

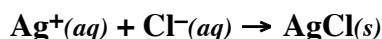
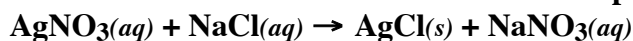
- 1a. Define the terms *precipitation* and *solubility*.

Precipitation is the act of precipitating or forming a precipitate. A precipitate is an insoluble solid formed by the reaction of two or more solutions of soluble compounds.

Solubility is a measure of the extent to which a compound will dissolve in a given solvent. In most cases, we are interested in the solubility of a compound in water.

- b. Write a chemical equation and a net ionic equation for a reaction which forms a precipitate.

Many different reactions can be used here. One example is



- c. Write the solubility equation for the precipitate formed above.



- 2a. Using the solubility table below predict whether the following compounds are soluble or insoluble in water.

Solubility Table

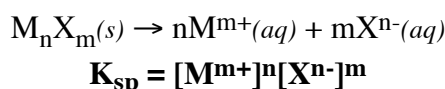
<u>Ion</u>	<u>Solubility</u>	<u>Exceptions</u>
NO ₃ ⁻	soluble	none
ClO ₄ ⁻	soluble	none
Cl ⁻	soluble	except Ag ⁺ , Hg ₂ ²⁺ , *Pb ²⁺
I ⁻	soluble	except Ag ⁺ , Hg ₂ ²⁺ , Pb ²⁺
SO ₄ ²⁻	soluble	except Ca ²⁺ , Ba ²⁺ , Sr ²⁺ , Hg ²⁺ , Pb ²⁺ , Ag ⁺
CO ₃ ²⁻	insoluble	except Group IA and NH ₄ ⁺
PO ₄ ³⁻	insoluble	except Group IA and NH ₄ ⁺
-OH	insoluble	except Group IA, *Ca ²⁺ , Ba ²⁺ , Sr ²⁺
S ²⁻	insoluble	except Group IA, IIA and NH ₄ ⁺
Na ⁺	soluble	none
NH ₄ ⁺	soluble	none
K ⁺	soluble	none

*slightly soluble

Soluble/Insoluble

- a) AgI **Insoluble**
 b) (NH₄)₂SO₄ **Soluble**
 c) Cu(OH)₂ **Insoluble**

3. Complete and balance the following reactions. Identify all products phases as either (g)as, (l)iquid, (s)olid or (aq)ueous. If no reaction occurs, write NR.
- $\text{Na}_2\text{SO}_4(\text{aq}) + \text{Ba}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaNO}_3(\text{aq})$
 - $\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$
 - $\text{Fe}(\text{NO}_3)_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NR}$ (both products are soluble)
 - $2\text{NH}_4\text{I}(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{NH}_4\text{NO}_3(\text{aq})$
4. Write the equilibrium expression for the reaction described by the general solubility equation below,



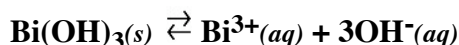
5. Define the term *solubility product constant*.

The solubility product constant is a measure of the extent to which a compound will dissolve in water. Very small values of K_{sp} suggest the compound is insoluble in water.

6. Complete the following problem:

a. Calculate the K_{sp} for $\text{Bi}(\text{OH})_3$ if 1.1×10^{-8} moles of $\text{Bi}(\text{OH})_3$ dissolve in 1.0 liter of water to form a saturated solution.

The equilibrium reaction is



and the equilibrium expression is

$$K_{\text{sp}} = [\text{Bi}^{3+}][\text{OH}^{-}]^3$$

Set up the equilibrium table:

		$\text{Bi}(\text{OH})_3(\text{s})$	\rightleftharpoons	$\text{Bi}^{3+}(\text{aq})$	+	$3\text{OH}^{-}(\text{aq})$	
initial	-	0		0		x=solubility of	
change	-	x		3x		$\text{Bi}(\text{OH})_3$	
equilibrium	-	0 + x		0 + 3x			

The problem indicates that the solubility of $\text{Bi}(\text{OH})_3$ is 1.1×10^{-8} M.

Therefore,

$$[\text{Bi}^{3+}] = x = 1.1 \times 10^{-8} \text{ M}$$

$$[\text{OH}^{-}] = 3x = 3(1.1 \times 10^{-8} \text{ M}) = 3.3 \times 10^{-8} \text{ M}$$

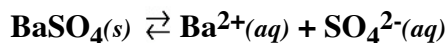
and

$$K_{\text{sp}} = [\text{Bi}^{3+}][\text{OH}^{-}]^3 = (1.1 \times 10^{-8})(3.3 \times 10^{-8})^3 = 4.0 \times 10^{-31}$$

7. Complete the following problem:

a. Calculate the solubility of BaSO_4 in H_2O . $K_{\text{sp}} = 1.1 \times 10^{-10}$.

Write the equilibrium equation



and the equilibrium expression

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

Setup the equilibrium table:

	$\text{BaSO}_4(s)$	\rightleftharpoons	$\text{Ba}^{2+}(aq)$	+	$\text{SO}_4^{2-}(aq)$
initial	-		0		0
change	-		x		x
equilibrium	-		0 + x		0 + x

Substituting in the K_{sp} expression

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

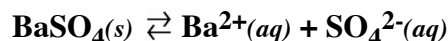
$$1.1 \times 10^{-10} = (x)(x)$$

$$1 \times 10^{-5} \text{ M} = x$$

The solubility of BaSO_4 is 1×10^{-5} moles/liter. Barium sulfate is not particularly soluble in water. Toxicity data indicates that Ba^{2+} is toxic at levels between 1 and 15 g (ingested). The solubility data shows that the amount of barium that might dissolve in 1 L of water is only 0.00137 g, a factor of over 700 less than the toxicity data indicate as hazardous. BaSO_4 is commonly used in medical procedures because of its insolubility and opacities to X-rays.

8. Complete the following problem:

a. Calculate the solubility of BaSO_4 in 0.100 M Na_2SO_4 .



and the equilibrium expression

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

Setup the equilibrium table:

Note the presence of 0.100 M Na_2SO_4 . A solution of Na_2SO_4 contains Na^+ ions and SO_4^{2-} ions. The SO_4^{2-} is a common ion as it appears in the solubility equilibrium for BaSO_4 . Now setup the equilibrium table and remember that the SO_4^{2-} ion is present initially:

	$\text{BaSO}_4(s)$	\rightleftharpoons	$\text{Ba}^{2+}(aq)$	+	$\text{SO}_4^{2-}(aq)$
initial	-		0		0.1
change	-		x		x
equilibrium	-		0 + x		0.1 + x

Substituting in the K_{sp} expression,

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1.1 \times 10^{-10} = (x)(0.1 + x)$$

We might become concerned here as it appears that the problems can only be solved using the quadratic equation. However, it is possible to consider the chemical implications of the mathematical relationship. 'x' is defined as the solubility of BaSO_4 in the solution. In pure water 'x' is 1×10^{-5} M, a very small number, certainly smaller than 0.100 M. So we would expect that 0.1 + x is approximately the same as 0.1. We are going to approximate the problem, to simplify the mathematics, by neglecting 'x' in 0.1 + x. We can not neglect the other 'x' as it is not compared to an initial concentration. Another piece of chemical intuition that we can invoke at this point is Le Chatelier's principle. The presence of the SO_4^{2-} in the solution will decrease the amount of BaSO_4 that will dissolve, making 'x' even smaller than 1×10^{-5} M.

$$1.1 \times 10^{-10} = (x)(0.1) \quad \text{assume } 0.1 + x = 0.1$$

$$1.1 \times 10^{-9} \text{ M} = x = \text{solubility of } \text{BaSO}_4$$

Now to be correct, we must check the calculated value of 'x' in our assumption to be sure that we are justified.

$$(0.1 + 1.1 \times 10^{-9}) = 0.100$$

We were justified in using the assumption to simplify the mathematics of the problem. We did not compromise the chemistry of the solubility equilibrium.

9. Complete the following problem;

a. A 50.0 mL sample of 0.0152 M Na_2SO_4 is added to 50.0 mL of 0.0125 M $\text{Ca}(\text{NO}_3)_2$.

i) Should precipitation of CaSO_4 occur?

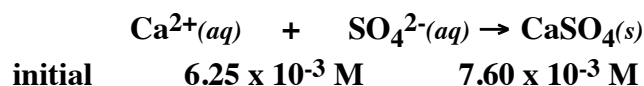
$$[\text{Ca}^{2+}] = 0.05 \text{ L} \left(\frac{0.0125 \text{ mol}}{\text{L}} \right) \left(\frac{1}{0.1 \text{ L}} \right) = 6.25 \times 10^{-3} \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.05 \text{ L} \left(\frac{0.0152 \text{ mol}}{\text{L}} \right) \left(\frac{1}{0.1 \text{ L}} \right) = 7.60 \times 10^{-3} \text{ M}$$

$$Q = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (6.25 \times 10^{-3})(7.60 \times 10^{-3}) = 4.75 \times 10^{-5}$$

$K_{\text{sp}} = 9.1 \times 10^{-6}$: therefore $Q > K_{\text{sp}}$ and precipitation will occur

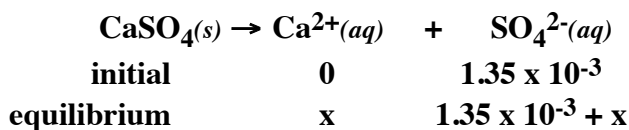
ii) What % of the Ca^{2+} will precipitate?



K_{ppt} is large for this reaction, so it will go to completion



So now the problem is a common ion problem. What is the concentration of Ca^{2+} in the solution?



$$K_{\text{sp}} = 9.1 \times 10^{-6} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$9.1 \times 10^{-6} = [x][1.35 \times 10^{-3} + x]$$

Must solve the quadratic equation because the initial concentration of SO_4^{2-} is large compared to K_{sp} . When the quadratic equation is solved,

$$x = 2.4 \times 10^{-3} \text{ M} = [\text{Ca}^{2+}]$$

$$\% \text{ Ca}^{2+} \text{ remaining} = (2.4 \times 10^{-3} / 6.25 \times 10^{-3}) * 100 = 38 \%$$

- 10a. Under what circumstances will the solubility of an ionic compound be dependent on the pH of the solution?

The solubility of a compound will be dependent on the pH, if the cation behaves as a weak acid or, and this is more likely, the anion acts as a weak base.

- b. Give two examples of ionic compounds that are more soluble in acidic solutions than basic solutions.

Many examples are possible:



- c. Give two examples of ionic compounds that are more soluble in basic solutions than acidic solutions.

Many examples are possible:

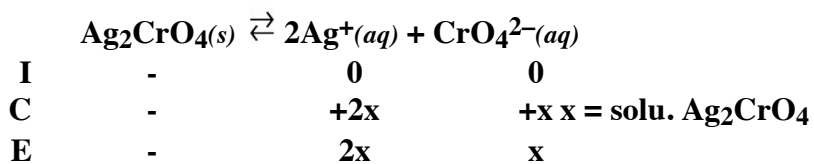


PS.1. Complete and balance the following reactions. Identify all products phases as either (g)as, (l)iquid, (s)olid or (aq)ueous. If no reaction occurs, write NR.

- $\text{Na}_2\text{CO}_3(\text{aq}) + \text{Ca}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + 2\text{NaNO}_3(\text{aq})$
- $\text{AgNO}_3(\text{aq}) + \text{KBr}(\text{aq}) \rightarrow \text{AgBr}(\text{s}) + \text{KNO}_3(\text{aq})$
- $3\text{NaOH}(\text{aq}) + \text{Al}(\text{NO}_3)_3(\text{aq}) \rightarrow 3\text{NaNO}_3(\text{aq}) + \text{Al}(\text{OH})_3(\text{s})$
- $(\text{NH}_4)_2\text{S}(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow 2\text{NH}_4\text{NO}_3(\text{aq}) + \text{PbS}(\text{s})$

PS.2. Calculate K_{sp} for the following salts using the information provided.

- The concentration of $\text{CrO}_4^{2-}(\text{aq})$ in a saturated solution of Ag_2CrO_4 is $6.50 \times 10^{-5} \text{ M}$.



$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2x)^2(x)$$

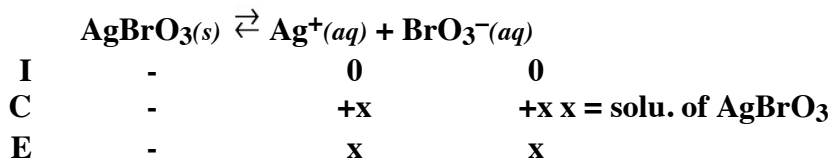
Since x is given as $6.50 \times 10^{-5} \text{ M}$, the solubility product constant can be calculated as;

$$K_{\text{sp}} = (2x)^2(x) = 4x^3 = 4(6.50 \times 10^{-5})^3 = 1.10 \times 10^{-12}$$

- b) The solubility of AgBrO_3 in water is 7.2×10^{-2} g/L.

The solubility of AgBrO_3 must be converted to $\frac{\text{mol}}{\text{L}}$, so

$$7.2 \times 10^{-2} \frac{\text{g}}{\text{L}} \left(\frac{1 \text{ mol AgBrO}_3}{236 \text{ g}} \right) = 3.05 \times 10^{-4} \text{ M}$$



$$K_{\text{sp}} = [\text{Ag}^+][\text{BrO}_3^-] = (x)(x)$$

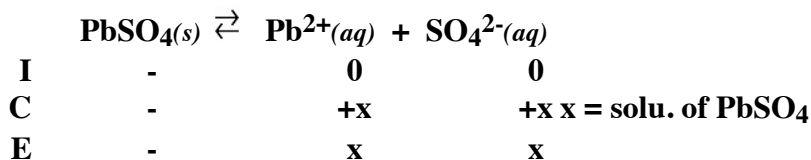
Since x is given as 3.05×10^{-4} M, the solubility product constant can be calculated as;

$$K_{\text{sp}} = (x)(x) = x^2 = (3.05 \times 10^{-4})^2 = 9.32 \times 10^{-8}$$

- c) A sample of a saturated solution of PbSO_4 contains .0262 g/L of Pb^{2+} .

The solubility of PbSO_4 must be converted to $\frac{\text{mol}}{\text{L}}$, so

$$0.0262 \frac{\text{g Pb}^{2+}}{1 \text{ L}} \left(\frac{1 \text{ mol Pb}^{2+}}{207 \text{ g}} \right) \left(\frac{1 \text{ mol PbSO}_4}{1 \text{ mol Pb}^{2+}} \right) = 1.26 \times 10^{-4} \text{ M}$$



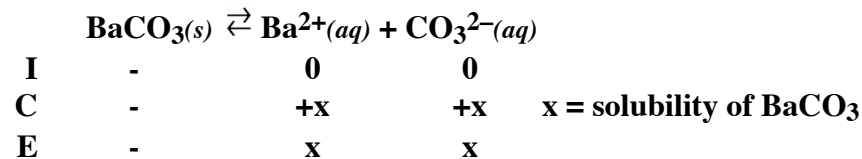
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (x)(x)$$

Since x is given as 1.26×10^{-4} M, the solubility product constant can be calculated as;

$$K_{\text{sp}} = (x)(x) = x^2 = (1.26 \times 10^{-4})^2 = 1.61 \times 10^{-8}$$

PS.3. Calculate the solubility of the following compounds in water. (Use a table of solubility product constants in your text or some other reference book.)

- a) BaCO_3



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

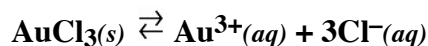
$$5.1 \times 10^{-9} = (x)(x)$$

$$5.1 \times 10^{-9} = x^2$$

$$7.1 \times 10^{-5} \text{ M} = x = \text{solubility of BaCO}_3$$

b) AuCl
Solubility of AuCl is 4.47×10^{-7} M by the same method as used in a).

c) AuCl₃



I	-	0	0	
C	-	+x	+3x	x = solubility of AuCl ₃
E	-	x	3x	

$$K_{sp} = [\text{Au}^{3+}][\text{Cl}^-]^3$$

$$3.2 \times 10^{-25} = (x)(3x)^3$$

$$3.2 \times 10^{-25} = 27x^4$$

$$1.2 \times 10^{-26} = x^4$$

$$3.3 \times 10^{-7} \text{ M} = x = \text{solubility of AuCl}_3$$

d) Cu₃(PO₄)₂



I	-	0	0	
C	-	+3x	+2x	x = solu. of Cu ₃ (PO ₄) ₂
E	-	3x	2x	

$$K_{sp} = [\text{Cu}^{2+}]^3[\text{PO}_4^{3-}]^2$$

$$1.3 \times 10^{-37} = (3x)^3(2x)^2$$

$$1.3 \times 10^{-37} = 108x^5$$

$$1.2 \times 10^{-39} = x^5$$

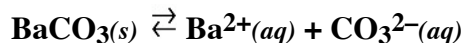
$$1.6 \times 10^{-8} \text{ M} = x = \text{solubility of Cu}_3(\text{PO}_4)_2$$

PS.4. Calculate the solubility of;

a) BaCO₃ in 0.500 M Ba(NO₃)₂

$$0.500 \text{ M Ba}(\text{NO}_3)_2 \left(\frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol Ba}(\text{NO}_3)_2} \right) = 0.500 \text{ M Ba}^{2+}$$

Notice Ba²⁺ is a common ion in this system.



I	-	0.5	0	
C	-	+x	+x	x = solubility of BaCO ₃
E	-	0.5 + x	x	

$$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$$

$$5.1 \times 10^{-9} = (0.5 + x)(x)$$

assume $x \ll 0.5$

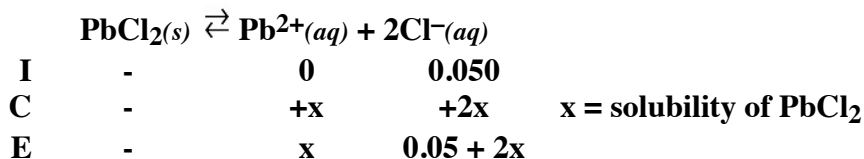
$$5.1 \times 10^{-9} = 0.5(x)$$

$$1.02 \times 10^{-8} \text{ M} = x = \text{solubility of BaCO}_3 \text{ in } 0.500 \text{ M Ba}(\text{NO}_3)_2.$$

Notice the solubility of BaCO₃ is considerably smaller when a common ion is present.

b) PbCl_2 in 0.0250 M CaCl_2

$$0.0250 \text{ M CaCl}_2 \left(\frac{2 \text{ mol Cl}^-}{1 \text{ mol CaCl}_2} \right) = 5.00 \times 10^{-2} \text{ M Cl}^-$$



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$1.6 \times 10^{-5} = (x)(0.05 + 2x)^2 \text{ assume } x \lll 0.05$$

$$1.6 \times 10^{-5} = (x)(0.05)^2$$

$$1.6 \times 10^{-5} = (x)(0.0025)$$

$$6.4 \times 10^{-3} \text{ M} = x = \text{solubility of } \text{PbCl}_2 \text{ in } 0.0250 \text{ M CaCl}_2.$$

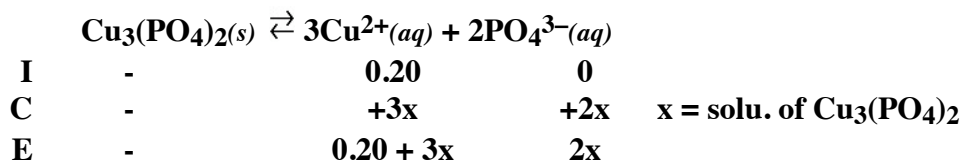
This is on the same order of magnitude as the initial concentration of chloride, so the assumption is not justified. If one guesses a value of x and substitute into the equation,

$$1.6 \times 10^{-5} = (x)(0.05 + 2x)^2$$

and iterates the guess, the value of x which is obtained is 4.5×10^{-3} M. So the solubility of PbCl_2 in 0.0250 M CaCl_2 is 4.5×10^{-3} M.

c) $\text{Cu}_3(\text{PO}_4)_2$ in 0.200 M $\text{Cu}(\text{NO}_3)_2$

$$0.200 \text{ M Cu}(\text{NO}_3)_2 \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu}(\text{NO}_3)_2} \right) = 0.200 \text{ M Cu}^{2+}$$



$$K_{\text{sp}} = [\text{Cu}^{2+}]^3[\text{PO}_4^{3-}]^2$$

$$1.3 \times 10^{-37} = (0.20 + 3x)^3(2x)^2 \text{ assume } x \lll 0.2$$

$$1.3 \times 10^{-37} = (0.20)^3(2x)^2$$

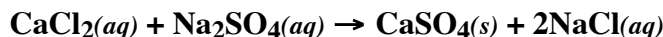
$$1.3 \times 10^{-37} = 8.0 \times 10^{-3}(4x^2)$$

$$4.06 \times 10^{-36} = x^2$$

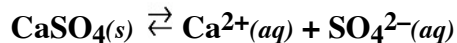
$$2.01 \times 10^{-18} \text{ M} = x = \text{solubility of } \text{Cu}_3(\text{PO}_4)_2$$

PS29.10. A 45 mL sample of 0.015 M calcium chloride is added to 55 mL of 0.010 M sodium sulfate. Is a precipitate expected? Explain. (Your answer must include a calculation!)

When CaCl_2 and Na_2SO_4 are mixed, the following reaction will occur,



The only insoluble product is CaSO_4 .



$$K_{\text{sp}} = 9.1 \times 10^{-6} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

If Q for the system is greater than $K_{\text{sp}}(\text{CaSO}_4)$ which is 9.1×10^{-6} , a precipitate will form. To determine Q for the reaction, the $[\text{Ca}^{2+}]$ and the $[\text{SO}_4^{2-}]$ in the solution must be calculated.

$$\text{mol Ca}^{2+} = 0.015 \frac{\text{mol CaCl}_2}{\text{L}} \cdot 0.045 \text{ L} \left(\frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol CaCl}_2} \right)$$

$$\text{mol Ca}^{2+} = 6.75 \times 10^{-4} \text{ mol Ca}^{2+} \text{ in 45 mL}$$

To determine the $[\text{Ca}^{2+}]$ in the mixture,

$$[\text{Ca}^{2+}] = \frac{6.75 \times 10^{-4} \text{ mol Ca}^{2+}}{0.100 \text{ L}} = 6.75 \times 10^{-3} \text{ M Ca}^{2+}$$

$$\text{mol SO}_4^{2-} = 0.010 \frac{\text{mol Na}_2\text{SO}_4}{\text{L}} \cdot 0.055 \text{ L} \left(\frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol Na}_2\text{SO}_4} \right)$$

$$\text{mol SO}_4^{2-} = 5.5 \times 10^{-4} \text{ mol SO}_4^{2-} \text{ in 55 mL}$$

To determine the $[\text{SO}_4^{2-}]$ in the mixture,

$$[\text{SO}_4^{2-}] = \frac{5.5 \times 10^{-4} \text{ mol SO}_4^{2-}}{0.100 \text{ L}} = 5.5 \times 10^{-3} \text{ M SO}_4^{2-}$$

$$Q = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = [6.75 \times 10^{-3}][5.5 \times 10^{-3}] = 3.7 \times 10^{-5}$$

$$3.7 \times 10^{-5} > 9.1 \times 10^{-6}$$

Q is greater than K_{sp} , so a precipitate of CaSO_4 will form.