***Chemistry***

**15: Equilibria of Other Reaction Classes**

**15.1: Precipitation and Dissolution**

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

(a) 

(b) 

(c) 

(d) 

(e) 

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) 

Dissolving AgI(*s*) must produce the same amount of I– ion as it does Ag+ ion.

(b) 

Dissolving CaCO3(*s*) must produce the same amount of Ca2+ ion as it does  ion.

(c) 

When one unit of Mg(OH)2 dissolves, two ions of OH– are formed for each Mg2+ ion.

(d) 

One unit of Mg3(PO4)2 provides two units of  ion and three units of Mg2+ ion.

(e) 

One unit of Ca5(PO4)3OH dissolves into five units of Ca2+ ion, three units of  ion, and one unit of OH– ion.

3. How do the concentrations of Ag+ and  in a saturated solution above 1.0 g of solid Ag2CrO4 change when 100 g of solid Ag2CrO4 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, BaSO4, CaF2, Hg2I2, MnCO3, ZnS, PbS?

Solution

CaF2, MnCO3, 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) LaF3

(b) CaCO3

(c) Ag2SO4

(d) Pb(OH)2

Solution

(a) ;

(b) ;

(c) ;

(d) 

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) BaSeO4, 0.0118 g/100 mL

(b) Ba(BrO3)2⋅H2O, 0.30 g/100 mL

(c) NH4MgAsO4⋅6H2O, 0.038 g/100 mL

(d) La2(MoO4)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) BaSeO4: ,

*K* = [Ba2+] = (4.21  10–4)(4.21 10–4) = 1.77  10–7;

(b) Ba(BrO3)2⋅H2O: ,

*K* = [Ba2+] = (7.3  10–3)(2  7.3  10–3)2 = 1.6  10–6;

(c) NH4MgAsO4⋅6H2O: ,

*K* = [Mg2+] = (1.3 10–3)3 = 2.2  10–9;

(d) La2(MoO4)3: ,

*K* = [La3+]2 = (2  2.36  10–5)2(3  2.36  10–5)3 = 2.228  10–9 3.549  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) KHC4H4O6

(b) PbI2

(c) Ag4[Fe(CN)6], a salt containing the ion

(d) Hg2I2

Solution

Let *x* be the molar solubility.

(a) *K*sp =  = 3  10–4 = *x*2, *x* = 2  10–2*M*;

(b) *K*sp = [Pb2+][I–]2 = 1.4  10–8 = *x*(2*x*)3 = 4*x*3, *x* = 1.5  10–3*M*;

(c) *K*sp =  = 1.55  10–41 = (4*x*)4*x* = 256*x*5, *x* = 2.27  10–9*M*;

(d) *K*sp =  = 4.5  10–29 = [*x*][2*x*]2 = 4*x*3, *x* = 2.2  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) CaF2(*s*) in 0.00133 *M* KF

(c) Ag2SO4(*s*) in 0.500 L of a solution containing 19.50 g of K2SO4

(d) Zn(OH)2(*s*) in a solution buffered at a pH of 11.45

Solution

(a) *K*sp = 1.6  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:



Check: , an insignificant change;

(b) *K*sp = 4.0  10–11 = [Ca2+][F–]2 = *x*(2*x* + 0.00133 *M*)2, where *x* = [Ca2+]. Assume that *x* is small when compared with 0.0013 *M* and disregard it:



Check: . This value is less than 5% and can be ignored.

(c) Find the concentration of K2SO4:





*K*sp = 1.12  10–5 = [Ag+]2 = 4*x*2(*x* + 0.2238)



*x* = 3.7  10–3[Ag+] = 2*x* = 7.4  10–3*M*

Check: ; the condition is satisfied.

(d) Find the concentration of OH– from the pH:

pOH = 14.00 – 11.45 = 2.55

[OH–] = 2.8  10–3*M*

*K*sp = 4.5  10–17 = [Zn2+][OH–]2 = *x*(2*x* + 2.8  10–3)2

Assume that *x* is small when compared with 2.8  10–3:



Check: ; *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* TlNO3

(b) BaF2(*s*) in 0.0313 *M* KF

(c) MgC2O4 in 2.250 L of a solution containing 8.156 g of Mg(NO3)2

(d) Ca(OH)2(*s*) in an unbuffered solution initially with a pH of 12.700

Solution

(a) *K*sp = 1.7  10–4 = [Ti+][Cl–]; Let *x* = [Cl–]:

1.7  10–4 = (*x* = 0.025)*x*

Assume that *x* is small when compared with 0.025:



Check: 

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



*x*2 + 0.025*x* – 1.7  10–4 = 0



(Use only the positive answer for physical sense.)

[Ti+] = 0.025 + 0.0056 = 3.1 10–2*M*

[Cl–] = 6.1  10–3

(b) *K*sp = 2.4  10–5 = [Ba2+][F–]2; Let *x* = [Ba2+]

If we drop *x* from *x* + 0.0313, *x* would be equal to 7.7  10–4 *M*

Check: 

This value is less than 5%, so

[Ba2+] = 7.7  10–4*M*

[F–] = 0.0321 *M*;

(c) Find the molar concentration of the Mg(NO3)2. The molar mass of Mg(NO3)2 is 148.3149 g/mol. The number of moles is 



Let *x* =  and assume that *x* is small when compared with 0.02444 *M*.

*K*sp = 7  10–7 = [Mg2+]= (*x*)(*x* + 0.02444)

0.02444*x* = 7  10–7

*x* =  = 2.9  10–5

Check: 

This value is less than 5%, so

[Ca2+] = 2.9  10–5 *M*

[OH–] = 0.0501 *M*

[Mg2+] = 0.0244 *M*

(d) pH = 12.700; pOH = 1.300

[OH–] = 0.0501 *M*; Let *x* = [Ca2+]

*K*sp = 7.9  10–6 = [Ca2+][OH–]2 = (*x*)(*x* + 0.050)2

Assume that *x* is small when compared with 0.050 *M*:

*x* = [Ca2+] = 3.15  10–3 (one additional significant figure is carried)

Check: 

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  10–3 + 0.0501)2 = 7.9  10–6 or



[Ca2+] = 2.8  10–3*M*

[OH–] = (2.8  10–3 + 0.0501) = 0.053  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: [Ca2+][OH–]2 = 1.3  10–6

Let *x* be [Ca2+] = molar solubility; then [OH–] = 2*x*

*K*sp = *x*(2*x*)2 = 4*x*3 = 1.3  10–6

*x*3 = 0.069  10–6

*x* = 0.069 *M*

CaCO3: [Ca2+]= 8.7  10–9

Let *x* be [Ca2+]; then  = [Ca2+] = molar solubility

*K*sp = *x*2 = 8.7  10–9

*x* = 9.3  10–5*M*

CaSO4·2H2O: [Ca2+][H2O]2 = 6.1  10–5

Let *x* be [Ca2+] = molar solubility =; then [H2O] = 2*x*

*K*sp = (*x*)(*x*)(2*x*)2 = 6.1  10–5

*x*4 = 1.53  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:

CaC2O4·H2O: [Ca2+][H2O] = 1.96 × 10–8

Let *x* be [Ca2+] = molar solubility =  = [H2O]

*x*3 = 1.96  10–8

*x* = 2.7  10–3*M*

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

Ca3(PO4)2: [Ca2+]3 = 1.3  10–32

Upon solution there are three Ca2+ and two  ions. Let the concentration of Ca2+ formed upon solution be *x*. Then  is the concentration of :



*x* = 4.9  10–7*M* = [Ca2+]

The solubility is then one-third the concentration of Ca2+, or 1.6  10–7. CaSO4 2H20 is the most soluble Ca salt.

23. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60  10–3*M*) of  because of its cathartic action (it is a laxative). Does natural water that is saturated with CaSO4 (“gyp” water) as a result or passing through soil containing gypsum, CaSO4.2H2O, meet these standards? What is  in such water?

Solution

First, find the concentration in a saturated solution of CaSO4. Before placing the CaSO4 in water, the concentrations of Ca2+ and  are 0. Let *x* be the change in concentration of Ca2+, which is equal to the concentration of :

*K*sp = [Ca2+] = 6.1  10–5

*x*  *x* = *x*2 = 6.1  10–5



*x* = 7.8  10–3*M* =  = [Ca2+]

Since this concentration is higher than 2.60  10–3*M*, “gyp” water does not meet the standards.

25. The solubility product of CaSO4⋅2H2O is 2.4  10–5. What mass of this salt will dissolve in1.0 L of 0.010 *M* ?

Solution

The amount of CaSO4⋅2H2O that dissolves is limited by the presence of a substantial amount of  already in solution from the 0.010 *M*. This is a common-ion problem. Let *x* be the change in concentration of Ca2+ and of  that dissociates from CaSO4:



*K*sp = [Ca2+] = 6.1  10–5

Addition of 0.010 *M* generated from the complete dissociation of 0.010 *M* SO4 gives

[*x*][*x* + 0.010] = 6.1  10–5. Here, *x* cannot be neglected in comparison with 0.010 *M*; the quadratic equation must be used. In standard form:

*x*2 + 0.010*x* – 6.1  10–5 = 0



Only the positive value will give a meaningful answer:

*x* = 4.2  10–3 = [Ca2+]

This is also the concentration of CaSO4⋅2H2O that has dissolved. The mass of the salt in 1 L is

Mass (CaSO4⋅2H2O) = 4.2  10–3 mol/L  172.16 g/mol = 0.72 g/L

Note that the presence of the common ion, , has caused a decrease in the concentration of Ca2+ that otherwise would be in solution:



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) Ag2SO4

(c) Mn(OH)2

(d) Sr(OH)2.8H2O

(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  10–5*M*; (b) *K*sp =  = 1.2  10–5 = [2*x*]2[*x*], 4*x*3 = 1.2  10–5, *x* = 1.44  10–2*M*

As there are 2 Ag+ ions for each  ion, [Ag+] = 2.88  10–2*M*, = 1.44  10–2*M*; (c) *K*sp = [Mn2+]2[OH–]2 = 2  10–13 = [*x*][2*x*]2, 4*x*3 = 2  10–13, *x* = 3.68  10–5*M*.

Since there are two OH– ions for each Mn2+ ion, multiplication of *x* by 2 gives 7.36  10–5*M*. If the value of *x* is rounded to the correct number of significant figures, [Mn2+] = 3.7  10–5*M*. [OH–] = 7.4  10–5*M*. We normally maintain one additional figure in the calculator throughout all calculations before rounding.

(d) *K*sp = [Sr2+][OH–]2 = 3.2  10–4 = [*x*][2*x*]2, 4*x*3 = 3.2  10–4, *x* = 4.3  10–2*M*.

Substitution gives [Sr2+] = 4.3  10–2*M*, [OH–] = 8.6  10–2*M*;

(e) *K*sp = [Mg2+]2[OH–]2 = 8.9  10–12 = [*x*][2*x*]2, 4*x*3 = 8.9  10–12, *x* = 1.31  10–4*M*, 2*x* = 2.6  10–4.

Substitution and taking the correct number of significant figures gives [Mg2+] = 1.3  10–4*M*, [OH–] = 2.6  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  10–2*M*, [Cl–] = 1.2  10–2*M*

(b) Ce(IO3)4: [Ce4+] = 1.8  10–4*M*,  = 2.6  10–13*M*

(c) Gd2(SO4)3: [Gd3+] = 0.132 *M*, = 0.198 *M*

(d) Ag2SO4: [Ag+] = 2.40  10–2*M*, = 2.05  10–2*M*

(e) BaSO4: [Ba2+] = 0.500 *M*, = 2.16  10–10*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  10–2)(1.2  10–2) = 1.7 10–4;

(b) Ce(IO3)4: *K*sp = (1.8  10–4)(2.6  10–13)4 = 8.2  10–55;

(c) Gd2(SO4)3: *K*sp = (0.132)2(0.198)3 = 1.35  10–4;

(d) Ag2SO4: *K*sp = (2.40  10–2)2(2.05  10–2) = 1.18  10–5;

(e) BaSO4: *K*sp = (0.500)(2.16  10–10) = 1.08  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) CaCO3: [Ca2+] = 0.003 *M*,  = 0.003 *M*

(b) Co(OH)2: [Co2+] = 0.01 *M*, [OH–] = 1  10–7*M*

(c) CaHPO4: [Ca2+] = 0.01 *M*,  = 2  10–6*M*

(d) Pb3(PO4)2: [Pb2+] = 0.01 *M*, = 1  10–13*M*

Solution

(a)

*K*sp = [Ca2+] = 8.7  10–9

test*K*sp against *Q* = [Ca2+]

*Q* = [Ca2+] = (0.003)(0.003) = 9  10–6

*K*sp = 8.7  10–9 < 9  10–6

The ion product does exceed *K*sp, so CaCO3 does precipitate.

(b) 

*K*sp = [Co2+][OH–]2 = 2.5  10–16

test *K*sp against *Q* = [Co2+][OH–]2

*Q* = [Co2+][OH–]2 = (0.01)(1  10–7)2 = 1  10–16

*K*sp = 2.5  10–16 > 1  10–16

The ion product does not exceed *K*sp, so the compound does not precipitate.

(c) CaHPO4: (*K*sp = 7  10–7):

*Q* = [Ca2+] = (0.01)(2  10–6) = 2  10–8 < *K*sp

The ion product does not exceed *K*sp, so compound does not precipitate.

(d) Pb3(PO4)2: (*K*sp = 1  10–54):

*Q* = [Pb2+]3 = (0.01)3(1  10–13)2 = 1  10–32 > *K*sp

The ion product exceeds *K*sp, so the compound precipitates.

33. Calculate the concentration of sulfate ion when BaSO4 just begins to precipitate from a solution that is 0.0758 *M* in Ba2+.

Solution

Precipitation of  will begin when the ion product of the concentration of the  and Ba2+ ions exceeds the *K*sp of BaSO4.

*K*sp = 2.3  10–8 = [Ba2+] = (0.0758)



35. Calculate the concentration of  when Ag3PO4 starts to precipitate from a solution that is 0.0125 *M* in Ag+.

Solution

Precipitation of Ag3PO4 will begin when the ion product of the concentrations of the Ag+ and  ions exceeds *K*sp:



*K*sp = 1.8  10–18 = [Ag+]3 = (0.0125)3



37. Calculate the concentration of Ag+ required to begin precipitation of Ag2CO3 in a solution that is 2.50  10–6*M* in .

Solution



[Ag+]2 = *K*sp = 8.1  10–12

[Ag+]2(2.5  10–6) = 8.1  10–12



[Ag+] = 1.8  10–3*M*

39. What [F–] is required to reduce [Ca2+] to 1.0  10–4*M* by precipitation of CaF2?

Solution

In the *K*sp expression, substitute the concentration of Ca2+ and solve for [F–].

*K*sp = 4.0  10–11 = [Ca2+][F–]2 = (1.0  10–4)[F–]2



[F–] = 6.3  10–4

41. Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing NiCO3 be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with NiCO3 (*K*sp = 1.36  10–7).

(b) If the NiCO3 were a contaminant in a sample of CoCO3 (*K*sp = 1.0  10–12), what mass of CoCO3 would have been lost? Keep in mind that both NiCO3 and CoCO3 dissolve in the same solution.

Solution

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

*K*sp = 1.4  10–7 = [Ni2+]

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  10–7

*x* = [Ni2+] =  = 3.742  10–4*M*

The molar mass of NiCO3 is 118.71 g/mol. Thus:

Concentration of NiCO3 = 118.71 g/mol  3.742  10–4 mol/L = 0.0444 g/L

To contain 0.1 g, ;

(b) During the process of removal of NiCO3, some CoCO3 would be lost. The  is controlled by the amount found in part (a). From the solubility product for CoCO3:

*K*sp = 1.0  10–12 = [Co2+][3.742 × 10–4]

[Co2+] = 2.67  10–9*M*

The molar mass of CoCO3 is 118.94 g/mol. Thus:

mass CoCO3 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 Cu2+ and Cd2+.What percentage of Cd2+ remains in the solution when 99.9% of the Cu2+ has been precipitated as CuS by adding sulfide?

Solution

When 99.9% of Cu2+ has precipitated as CuS, then 0.1% remains in solution.

 0.010 mol/L = 1  10–5*M* = [Cu2+]

[Cu2+][S2–] = *K*sp = 8.5  10–45

(1  10–5)[S2–] = 8.5  10–45

[S2–] = 8.5  10–40*M*

[Cd2+][S2–]*K*sp = 1.0  10–28

[Cd2+](7  10–37) = 1.0  10–28

[Cd2+] = 1.2  1011*M*

Thus [Cd2+] can increase to 1.2  1011 *M* before precipitation begins. [Cd2+] 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) and Cu2+

(b) and Cl–

(c) Hg2+ and Co2+

(d) Zn2+ and Sr2+

(e) Ba2+ and Mg2+

(f)  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) and Cu2+: Add . CuSO4 is soluble (see Appendix J), but *K*sp for Hg2SO4 is 7.4  10–7. When only 0.1%  remains in solution:



and

;

(b)  and Cl–: Add Ba2+. BaCl2 is soluble (see the section on catalysis), but *K*sp for BaSO4 is 2.3  10–8. When only 0.1%  remains in solution,  = 1  10–4*M* and

;

(c) Hg2+ and Co2+: Add S2–: For the least soluble form of CoS, *K*sp = 3  10–26 and for HgS, *K*sp = 1.6  10–54. CoS will not begin to precipitate until:

[Co2+][S2–] = *K*sp = 3  10–26

(0.10)[S2–] = 3  10–26

[S2–] = 3  10–25

At that concentration:

[Hg2+](3  10–25) = 1.6  10–54

[Hg2+] = 5.3  10–30 *M*

That is, it is virtually 100% precipitated. For a saturated (0.10 *M*) H2S solution, the corresponding  is:





A solution more basic than this would supply enough S2– for CoS to precipitate.

(d) Zn2+ and Sr2+: Add OH– until [OH–] = 0.050 *M*. For Sr(OH)2⋅8H2O, *K*sp = 3.2  10–4. For Zn(OH)2, *K*sp = 4.5  10–11. When Zn2+ is 99.9% precipitated, then [Zn2+] = 1  10–4*M* and



[OH–] = 7  10–4*M*

When Sr(OH)2⋅8H2O just begins to precipitate:



[OH–] = 0.057 *M*

If [OH–] is maintained less than 0.056 *M*, then Zn2+ will precipitate and Sr2+ will not.

(e) Ba2+ and Mg2+: Add . MgSO4 is soluble and BaSO4 is not (*K*sp = 2.3  10–8).

(f)  and OH–: Add Ba2+. For Ba(OH)2, 8H2O, *K*sp = 5.0  10–3; for BaCO3, *K*sp = 1.6 10–9. When 99.9% of  has been precipitated  = 1  10–4*M* and



Ba(OH)2⋅8H2O begins to precipitate when:



As long as [Ba2+] is maintained at less than 0.50 *M*, BaCO3 precipitates and Ba(OH)2⋅8H2O does not.

47. A solution contains 1.0  10–2 mol of KI and 0.10 mol of KCl per liter. AgNO3 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  10–10 = [Ag+][Cl–]



For AgI: *K*sp = 1.5  10–16 = [Ag+][I–]



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, Ca3(PO4)2. The normal mid range calcium content excreted in the urine is 0.10 g of Ca2+ 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 Ca3(PO4)2 yields:



Given the concentration of Ca2+ in solution, the maximum  can be calculated by using the *K*sp expression for Ca3(PO4)2:

*K*sp = 1.3  10–32 = [Ca2+]3







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:







Sea water has a density of 1.026 g/cm3 and contains 1272 parts per million of magnesium as Mg2+(*aq*) by mass. What mass, in kilograms, of Ca(OH)2 is required to precipitate 99.9% of the magnesium in 1.00  103 L of sea water?

Solution

Calculate the amount of Mg2+ 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  103 L  1000 cm3/L  1.026 g/cm3  1272 ppm  10–6 ppm–1 = 1.305  103 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:



As the Ca(OH)2 reacts with Mg2+ on a 1:1 mol basis, the amount of Ca(OH)2 required to precipitate 99.9% of the Mg2+ in 1 L is:

0.05365 M  74.09 g/mol Ca(OH)2 = 3.97 g/L

For treatment of 1000 L, 1000 L  3.97 g/L = 3.97  103 g = 3.97 kg. However, additional [OH–] must be added to maintain the equilibrium:



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



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

[Mg2+][OH–]2 = (5.369  10–5)[OH–]2 = 8.9  10–12 = *K*sp

[OH–] = 4.07  10–4

Thus an additional  4.07  10–4 mol (2.65  10–4 mol) of Ca(OH)2 per liter is required to supply the OH–. For 1000 L:



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(IO3)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(IO3)2 (*K*sp = 7.4  10–8).

Solution

(a) *K*sp = [La3+] =  (3.1  10–3)3 = (0.0010)(3.0  10–8) = 3.1  10–11;

(b) *K*sp = [Cu2+] = *x*(2*x*)2 = 7.4  10–8

4*x*3 = 7.4  10–8

*x*3 = 1.85  10–8

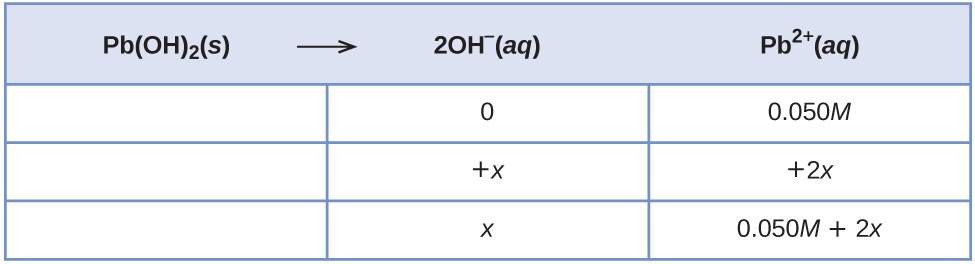
*x* = 2.64  10–3

[Cu2+] = 2.6  10–3

 = 2*x* = 5.3  10–3

55. How many grams of Pb(OH)2 will dissolve in 500 mL of a 0.050-*M* PbCl2 solution (*K*sp = 1.2  10–15)?

Solution



(2*x*)(0.050 *M* + *x*) = 1.2  10–15

If we ignore the +*x*, then *x* is equal to 1.2  10–14*M*. This is well below the 5% rule, so we can ignore the +*x*:



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  10–12.Include the ionic reaction and the expression for *K*sp in your answer. What is the pH? (*K*w = 1  10–14 = [OH–])

Solution



8.9  10–12 = (*x*)(2*x*)2 = 4*x*3

*x* = 1.31  10–4*M* = [Mg2+]



59. Which of the following carbonates will form first? Which of the following will form last?

Explain.

(a) 

(b) 

(c) 

(d) 

(e) 

Solution

MnCO3 will form first, since it has the smallest *K*sp value it is the least soluble. MgCO3 will be the last to precipitate, it has the largest *K*sp value.

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