1
Solubility equilibria

I NSOLUBLE compounds and the solubility of solid chemicals in water is critical in fields such as engineering, medicine, and dentistry. For example, the presence of acids in the saliva enables tooth decay as they enhance the solubility of tooth enamel made of $Ca_5(PO_4)_3OH$. On a similar note, barium sulfate $BaSO_4$, an insoluble compound, is opaque to x-rays and helps reveal digestive track issues. This chapter applies concepts of chemical equilibrium to the study of insoluble compounds. We will learn how to compute chemical solubilities using the equilibrium constant associated with the solubility equilibrium, and to assess the effect on the solubility of a common ion in solution.

GOALS

1. Compute solubility product constants
2. Compute solubility from solubility product constants
3. Predict the precipitation of a ion mixture
4. Assess the impact of a common ion on solubility
5. Relate solubility to PH for acid-base insoluble compounds

1.1 Solubility

The solubility of an insoluble solute is the concentration of a saturated solution. A solution is saturated when no more solute can dissolve on it. One can express solubility in two different ways, with respect to the solution and with respect to the solvent. If we refer solubility to the solution, we have two different solubility units: molar or mass-based solubility. Molar solubility is the molarity of a saturated solution, whereas mass-based solubility–or simply solubility–is the concentration in grams per liter of a saturated solution. Both types of solubilities–molar and mass-based–are related. If we refer to solubility with respect to the solvent, the solubility values are often expressed in g/100mL units, where mL refers to the volume of water.

Solubility Molar solubility or simply solubility s is defined as the moles of solute dissolved in 1L of a saturated solution. For example, the solubility of silver iodide (AgI) at 25°C is 9.0×10^{-9} mol/L. This means that 9.0×10^{-9} moles of silver iodide will dissolve in one liter of a saturated solution.

Mass-based solubility Mass-based solubility $\overline{s}$ is defined as the number of grams of solute dissolved in a liter of a saturated solution. For example, the solubility of silver iodide (AgI) at 25° is 2.1×10^{-6} g/L. This means that 2.1×10^{-6} grans of silver iodide will dissolve in one liter of a saturated solution.

Relating solubility and mass-based solubility We can convert solubility values in terms of mass into solubility values in terms of moles by means of the molar mass of the insoluble solute

$$\overline{s} = s \cdot MW \qquad (1.1)$$

where:

⚙ Discussion: You have two chemicals A and B. Given that the K_s of A is larger than the one for B, does this means that the solubility of A is larger than the one of a solution of B? Elaborate.

s is solubility in mol/L

$\bar{s}$ is solubility in g/L

MW the molar weight of the insoluble compound

Sample Problem 1

How many grams of AgCl will dissolve in 5mL of a AgCl saturated solution, given that $s=1.33 \times 10^{-5}$M?

SOLUTION

As we have the molar solubility, we will convert this value into g/mol:

$$1.33 \times 10^{-5}\frac{mol}{L} \times \frac{143g}{mol} = 1.90 \times 10^{-3}\frac{g}{L}$$

In order to calculate the number of grams of solute in 5mL, we can do:

$$1.90 \times 10^{-3}\frac{g}{L} \times 0.005L = 9.51 \times 10^{-5}g$$

◈ **STUDY CHECK**

How many mL of solution contains 1ng of solute in a saturated ScF$_3$ solution, given $s=2.41 \times 10^{-12}$M. The molar mass of is ScF$_3$ 101.9g/mol.

▶Answer: 4072mL

Solubility based on water volume Often we will find solubility expressed in terms of 100mL of water. For example, the solubility of Aluminium chloride is 45.8 g/100 mL at 20°. This unit is defined with respect to the volume of water and ultimately is useful to find out the amount of solute that will dissolve in a given volume of water. For AlCl$_3$, we have that 45.8 grams of solute will dissolve in 100 mL of solvent.

1.2 Solubility equilibrium

When insoluble compounds dissolve in water an equilibrium between the solid and the dissolved ions establishes. Based on the stoichiometry of the compound we will obtain a different number of moles of ions in solution.

Solubility equilibrium Insoluble compounds dissolve in small amounts in water. Solubility equilibrium is the equilibrium that describes the dissolution of an insoluble compound to produced an aqueous solution of ions. For example, for the case of silver chloride, we have:

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
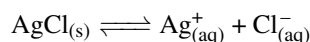
The solubility equilibrium above represents the dissolution of the insoluble salt–a solid–to produce ions, silver and chloride in solution. In general terms, solubility equilibriums start with a solid and generate ions in solution. In order to break down the insoluble compound into ions, we just need to take into account the stoichiometry of the compound. For example, for the case of Cobalt(II) phosphate, we have:
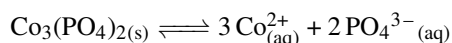
$$Co_3(PO_4)_{2(s)} \rightleftharpoons 3\,Co^{2+}_{(aq)} + 2\,PO_4{}^{3-}{}_{(aq)}$$

Table 1.1 Solubility product constants on water at 25°C

| Name	Formula	K_{sp}	Name	Formula	K_{sp}
Aluminium hydroxide	$Al(OH)_3$	3.00×10^{-34}	Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Aluminium phosphate	$AlPO_4$	9.84×10^{-21}	Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}	Manganese(II) hydroxide	$Mn(OH)_2$	2.00×10^{-13}
Barium carbonate	$BaCO_3$	2.58×10^{-9}	Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Barium chromate	$BaCrO_4$	1.17×10^{-10}	Manganese(II) sulfide (green)	MnS	3.00×10^{-14}
Barium fluoride	BaF_2	1.84×10^{-7}	Manganese(II) sulfide (pink)	MnS	3.00×10^{-11}
Barium hydroxide octahydrate	$Ba(OH)_2 \cdot 8\,H_2O$	2.55×10^{-4}	Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}	Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Barium iodate monohydrate	$Ba(IO_3)_2 \cdot H_2O$	1.67×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Barium molybdate	$BaMoO_4$	3.54×10^{-8}	Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}	Mercury(I) iodide	Hg_2I_2	5.20×10^{-29}
Barium selenate	$BaSeO_4$	3.40×10^{-8}	Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Barium sulfate	$BaSO_4$	1.08×10^{-10}	Mercury(I) sulfate	Hg_2SO_4	6.50×10^{-7}
Barium sulfite	$BaSO_3$	5.00×10^{-10}	Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.20×10^{-20}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}	Mercury(II) bromide	$HgBr_2$	6.20×10^{-20}
Cadmium arsenate	$Cd_3(AsO_4)_2$	2.20×10^{-33}	Mercury(II) hydroxide	HgO	3.60×10^{-26}
Cadmium carbonate	$CdCO_3$	1.00×10^{-12}	Mercury(II) iodide	HgI_2	2.90×10^{-29}
Cadmium fluoride	CdF_2	6.44×10^{-3}	Mercury(II) sulfide (black)	HgS	2.00×10^{-53}
Cadmium hydroxide	$Cd(OH)_2$	7.20×10^{-15}	Mercury(II) sulfide (red)	HgS	2.00×10^{-54}
Cadmium iodate	$Cd(IO_3)_2$	2.50×10^{-8}	Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}	Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Cadmium sulfide	CdS	1.00×10^{-27}	Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Calcium carbonate (calcite)	$CaCO_3$	3.36×10^{-9}	Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Calcium fluoride	CaF_2	3.45×10^{-11}	Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}	Nickel(II) sulfide (alpha)	NiS	4.00×10^{-20}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}	Nickel(II) sulfide (beta)	NiS	1.30×10^{-25}
Calcium molybdate	$CaMoO$	1.46×10^{-8}	Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}	Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}	Potassium periodate	KIO_4	3.71×10^{-4}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}	Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}
Cobalt(II) carbonate	$CoCO_3$	1.00×10^{-10}	Radium iodate	$Ra(IO_3)_2$	1.16×10^{-9}
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}	Radium sulfate	$RaSO_4$	3.66×10^{-11}
Copper(I) bromide	$CuBr$	6.27×10^{-9}	Rubidium perchlorate	$RuClO_4$	3.00×10^{-3}
Copper(I) chloride	$CuCl$	1.72×10^{-7}	Scandium fluoride	ScF_3	5.81×10^{-24}
Copper(I) cyanide	$CuCN$	3.47×10^{-20}	Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Copper(I) hydroxide	Cu_2O	2.00×10^{-15}	Silver(I) acetate	$AgCH_3COO$	1.94×10^{-3}
Copper(I) iodide	CuI	1.27×10^{-12}	Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Copper(I) thiocyanate	$CuSCN$	1.77×10^{-13}	Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}	Silver(I) bromide	$AgBr$	5.35×10^{-13}
Copper(II) hydroxide	$Cu(OH)_2$	4.80×10^{-20}	Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Copper(II) iodate monohydrate	$Cu(IO_3)_2 \cdot H_2O$	6.94×10^{-8}	Silver(I) chloride	$AgCl$	1.77×10^{-10}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}	Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}	Silver(I) cyanide	$AgCN$	5.97×10^{-17}
Copper(II) sulfide	CuS	8.00×10^{-37}	Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}	Silver(I) iodide	AgI	8.52×10^{-17}
Iron(II) fluoride	FeF_2	2.36×10^{-6}	Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}
Iron(II) sulfide	FeS	8.00×10^{-19}	Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}	Silver(I) sulfide	Ag_2S	8×10^{-51}
Iron(III) phosphate dihydrate	$FePO_4 \cdot 2\,H_2O$	9.91×10^{-16}	Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}

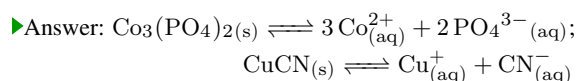Write down the solubility equilibrium for: Lead(II) iodate, and $FeCO_3$.

SOLUTION

The first insoluble compound, Lead(II) iodate, with formula $Pb(IO_3)_2$, contains cation lead(II) Pb^{2+} and anion IO_3^{2-} (iodate). The solubility equilibrium will be given by:

$$Pb(IO_3)_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,IO_3^{-}{}_{(aq)}$$
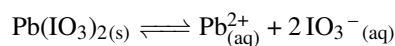
The solubility equilibrium for the second insoluble compound iron(II) carbonate will be:

$$FeCO_{3(s)} \rightleftharpoons Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$
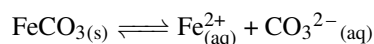
💎 **STUDY CHECK**

Write down the solubility equilibrium for: Copper(II) phosphate, and CuCN.

▶Answer: $Co_3(PO_4)_{2(s)} \rightleftharpoons 3\,Co^{2+}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)}$;
$CuCN_{(s)} \rightleftharpoons Cu^{+}_{(aq)} + CN^{-}_{(aq)}$

1.3 Solubility product

When an insoluble solid solves in liquid a solubility equilibrium establishes between the solid and the dissolved solid with an equilibrium constant associated. This equilibrium constant informs about the amount of solid that dissolves, which in general is small. Unless otherwise stated, all solutions in this chapter are water-based solutions at 25°C–remember equilibrium constants are temperature and solvent-dependent.

Solubility product in terms of molarities, K_{sp} Silver chloride, AgCl is an insoluble compound in water which means this compound will not fully dissolve in water. Still, small quantities of the salt will indeed dissolve leading to a small amount of silver and chlorine ions. As this compound is insoluble the ion concentration will be very small. The dissociation equilibrium involved in the dissolution, indicate below, is characterized by an equilibrium constant K_{sp} called *solubility product constant* or simply *solubility product*:

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \qquad\qquad K_{sp} = \left[Ag^{+}\right] \cdot \left[Cl^{-}\right]$$
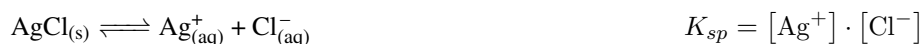
As pure solids are not included in any equilibrium constant, the formula above does not include $AgCl_{(s)}$. Hence, all solubility products simply result from the product of the molarities of the ions involved in the dissociation with the corresponding powers based on the stoichiometry of the salt. This is why the term *product* is included on its name. K_{sp} will have a different explicit expression depending on the formula of the insoluble compound–deppending on its stoichiometry. For example, K_{sp} for calcium fluoride–a 1:2 compund–would be:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\,F^{-}_{(aq)} \qquad\qquad K_{sp} = \left[Ca^{2+}\right] \cdot \left[F^{-}\right]^2$$

Solubility products are related to the solubility of chemicals. However, the relation is not one-on-one. In other words, a larger K_{sp} does not necessarely imply a larger
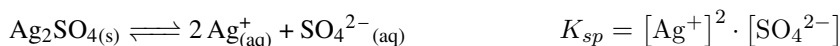
solubility. For example, K_{sp} for PbBr$_2$ is 6.6×10^{-3}M whereas K_{sp} for MgCO$_3$ is 4.0×10^{-5}M. We have that K_{sp} for PbBr$_2$ is smaller than K_{sp} for MgCO$_3$. However, the solubility of PbBr$_2$ is indeed larger than the solubility of MgCO$_3$. Table 1.1 reports numerous solubility product constant values.
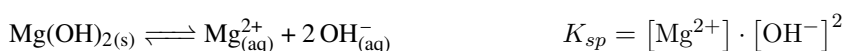

Sample Problem 3

Write down the expression of K_{sp} in terms of the ion concentration for the following compounds: Ag$_2$SO$_4$, Mg(OH)$_2$, and MgCO$_3$.

SOLUTION

The solubility equilibrium for first compound, silver sulfate, is

$$\text{Ag}_2\text{SO}_{4(s)} \rightleftharpoons 2\,\text{Ag}^+_{(aq)} + \text{SO}_4{}^{2-}{}_{(aq)} \qquad K_{sp} = \left[\text{Ag}^+\right]^2 \cdot \left[\text{SO}_4{}^{2-}\right]$$

The solubility product depends on the square concentration of silver ions. For magnesium hydroxide:

$$\text{Mg(OH)}_{2(s)} \rightleftharpoons \text{Mg}^{2+}_{(aq)} + 2\,\text{OH}^-_{(aq)} \qquad K_{sp} = \left[\text{Mg}^{2+}\right] \cdot \left[\text{OH}^-\right]^2$$

Finally, for magnesium carbonate:

$$\text{MgCO}_{3(s)} \rightleftharpoons \text{Mg}^{2+}_{(aq)} + \text{CO}_3{}^{2-}{}_{(aq)} \qquad K_{sp} = \left[\text{Mg}^{2+}\right] \cdot \left[\text{CO}_3{}^{2-}\right]$$

◈ **STUDY CHECK**

Write down the expression of K_{sp} in terms of the ion concentration for the following compounds: PbCl$_2$, and manganese(II) sulfide.

▶Answer: $\left[\text{Pb}^{2+}\right] \cdot \left[\text{Cl}^-\right]^2; \left[\text{Mn}^{2+}\right] \cdot \left[\text{S}^{2-}\right]$

Relating solubility to the concentration of ions We have that insoluble compounds dissolve to produce small amounts of ions in solutions. The concentration of these ions is directly related to solubility s by means of the stoichiometry of the compound. For example, for silver chloride–a salt with a 1:1 stoichiometry–we have that solubility is has a 1 and 1 relationship with the concentration of ions:

$$\left[\text{Ag}^+\right] = s \text{ and } \left[\text{Cl}^-\right] = s$$

Similarly, for barium sulfate we have that solubility has a 1:1 relationship with the concentration of ions:

$$\left[\text{Ba}^{+2}\right] = s \text{ and } \left[\text{SO}_4{}^{-2}\right] = s$$

When the stoichiometry of the compound is not 1:1 we need to include the stoichiometry coefficients in the relationship between solubility and ion concentration. For example, for Ag$_2$SO$_4$–a compound with 2:1 stoichiometry, we have that

$$\left[\text{Ag}^+\right] = 2 \cdot s \text{ and } \left[\text{SO}_4{}^{-2}\right] = s$$

This is because for every mole of silver sulfate we produce two moles of silver–and hence the factor two–and one mole of sulfate in solution. Similarly, for Nd$_2$(CO$_3$)$_3$ we have

$$\left[\text{Nd}^{+3}\right] = 2 \cdot s \text{ and } \left[\text{CO}_3{}^{-2}\right] = 3 \cdot s$$

1.4 Predicting precipitation

At this point, we have used the solubility product to calculate the concentration of ions in a saturated solution of a solid. Imagine we have a solution containing a mixture of two different ions given that the ions in the solution can combine to form a precipitate. The question is, will a solid precipitate? Similar to the solubility product, we can use a construct called the concentration product to predict whether a mixture of ions will precipitate.

Predicting precipitation: an introduction The values of the solubility product constant can be used to predict the precipitation of a salt when mixing two reagents. Imagine for example that we have a 0.1M Cu^+ solution and you gradually add a solution containing I^-. Given that CuI is an insoluble compound with a K_{sp} of 1.27×10^{-12}, the goal would be to compute the I^- concentration that would make CuI precipitate. We will answer this question by obtaining first the expression for K_{sp}:

$$CuI_{(s)} \rightleftharpoons Cu^+_{(aq)} + I^-_{(aq)} \qquad\qquad K_{sp} = \left[Cu^+\right] \cdot \left[I^-\right] = 1.27 \times 10^{-12}$$
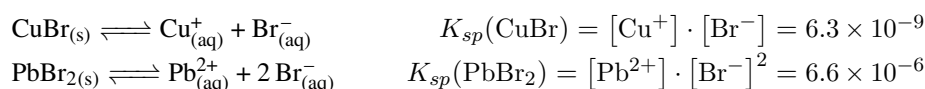
As we know the concentration of Cu^+, and we have that the concentration of both ions is related by means of the solubility products constant, hence we can solve for the critical $\left[I^-\right]_c$ that would make CuI precipitate:

$$K_{sp} = \left[Cu^+\right] \cdot \left[I^-\right]_c = (0.1) \cdot \left[I^-\right]_c = 1.27 \times 10^{-12}$$

We have that $\left[I^-\right]_c = 1.27 \times 10^{-11}$M. Hence, Copper(I) iodide will precipitate when its concentration is larger than 1.27×10^{-11}M.

Selective precipitation When we have a mixture of different ions that form insoluble precipitates (e.g. Pb^{2+} and Cu^+ both form insoluble bromides) we can use the principles of selective precipitation to separate the ions. We know that $PbBr_2$ and CuBr are insoluble compounds. Let us say we have a mixture of both ions with 0.01M concentration, and we add a solution containing Br^-. As two different precipitates will form (CuBr and $PbBr_2$) the question is: are we going to be able to separate both compounds? Or the precipitation of both will overlap? If the concentration needed to precipitate both insoluble compounds is ten times different we will be able to selectively precipitate both compounds. Here we assume that the addition of the cation will not modify the volume of the mixture. We will calculate the amount solution added needed to precipitate each of the solids. Let us first address the expressions for the solubility product for each solid:

$$CuBr_{(s)} \rightleftharpoons Cu^+_{(aq)} + Br^-_{(aq)} \qquad K_{sp}(CuBr) = \left[Cu^+\right] \cdot \left[Br^-\right] = 6.3 \times 10^{-9}$$
$$PbBr_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,Br^-_{(aq)} \qquad K_{sp}(PbBr_2) = \left[Pb^{2+}\right] \cdot \left[Br^-\right]^2 = 6.6 \times 10^{-6}$$

We will calculate the critical concentration of bromide $\left[Br^-\right]_c$ needed to precipitate each of the solids, first Copper(I) bromide:

$$K_{sp}(CuBr) = \left[Cu^+\right] \cdot \left[Br^-\right] = (0.01) \cdot \left[Br^-\right]_{c,CuBr} = 6.3 \times 10^{-9}$$

Solving for $\left[Br^-\right]_{c,CuBr}$ we have: $\left[Br^-\right]_{c,CuBr} = 6.3 \times 10^{-9}/0.01 = 6.3 \times 10^{-7}$M for the precipitation of CuBr. Now, we calculate the concentration of bromide needed to precipitate Lead(II) bromide: $\left[Br^-\right]^2_{c,PbBr_2} = \frac{6.6 \times 10^{-6}}{0.01}$ hence $\left[Br^-\right]_{c,PbBr_2} = \left(\frac{6.6 \times 10^{-6}}{0.01}\right)^{\frac{1}{2}} = 2.5 \times 10^{-2}$M for $PbBr_2$. Comparing both concentrations we have that the values are separate enough so it would be feasible to separate both ions in solution. We will have to add 6.3×10^{-3}mL of the solution to precipitate Copper(I) bromide and 2.5×10^2mL to precipitate Lead(II) bromide.

1.5 Solubility and K_{sp}

The solubility product is the equilibrium constant associated to the solubility equilibrium. At the same time, the solubility product constant is related to the solubility of the insoluble compound and the relationship is not direct. This section will cover how to express K_{sp} in terms of solubility, and at the same time, how to express solubility in terms of K_{sp}. Before that, we will start by addressing the idea of solubility.
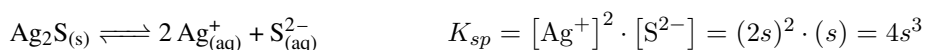
K_{sp} `in terms of molar solubility` The solubility product is directly related to molar solubility s. We will demonstrate how to obtain this relationship by means of three examples. First, the solubility product of AgCl is:

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad\qquad K_{sp} = \left[Ag^+\right] \cdot \left[Cl^-\right]$$

As the concentration of each ion, Ag^+ and Cl^-, is related to the molar solubility of the salt, we have

$$K_{sp} = \left[Ag^+\right] \cdot \left[Cl^-\right] = (s) \cdot (s) = s^2$$

Second, for silver sulfide, an insoluble compound with a more complex stoichiometry, we have:

$$Ag_2S_{(s)} \rightleftharpoons 2\,Ag^+_{(aq)} + S^{2-}_{(aq)} \qquad K_{sp} = \left[Ag^+\right]^2 \cdot \left[S^{2-}\right] = (2s)^2 \cdot (s) = 4s^3$$

Third, the solubility equilibrium and K_{sp} expression for $Nd_2(CO_3)_3$ is

$$Nd_2(CO_3)_{3(s)} \rightleftharpoons 2\,Nd^{3+}_{(aq)} + 3\,CO_3{}^{2-}{}_{(aq)} \qquad\qquad K_{sp} = \left[Nd^{3+}\right]^2 \cdot \left[CO_3{}^{2-}\right]^3$$
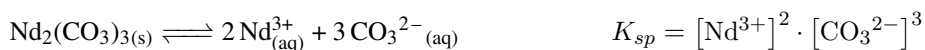
As the ion concentrations are related to solubility, we have

$$K_{sp} = (2s)^2 \cdot (3s)^3 = 108s^5$$

K_{sp} `in terms of molar solubility: general formula` For any insoluble salt A_xB_y, we have that K_{sp} is related to s by means of a general formula:

$$\boxed{K_{sp} = a \cdot s^b} \qquad\qquad (1.2)$$

where:

a is $x^x \cdot y^y$

b is $x + y$

For example, for Ba_1F_2 the constant a would be $1^1 \cdot 2^2$, that is four, whereas the constant b will be $1 + 2$ that equals to three. As such, the expression of K_{sp} in terms of s would be: $K_{sp} = 4s^3$. This approach is useful when the we need to compute the solubility product constant given the molar solubility.

Sample Problem 4

Write down the relationship between K_{sp} and s for the following salts: $Co_3(PO_4)_2$ and HgS.

SOLUTION

We will use Equation 1.2. For the first salt, we have:

$$K_{sp}(\text{Co}_3(\text{PO}_4)_2) = (3^3 \cdot 2^2) \cdot s^{3+2} = 108 \cdot s^5$$

For the second salt:

$$K_{sp}(\text{HgS}) = (1^1 \cdot 1^1) \cdot s^{1+1} = s^2$$

💎 **STUDY CHECK**

Write down the relationship between K_{sp} and s for the following salts: ceAg2CO3 and Fe(OH)$_3$.

▶Answer: $4s^3$; $27s^4$

Molar solubility in terms of K_{sp}: general formula We previously explored the relationship between K_{sp} and molar solubility. Here we will explore the relationship between molar solubility and K_{sp}, simply solving for s in Equation 1.2. Again, for any insoluble salt A$_x$B$_y$, we have:

$$s = \left(\frac{K_{sp}}{a}\right)^{\frac{1}{b}}$$

(1.3)

where:

a is $x^x \cdot y^y$

b is $x + y$

For example, for Ba$_1$F$_2$ the constant a would be $1^1 \cdot 2^2$, that is four, whereas the constant b will be $1 + 2$ that equals to three. As such, the expression of s in terms of K_{sp} would be: $s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$. This approach is useful when the solubility product constant is given and we need to calculate the molar solubility. As the relation between molar solubility and K_{sp} is not a one-to-one relationship, K_{sp} are not directly related to solubility. For salts with a similar stoichiometry, it would be safe to compare solubilities in terms of K_{sp}. For example:

CuS	K_{sp}=8×10^{-37}	$s = 6 \times 10^{-19}$
PbS	K_{sp}=3×10^{-28}	$s = 1 \times 10^{-14}$
LiF	K_{sp}=2×10^{-3}	$s = 3 \times 10^{-2}$

and we have that the lower K_{sp} the lower solubility. When the salt stoichiometry differs

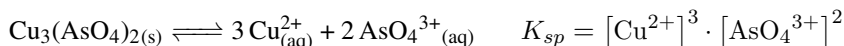|		
MgF$_2$	K_{sp}=5×10^{-11}	$s = 2 \times 10^{-4}$
Li$_3$PO$_4$	K_{sp}=2×10^{-4}	$s = 7 \times 10^{-2}$
Li$_2$CO$_3$	K_{sp}=8×10^{-4}	$s = 6 \times 10^{-2}$

then an increase in K_{sp} do not necessarily follows an increase in solubility.

Sample Problem 5

The solubility product of Copper(II) arsenate Cu$_3$(AsO$_4$)$_2$ is 7.95×10^{-36}. Calculate the molar solubility of the salt.

SOLUTION

In order to calculate the salt solubility, we will first break it down into ions. Copper(II) arsenate contains Cu^{2+} ions and arsenate ions $AsO_4{}^{3+}$. The solubility dissociation is given by:

$$Cu_3(AsO_4)_{2(s)} \rightleftharpoons 3\,Cu^{2+}_{(aq)} + 2\,AsO_4{}^{3+}{}_{(aq)} \qquad K_{sp} = \left[Cu^{2+}\right]^3 \cdot \left[AsO_4{}^{3+}\right]^2$$

The molar concentration of copper and arsenate are related to solubility, taking into account the stoichiometric coefficients:

$$K_{sp} = \left[Cu^{2+}\right]^3 \cdot \left[AsO_4{}^{3+}\right]^2 = (3s)^3 \cdot (2s)^2 = 108s^5$$

As we know the value of the solubility product, we can solve for s:

$$7.95 \times 10^{-36} = 108s^5$$

Solving for s we have:

$$s^5 = \frac{7.95 \times 10^{-36}}{108} \text{ and } s = \sqrt[5]{\frac{7.95 \times 10^{-36}}{108}} = \left(\frac{7.95 \times 10^{36}}{108}\right)^{\frac{1}{5}} = 3.7 \times 10^{-8}M$$

◈ **STUDY CHECK**

The solubility product of Nickel(II) phosphate $Ni_3(PO_4)_2$ is 4.74×10^{-32}. Calculate the molar solubility of the salt.

▶Answer: 2.13×10^{-7}M

1.6 Solubility , PH and common ion effect

The solubility value of an insoluble compound refers to the amount of ions produced by an insoluble compound when dissolved in clean water. Instead of clean water, we can think of a solution containing ions. If the ions have no relation with the solubility equilibrium, the value of solubility in pure water and a solution with ions will be the same. Differently, if the solution contains ions involved in the equilibrium the value of solubility will be affected by the presence of these ions. In particular, solubility will be reduced. This effect is referred to as the common ion effect. For example, the solubility of $PbCl_2$ in pure water is 1.6×10^{-2}M. In contrast, the solubility in a 0.1M NaCl solution–a solution containing chloride a common ion–is 1.5×10^{-3}M. Similarly, the solubility in a 0.5M NaCl solution is 6.4×10^{-5}M. Some insoluble compounds have acid-base properties. For example, $Mg(OH)_2$ is an insoluble compound with basic character. This means that its solubility will be related to the OH of the solution. In acidic solutions, its solubility will increase, whereas in basic solutions its solubility will be reduced. For these types of chemicals, it is important to establish a relationship between PH and solubility.

Solubility and PH Some insoluble salts have acid-base character. For example, $Ba(OH)_2$ is an insoluble salt with basic character–mind OH^- is a base–and FeF_2 is also a basic salt, as F^- is a moderately strong base resulting from the dissociation of HF, a weak acid. Therefore, for these salts, solubility is related to the PH. Only salts that result from weak acids or bases would have an acid-base character. For example, $CaCO_3$ or CuCN are all basic insoluble salts as carbonic acid and hydrocyanic acid are both weak acids. Let us calculate the PH of a $Ba(OH)_2$ solution. We have that the solubility equilibrium is given by

$$Ba(OH)_{2(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2\,OH^{-}_{(aq)}$$
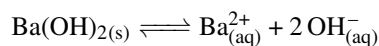
and K_{sp} is reates to solubility s by means the following formula

$$K_{sp} = 4s^3$$

As the solubility product of $Ba(OH)_2$ is 2.5×10^{-4} we have that the solubility of the hydroxide is 0.04M. We have that the concentration of the ions in solution is related to solubility by

$$\left[Ba^{2+}\right] = s \hspace{6cm} \left[OH^{-}\right] = 2s$$

Hence we have that the PH is directly related to solubility

$$POH = -log(\left[OH^{-}\right]) = -log(2s) = 1.09$$

and PH will be 12.9. At the same time, solubility of insoluble compounds with acid-base properties will be affected by the PH of the solution. In the example above, as $Ba(OH)_2$ is a basic compound, increasing PH towards even more basic values would impede the salt dissociation and hence decrease its solubility. Differently, decreasing PH would increase solubility as the amount of hydroxils in solution would hence decrease and hence, more would need to be formed.

Common ion effect Insoluble compounds dissociate to produce ions in solution. For example, a saturated AgCl solution will contain 1.3×10^{-5}M-Ag^{+} and Cl^{-}. By adding a chemical with a common ion (e.g. NaCl) into the solution we can decrease solubility as common ions will decrease the salt dissociation. Let us work on a problem: we want to calculate the solubility of AgCl in a 0.1M-NaCl solution given that $K_{sp}(AgCl) = 1.8 \times 10^{-10}$. In order to do this, we will first display the solubility equilibriu of the salt

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \hspace{3cm} K_{sp} = \left[Ag^{+}\right] \cdot \left[Cl^{-}\right] = 1.8 \times 10^{-10}$$
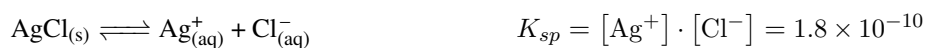
The concentration of the different ions in solution are related to the salt solubility. However, as we now have a common ion (Cl^{-}), we should add this new concentration to the original solubility of the salt

$$\left[Ag^{+}\right] = s \hspace{6cm} \left[Cl^{-}\right] = 0.1 + s$$

Solving for s we have:

$$K_{sp} = \left[Ag^{+}\right] \cdot \left[Cl^{-}\right] = (s) \cdot (0.1 + s) = 1.8 \times 10^{-10}$$

that leads to a polynomial

$$s^2 + 0.1s - 1.8 \times 10^{-10} = 0$$

1.7 Predicting precipitation from mixtures and solutions

At this point, we have used the solubility product to calculate the concentration of ions in a saturated solution of a solid. Imagine we have a solution containing a mixture of two different ions given that the ions in the solution can combine to form a precipitate. The question is, will a solid precipitate? Similar to the solubility product, we can use a construct called the concentration product to predict whether a mixture of ions will precipitate.

*Predicting precipitation in ion mixtures: concentration product*

Let us analyze a situation in which we dissolve in water an insoluble compound such as lead(II) fluoride. The solubility products constant K_{sp} is just an equilibrium constant that described the process of solubility, that is the dissolution of a solid. K_{sp} depends on the equilibrium concentration of the ions in solution. With equilibrium, we mean that the concentrations were measured after a long long time, so that the system has reached equilibrium. For example, K_{sp} for lead(II) fluoride is 3.3×10^{-8} and its mathematical expression is presented below

$$PbF_2(s) \rightleftharpoons Pb^{2+}_{(aq)} + 2\,F^-_{(aq)} \qquad\qquad K_{sp} = \left[Pb^{2+}\right] \cdot \left[F^-\right]^2 = 3.3 \times 10^{-8}$$

In the expression above, $\left[Pb^{2+}\right]$ represents the equilibrium concentration of ions Lead(II) and $\left[F^-\right]$ is the equilibrium concentration of fluoride. These concentrations result from dissolving the insoluble chemical in water. Let us now analyze a situation in which we have a mixture of ions containing 0.1M-Pb^{2+} ions and 0.1M-F^-. We want to assess if a precipitate will form, given that both ions can combine to produce lead(II) fluoride. To predict precipitation, we will use the reaction concentration product Q_c, and we will compare this product with the solubility product constant K_{sp}:

$$\boxed{Q_c = \left[Products\right]_{noneq}} \quad \text{concentration product} \qquad (1.4)$$

A precipitate will appear only the computed Q_c value is larger than K_{sp}. In other words, mixtures of solutions more concentrated that the compound's solubility will precipitate, whereas less concentrated mixtures will not.
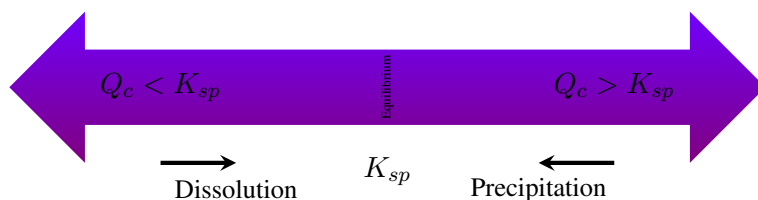
You might have noticed that K_{sp} and Q_c have a very similar formula. The difference beholds on the nature of the concentrations included in each of the formulas. K_{sp} includes *equilibrium* concentration, that is concentrations resulting of the slow dissolution of an insoluble compound measured after a long time, whereas Q_c includes *nonequilibrium* concentrations resulting of artificially preparing and quickly mixing ion solutions. For the example we are considering, after mixing a 0.1M-Pb^{2+} solution and a 0.1M-F^- solution, we have that Q_c is larger than K_{sp} and therefore a precipitate will form:

$$Q_c = \left[Pb^{2+}\right]_{noneq} \cdot \left[F^-\right]^2_{noneq} = 0.1 \cdot 0.1^2 = 1 \times 10^{-3} > K_{sp} = 3.3 \times 10^{-8}$$
$$\text{hence } (\downarrow)$$

Imaging that we mix now a 10^{-3}M-Pb^{2+} solution and a 10^{-3}M-F^- solution. For this case, we have that Q_c is smaller than K_{sp} and therefore no precipitate will form:

$$Q_c = \left[Pb^{2+}\right]_{noneq} \cdot \left[F^-\right]^2_{noneq} = 10^{-3} \cdot (10^{-3})^2 = 10^{-9} < K_{sp} = 3.3 \times 10^{-8}$$
$$\text{hence } (\cancel{\downarrow})$$

> **Sample Problem 6**
>
> Predict if a precipitate will form in any of the following mixtures: (a) $\left[Cu^+\right]=10^{-6}M$ and $\left[I^-\right]=10^{-7}M$ given that $K_{sp}(CuI) = 1.27 \times 10^{-12}M$ (b) $\left[Cd^{2+}\right]=0.5M$ and $\left[F^-\right]=0.5M$ given that $K_{sp}\left(CdF_2\right) = 6.44 \times 10^{-3}M$
>
> **SOLUTION**
>
> We will calculate Q_c for each of the mixtures and we will compare the value with K_{sp}. Q_c values larger than K_{sp} will produce a precipitate, whereas Q_c values smaller than K_{sp} will not produce a precipitate. For the first mixture, we have that:
>
> $$Q_c(CuI) = \left[Cu^+\right]_{noneq} \cdot \left[I^-\right]_{noneq} = (10^{-6}) \cdot (10^{-7}) = 10^{-13} < K_{sp}(CuI)$$
>
> Therefore in the first mixture no precipitate will form. For the second mixture:
>
> $$Q_c(CdF_2) = \left[Cd^{2+}\right]_{noneq} \cdot \left[F^-\right]^2_{noneq} = (0.5) \cdot (0.5)^2 = 3.1 \times 10^{-2} > K_{sp}(CdF_2)$$
>
> Therefore in the second mixture a precipitate will form.
>
> ◈ **STUDY CHECK**
>
> Predict if a precipitate will form in a mixtures of $\left[Li^+\right]=10^{-1}M$ and $\left[CO_3{}^{2-}\right]=10^{-1}M$ given that $K_{sp}(Li_2CO_3) = 8.15 \times 10^{-4}M$
>
> ▶Answer: yes

Predicting precipitation from mixing solutions Let us now analyze a situation in which we mix two different solutions, 5mL of a solution containing 0.1M Pb(NO₃)₂ and 6mL of a solution containing 0.01M NaF. Assuming that liquid volume can be added, we would like to know whether lead(II) fluoride would precipitate. To answer this question, we need to calculate the concentration of lead(II) and of fluoride in the resulting mixture. With this information, we could compute the ion product and compare this value with the solubility product (3.3×10^{-8}). We will first calculate the concentration of lead(II) produced from Pb(NO₃)₂, given that the salt dissociates giving one lead cation and two nitrate anions:

$$\left[Pb^{2+}\right] = \frac{0.1M \cdot 5mL}{11mL} = 4.5 \times 10^{-2}M$$

and then calculate the fluoride concentration produced from NaF, given that the salt dissociates giving one sodium cation and one fluoride anion:

$$\left[F^-\right] = \frac{0.01M \cdot 6mL}{11mL} = 5.4 \times 10^{-3}M$$

With these two concentrations, we can compute the ion product Q_c and compare it with K_{sp}:

$$Q_c = \left[Pb^{2+}\right]_{noneq} \cdot \left[F^-\right]^2_{noneq} = (4.5 \times 10^{-2}) \cdot (5.4 \times 10^{-3})^2 =$$
$$= 1.3 \times 10^{-6} < K_{sp} = 3.3 \times 10^{-8} \text{ hence } (\downarrow)$$

Based on this comparison, we can predict that after mixing the two solutions PbF₂ will precipitate.

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Sample Problem 7

Predict if a $Cu_3(AsO_4)_2$ precipitate will form after mixing 10mL of a 10^{-9}M Na_3AsO_4 with 10mL of a 10^{-10}M $CuCl_2$, given that $K_{sp}(Cu_3(AsO_4)_2){=}8 \times 10^{-36}$.

SOLUTION

We will first calculate the concentration of Cu^{2+} resulting from mixing 10mL of a 10^{-10}M $CuCl_2$ with 10mL of another solution:

$$\left[Cu^{2+}\right] = \frac{10^{-10}M \cdot 10mL}{20mL} = 5 \times 10^{-11} M$$

and then calculate the concentration of $AsO_4{}^{3-}$ resulting from mixing 10mL of a 10^{-9}M Na_3AsO_4 with 10mL of another solution:

$$\left[AsO_4{}^{3-}\right] = \frac{10^{-9}M \cdot 10mL}{20mL} = 5 \times 10^{-10} M$$

We can now calculate the ion product and compare it with the solubility product:

$$Q_c = \left[Cu^{2+}\right]_{noneq}^3 \cdot \left[AsO_4{}^{3-}\right]_{noneq}^2 = (5 \times 10^{-11})^3 \cdot (5 \times 10^{-10})^2 =$$
$$= 3.3 \times 10^{-50} < K_{sp} = 8 \times 10^{-36} \text{ hence } (\downarrow)$$

The insoluble salt will precipitate.

💎 **STUDY CHECK**

Predict if a $FeCO_3$ precipitate will form after mixing 4mL of a 10^{-6}M $FeSO_4$ with 5mL of a 10^{-6}M Na_2CO_3, given that $K_{sp}(FeCO_3){=}3 \times 10^{-11}$.

▶Answer: no precipitate

Predicting the amount of precipitate formed A precipitate can form when mixing two solutions containing specific ions. For example, AgCl is an insoluble compound. A precipitate will form if you mix solutions of $AgNO_3$ and NaCl. In these chemicals, Ag^+ and Cl^- are directly involved in the precipitate formation, whereas $NO_3{}^-$ and Na^+ are spectators. In this section, we will cover how to compute the amount of precipitate formed and the concentration of the leftover ions that will contribute to reduce the solubility of the solid, in comparison to plan water. We will leave aside the spectator ions knowing that they will remain in solution and we will focus mainly on the ions involved in the precipitate. Let us consider the situation in which we mix 5mL of 0.01M-$AgNO_3$ with 6mL of 0.005M-$AgNO_3$. In order to determine the amount of precipitate formed, we will first set up the precipitation reaction:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$$
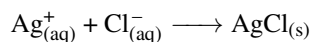
Then, we will identify the limiting reactant by comparing the moles of ions reacting. We will calculate the moles of Ag^+ by computing the moles of silver(I) coming from $AgNO_3$–when multiplying volume by molarity we obtain milimoles:

$$n^{Ag^+} = 5mL \cdot 0.01M = 5 \times 10^{-2} mmol$$

We will now calculate the number of moles of chloride:

$$n^{Cl^-} = 6mL \cdot 0.005M = 3 \times 10^{-2} mmol$$

We have that in order to react with the amount of Ag^+ in the mixture, we would need $n^{Cl^-} = 5 \times 10^{-2}$mmol and we only have 3×10^{-2}mmol of chloride, hence chloride is the limiting reagent and the leftovers will be:

$$n_{left}^{Ag^+} = 5 \times 10^{-2} - 3 \times 10^{-2} = 2 \times 10^{-2}\text{mmol}$$

The number of moles of precipitate formed will be given by:

$$n^{AgCl} = 3 \times 10^{-2}\text{mmol of Cl}^- \times \frac{1\text{mol of AgCl}}{1\text{mol of Cl}^-} = 3 \times 10^{-2}\text{mmol of AgCl}$$

When AgCl forms at the same time there will be silver(I) ion leftovers. We will finally calculate the concentration of the leftover ion simply by dividing the leftover moles by the overall volume of the mixture–mind we mix two different volumes assuming liquid volumes can be added:

$$c_{Ag^+,left} = \frac{n_{left}^{Ag^+}}{V} = \frac{2 \times 10^{-2}\text{mmol}}{(5+6)\text{mL}} = 1.8 \times 10^{-3}\text{M}$$

The ions Silver(I) is a common ion that will affect the solubility of silver chloride, in fact reducing its value:

$$K_{sp} = \left[Ag^+\right] \cdot \left[Cl^-\right] = (s + c_{Ag^+,left}) \cdot (s) = 1.8 \times 10^{-10}$$

that leads to a polynomial

$$s^2 + c_{Ag^+,left} \cdot s - 1.8 \times 10^{-10} = 0$$

Solving for s given that $c_{Ag^+,left} = 1.8 \times 10^{-3}$M we have that $s = 1.0 \times 10^{-7}$M, lower than the solubility of silver chloride in water (1.3×10^{-5}M).

Sample Problem 8

A mixture is prepared by adding 100mL of 0.01M-$CaNO_3$ with 50mL of 0.02M-NaF. Calculate the number of moles of CaF_2 that precipitate–CaF_2 is insoluble– and the concentration of the leftover ion in solution.

SOLUTION

Given that CaF_2 precipitates, we will have the following ions in the solution:

$$Ca^{2+}_{(aq)} + 2\,NO_3^-{}_{(aq)} + Na^+_{(aq)} + F^-_{(aq)} \longrightarrow CaF_{2(s)} \downarrow + 2\,NO_3^-{}_{(aq)} + Na^+_{(aq)}$$
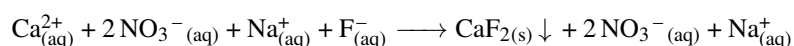
The spectators will be NO_3^- and Na^+, whereas Ca^{2+} and F^- are involved in the precipitation reaction. We will first calculate the number of moles the ions involved in the precipitation

$$n^{Ca^{2+}} = 100\text{mL} \cdot 0.01\text{M} = 1\text{mmol and } n^{F^-} = 50\text{mL} \cdot 0.02\text{M} = 1\text{mmol}$$

to then identify the limiting reagent, calculating the number of moles needed to react with 1mmol of Ca^{2+}

$$n_{needed}^{F^-} = 1\text{mmol of Ca}^{2+} \times \frac{2\text{mol of F}^-}{1\text{mol of Ca}^{2+}} = 2\text{mmol of F}^-$$

As we will need 2-mmol of F^- but we only have 1-mmol, F^- will limit the precipitation whereas Ca^{2+} will be in excess. We will based our calculations on F^- to predict the moles of precipitate formed

$$n^{CaF_2} = 1\text{mmol of F}^- \times \frac{1\text{mol of CaF}_2}{2\text{mol of F}^-} = 0.5\text{mmol of CaF}_2$$

and the leftover moles of Ca^{2+}, given that the we have 1mmol of Ca^{2+} and we need

$$n_{needed}^{Ca^{2+}} = 1\text{mmol of } F^- \times \frac{1\text{mol of } Ca^{2+}}{2\text{mol of } F^-} = 0.5\text{mmol of } Ca^{2+}$$

the leftovers will be 0.5mmol. Finally, we can calculate the concentration of leftover ions by doing

$$\left[Ca^{2+}\right] = \frac{n_{left}^{Ag^+}}{V} = \frac{0.5\text{mmol}}{(50+100)\text{mL}} = 3.3 \times 10^{-3}\text{M}$$

◈ STUDY CHECK

A mixture is prepared by adding 50mL of 0.03M-$GaCl_3$ with 75mL of 0.05M-NaOH. Calculate the number of moles of $Ga(OH)_3$ that precipitate and the concentration of the leftover ion in solution.

▶Answer: 1.25mmol; 2×10^{-3}M