**Answer Key to Problem Set on Solubility Equilibrium**

1. a.The equilibrium taking place is:

 PbCO3(s) ⮀ Pb2+(aq) + CO32-(aq)

The equilibrium constant expression is: Ksp = [Pb2+][CO32-] = 7.4 x 10-14. Notice that a denominator term is absent (actually equal to one), because the reactant in the chemical equilibrium is a solid. Equal amounts of lead(II) ions and carbonate ions are produced in solution for every lead(II) carbonate particle that dissociates. Let us use “x” for the amount of each of these ions in the equilibrium constant expression:

 Ksp = [Pb2+][CO32-] = 7.4 x 10-14 = (x)(x) = x2

The molar solubility will be “x” and represents the moles of solute soluble in one liter of solution:

$$x = \sqrt{7.4 x 10^{-14} } = 2.7 x 10^{-7} M$$

1. b. The equilibrium taking place is:

 Ag2CrO4(s) ⮀ 2 Ag+(aq) + CrO42-(aq)

The equilibrium constant expression is: Ksp = [Ag+]2[CrO42-] = 1.3 x 10-12. Notice that a denominator term is absent (actually equal to one), because the reactant in the chemical equilibrium is a solid. The amount of silver(I) cation produced in solution is twice the amount of chromate ion. Let us use “2x” for the amount of silver(I) ion, and “x” for the amount of chromate ion in the equilibrium constant expression:

 Ksp = [Ag+]2[CO32-] = 1.3 x 10-12 = (2x)2(x) = 4x3

The molar solubility will be “x” and represents the moles of solute soluble in one liter of solution:

$$4x^{3} = 1.3 x 10^{-12}$$

$$x^{3} = \frac{1.3 x 10^{-12}}{4} = 3.25 x 10^{-13}$$

$$x = \sqrt[3]{3.25 x 10^{-13}} = 6.9 x 10^{-5} M$$

1. c. The equilibrium taking place is:

 La(IO3)3(s) ⮀ La3+(aq) + 3 IO3¯(aq)

The equilibrium constant expression is: Ksp = [La3+][ IO3¯]3 = 1.2 x 10-11. Notice that a denominator term is absent (actually equal to one), because the reactant in the chemical equilibrium is a solid. The amount of iodate ion produced in solution is three times as much as the amount of lanthanum(III) ions. Let us use “x” for the amount of lanthanum(II) ions and “3x” for the amount of iodate ions in the equilibrium constant expression:

 Ksp = [La3+][IO3¯] = 1.2 x 10-11 = (x) (3x)3 = 27x4

The molar solubility will be “x” and represents the moles of solute soluble in one liter of solution:

$$27x^{4} = 1.2 x 10^{-11}$$

$$x^{4} = \frac{1.2 x 10^{-11}}{27} = 4.4 x 10^{-13}$$

$$x = \sqrt[4]{4.4 x 10^{-13}} = 8.2 x 10^{-4} M$$

1. d. The equilibrium taking place is:

 Fe3(PO4)2(s) ⮀ 3 Fe2+(aq) + 2 PO43- (aq)

The equilibrium constant expression is: Ksp = [Fe2+]3[ PO43-]2 = 1.0 x 10-36. Notice that a denominator term is absent (actually equal to one), because the reactant in the chemical equilibrium is a solid. Three particles of iron(II) ions and two particles of phosphate ions form in solution for every particle of iron(II) phosphate. Let us use “3x” for the amount of iron(II) ions in solution and “2x” for the amount of phosphate ions in solution:

 Ksp = [Fe2+]3[ PO43-]2 = 1.0x 10-36 = (3x)3(2x)2 = 108x5

The molar solubility will be “x” and represents the moles of solute soluble in one liter of solution:

$$108x^{5} = 1.0 x 10^{-36} $$

$$x^{5} = \frac{1.0 x 10^{-36}}{108} = 9.3 x 10^{-39}$$

$$x = \sqrt[5]{9.3 x 10^{-39}} = 2.5 x 10^{-8} M$$

2. Since the molar solubility has units of moles solute per liter of solution, convert the moles of solute to grams using the molar mass of the compound. Using the molar solubilities calculated from problem 1:

a. Molar mass of PbCO3 = AW Pb + AW C + 3 AW O where AW = atomic weight in g/mol

 MM PbCO3 = 207.2 g/mol + 12.01 g/mol + 3(16.00 g/mol) = 235.2 g/mol

$$\frac{2.7 x 10^{-7} mol PbCO\_{3}}{1 L solution} x \frac{235.2 g PbCO\_{3}}{1 mol PbCO\_{3}} = 6.4 x 10^{-5} g PbCO\_{3}/L soln$$

b. Molar mass of Ag2CrO4 = 2 AW Ag + AW Cr + 4 AW O

 MM Ag2CrO4 = 2(107.9 g/mol) + 52.00 g/mol + 4(16.00 g/mol) = 331.8 g/mol

$$\frac{6.9 x 10^{-5} mol Ag\_{2}CrO\_{4}}{L solution} x \frac{331.8 g Ag\_{2}CrO\_{4}}{1 mol Ag\_{2}CrO\_{4}} = 0.023 g Ag\_{2}CrO\_{4}/L soln$$

2. c. Molar mass of La(IO3)3 = AW La + 3 AW I + 9 AW O

 MM La(IO3)3 = 138.9 g/mol + 3(126.9 g/mol) + 9(16.00 g/mol) = 663.6 g/mol

$$\frac{8.2 x 10^{-4} mol La(IO\_{3})\_{3}}{1 L solution} x \frac{663.6 g La(IO\_{3})\_{3}}{1 mol La(IO\_{3})\_{3}} = 0.54 g La(IO\_{3})\_{3}/L soln$$

 d. Molar mass of Fe3(PO4)2 = 3 AW Fe + 2 AW P + 8 AW O

 MM Fe3(PO4)2 = 3(55.85 g/mol) + 2(30.97 g/mol) + 8(16.00 g/mol) = 357.5 g/mol

$$\frac{2.5 x 10^{-8} mol Fe\_{3}(PO\_{4})\_{2}}{1 L solution} x \frac{357.5 g Fe\_{3}(PO\_{4})\_{2}}{1 mol Fe\_{3}(PO\_{4})\_{2}} = 8.9 x 10^{-6} g Fe\_{3}(PO\_{4})\_{2}/L soln$$

3. One cannot easily predict the relative solubility of a series of compounds solely by looking at the Ksp value. For BaCO3, the Ksp = 5.0 x 10-9; for SrF2, the Ksp = 3.2 x 10-9. Initially one might think that the larger equilibrium constant for BaCO3 means the equilibrium lies further to the right, and thus BaCO3 would have a higher solubility. However, upon calculation of the actual molar solubility of each of these compounds, one discovers that the opposite is true. Notice that the numbers of particles produced by each compound in solution are not identical. BaCO3 produces 2 moles of ions per mole of substance in solution while SrF2 produces 3 moles of ions per mole of substance:

BaCO3(s) ⮀ Ba2+ (aq) + CO32─ (aq)

SrF2(s) ⮀ Sr2+(aq) + 2 F¯(aq)

An approximation could be done quickly by noting that one will have to take the square root of the Ksp of barium carbonate, while one will be taking the cube root of the Ksp of strontium fluoride. This will make the magnitude of the molar solubility of barium carbonate around 10-5 and the magnitude of the molar solubility of strontium fluoride around 10-3. Thus, even though it appears to have a smaller equilibrium constant, the strontium fluoride turns out to be more soluble. For those who are still skeptical, calculate the actual molar solubility of each compound:

 Ksp = [Ba2+][ CO32─] = 5.0 x 10-9 = x2

 molar solubility = x = $\sqrt{5.0 x 10^{-9}} = 7.1 x 10^{-5} M$

 Ksp = [Sr2+][ F─]2 = 3.2 x 10-9 = (x)(2x)2 = 4x3

 molar solubility = x = $\sqrt[3]{\frac{3.2 x 10^{-9}}{4}} = 9.3 x 10^{-4} M$

4. This problem demonstrates LeChatelier’s Principle. Qualitatively, the stress is excess lead(II) ion which would drive the equilibrium towards products and lower the solubility. Let’s compare the solubility in pure water to the solubility in 0.020 M lead(II) ion. The equilibrium involved is:

 PbCO3(s) ⮀ Pb2+(aq) + CO32─ (aq)

The equilibrium constant expression for this equilibrium would be:

 Ksp = [Pb2+][ CO32─] = 7.4 x 10-14

Equal amounts of lead(II) ions and carbonate ions are produced for every particle of lead(II) carbonate. Thus an “x” amount of both lead(II) and carbonate ions are produced in solution:

 Ksp = [Pb2+][ CO32─] = 7.4 x 10-14 = (x)(x) = x2

Solving for x gives the molar solubility in pure water:

$$Molar solubility = x = \sqrt{7.4 x 10^{-14}} = 2.7 x 10^{-7}$$

By adjusting lead(II) cations into solution to 0.020 M, the amount of lead(II) is no longer “x”. Adding extra lead(II) cations into solution totally disrupts the initial equilibrium. We can make the assumption that the intial concentration of lead(II) is 0.020 M, and that the initial concentration of carbonate after the equilibrium was stressed is zero. To re-establish the equilibrium, an x amount of additional lead(II) cations must form for an x amount of carbonate ions:

 Ksp = [Pb2+][ CO32─] = 7.4 x 10-14 = (0.020 + x)(x)

Using a quadratic equation will not be necessary here. One can assume the “x” amount of additional lead(II) cations will be negligibly small. The approximation can be tested once the solution to the problem is calculated. This simplifies the above expression to:

 Ksp = [Pb2+][ CO32─] = 7.4 x 10-14 = (0.020)(x)

Solving for x:

$$x = \frac{7.4 x 10-14}{0.020} = 3.7 x 10^{-12} M$$

Notice that the solubility dropped from 2.7 x 10-7 in a pure solution of lead(II) carbonate to 3.7 x 10-12 in a solution to which additional carbonate ions was introduced. The solubility is approximately 105 times lower! Also notice that our assumption that the additional “x” amount of lead(II) ions was negligibly small was valid: 0.020 + 3.7 x 10-12 = 0.020M. Thus, these results show quantitatively LeChatelier’s Principle in action. The stress of excess carbonate shifted the equilibrium towards reactants as indicated by the lower solubility.

5. The equilibrium constant expression for lead(II) phosphate is shown below. There will be a 3x amount of lead(II) ions in solution from the lead(II) precipitate. The phosphate ion concentration will be 0.50 M from whatever source of phosphate was used to adjust the concentration plus an additional 2x amount from the dissociation of lead(II) phosphate precipitate.

Pb3(PO4)2 (s) ⮀ 3 Pb2+(aq) + 2 PO43-(aq)

The equilibrium constant expression is:

Ksp = [Pb2+]3 [PO43-]2 = 1 x 10-36

Substitute the algebraic amounts into the above expression:

Ksp = [Pb2+]3 [PO43-]2 = 1 x 10-36 = (3x)3(0.50 + 2x)2

Luckily, the equilibrium constant is very small (1 x 10-6). This allows us to neglect the additional 2x amount of phosphate from the dissociation of lead(II) phosphate. Otherwise, we would have to solve a polynomial equation using a serial approximation method. With our approximation, the equation simplifies to:

1 x 10-36 = (3x)3(0.50)2 = (27x3)(0.25) = 6.75x3

Solve for x:

$$x^{3} = \frac{1 x 10^{-36}}{6.75} = 1.5 x 10^{-37}$$

$$x = \sqrt[3]{1.5 x 10^{-37}} = 5.3 x 10^{-13}$$

3x = [Pb2+] = 3(5.3 x 10-13) = 1.6 x 10-12 M

To demonstrate how this quantitatively demonstrates LeChatelier’s Principle, we will compare this concentration of lead(II) ions in solution that the lead(II) ion concentration that would be present if the stress of additional phosphate were not added. To do this we will find the lead(II) ion concentration in a pure solution of saturated lead(II) phosphate. Using the same equilibrium constant expression, there will be a 3x amount of lead(II) ions in solution and a 2x amount of phosphate ions in solution at equilibrium. Substituting these algebraic amounts into the equilibrium constant expression gives:

Ksp = [Pb2+]3 [PO43-]2 = 1 x 10-36 = (3x)3(2x)2

Solve for x:

1 x 10-36 = (3x)3(2x)2 = 108x5

$$x^{5} = \frac{1 x 10^{-36}}{108} = 9.3 x 10^{-39}$$

$$x = \sqrt[5]{9.3 x 10^{-39}} = 2.5 x 10^{-8} M$$

3x = [Pb2+] = 3(2.5 x 10-8) = 7.5 x 10-8 M

A comparison of the results shows that the lead(II) concentration has been significantly reduced upon introducing additional phosphate into solution: 1.6 x 10-12 M Pb2+ in 0.50 M PO43- << 7.5 x 10-8 M Pb2+ in pure, saturated lead(II) phosphate solution. The stress placed on the equilibrium was the additional phosphate, hence the equilibrium shifted towards solid lead(II) phosphate to reduce the stress and the lead(II) ion concentration in solution has been decreased.

6. a. This problem has competing equilibria. To determine which compound will precipitate first, find the molar solubility of each compound.

The equilibrium for calcium carbonate is:

CaCO3(s) ⮀ Ca2+(aq) + CO32-(aq)

The equilibrium constant expression for the above equilibrium is:

Ksp = [Ca2+][CO32-] = 4.5 x 10-9

The initial concentration of calcium ion is 0.30 M. Once precipitation begins, every particle of calcium carbonate produces one calcium ion and one carbonate ion in solution, so we will use x as the unknown amount of additional calcium ions and an x amount of carbonate ions produced in solution. Substitute these algebraic amounts into the equilibrium constant expression:

Ksp = [Ca2+][CO32-] = 4.5 x 10-9 = (0.30 + x)(x)

Since the equilibrium constant of calcium carbonate is very small, we can neglect the additional x amount of calcium ions coming from the dissociation of calcium carbonate. This simplifies the problem of solving for x. The x amount represents the maximum amount of carbonate ion that will remain in solution. Any concentration exceeding this amount will cause calcium carbonate to precipitate.

$$x = [CO\_{3}^{2-}] = \frac{K\_{sp}}{[Ca^{2+}]} = \frac{4.5 x 10^{-9}}{0.30} = 1.5 x 10^{-8} M$$

Thus, any carbonate ion concentration greater than 1.5 x 10-8 M will cause calcium carbonate to precipitate under these conditions.

We will do the analogous calculation for the nickel(II) carbonate. The equilibrium for nickel(II) carbonate is:

NiCO3(s) ⮀ Ni2+(aq) + CO32-(aq)

The equilibrium constant expression for the above equilibrium is:

Ksp = [Ni2+][CO32-] = 1.3 x 10-7

The initial concentration of nickel(II) ion is 0.30 M. Once precipitation begins, every particle of nickel(II) carbonate produces one nickel(II) ion and one carbonate ion in solution, so we will use x as the unknown amount of additional nickel(II) ions and an x amount of carbonate ions produced in solution. Substitute these algebraic amounts into the equilibrium constant expression:

Ksp = [Ni2+][CO32-] = 1.3 x 10-7 = (0.30 + x)(x)

Since the equilibrium constant of nickel(II) carbonate is very small, we can neglect the additional x amount of nickel(II) ions coming from the dissociation of nickel(II) carbonate. This simplifies the problem of solving for x. The x amount represents the maximum amount of carbonate ion that will remain in solution. Any concentration exceeding this amount will cause nickel(II) carbonate to precipitate.

$$x = [CO\_{3}^{2-}] = \frac{K\_{sp}}{[Ni^{2+}]} = \frac{1.3 x 10^{-7}}{0.30} = 4.3 x 10^{-7} M$$

Thus, any carbonate ion concentration greater than 4.3 x 10-7 M will cause nickel(II) carbonate to precipitate under these conditions.

Based on these calculations, one can see that calcium carbonate is less soluble than nickel(II) carbonate, hence calcium carbonate will precipitate first. (1.5 x 10-8 M [CO32-] < 4.3 x 10-7 M [CO32-])

6. b. One must find the concentration of calcium at the carbonate ion concentration at which nickel(II) carbonate begins to precipitate. The solubility of nickel(II) carbonate is 4.3 x 10-8 M as found in the previous problem. This means that any carbonate ion concentration greater than 4.3 x 10-7 M will exceed the solubility limit of nickel(II) carbonate and precipitation will begin. Using this concentration of carbonate, we can calculate what concentration of calcium ion remains in solution:

Ksp = [Ca2+][CO32-] = 4.5 x 10-9

$$[Ca^{2+}] = \frac{K\_{sp}}{[CO\_{3}^{2-}]} = \frac{4.5 x 10^{-9}}{4.3 x 10^{-7}} = 1.0 x 10^{-2} M$$

Thus, at the point that nickel(II) carbonate begins to precipitate, 1.0 x 10-2 M Ca2+ ions remain in solution.

7. The equilibrium taking place is:

Co(OH)3(s) ⮀ Co2+(aq) + 3 OH¯(aq)

The Ksp expression for this equilibrium is:

Ksp = [Co2+][OH¯]3 = 3.0 x 10-45

In this equilibrium, the hydroxide ion concentration has been adjusted by controlling the pH by introducing hydroxide from a source other than cobalt(III) hydroxide . The initial concentration of hydroxide is calculated from the pH:

 pOH = 14 – pH = 14 – 9.00 = 5.00

 [OH¯] = 10 ─pOH = 10─5.00 = 1.0 x 10-5 M

At equilibrium, there will be an x amount of cobalt(II) ions present and 1.0 x 10-5 plus an additional 3x amount of hydroxide from the dissociation of cobalt(III) hydroxide. We can substitute these algebraic expressions into the Ksp expression:

Ksp = [Co2+][OH¯]3 = 3.0 x 10-45 = (x)(1.0 x 10-5 + 3x)3

Due to the low solubility of this compound, we can simplify the above algebraic expression by neglecting the 3x amount of additional hydroxide. This simplifies the above polynomial expression to:

Ksp = [Co2+][OH¯]3 = 3.0 x 10-45 = (x)(1.0 x 10-5)3

Solve for x which is equal to the [Co2+]:

$$x = [Co^{2+}] = \frac{K\_{sp}}{(1.0 x 10^{-5})^{3}} = \frac{3.0 x 10^{-45}}{1.0 x 10^{-15}} = 3.0 x 10^{-30}$$

8. . From the solubility rules, one can write a chemical reaction that result from the mixing of these two solutions:

Ca(NO3)2(aq) + Cd(IO3)2(aq) → Cd(IO3)2(s) + NaNO3(aq)

We need to find out whether or not the solubility limit for cadmium iodate has been exceeded from the mixing the two solutions. Calculating the initial concentration of cadmium ions and iodate ions is basically a dilution problem:

C1V1 = C2V2

For Cd2+ , C1 = 2.0 x 10-4 M, V1 = 400 mL and V2 = 600 mL + 400 mL = 1000 mL = total volume

$$\left[Cd^{2+}\right]= 400 mL x \frac{2.0 x 10^{-4} mol Cd(NO\_{3})\_{2}}{L} x \frac{1mol Cd^{2+}}{1 mol Cd(NO\_{3})\_{2}} x \frac{1}{1000 mL} = 8.0x 10^{-5} M$$

For IO3¯, C1 = 1.5 x 10-3 M, V1 = 600 mL and V2 = 600 mL + 400 mL = 1000 mL = total volume

$$\left[IO\_{3}^{─}\right]= 600 mL x \frac{1.5 x 10^{-3} mol KIO\_{3}}{L} x \frac{1mol IO\_{3}^{-}}{1 mol KIO\_{3}} x \frac{1}{1000 mL} = 9.0 x 10^{-4} M$$

Calculate the solubility quotient, Qsp, and compare this to the Ksp for calcium carbonate:

Qsp = [Cd2+][IO3-]2

Qsp = (8.0 x 10-5)(9.0 x 10-4)2 = 6.5 x 10-11

Compare the Qsp with the Ksp of cadmium iodate. The Ksp of cadmium iodate is 2.3 x 10-8.

6.5 x 10-11 < 2.3 x 10-8

Qsp < Ksp

Since the Qsp < Ksp, the solubility limit for calcium carbonate has not been exceeded, and thus a precipitate will not form.

9. From the solubility rules, one can write a chemical reaction that result from the mixing of these two solutions:

Ca(NO3)2(aq) + Na2CO3(aq) → CaCO3(s) + 2 NaNO3(aq)

We need to find out whether or not the solubility limit for calcium carbonate has been exceeded from the mixing the two solutions. Calculating the initial concentration of calcium ions and carbonate ions is basically a dilution problem:

C1V1 = C2V2

For Ca2+ , C1 = 5.0 x 10-3M, V1 = 400 mL and V2 = 300 mL + 400 mL = 700 mL = total volume

$$\left[Ca^{2+}\right]= 300 mL x \frac{5.0 x 10^{-3} mol Ca(NO\_{3})\_{2}}{L} x \frac{1mol Ca^{2+}}{1 mol Ca(NO\_{3})\_{2}} x \frac{1}{700 mL} = 2.1x 10^{-3} M$$

For CO32-, C1 = 3.5 x 10-4 M , V1 = 400 mL and V2 = 300 mL + 400 mL = 700 mL = total volume

$$\left[CO\_{3}^{2-}\right]= 400 mL x \frac{5.0 x 10^{-3} mol Ca(NO\_{3})\_{2}}{L} x \frac{1mol CO\_{3}^{2-}}{1 mol Ca(NO\_{3})\_{2}} x \frac{1}{700 mL} = 2.9 x 10^{-3} M$$

Calculate the solubility quotient, Qsp, and compare this to the Ksp for calcium carbonate:

Qsp = [Ca2+][CO32-]

Qsp = (2.1 x 10-3)(2.9 x 10-3) = 6.1 x 10-6

Compare the Qsp with the Ksp of calcium carbonate. The Ksp of calcium carbonate is 4.5 x 10-9.

6.1 x 10-6 > 4.5 x 10-9

Qsp > Ksp

Since the Qsp > Ksp, the solubility limit for calcium carbonate has been exceeded, and thus a precipitate will form.

10. The equilibrium involved is:

Ba3(PO4)2(s) ⮀ 3 Ba2+(aq) + 2 PO43-(aq)

 a. Addition of barium ions into the solution creates a stress on the products side of the equilibrium (too much barium ions), so the equilibrium will shift towards reactants to remove the excess barium ions. Thus, one observes additional precipitate form in the container.

 b. Addition of hydronium ions from an acid will consume phosphate ions by:

H3O+(aq) + PO43-(aq) ⮀ HPO42-(aq) + H2O(l)

The stress created by this formation of hydrogen phosphate ions is the removal of phosphate ions from the solubility equilibrium (not enough phosphate), so the equilibrium will shift towards products to replenish the phosphate ions removed. Thus, one observes the precipitate dissolve.

 c. Addition of hydroxide ions will deplete hydronium ions from solution:

H3O+(aq) + OH¯(aq) ⮀ 2 H2O(l)

This also removes hydronium ion from the previous equilibrium:

H3O+(aq) + PO43-(aq) ⮀ HPO42-(aq) + H2O(l)

The stress on this equilibrium is now too little hydronium, so the equilibrium will shift towards reactants to replenish the hydronium removed by hydroxide ion. As a result, the phosphate ion concentration in solution will increase. This increase of phosphate ion will now impact the solubility equilibrium by creating a stress of too much phosphate:

Ba3(PO4)2(s) ⮀ 3 Ba2+(aq) + 2 PO43-(aq)

The equilibrium will shift towards reactants to remove the excess phosphate, and one will observe the reappearance of the precipitate of barium phosphate.