2x)^3 = 4x^3$, $x = 1.5 \times 10^{-3} M$;
(c) $K_{sp} = [Ag^{+}]^4[Fe(CN)_6^{4-}] = 1.55 \times 10^{-41} = (4x)^4x = 256x^5$, $x = 2.27 \times 10^{-9} M$;
(d) $K_{sp} = [Hg_2^{2+}][I^{-}]^2 = 4.5 \times 10^{-29} = [x][2x]^2 = 4x^3$, $x = 2.2 \times 10^{-10} M$

15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.
(a) $AgCl(s)$ in 0.025 *M* NaCl
(b) $CaF_2(s)$ in 0.00133 *M* KF
(c) $Ag_2SO_4(s)$ in 0.500 L of a solution containing 19.50 g of K_2SO_4
(d) $Zn(OH)_2(s)$ in a solution buffered at a pH of 11.45

Solution
(a) $K_{sp} = 1.6 \times 10^{-10} = [Ag^{+}][Cl^{-}] = x(x + 0.025)$, where $x = [Ag^{+}]$. Assume that x is small when compared with 0.025 and therefore ignore it:

$$x = \frac{1.6 \times 10^{-10}}{0.025} = 6.4 \times 10^{-9}\ M = [Ag^{+}],\ [Cl^{-}] = 0.025\ M$$

Check: $\dfrac{6.4 \times 10^{-9}\ M}{0.025\ M} \times 100\% = 2.6 \times 10^{-5}\%$, an insignificant change;

(b) $K_{sp} = 4.0 \times 10^{-11} = [Ca^{2+}][F^{-}]^2 = x(2x + 0.00133\ M)^2$, where $x = [Ca^{2+}]$. Assume that x is small when compared with 0.0013 *M* and disregard it:

$$x = \frac{4.0 \times 10^{-11}}{(0.00133)^2} = 2.2 \times 10^{-5}\ M = [Ca^{2+}],\ [F^{-}] = 0.0013\ M$$

Check: $\dfrac{2.26 \times 10^{-5}\ M}{0.00133\ M} \times 100\% = 1.70\%$. This value is less than 5% and can be ignored.

(c) Find the concentration of K_2SO_4:

$$\frac{19.50\text{ g}}{174.260\text{ g mol}^{-1}} = 0.1119\text{ mol}$$

$$\frac{0.1119\text{ mol}}{0.5\text{ L}} = 0.2238\ M = [SO_4{}^{2-}]$$

$K_{sp} = 1.12 \times 10^{-5} = [Ag^+]^2[SO_4{}^{2-}] = 4x^2(x + 0.2238)$

$$x^2 = \frac{1.2 \times 10^{-5}}{4(0.2238)} = 1.34 \times 10^{-5}$$

$x = 3.7 \times 10^{-3}[Ag^+] = 2x = 7.4 \times 10^{-3}M$

Check: $\dfrac{3.7 \times 10^{-3}}{0.2238} \times 100\% = 1.64 \times 10^{-2}$; the condition is satisfied.

(d) Find the concentration of OH^- from the pH:

pOH = 14.00 – 11.45 = 2.55

$[OH^-] = 2.8 \times 10^{-3}M$

$K_{sp} = 4.5 \times 10^{-17} = [Zn^{2+}][OH^-]^2 = x(2x + 2.8 \times 10^{-3})^2$

Assume that x is small when compared with 2.8×10^{-3}:

$$x = \frac{4.5 \times 10^{-17}}{(2.8 \times 10^{-3})^2} = 5.7 \times 10^{-12}\ M = [Zn^{2+}]$$

Check: $\dfrac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\%$; x is less than 5% of $[OH^-]$ and is, therefore, negligible. In each case the change in initial concentration of the common ion is less than 5%.

17. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

(a) $TlCl(s)$ in 0.025 M $TlNO_3$

(b) $BaF_2(s)$ in 0.0313 M KF

(c) MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$

(d) $Ca(OH)_2(s)$ in an unbuffered solution initially with a pH of 12.700

Solution

(a) $K_{sp} = 1.7 \times 10^{-4} = [Ti^+][Cl^-]$; Let $x = [Cl^-]$:

$1.7 \times 10^{-4} = (x = 0.025)x$

Assume that x is small when compared with 0.025:

$$x = \frac{1.7 \times 10^{-4}}{0.025} = 6.8 \times 10^{-3}\ M$$

Check: $\dfrac{6.8 \times 10^{-3}}{0.025} \times 100\% = 27\%$

This value is too large to drop x. Therefore solve by using the quadratic equation:

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x^2 + 0.025x - 1.7 \times 10^{-4} = 0$

$$x = \frac{-0.025 \pm \sqrt{6.25 \times 10^{-4} + 6.8 \times 10^{-4}}}{2} = \frac{-0.025 \pm \sqrt{1.305 \times 10^{-3}}}{2}$$

$$= \frac{-0.025 \pm 0.0361}{2} = 0.0056\ M$$

(Use only the positive answer for physical sense.)

$[Ti^+] = 0.025 + 0.0056 = 3.1 \times 10^{-2} M$

$[Cl^-] = 6.1 \times 10^{-3}$

(b) $K_{sp} = 2.4 \times 10^{-5} = [Ba^{2+}][F^-]^2$; Let $x = [Ba^{2+}]$

If we drop x from $x + 0.0313$, x would be equal to $7.7 \times 10^{-4}\ M$

Check: $\frac{7.7 \times 10^{-4}}{0.0313} \times 100\% = 2.4\%$

This value is less than 5%, so

$[Ba^{2+}] = 7.7 \times 10^{-4} M$

$[F^-] = 0.0321\ M$;

(c) Find the molar concentration of the $Mg(NO_3)_2$. The molar mass of $Mg(NO_3)_2$ is 148.3149 g/mol. The number of moles is $\frac{8.156\text{ g}}{148.3149\text{ g mol}^{-1}} = 0.05499\text{ mol}$

$$M = \frac{0.05499\text{ mol}}{2.250\text{ L}} = 0.02444\ M$$

Let $x = [C_2O_4^{2-}]$ and assume that x is small when compared with 0.02444 M.

$K_{sp} = 7 \times 10^{-7} = [Mg^{2+}][C_2O_4^{2-}] = (x)(x + 0.02444)$

$0.02444x = 7 \times 10^{-7}$

$x = [C_2O_4^{2-}] = 2.9 \times 10^{-5}$

Check: $\frac{2.9 \times 10^{-5}}{0.02444} \times 100\% = 0.12\%$

This value is less than 5%, so

$[Ca^{2+}] = 2.9 \times 10^{-5} M$

$[OH^-] = 0.0501\ M$

$[Mg^{2+}] = 0.0244\ M$

(d) pH = 12.700; pOH = 1.300

$[OH^-] = 0.0501\ M$; Let $x = [Ca^{2+}]$

$K_{sp} = 7.9 \times 10^{-6} = [Ca^{2+}][OH^-]^2 = (x)(x + 0.050)^2$

Assume that x is small when compared with 0.050 M:

$x = [Ca^{2+}] = 3.15 \times 10^{-3}$ (one additional significant figure is carried)

Check: $\frac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$

This value is greater than 5%, so a more exact method, such as successive approximations, must be used. Begin by choosing the value of x that has just been calculated:

$x'(3.15 \times 10^{-3} + 0.0501)^2 = 7.9 \times 10^{-6}$ or

$$x' = \frac{7.9 \times 10^{-6}}{2.836 \times 10^{-3}} = 2.8 \times 10^{-3}$$

$[Ca^{2+}] = 2.8 \times 10^{-3} M$

$[OH^-] = (2.8 \times 10^{-3} + 0.0501) = 0.053 \times 10^{-2} M$

In each case, the initial concentration of the common ion changes by more than 5%.

19. Explain why the changes in concentrations of the common ions in Exercise 18 cannot be neglected.

Solution

The changes in concentration are greater than 5% and thus exceed the maximum value for disregarding the change.

21. Refer to Appendix J for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

Solution

$Ca(OH)_2$: $[Ca^{2+}][OH^-]^2 = 1.3 \times 10^{-6}$

Let x be $[Ca^{2+}]$ = molar solubility; then $[OH^-] = 2x$

$K_{sp} = x(2x)^2 = 4x^3 = 1.3 \times 10^{-6}$

$x^3 = 0.069 \times 10^{-6}$

$x = 0.069\ M$

$CaCO_3$: $[Ca^{2+}][CO_3^{\ 2-}] = 8.7 \times 10^{-9}$

Let x be $[Ca^{2+}]$; then $[CO_3^{\ 2-}] = [Ca^{2+}]$ = molar solubility

$K_{sp} = x^2 = 8.7 \times 10^{-9}$

$x = 9.3 \times 10^{-5} M$

$CaSO_4 \cdot 2H_2O$: $[Ca^{2+}][SO_4^{\ 2-}][H_2O]^2 = 6.1 \times 10^{-5}$

Let x be $[Ca^{2+}]$ = molar solubility $= [SO_4^{\ 2-}]$; then $[H_2O] = 2x$

$K_{sp} = (x)(x)(2x)^2 = 6.1 \times 10^{-5}$

$x^4 = 1.53 \times 10^{-5}$

$x = 0.062\ M$

This value is more than four times the value given by *Handbook of Chemistry and Physics* (http://www.hbcpnetbase.com/) of ($0.014\ M$) and reflects the complex interaction of water within the precipitate:

$CaC_2O_4 \cdot H_2O$: $[Ca^{2+}][C_2O_4^{\ 2-}][H_2O] = 1.96 \times 10^{-8}$

Let x be $[Ca^{2+}]$ = molar solubility $= [C_2O_4^{\ 2-}] = [H_2O]$

$x^3 = 1.96 \times 10^{-8}$

$x = 2.7 \times 10^{-3} M$

In this case, the interaction of water is also complex and the solubility is considerably less than that calculated.

$Ca_3(PO_4)_2$: $[Ca^{2+}]^3[PO_4^{\ 3-}]^2 = 1.3 \times 10^{-32}$

Upon solution there are three Ca^{2+} and two $PO_4^{\ 3-}$ ions. Let the concentration of Ca^{2+} formed upon solution be x. Then $\frac{2}{3}x$ is the concentration of $PO_4^{\ 3-}$:

$$x^3\left(\frac{2}{3}x\right)^2 x^3 = 1.3 \times 10^{-32} = 0.4444x^5$$

$x = 4.9 \times 10^{-7} M = [Ca^{2+}]$

The solubility is then one-third the concentration of Ca^{2+}, or 1.6×10^{-7}. $CaSO_4$ $2H_20$ is the most soluble Ca salt.

23. Public Health Service standards for drinking water set a maximum of 250 mg/L ($2.60 \times 10^{-3} M$) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ ("gyp" water) as a result or passing through soil containing gypsum, $CaSO_4{\cdot}2H_2O$, meet these standards? What is SO_4^{2-} in such water?

Solution

First, find the concentration in a saturated solution of $CaSO_4$. Before placing the $CaSO_4$ in water, the concentrations of Ca^{2+} and SO_4^{2-} are 0. Let x be the change in concentration of Ca^{2+}, which is equal to the concentration of SO_4^{2-}:

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 6.1 \times 10^{-5}$

$x \times x = x^2 = 6.1 \times 10^{-5}$

$x = \sqrt{6.1 \times 10^{-5}}$

$x = 7.8 \times 10^{-3} M = [SO_4^{2-}] = [Ca^{2+}]$

Since this concentration is higher than $2.60 \times 10^{-3} M$, "gyp" water does not meet the standards.

25. The solubility product of $CaSO_4{\cdot}2H_2O$ is 6.1×10^{-5}. What mass of this salt will dissolve in1.0 L of 0.010 M SO_4^{2-}?

Solution

The amount of $CaSO_4{\cdot}2H_2O$ that dissolves is limited by the presence of a substantial amount of SO_4^{2-} already in solution from the 0.010 $M\,SO_4^{-}$. This is a common-ion problem. Let x be the change in concentration of Ca^{2+} and of SO_4^{2-} that dissociates from $CaSO_4$:

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 6.1 \times 10^{-5}$

Addition of 0.010 $M\,SO_4^{2-}$ generated from the complete dissociation of 0.010 M SO_4 gives $[x][x + 0.010] = 6.1 \times 10^{-5}$. Here, x cannot be neglected in comparison with 0.010 M; the quadratic equation must be used. In standard form:

$x^2 + 0.010x - 6.1 \times 10^{-5} = 0$

$$x = \frac{-0.01 \pm \sqrt{1 \times 10^{-4} + 2.4 \times 10^{-4}}}{2} = \frac{-0.01 \pm 1.8 \times 10^{-2}}{2}$$

Only the positive value will give a meaningful answer:

$x = 4.2 \times 10^{-3} = [Ca^{2+}]$

This is also the concentration of $CaSO_4{\cdot}2H_2O$ that has dissolved. The mass of the salt in 1 L is

Mass ($CaSO_4{\cdot}2H_2O$) = 4.2×10^{-3} mol/L × 172.16 g/mol = 0.72 g/L

Note that the presence of the common ion, $SO_4^{\;2-}$, has caused a decrease in the concentration of Ca^{2+} that otherwise would be in solution:

$\sqrt{6.1 \times 10^{-5}} = 7.8 \times 10^{-3}\ M$

27. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Appendix J for solubility products):
(a) AgI
(b) Ag_2SO_4
(c) $Mn(OH)_2$
(d) $Sr(OH)_2{\cdot}8H_2O$
(e) themineral brucite, $Mg(OH)_2$

Solution
In each of the following, allow *x* to be the molar concentration of the ion occurring only once in the formula.
(a) $K_{sp} = [Ag^+][Cl^-] = 1.6 - 10^{-10} = [x^2]$, $[x] = 1.3 - 10^{-5}M$, $[Ag^+] = [I^-] = 1.3 \times 10^{-5}M$; (b) $K_{sp} = [Ag^+]^2[SO_4^{\;2-}] = 1.2 \times 10^{-5} = [2x]^2[x]$, $4x^3 = 1.2 \times 10^{-5}$, $x = 1.44 \times 10^{-2}M$

As there are 2 Ag^+ ions for each $SO_4^{\;2-}$ ion, $[Ag^+] = 2.88 \times 10^{-2}M$, $[SO_4^{\;2-}] = 1.44 \times 10^{-2}M$; (c) $Ksp = [Mn^{2+}]^2[OH^-]^2 = 2 \times 10^{-13} = [x][2x]^2$, $4x^3 = 2 \times 10^{-13}$, $x = 3.68 \times 10^{-5}M$.
Since there are two OH^- ions for each Mn^{2+} ion, multiplication of *x* by 2 gives $7.36 \times 10^{-5}M$. If the value of *x* is rounded to the correct number of significant figures, $[Mn^{2+}] = 3.7 \times 10^{-5}M$. $[OH^-] = 7.4 \times 10^{-5}M$. We normally maintain one additional figure in the calculator throughout all calculations before rounding.
(d) $K_{sp} = [Sr^{2+}][OH^-]^2 = 3.2 \times 10^{-4} = [x][2x]^2$, $4x^3 = 3.2 \times 10^{-4}$, $x = 4.3 \times 10^{-2}M$.
Substitution gives $[Sr^{2+}] = 4.3 \times 10^{-2}M$, $[OH^-] = 8.6 \times 10^{-2}M$;
(e) $K_{sp} = [Mg^{2+}]^2[OH^-]^2 = 8.9 \times 10^{-12} = [x][2x]^2$, $4x^3 = 8.9 \times 10^{-12}$, $x = 1.31 \times 10^{-4}M$, $2x = 2.6 \times 10^{-4}$.
Substitution and taking the correct number of significant figures gives $[Mg^{2+}] = 1.3 \times 10^{-4}M$, $[OH^-] = 2.6 \times 10^{-4}M$.

29. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:
(a) TlCl: $[Tl^+] = 1.21 \times 10^{-2}M$, $[Cl^-] = 1.2 \times 10^{-2}M$
(b) $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}M$, $[IO_3^{\;-}] = 2.6 \times 10^{-13}M$
(c) $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\ M$, $[SO_4^{\;2-}] = 0.198\ M$
(d) Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2}M$, $[SO_4^{\;2-}] = 2.05 \times 10^{-2}M$
(e) $BaSO_4$: $[Ba^{2+}] = 0.500\ M$, $[SO_4^{\;2-}] = 4.6 \times 10^{-8}M$

Solution
In each case the value of K_{sp} is found by multiplication of the concentrations raised to the ion's stoichiometric power. Molar units are not normally shown in the value of *K*.
(a) TlCl: $K_{sp} = (1.21 \times 10^{-2})(1.2 \times 10^{-2}) = 1.7 \times 10^{-4}$;
(b) $Ce(IO_3)_4$: $K_{sp} = (1.8 \times 10^{-4})(2.6 \times 10^{-13})^4 = 8.2 \times 10^{-55}$;
(c) $Gd_2(SO_4)_3$: $K_{sp} = (0.132)^2(0.198)^3 = 1.35 \times 10^{-4}$;
(d) Ag_2SO_4: $K_{sp} = (2.40 \times 10^{-2})^2(2.05 \times 10^{-2}) = 1.18 \times 10^{-5}$;

(e) $BaSO_4$: $K_{sp} = (0.500)(2.16 \times 10^{-10}) = 1.08 \times 10^{-10}$

31. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix J for K_{sp} values.)

(a) $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $[CO_3^{\ 2-}] = 0.003\ M$

(b) $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7} M$

(c) $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $[HPO_4^{\ 2-}] = 2 \times 10^{-6} M$

(d) $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $[PO_4^{\ 3-}] = 1 \times 10^{-13} M$

Solution

(a) $CaCO_3 : CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3^{\ 2-}(aq)$

$K_{sp} = [Ca^{2+}][CO_3^{\ 2-}] = 8.7 \times 10^{-9}$

test K_{sp} against $Q = [Ca^{2+}][CO_3^{\ 2-}]$

$Q = [Ca^{2+}][CO_3^{\ 2-}] = (0.003)(0.003) = 9 \times 10^{-6}$

$K_{sp} = 8.7 \times 10^{-9} < 9 \times 10^{-6}$

The ion product does exceed K_{sp}, so $CaCO_3$ does precipitate.

(b) $Co(OH)_2 : Co(OH)_2(s) \longrightarrow Co^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Co^{2+}][OH^-]^2 = 2.5 \times 10^{-16}$

test K_{sp} against $Q = [Co^{2+}][OH^-]^2$

$Q = [Co^{2+}][OH^-]^2 = (0.01)(1 \times 10^{-7})^2 = 1 \times 10^{-16}$

$K_{sp} = 2.5 \times 10^{-16} > 1 \times 10^{-16}$

The ion product does not exceed K_{sp}, so the compound does not precipitate.

(c) $CaHPO_4$: ($K_{sp} = 7 \times 10^{-7}$):

$Q = [Ca^{2+}][HPO_4^{\ 2-}] = (0.01)(2 \times 10^{-6}) = 2 \times 10^{-8} < K_{sp}$

The ion product does not exceed K_{sp}, so compound does not precipitate.

(d) $Pb_3(PO_4)_2$: ($K_{sp} = 1 \times 10^{-54}$):

$Q = [Pb^{2+}]^3[PO_4^{\ 3-}]^2 = (0.01)^3(1 \times 10^{-13})^2 = 1 \times 10^{-32} > K_{sp}$

The ion product exceeds K_{sp}, so the compound precipitates.

33. Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}.

Solution

Precipitation of $SO_4^{\ 2-}$ will begin when the ion product of the concentration of the $SO_4^{\ 2-}$ and Ba^{2+} ions exceeds the K_{sp} of $BaSO_4$.

$K_{sp} = 2.3 \times 10^{-8} = [Ba^{2+}][SO_4^{2-}] = (0.0758)[SO_4^{2-}]$

$$[SO_4^{\ 2-}] = \frac{2.3 \times 10^{-8}}{0.0758} = 3.03 \times 10^{-7}\ M$$

35. Calculate the concentration of $PO_4^{\ 3-}$ when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+.

Solution

Precipitation of Ag_3PO_4 will begin when the ion product of the concentrations of the Ag^+ and PO_4^{3-} ions exceeds K_{sp}:

$$Ag_3PO_4(s) \longrightarrow 3Ag^+(aq) + PO_4^{3-}(aq)$$

$K_{sp} = 1.8 \times 10^{-18} = [Ag^+]^3[PO_4^{3-}] = (0.0125)^3[PO_4^{3-}]$

$$[PO_4^{3-}] = \frac{1.08 \times 10^{-18}}{(0.0125)^3} = 9.2 \times 10^{-13}\ M$$

37. Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50 \times 10^{-6}M$ in CO_3^{2-}.

Solution

$$Ag_2CO_3(s) \longrightarrow 2Ag^+(aq) + CO_3^{2-}(aq)$$

$[Ag^+]^2[CO_3^{2-}] = K_{sp} = 8.1 \times 10^{-12}$

$[Ag^+]^2(2.5 \times 10^{-6}) = 8.1 \times 10^{-12}$

$$[Ag^+]^2 = \frac{8.1 \times 10^{-12}}{2.50 \times 10^{-6}} = 3.28 \times 10^{-6}$$

$[Ag^+] = 1.8 \times 10^{-3}M$

39. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4}M$ by precipitation of CaF_2?

Solution

In the K_{sp} expression, substitute the concentration of Ca^{2+} and solve for $[F^-]$.

$K_{sp} = 4.0 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (1.0 \times 10^{-4})[F^-]^2$

$$[F^-]^2 = \frac{4.0 \times 10^{-11}}{1.0 \times 10^{-4}} = 4.0 \times 10^{-7}$$

$[F^-] = 6.3 \times 10^{-4}$

41. Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).

(b) If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

Solution

(a) Calculate the molar solubility. Then calculate the number of grams per liter.

$K_{sp} = 1.4 \times 10^{-7} = [Ni^{2+}][CO_3^{2-}]$

Before placement of the sample into water, the concentration of the ions is 0. Let x be the change in concentration of the two ions formed. The total concentration of each is thus $0 + x = x$. Thus:

$x^2 = 1.4 \times 10^{-7}$

$x = [Ni^{2+}] = [CO_3^{2-}] = 3.742 \times 10^{-4}M$

The molar mass of $NiCO_3$ is 118.71 g/mol. Thus:

Concentration of $NiCO_3$ = 118.71 g/mol × 3.742×10^{-4} mol/L = 0.0444 g/L

To contain 0.1 g, $\dfrac{0.1\ \text{g}}{0.0444\ \text{g L}^{-1}} = 2.25\ \text{L}$;

(b) During the process of removal of $NiCO_3$, some $CoCO_3$ would be lost. The $[CO_3^{2-}]$ is controlled by the amount found in part (a). From the solubility product for $CoCO_3$:
$K_{sp} = 1.0 \times 10^{-12} = [Co^{2+}][3.742 \times 10^{-4}]$
$[Co^{2+}] = 2.67 \times 10^{-9} M$
The molar mass of $CoCO_3$ is 118.94 g/mol. Thus:
mass $CoCO_3$ in 2.28 L = 118.94 g/mol × 2.67 × 10^{-9} mol/L × 2.28 L = 7.2 × 10^{-7} g

43. A solution is 0.010 *M* in both Cu^{2+} and Cd^{2+}.What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

Solution
When 99.9% of Cu^{2+} has precipitated as CuS, then 0.1% remains in solution.

$$\frac{0.1}{100} \times 0.010 \text{ mol/L} = 1 \times 10^{-5} M = [Cu^{2+}]$$

$[Cu^{2+}][S^{2-}] = K_{sp} = 8.5 \times 10^{-45}$
$(1 \times 10^{-5})[S^{2-}] = 8.5 \times 10^{-45}$
$[S^{2-}] = 8.5 \times 10^{-40} M$
$[Cd^{2+}][S^{2-}]K_{sp} = 1.0 \times 10^{-28}$
$[Cd^{2+}](7 \times 10^{-37}) = 1.0 \times 10^{-28}$
$[Cd^{2+}] = 1.2 \times 10^{11} M$
Thus $[Cd^{2+}]$ can increase to 1.2 × 10^{11} *M* before precipitation begins. $[Cd^{2+}]$ is only 0.010 *M*, so 100% of it is dissolved.

45. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 *M* with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix J.)
(a) Hg_2^{2+} and Cu^{2+}
(b) SO_4^{2-} and Cl^-
(c) Hg^{2+} and Co^{2+}
(d) Zn^{2+} and Sr^{2+}
(e) Ba^{2+} and Mg^{2+}
(f) CO_3^{2-} and OH^-

Solution
To compare ions of the same oxidation state, look for compounds with a common counter ion that have very different K_{sp} values, one of which has a relatively large K_{sp}—that is, a compound that is somewhat soluble.
(a) Hg_2^{2+} and Cu^{2+}: Add SO_4^{2-}. $CuSO_4$ is soluble (see Appendix J), but K_{sp} for Hg_2SO_4 is 7.4 × 10^{-7}. When only 0.1% Hg_2^{2+} remains in solution:

$$[Hg_2^{2+}] = \frac{0.1\%}{100\%} \times 0.10 = 1 \times 10^{-4}\ M$$

and

$$[SO_4^{2-}] = \frac{K_{sp}}{[Hg_2^{2+}]} = \frac{7.4 \times 10^{-7}}{1 \times 10^{-4}} = 7.4 \times 10^{-3}\ M;$$

(b) SO_4^{2-} and Cl^-: Add Ba^{2+}. $BaCl_2$ is soluble (see the section on catalysis), but K_{sp} for $BaSO_4$ is 2.3 × 10^{-8}. When only 0.1% SO_4^{2-} remains in solution, $[SO_4^{2-}] = 1 \times 10^{-4} M$ and

$$[\mathrm{Ba^{2+}}] = \frac{2.3 \times 10^{-8}}{1 \times 10^{-4}} = 2.3 \times 10^{-4}\ M;$$

(c) Hg^{2+} and Co^{2+}: Add S^{2-}: For the least soluble form of CoS, $K_{sp} = 3 \times 10^{-26}$ and for HgS, $K_{sp} = 1.6 \times 10^{-54}$. CoS will not begin to precipitate until:

$[Co^{2+}][S^{2-}] = K_{sp} = 3 \times 10^{-26}$

$(0.10)[S^{2-}] = 3 \times 10^{-26}$

$[S^{2-}] = 3 \times 10^{-25}$

At that concentration:

$[Hg^{2+}](3 \times 10^{-25}) = 1.6 \times 10^{-54}$

$[Hg^{2+}] = 5.3 \times 10^{-30}\ M$

That is, it is virtually 100% precipitated. For a saturated (0.10 *M*) H_2S solution, the corresponding $[\mathrm{H_3O^+}]$ is:

$$[\mathrm{H_3O^+}] = \frac{[\mathrm{H_2S}]}{[\mathrm{S^{2-}}]}K_a = \frac{(0.10)}{(3 \times 10^{-25})} = 8.9 \times 10^{-27}$$

$[\mathrm{H_3O^+}] = 0.0030\ M$

A solution more basic than this would supply enough S^{2-} for CoS to precipitate.

(d) Zn^{2+} and Sr^{2+}: Add OH^- until $[OH^-] = 0.050\ M$. For $Sr(OH)_2{\cdot}8H_2O$, $K_{sp} = 3.2 \times 10^{-4}$. For $Zn(OH)_2$, $K_{sp} = 4.5 \times 10^{-11}$. When Zn^{2+} is 99.9% precipitated, then $[Zn^{2+}] = 1 \times 10^{-4} M$ and

$$[\mathrm{OH^-}]^2 = \frac{K_{sp}}{[\mathrm{Zn^{2+}}]} = \frac{4.5 \times 10^{-11}}{1 \times 10^{-4}} = 4.5 \times 10^{-7}$$

$[OH^-] = 7 \times 10^{-4} M$

When $Sr(OH)_2{\cdot}8H_2O$ just begins to precipitate:

$$[\mathrm{OH^-}]^2 = \frac{K_{sp}}{[\mathrm{Sr^{2+}}]} = \frac{3.2 \times 10^{-4}}{0.10} = 3.2 \times 10^{-3}$$

$[OH^-] = 0.057\ M$

If $[OH^-]$ is maintained less than 0.056 *M*, then Zn^{2+} will precipitate and Sr^{2+} will not.

(e) Ba^{2+} and Mg^{2+}: Add $\mathrm{SO_4}^{2-}$. $MgSO_4$ is soluble and $BaSO_4$ is not ($K_{sp} = 2.3 \times 10^{-8}$).

(f) $\mathrm{CO_3}^{2-}$ and OH^-: Add Ba^{2+}. For $Ba(OH)_2$, $8H_2O$, $K_{sp} = 5.0 \times 10^{-3}$; for $BaCO_3$, $K_{sp} = 1.6 \times 10^{-9}$. When 99.9% of $\mathrm{CO_3}^{2-}$ has been precipitated $[\mathrm{CO_3}^{2-}] = 1 \times 10^{-4} M$ and

$$[\mathrm{Ba^{2+}}] = \frac{K_{sp}}{[\mathrm{CO_3}^{2-}]} = \frac{1.6 \times 10^{-9}}{1 \times 10^{-4}} = 1.6 \times 10^{-5}\ M$$

$Ba(OH)_2{\cdot}8H_2O$ begins to precipitate when:

$$[\mathrm{Ba^{2+}}] = \frac{K_{sp}}{[\mathrm{OH^-}]^2} = \frac{5.0 \times 10^{-3}}{(0.10)^2} = 0.50\ M$$

As long as $[Ba^{2+}]$ is maintained at less than 0.50 *M*, $BaCO_3$ precipitates and $Ba(OH)_2{\cdot}8H_2O$ does not.

47. A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Solution

Compare the concentration of Ag^+ as determined from the two solubility product expressions. The one requiring the smaller $[Ag^+]$ will precipitate first.

For AgCl: $K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{[0.10]} = 1.6 \times 10^{-9}\ M$$

For AgI: $K_{sp} = 1.5 \times 10^{-16} = [Ag^+][I^-]$

$$[Ag^+] = \frac{1.5 \times 10^{-16}}{1.0 \times 10^{-2}} = 1.5 \times 10^{-9}\ M$$

As the value of $[Ag^+]$ is smaller for AgI, AgI will precipitate first.

49. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

Solution

The dissolution of $Ca_3(PO_4)_2$ yields:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4{}^{3-}(aq)$$

Given the concentration of Ca^{2+} in solution, the maximum $[PO_4{}^{3-}]$ can be calculated by using the K_{sp} expression for $Ca_3(PO_4)_2$:

$K_{sp} = 1.3 \times 10^{-32} = [Ca^{2+}]^3[PO_4{}^{3-}]^2$

$$[Ca^{2+}]_{\text{urine}} = \frac{0.10\ \text{g}\left(\dfrac{1\ \text{mol}}{40.08\ \text{g}}\right)}{1.4\ \text{L}} = 1.8 \times 10^{-3}\ M$$

$$[PO_4{}^{3-}]^2 = \frac{1.3 \times 10^{-32}}{(1.8 \times 10^{-3})^3} = 2.2 \times 10^{-24}$$

$$[PO_4{}^{3-}]^2 = 1.5 \times 10^{-12}\ M$$

51. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$Mg^{2+}(aq) + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(s) + 2H_2O(l)$$

$$MgCl_2(l) \xrightarrow{\text{electrolysis}} Mg(s) + Cl_2(g)$$

Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water?

Solution

Calculate the amount of Mg^{2+} present in sea water; then use K_{sp} to calculate the amount of $Ca(OH)_2$ required to precipitate the magnesium.

mass Mg = 1.00×10^3 L × 1000 cm^3/L × 1.026 g/cm^3 × 1272 ppm × 10^{-6} ppm^{-1} = 1.305×10^3 g

The concentration is 1.305 g/L. If 99.9% is to be recovered 0.999 × 1.305 g/L = 1.304 g/L will be obtained. The molar concentration is:

$$\frac{1.304\ \text{g L}^{-1}}{24.305\ \text{g mol}^{-1}} = 0.05365\ M$$

As the $Ca(OH)_2$ reacts with Mg^{2+} on a 1:1 mol basis, the amount of $Ca(OH)_2$ required to precipitate 99.9% of the Mg^{2+} in 1 L is:

$0.05365\ M \times 74.09\ g/mol\ Ca(OH)_2 = 3.97\ g/L$

For treatment of 1000 L, $1000\ L \times 3.97\ g/L = 3.97 \times 10^3\ g = 3.97\ kg$. However, additional $[OH^-]$ must be added to maintain the equilibrium:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad (K_{sp} = 8.9 \times 10^{-12})$$

When the initial 1.035 g/L is reduced to 0.1% of the original, the molarity is calculated as:

$$\frac{0.001 \times 1.305\ g\ L^{-1}}{24.305\ g\ mol^{-1}} = 5.369 \times 10^{-5}\ M$$

The added amount of OH^- required is found from the solubility product:

$[Mg^{2+}][OH^-]^2 = (5.369 \times 10^{-5})[OH^-]^2 = 8.9 \times 10^{-12} = K_{sp}$

$[OH^-] = 4.07 \times 10^{-4}$

Thus an additional $\frac{1}{2} \times 4.07 \times 10^{-4}$ mol (2.65×10^{-4} mol) of $Ca(OH)_2$ per liter is required to supply the OH^-. For 1000 L:

$$\text{mass } Ca(OH)_2 = 2.04 \times 10^{-4}\ \text{mol } Ca(OH)_2\ L^{-1} \times 1.00 \times 10^3\ L \times \frac{74.0946\ g}{\text{mol } Ca(OH)_2} = 15\ g$$

The total $Ca(OH)_2$ required is 3.97 kg + 0.015 kg = 3.99 kg.

53. Perform the following calculations involving concentrations of iodate ions:

(a) The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.

(b) Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).

Solution

(a) $K_{sp} = [La^{3+}][IO_3^-]^3 = \left(\frac{1}{3} \times 3.1 \times 10^{-3}\right)(3.1 \times 10^{-3})^3 = (0.0010)(3.0 \times 10^{-8}) = 3.1 \times 10^{-11}$;

(b) $K_{sp} = [Cu^{2+}][IO_3^-]^2 = x(2x)^2 = 7.4 \times 10^{-8}$

$4x^3 = 7.4 \times 10^{-8}$

$x^3 = 1.85 \times 10^{-8}$

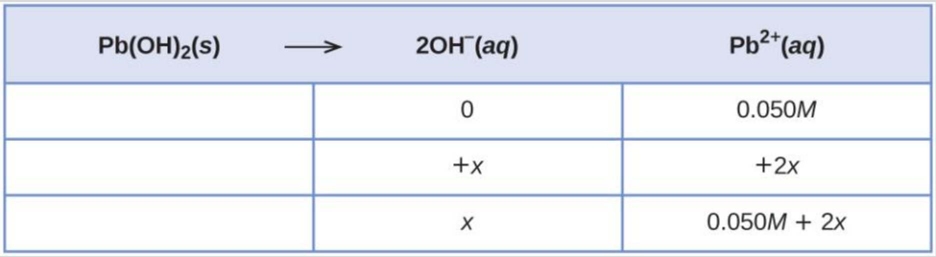
$x = 2.64 \times 10^{-3}$

$[Cu^{2+}] = 2.6 \times 10^{-3}$

$[IO_3^-] = 2x = 5.3 \times 10^{-3}$

55. How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)?

Solution



$Pb(OH)_2(s) \longrightarrow$	$2OH^-(aq)$	$Pb^{2+}(aq)$
	0	0.050*M*
	$+x$	$+2x$
	x	$0.050M + 2x$

$(2x)(0.050\ M + x) = 1.2 \times 10^{-15}$

If we ignore the $+x$, then x is equal to $1.2 \times 10^{-14} M$. This is well below the 5% rule, so we can ignore the $+x$:

$$0.500\ \cancel{\text{L}} \times \frac{1.2 \times 10^{-14}\ \cancel{\text{mol}}}{1\ \cancel{\text{L}}} \times \frac{241.22\ \text{g}}{1\ \cancel{\text{mol}}} = 1.4 \times 10^{-12}\ \text{g}$$

1.8×10^{-5} g $Pb(OH)_2$

57. How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 8.9 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. What is the pH? ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)

Solution

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp} = [Mg^{2+}][OH^-]^2$$

$8.9 \times 10^{-12} = (x)(2x)^2 = 4x^3$

$x = 1.31 \times 10^{-4} M = [Mg^{2+}]$

$$\frac{1.31 \times 10^{-4}\ \text{mol}}{\text{L}} \times 0.200\ \text{L} \times \frac{1\ \text{mol Mg(OH)}_2}{1\ \text{mol Mg}^{2+}} \times \frac{58.3\ \text{g Mg(OH)}_2}{1\ \text{mol Mg(OH)}_2} = 1.23 \times 10^{-3}\ \text{g Mg(OH)}_2$$

59. The carbonate ion concentration is gradually increased in a solution containing equal concentrations of the divalent cations of magnesium, calcium, strontium, barium, and manganese. Which of the following carbonates will precipitate first? Which will precipitate last? Explain.

(a) $MgCO_3 \cdot 3H_2O \quad K_{sp} = 1 \times 10^{-5}$

(b) $CaCO_3 \quad K_{sp} = 8.7 \times 10^{-9}$

(c) $SrCO_3 \quad K_{sp} = 7 \times 10^{-10}$

(d) $BaCO_3 \quad K_{sp} = 1.6 \times 10^{-9}$

(e) $MnCO_3 \quad K_{sp} = 8.8 \times 10^{-11}$

Solution

$MnCO_3$ will form first since it has the smallest K_{sp} value among these homologous compounds and is therefore the least soluble. $MgCO_3 \cdot 3H_2O$ will be the last to precipitate since it has the largest K_{sp} value and is the most soluble.

Chemistry 2e
15: Equilibria of Other Reaction Classes
15.2: Lewis Acids and Bases

62. Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

Solution

when the amount of solid is so small that a saturated solution is not produced

64. Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 *M* $Cd(NO_3)_2$ with 0.150 L of 0.100 $NH_3(aq)$.

Solution

Cadmium ions associate with ammonia molecules in solution to form the complex ion $[Cd(NH_3)_4]^{2+}$, which is defined by the following equilibrium:

$$Cd^{2+}(aq) + 4NH_3(aq) \longrightarrow \left[Cd\left(NH_3\right)_4\right]^{2+}(aq) \qquad K_f = 1.3 \times 10^7$$

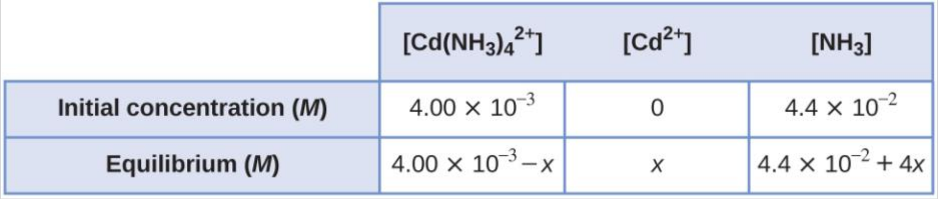
The formation of the complex ion requires 4 mol of NH_3 for each mol of Cd^{2+}. First, calculate the initial amounts of Cd^{2+} and of NH_3 available for association:

$$[Cd^{2+}] = \frac{(0.100\text{ L})(0.0100\text{ mol L}^{-1})}{0.250\text{ L}} = 4.00 \times 10^{-3}\ M$$

$$[NH_3] = \frac{(0.150\text{ L})(0.100\text{ mol L}^{-1})}{0.250\text{ L}} = 6.00 \times 10^{-2}\ M$$

For the reaction, 4.00×10^{-3}mol/L of Cd^{2+} would require $4(4.00 \times 10^{-3}$ mol/L) of NH_3 or a 1.6×10^{-2}-*M* solution. Due to the large value of K_f and the substantial excess of NH_3, it can be assumed that the reaction goes to completion with only a small amount of the complex dissociating to form the ions. After reaction, concentrations of the species in the solution are $[NH_3] = 6.00 \times 10^{-2}$ mol/L – 1.6×10^{-2} mol $L^{-1} = 4.4 \times 10^{-2}\ M$

Let *x* be the change in concentration of $[Cd^{2+}]$:



	$[Cd(NH_3)_4{}^{2+}]$	$[Cd^{2+}]$	$[NH_3]$
Initial concentration (*M*)	4.00×10^{-3}	0	4.4×10^{-2}
Equilibrium (*M*)	$4.00 \times 10^{-3} - x$	x	$4.4 \times 10^{-2} + 4x$

$$K_f = 4.0 \times 10^6 = \frac{[Cd(NH_3)_4{}^{2+}]}{[Cd^{2+}][NH_3]^4}$$

$$1.3 \times 10^7 = \frac{(4.00 \times 10^{-3} - x)}{(x)(4.4 \times 10^{-2} + 4x)^4}$$

As *x* is expected to be about the same size as the number from which it is subtracted, the entire expression must be expanded and solved, in this case, by successive approximations where substitution of values for *x* into the equation continues until the remainder is judged small enough. This is a slightly different method than used in most problems. We have:

$1.3 \times 10^7 x\,(4.4 \times 10^{-2} + 4x)^4 = 4.00 \times 10^{-3} - x$

$1.3 \times 10^7 x\,(3.75 \times 10^{-6} + 1.36 \times 10^{-3}x + 0.186x^2 + 11.264x^3 + 256x^4) = 4.00 \times 10^{-3}$

$16x + 5440x^2 + 7.44 \times 10^5x^3 + 4.51 \times 10^7x^4 + 1.024 \times 10^9x^5 = 4.00 \times 10^{-3}$

Substitution of different values *x* will give a number to be compared with 4.00 × 10^{-3}. Using 8 × 10^{-5} gives 4.01 × 10^{-3}, this is a good fit. Thus 1.8 × 10^{-5} is close enough to the true value of *x* to make the difference equal to zero. The decision to drop 4*x* compared with 4.4 x 10^{-2} is justified.

66. Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion AlF_6^{3-} the dissociation reaction is:

$$AlF_6^{3-} \rightleftharpoons Al^{3+} + 6F^- \text{ and } K_d = \frac{[Al^{3+}][F^-]^6}{[AlF_6^{3-}]} = 2 \times 10^{-24}$$

Calculate the value of the formation constant, K_f, for AlF_6^{3-}.

Solution

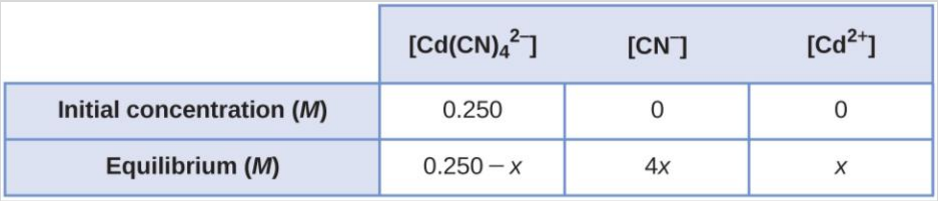
For the formation reaction:

$$Al^{3+}(aq) + 6F^-(aq) \rightleftharpoons AlF_6^{3-}(aq)$$

$$K_f = \frac{[AlF_6^{3-}]}{[Al^{3+}][F^-]^6} = \frac{1}{K_d} = \frac{1}{2 \times 10^{-24}} = 5 \times 10^{23}$$

68. Using the dissociation constant, K_d = 7.8 × 10^{-18}, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-*M* solution of $Cd(CN)_4^{2-}$.

Solution



	$[Cd(CN)_4^{2-}]$	$[CN^-]$	$[Cd^{2+}]$
Initial concentration (*M*)	0.250	0	0
Equilibrium (*M*)	0.250 − *x*	4*x*	*x*

$$K_d = \frac{[Cd^{2+}][CN^-]}{[Cd(CN)_4^{2-}]} = 7.8 \times 10^{-18} = \frac{x(4x)^4}{0.250 - x}$$

Assume that *x* is small when compared with 0.250 *M*.

$256x^5$ = 0.250 × 7.8 × 10^{-18}

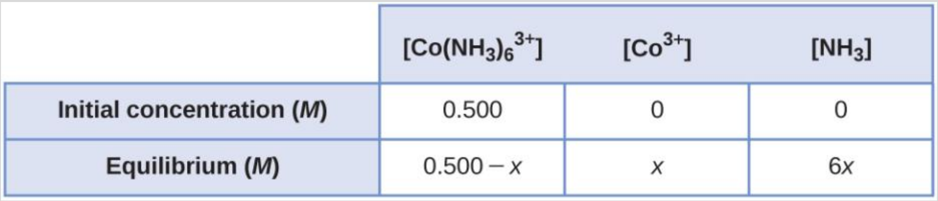
x^5 = 7.617 × 10^{-21}

x = $[Cd^{2+}]$ = 9.5 × 10^{-5} *M*

4*x* = $[CN^-]$ = 3.8 × 10^{-4} *M*

70. Using the dissociation constant, K_d = 2.2 × 10^{-34}, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of $Co(NH_3)_6^{3+}$.

Solution



	$[Co(NH_3)_6^{3+}]$	$[Co^{3+}]$	$[NH_3]$
Initial concentration (*M*)	0.500	0	0
Equilibrium (*M*)	0.500 − *x*	*x*	6*x*

$$K_d = \frac{[Co^{2+}][NH_3]^6}{[Co(NH_3)_6^{3+}]} = \frac{x(6x)^6}{0.500 - x} = 2.2 \times 10^{-34}$$

Assume that *x* is small when compared with 0.500 *M*.

4.67 × 104x^7 = 0.500 × 2.2 × 10^{-34}

x^7 = 2.358 × 10^{-39}

$x = [Co^{3+}] = 3.0 \times 10^{-6}\ M$
$6x = [NH_3] = 1.8 \times 10^{-5}\ M$

72. Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

Solution

Because K_{sp} is small and K_f is large, most of the Ag^+ is used to form $Ag(CN)_2{}^-$; that is:

$[Ag^+] < [Ag(CN)_2{}^-]$

$[Ag(CN)_2{}^-] \approx 2.0 \times 10^{-1}\ M$

The CN^- from the dissolution and the added CN^- exist as $CN^-$and $Ag(CN)_2{}^-$. Let x be the change in concentration upon addition of CN^-. Its initial concentration is approximately 0.

$[CN^-] + 2[Ag(CN)_2{}^-] = 2 \times 10^{-1} + x$

Because K_{sp} is small and K_f is large, most of the CN^- is used to form $[Ag(CN)_2{}^-]$; that is:

$[CN^-] < 2[Ag(CN)_2{}^-]$.

$2[Ag(CN)_2{}^-] \approx 2.0 \times 10^{-1} + x$

$2(2.0 \times 10^{-1}) - 2.0 \times 10^{-1} = x$

$2.0 \times 10^{-1}\ M \times L$ = mol CN^- added

The solution has a volume of 100 mL.

2×10^{-1} mol/L $\times$ 0.100 L $= 2 \times 10^{-2}$ mol

mass KCN $= 2.0 \times 10^{-2}$ mol KCN $\times$ 65.120 g/mol = 1.3 g

74. A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3{\cdot}5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$)?

Solution

The reaction is governed by two equilibria, both of which must be satisfied:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5 \times 10^{-13}$$

$$Ag^+(aq) + 2S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) \qquad K_f = 4.7 \times 10^{13}$$

The overall equilibrium is obtained by adding the two equations and multiplying their Ks:

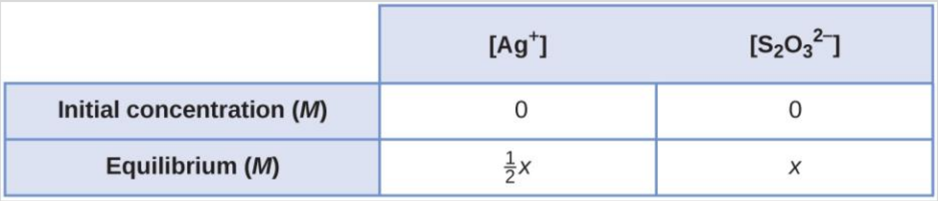
$$\frac{[Ag(S_2O_3)^{3-}][Br^-]}{[S_2O_3{}^{2-}]^2} = 23.5$$

If all Ag is to be dissolved, the concentration of the complex is the molar concentration of AgBr.

formula mass (AgBr) = 187.772 g/mol

$$\text{moles present} = \frac{0.27\text{ g AgBr}}{187.772\text{ g mol}^{-1}} = 1.438 \times 10^{-3}\text{ mol}$$

Let x be the change in concentration of $S_2O_3{}^{2-}$:



	$[Ag^+]$	$[S_2O_3{}^{2-}]$
Initial concentration (*M*)	0	0
Equilibrium (*M*)	$\frac{1}{2}x$	x

$$\frac{(1.438 \times 10^{-3})(1.438 \times 10^{-3})}{x^2} = 23.5$$

$x^2 = 8.799 \times 10^{-8}$

$x = 2.97 \times 10^{-4}\ M = [S_2O_3^{\ 2-}]$

The formula mass of $Na_2S_2O_3 \cdot 5H_2O$ is 248.13 g/mol. The total $[S_2O_3^{\ 2-}]$ needed is:

$2(1.438 \times 10^{-3}) + 2.97 \times 10^{-4} = 3.173 \times 10^{-3}$ mol

g(hypo) = 3.173×10^{-3} mol × 248.13 g/mol = 0.79 g

76. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CO_2 + OH^- \longrightarrow HCO_3^{\ -}$

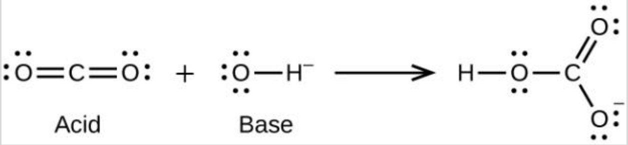
(b) $B(OH)_3 + OH^- \longrightarrow B(OH)_4^{\ -}$

(c) $I^- + I_2 \longrightarrow I_3^{\ -}$

(d) $AlCl_3 + Cl^- \longrightarrow AlCl_4^{\ -}$ (use Al-Cl single bonds)

(e) $O^{2-} + SO_3 \longrightarrow SO_4^{\ 2-}$

Solution

(a)


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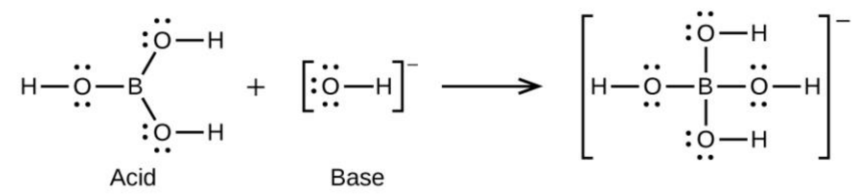
(b)


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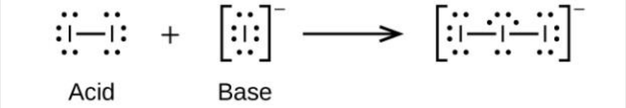
(c)


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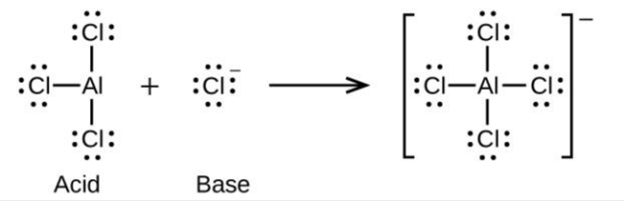
(d)


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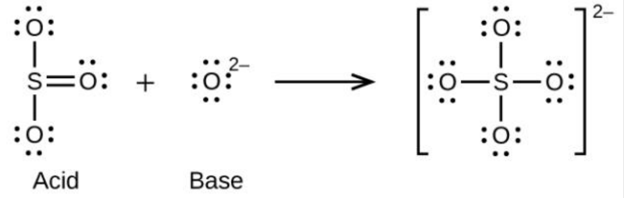
(e)


78. Using Lewis structures, write balanced equations for the following reactions:

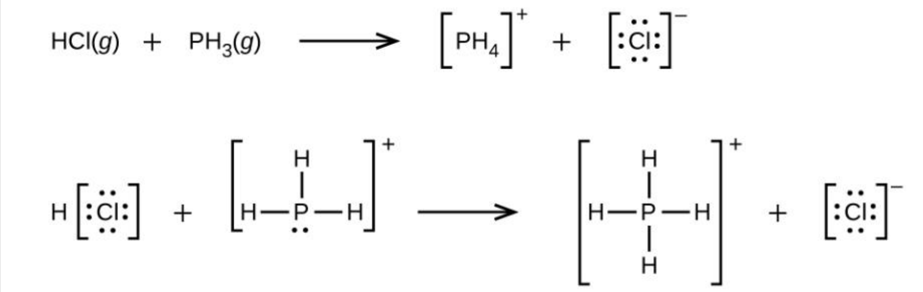
(a) $HCl(g) + PH_3(g) \longrightarrow$

(b) $H_3O^+ + CH_3^{\ -} \longrightarrow$

(c) $CaO + SO_3 \longrightarrow$

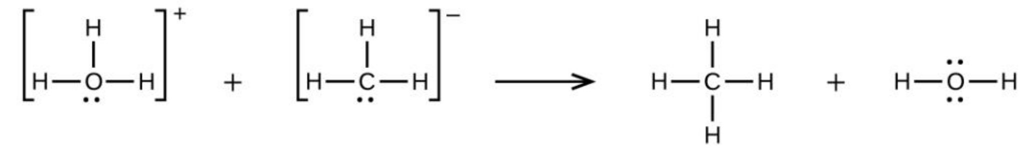
(d) $NH_4^+ + C_2H_5O^- \longrightarrow$

Solution

(a) 

;

(b) $H_3O^+ + CH_3^- \longrightarrow CH_4 + H_2O$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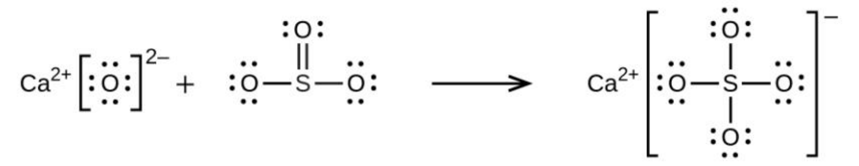
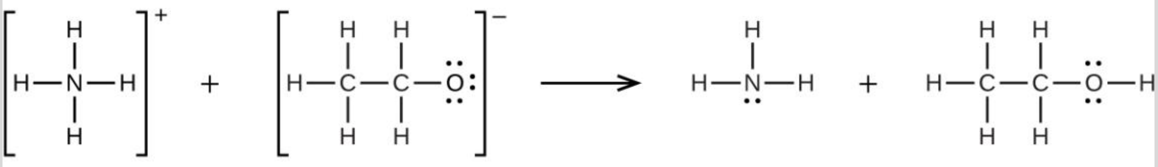
(c) $CaO + SO_3 \longrightarrow$ CaSO4


;

(d) $NH_4^+ + C_2H_5O^- \longrightarrow C_2H_5OH + NH_3$



80. In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the $Ag(CN)_2^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $Ag(CN)_2^-$. How many grams of NaCN were in the original sample?

Solution

The equilibrium is:

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) \qquad K_f = 1 \times 10^{21}$$

The number of moles of $AgNO_3$ added is:

$0.02872 \text{ L} \times 0.0100 \text{ mol/L} = 2.87 \times 10^{-4}$ mol

This compound reacts with CN^- to form $Ag(CN)_2^-$, so there are 2.87×10^{-4} mol $Ag(CN)_2^-$.

This amount requires $2 \times 2.87 \times 10^{-4}$ mol, or 5.74×10^{-4} mol, of CN^-. The titration is stopped just as precipitation of AgCN begins:

$$AgCN_2^-(aq) + Ag^+(aq) \rightleftharpoons 2AgCN(s)$$

so only the first equilibrium is applicable. The value of K_f is very large.

mol $CN^- < [Ag(CN)_2^-]$

mol NaCN = 2 mol [$Ag(CN)_2^-$] = 5.74×10^{-4} mol

$$\text{mass (NaCN)} = 5.74 \times 10^{-4}\ \text{mol} \times \frac{49.007\ \text{g}}{1\ \text{mol}} = 0.0281\ \text{g}$$

82. In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

Solution

$HNO_3(l) + HF(l) \longrightarrow H_2NO_3^+ + F^-$; $HF(l) + BF_3(g) \longrightarrow H^+ + BF_4$

84. Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

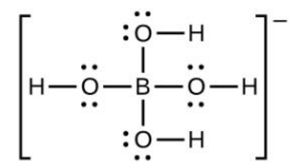
(a) Write an equation for its reaction with water.

(b) Predict the shape of the anion thus formed.

(c) What is the hybridization on the boron consistent with the shape you have predicted?

Solution

(a) $H_3BO_3 + H_2O \longrightarrow H_4BO_4^- + H^+$; (b) First, form a symmetrical structure with the unique atom, B, as the central atom. Then include the $32e^-$ to form the Lewis structure:



Because there are four bonds and no lone pair (unshared pair) on B, the electronic and molecular shapes are the same—both tetrahedral. (c) The tetrahedral structure is consistent with sp^3 hybridization.

Chemistry 2e
15: Equilibria of Other Reaction Classes
15.3: Coupled Equilibria

86. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

Solution

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) \qquad K_f = 2.0 \times 10^8$$

Let x be the change in concentration as Ni^{2+} dissociates. Because the initial Ni^{2+} concentration is 0, the concentration at any times is x:

$$2.0 \times 10^8 = \frac{[Ni(NH_3)_6]^{2+}}{[Ni^{2+}][NH_3]^6} = \frac{(1.0 - x)}{x(6x)^6}$$

$2.0 \times 10^8(46656x^7) = 1.0 – x$
$9.33 \times 10^{12}(x^2) = 1.0 – x$
Since x is small in comparison with 1.0, drop x:
$9.33 \times 10^{12}(x^7) = 1.0$
$x^7 = 1.07 \times 10^{–13}$
$x = 0.014\ M$

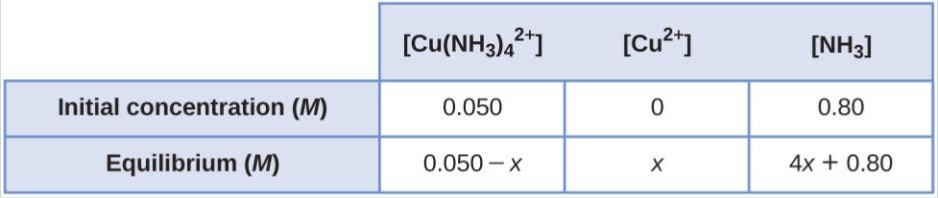
88. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

Solution

Assume that all Cu^{2+} forms the complex whose concentration is 0.050 *M* and the remaining NH_3 has a concentration of 1.00 *M* – 4(0.050 *M*) = 0.80 *M*. The complex dissociates:

$$[Cu(NH_3)_4]^{2+} \rightleftharpoons [Cu^{2+}] + 4[NH_3]$$

Let x be the change in concentration of Cu^{2+} that dissociates:



	$[Cu(NH_3)_4{}^{2+}]$	$[Cu^{2+}]$	$[NH_3]$
Initial concentration (*M*)	0.050	0	0.80
Equilibrium (*M*)	$0.050 - x$	x	$4x + 0.80$

$$\frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.7 \times 10^{13} = \frac{0.050 - x}{x(4x + 0.80)^4}$$

Assume that $4x$ is small when compared with 0.80 and that x is small when compared with 0.050:
$(0.80)^4 \times 1.7 \times 10^{13} x = 0.050$
$x = 7.2 \times 10^{–15} M$

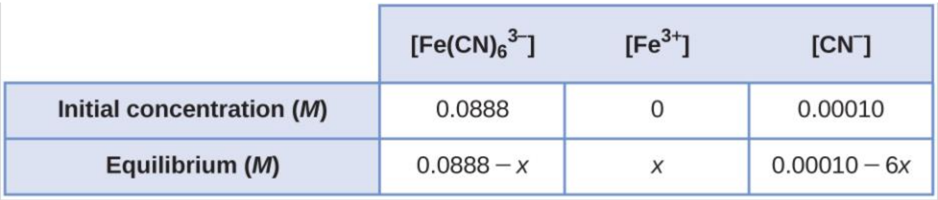
90. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* $CN^–$.

Solution

Set up a table listing initial and equilibrium concentrations for the reaction:

$$Fe^{3+} + 6CN^- \rightleftharpoons (Fe(CN)_6]^{3-} \qquad K_f = 2 \times 10^{43}$$

Let x be the concentration of Fe^{3+} that dissociates when 0.0888 mol dissolves in 1.00 L of 0.00010 *M* $CN^–$. Assume no volume change upon dissolution:



	$[Fe(CN)_6{}^{3-}]$	$[Fe^{3+}]$	$[CN^-]$
Initial concentration (*M*)	0.0888	0	0.00010
Equilibrium (*M*)	0.0888 – *x*	*x*	0.00010 – 6*x*

$$\frac{[Fe(CN)_6{}^{3-}]}{[Fe^{3+}][CN^-]^6} = \frac{0.0888 - x}{x(0.000010 - 6x)^6} = 2 \times 10^{43}$$

Assume that x is small when compared with the terms from which it is subtracted:

$0.0888 = (0.00010)^6(x)(1 \times 10^{43})$

$$x = \frac{0.0888}{2 \times 10^{19}} = 4.4 \times 10^{-22}\ M$$

93. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M* $NH_4{}^+$.

Solution

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{(0.400)[OH^-]}{(0.100)} = 1.8 \times 10^{-5}$$

$$[OH^-] = \frac{(0.100)(1.8 \times 10^{-5})}{0.0400} = 4.5 \times 10^{-6}$$

$K_{sp} = [Al^{3+}][OH^-]^3 = [Al^{3+}](4.5 \times 10^{-6})^3 = 2 \times 10^{-32}$

$[Al^{3+}] = 2 \times 10^{-16}$ (molar solubility)

95. What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for $HSO_4{}^- = 1.2 \times 10^{-2}$.

Solution

Find the amount of $SO_4{}^{2-}$ present from K_a for the equilibrium:

$$HSO_4{}^- + H_2O \longrightarrow H_3O^+ + SO_4{}^{2-}$$

Let x be $[SO_4{}^{2-}]$:

$$K_a = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{x^2}{0.250 - x} = 1.2 \times 10^{-2}$$

Because K_a is too large to disregard x in the expression $0.250 - x$, we must solve the quadratic equation:

$x^2 + 1.2 \times 10^{-2}x - 0.250(1.2 \times 10^{-2}) = 0$

$$x = \frac{-1.2 \times 10^{-2} \pm \sqrt{(1.2 \times 10^{-2})^2 + 4(3.0 \times 10^{-3})}}{2} = \frac{-1.2 \times 10^{-2} \pm 0.11}{2} = 0.049\ M$$

$K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = [Ba^{2+}](0.049) = 2.3 \times 10^{-8}$

$[Ba^{2+}] = 4.7 \times 10^{-7}$ (molar solubility)

97. What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2?

Solution

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3{}^+ + OH^-$$

$$K_b = \frac{[CH_3NH_3{}^+][OH^-]}{[CH_3NH_2]} = \frac{(x)(x)}{0.138 - x} = 4.4 \times 10^{-4}$$

Solve the quadratic equation using the quadratic formula:

$x^2 + 4.4 \times 10^{-4}x - 0.138(4.4 \times 10^{-4}) = 0$

$$x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 + 4(6.07 \times 10^{-5})}}{2} = \frac{-4.4 \times 10^{-4} \pm \sqrt{2.43 \times 10^{-4}}}{2}$$

$$= \frac{0.0152}{2} = 7.6 \times 10^{-3}\ M$$

$K_{sp} = [Pb^{2+}][OH^-]^2 = [Pb^{2+}](7.6 \times 10^{-3})^2 = 1.2 \times 10^{-15}$

$[Pb^{2+}] = 2.1 \times 10^{-11}$ (molar solubility)

99. A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S] = 0.10\ M$). At what pH does MnS begin to precipitate?

$$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 2.3 \times 10^{-13}$$

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 8.9 \times 10^{-27}$$

Solution

Two equilibria are in competition for the ions and must be considered simultaneously. Precipitation of MnS will occur when the concentration of S^{2-} in conjunction with 0.125 *M* Mn^{2+} exceeds the K_{sp} of MnS. The $[S^{2-}]$ must come from the ionization of H_2S as defined by the equilibrium:

$$H_2S(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + S^{2-}(aq)$$

$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_1K_2(H_2S) = 8.9 \times 10^{-27}$$

As a saturated solution of H_2S is 0.10 *M*, this later expression becomes:

$[H_3O^+]^2[S^{2-}] = 8.9 \times 10^{-28}$

From the equilibrium of MnS, the minimum concentration of S^{2-} required to cause precipitation is calculated as:

$$MnS(s) \longrightarrow Mn^{2+}(aq) + S^{2-}(aq)$$

$K_{sp} = [Mn^{2+}][S^{2-}] = 2.3 \times 10^{-13}$

$$[S^{2-}] = \frac{2.3 \times 10^{-13}}{0.125} = 1.84 \times 10^{-12}$$

This amount of S^{2-} will exist in solution at a pH defined by the H_2S equilibrium:

$[H_3O^+]^2(1.84 \times 10^{-12}) = 8.9 \times 10^{-28}$

$[H_3O^+]^2 = 4.84 \times 10^{-16}$

$[H_3O^+] = 2.20 \times 10^{-8}\ M$

$pH = -\log[H_3O^+] = 7.66$

101. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

In a saturated solution of MgF_2 at 18°C, the concentration of Mg^{2+} is 1.21×10^{-3} *M*. The equilibrium is represented by the equation above.

(a) Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
(c) Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}-*M* solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}-*M* solution of NaF at 18 °C. Show the calculations to support your prediction.
(d) At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is $1.17 \times 10^{-3} M$. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

Solution
(a) $K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$;
(b) $K_{sp} = [Mg^{2+}][F^-]^2 = [x][0.100 + 2x]^2 = 7.09 \times 10^{-9}$
Assume that $2x$ is small when compared with 0.100 *M*.
$0.100x = 7.09 \times 10^{-9}$
$x = [MgF_2] = 7.09 \times 10^{-7}\,M$
The value $7.09 \times 10^{-7}\,M$ is quite small when compared with 0.100 *M*, so the assumption is valid.
(c) Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur.
$0.1000\text{ L} \times 3.00 \times 10^{-3}\,M\ Mg(NO_3)_2 = 0.3000\text{ L} \times M\ Mg(NO_3)_2$
$M\ Mg(NO_3)_2 = 1.00 \times 10^{-3}\,M$
$0.2000\text{ L} \times 2.00 \times 10^{-3}\,M\text{ NaF} = 0.3000\text{ L} \times M\text{ NaF}$
$M\text{ NaF} = 1.33 \times 10^{-3}\,M$
ion product $= (1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$
This value is smaller than K_{sp}, so no precipitation will occur.
(d) MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Châtelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.

103. Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_3$, ZnS, PbI_2? Explain your answer.

Solution
BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the $[H_3O^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

105. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and $HPO_4^{\;2-}$ when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?
(a) $CaCl_2$
(b) HCl
(c) $KClO_4$
(d) NaOH
(e) $CaHPO_4$

Solution
Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: (a) increase, increase, decrease; (b) decrease, increase, decrease; (c) no effect, no effect, no effect; (d) decrease, increase, decrease; (e) increase, no effect, no effect