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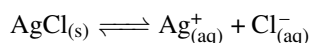
Solubility equilibria

INSOLUBLE 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 $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ in saliva. On a similar note, barium sulfate is an insoluble compound opaque to x-rays used to 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. The chapter also covers the basis properties and naming of complex ions, ions composed of a central atom bonded to one or more molecules or ions.

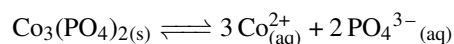
1.1 Solubility equilibrium

Insoluble compounds are in reality slightly soluble. As such, it exist an equilibrium that leads to the solubility of a so called insoluble compound, with a corresponding equilibrium constant called solubility product, K_{sp} . This section covers the obtention of the solubility product expression in terms of equilibrium concentrations of ions, and the relationship between this constant and the compound solubility. Ultimately, the goal would be to calculate the solubility value by means of the tabulated solubility constants. Unless otherwise stated, all solutions in this chapter are water-based solutions at 298K—remember equilibrium constants are temperature and solvent dependent.

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:



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:



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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 Name complex ions

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.

Table 1.1 Solubility product constants on water at 25°C

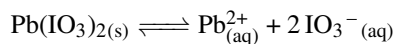
Name	Formula	K_{sp}	Name	Formula	K_{sp}
Aluminium hydroxide	$\text{Al}(\text{OH})_3$	3.00×10^{-34}	Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2$	1.04×10^{-24}
Aluminium phosphate	AlPO_4	9.84×10^{-21}	Manganese(II) carbonate	MnCO_3	2.24×10^{-11}
Barium bromate	$\text{Ba}(\text{BrO}_3)_2$	2.43×10^{-4}	Manganese(II) hydroxide	$\text{Mn}(\text{OH})_2$	2.00×10^{-13}
Barium carbonate	BaCO_3	2.58×10^{-9}	Manganese(II) iodate	$\text{Mn}(\text{IO}_3)_2$	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	$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$	2.55×10^{-4}	Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Barium iodate	$\text{Ba}(\text{IO}_3)_2$	4.01×10^{-9}	Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Barium iodate monohydrate	$\text{Ba}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	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	$\text{Ba}(\text{NO}_3)_2$	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	$\text{Hg}_2\text{C}_2\text{O}_4$	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	$\text{Hg}_2(\text{SCN})_2$	3.20×10^{-20}
Beryllium hydroxide	$\text{Be}(\text{OH})_2$	6.92×10^{-22}	Mercury(II) bromide	HgBr_2	6.20×10^{-20}
Cadmium arsenate	$\text{Cd}_3(\text{AsO}_4)_2$	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	$\text{Cd}(\text{OH})_2$	7.20×10^{-15}	Mercury(II) sulfide (red)	HgS	2.00×10^{-54}
Cadmium iodate	$\text{Cd}(\text{IO}_3)_2$	2.50×10^{-8}	Neodymium carbonate	$\text{Nd}_2(\text{CO}_3)_3$	1.08×10^{-33}
Cadmium phosphate	$\text{Cd}_3(\text{PO}_4)_2$	2.53×10^{-33}	Nickel(II) carbonate	NiCO_3	1.42×10^{-7}
Cadmium sulfide	CdS	1.00×10^{-27}	Nickel(II) hydroxide	$\text{Ni}(\text{OH})_2$	5.48×10^{-16}
Calcium carbonate (calcite)	CaCO_3	3.36×10^{-9}	Nickel(II) iodate	$\text{Ni}(\text{IO}_3)_2$	4.71×10^{-5}
Calcium fluoride	CaF_2	3.45×10^{-11}	Nickel(II) phosphate	$\text{Ni}_3(\text{PO}_4)_2$	4.74×10^{-32}
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	5.02×10^{-6}	Nickel(II) sulfide (alpha)	NiS	4.00×10^{-20}
Calcium iodate	$\text{Ca}(\text{IO}_3)_2$	6.47×10^{-6}	Nickel(II) sulfide (beta)	NiS	1.30×10^{-25}
Calcium molybdate	CaMoO_4	1.46×10^{-8}	Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	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	$\text{Co}_3(\text{AsO}_4)_2$	6.80×10^{-29}	Praseodymium hydroxide	$\text{Pr}(\text{OH})_3$	3.39×10^{-24}
Cobalt(II) carbonate	CoCO_3	1.00×10^{-10}	Radium iodate	$\text{Ra}(\text{IO}_3)_2$	1.16×10^{-9}
Cobalt(II) phosphate	$\text{Co}_3(\text{PO}_4)_2$	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	$\text{Sc}(\text{OH})_3$	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	$\text{Cu}_3(\text{AsO}_4)_2$	7.95×10^{-36}	Silver(I) bromide	AgBr	5.35×10^{-13}
Copper(II) hydroxide	$\text{Cu}(\text{OH})_2$	4.80×10^{-20}	Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Copper(II) iodate monohydrate	$\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	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	$\text{Cu}_3(\text{PO}_4)_2$	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	$\text{Ag}_2\text{C}_2\text{O}_4$	5.40×10^{-12}
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	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	$\text{Fe}(\text{OH})_3$	2.79×10^{-39}	Silver(I) sulfide	Ag_2S	8×10^{-51}
Iron(III) phosphate dihydrate	$\text{FePO}_4 \cdot 2 \text{H}_2\text{O}$	9.91×10^{-16}	Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}

Sample Problem 1

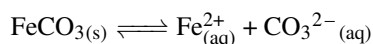
Write down the solubility equilibrium for: Lead(II) iodate, and FeCO_3 .

SOLUTION

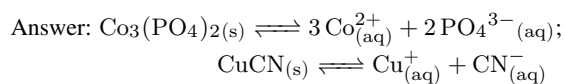
The first insoluble compound, Lead(II) iodate, with formula $\text{Pb}(\text{IO}_3)_2$, contains cation lead(II) Pb^{2+} and anion IO_3^{2-} (iodate). The solubility equilibrium will be given by:



The solubility equilibrium for the second insoluble compound iron(II) carbonate will be:

**STUDY CHECK**

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



1.2 Solubility product

Acid-base equilibrium have an acidity or a basicity constant associated. This equilibrium constant tells about the dissociation of the acid or base. Similarly, chemical reactions have an equilibrium constant associated which can be expressed in terms of concentrations or pressures. This equilibrium constant inform about the reacting mixture giving information about what is more abundant in the mixture, either reactants or products. When a solid dissolved in liquid, this equilibrium also has an equilibrium constant associated. This time, the constant informs about the amount of solid that actually dissolves.

Solubility product in terms of molarities, K_{sp} Silver chloride, AgCl is normally considered an insoluble compound in water. That means this compound will not fully dissolve in water. However, small quantities of the salt will certainly dissolve leading to a small amount of silver and chlorine ions. The dissociation equilibrium involved, indicate below, is characterized by an equilibrium constant K_{sp} called *solubility product constant* or simple *solubility product*:



As pure solids are not part of any equilibrium constant, the formula above does not include silver chloride. As such, all solubility products simply result from the product of the molarities of the ions involved in the dissociation, as hence its name *product*. K_{sp} will have a different explicit expression depending on the formula of the insoluble compound. For example, K_{sp} for calcium fluoride would be:



The solubility product is related to the solubility of the chemical. However, the relation is not one-on-one. For example, K_{sp} for PbBr_2 is $6.6 \times 10^{-3}\text{M}$, and K_{sp} for MgCO_3 is

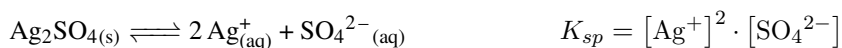
$4.0 \times 10^{-5}\text{M}$. As such, K_{sp} is smaller for PbBr_2 . Differently, the solubility of MgCO_3 is indeed smaller than the solubility of PbBr_2 . This is because, the relationship between K_{sp} and solubility is not linear. Table 1.1 reports solubility product constant values.

Sample Problem 2

Write down the expression of K_{sp} in terms of the ion concentration for the following compounds: Ag_2SO_4 , $\text{Mg}(\text{OH})_2$, and MgCO_3 .

SOLUTION

The solubility equilibrium for first compound, silver sulfate, is



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



Finally, for magnesium carbonate:



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.

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

1.3 Predicting precipitation

Imagine we have a clear solution with any sign of precipitate. Now we add a second solution knowing that the mixture will produce a precipitate. The question here is when would the precipitate form. Some precipitates will form after adding just a few drops. Other would require a larger amount of reagents. Where is the limit for precipitation when we mix two reagents? As you can see is crucial to predict at what point of the addition will a precipitate form.

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

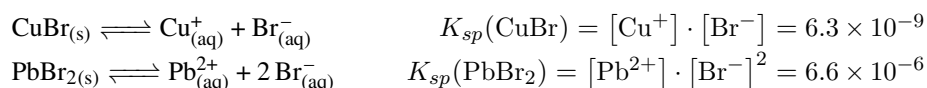


As we know the concentration of Cu^+ , we can solve for $[\text{I}^-]$:

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

We have that $[\text{I}^-] = 1.27 \times 10^{-11}\text{M}$. Hence, Copper(I) iodide will precipitate with a very small concentration of iodide in the solution.

Selective precipitation When we have a mixture of different ions that form insoluble precipitates (e.g. Pb^{2+} and Cu^+) we can use the principles of selective precipitation to separate the ions. Imagine that the concentration of both ions in the mixture is 0.01M. We will add a common anion (e.g. Br^-) that will produce two different precipitates (CuBr and PbBr_2). We will also assume that the addition of the cation will not modify much the volume of the mixture. If the solubility product of both insoluble compounds is different enough, we will be able to selectively precipitate first the less soluble compound and the more soluble. We will calculate the amount of the added solution needed to precipitate each solid. Let us first address the expressions for the solubility product for each solid:



We will calculate the concentration of bromide needed to precipitate each of the solids, first Copper(I) bromide:

$$K_{sp}(\text{CuBr}) = [\text{Cu}^+] \cdot [\text{Br}^-] = (0.01) \cdot [\text{Br}^-] = 6.3 \times 10^{-9}$$

Solving for $[\text{Br}^-]$ we have: $[\text{Br}^-] = 6.3 \times 10^{-9} / 0.01 = 6.3 \times 10^{-7} \text{M}$ for the precipitation of CuBr. Now, the concentration of bromide needed to precipitate Lead(II) bromide would be: $[\text{Br}^-]^2 = \frac{6.6 \times 10^{-6}}{0.01}$ hence $[\text{Br}^-] = \left(\frac{6.6 \times 10^{-6}}{0.01} \right)^{\frac{1}{2}} = 2.5 \times 10^{-2} \text{M}$ for PbBr_2 . Comparing both concentrations we have that the values are separate enough (more than 99%) so it would be feasible to separate both ions in solution.

1.4 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.

Molar solubility In general terms, solubility is the amount of solute in 1L of saturated solution. There are two main ways to describe solubility. On one hand, molar solubility s is the number of moles of solute per liter of saturated solution. On the other hand, solubility \bar{s} is normally defined as the number of grams of solute per liter of saturated solution. Both types of solubility are simply related by the molar mass:

$$\bar{s} = s \cdot MW \quad (1.1)$$

where:

\bar{s} is solubility in mol/L

s is solubility in g/L

MW the molar weight of the insoluble compound

Sample Problem 3

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

SOLUTION

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

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

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

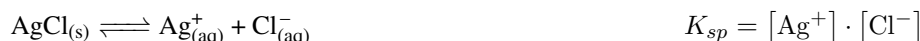
$$1.90 \times 10^{-3} \frac{\text{g}}{\text{L}} \times 0.005\text{L} = 9.51 \times 10^{-5}\text{g}$$

STUDY CHECK

How many mL of solution contains 1ng of solute in a saturated ScF_3 solution, given $s=2.41 \times 10^{-12}\text{M}$. The molar mass of ScF_3 is 101.9g/mol.

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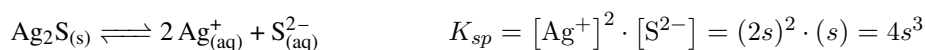
K_{sp} in terms of molar solubility The solubility product is directly related to molar solubility s . We will demonstrate how to obtain this relationship by means of three examples. First, the solubility product of AgCl is:



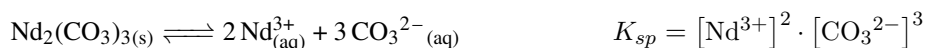
As the concentration of each ion, Ag^{+} and Cl^{-} , is related to the molar solubility of the salt, we have

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

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



Third, the solubility equilibrium and K_{sp} expression for $\text{Nd}_2(\text{CO}_3)_3$ is



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:

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

where:

$$a \text{ is } x^x \cdot y^y$$

$$b \text{ is } x + y$$

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 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:
 $\text{Co}_3(\text{PO}_4)_2$ 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:
 ceAg_2CO_3 and $\text{Fe}(\text{OH})_3$.

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_xB_y , we have:

$$s = \left(\frac{K_{sp}}{a} \right)^{\frac{1}{b}} \quad (1.3)$$

where:

$$a \text{ is } x^x \cdot y^y$$

$$b \text{ is } x + y$$

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

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

MgF ₂	$K_{sp}=5 \times 10^{-11}$	$s = 2 \times 10^{-4}$
Li ₃ PO ₄	$K_{sp}=2 \times 10^{-4}$	$s = 7 \times 10^{-2}$
Li ₂ CO ₃	$K_{sp}=8 \times 10^{-4}$	$s = 6 \times 10^{-2}$

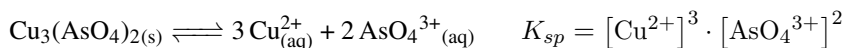
then an increase in K_{sp} do not necessarily follows an increase in solubility.

Sample Problem 5

The solubility product of Copper(II) arsenate $\text{Cu}_3(\text{AsO}_4)_2$ 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:



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

$$K_{sp} = [\text{Cu}^{2+}]^3 \cdot [\text{AsO}_4^{3-}]^2 = (3s)^3 \cdot (2s)^2 = 108s^5$$

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

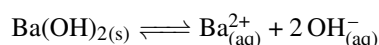
The solubility product of Nickel(II) phosphate $\text{Ni}_3(\text{PO}_4)_2$ is 4.74×10^{-32} . Calculate the molar solubility of the salt.

Answer: $2.13 \times 10^{-7} M$

1.5 Solubility and K_{sp}

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Solubility and PH Some insoluble salts have acid-base character. For example, $\text{Ba}(\text{OH})_2$ 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 $\text{Ba}(\text{OH})_2$ solution. We have that the solubility equilibrium is given by



and K_{sp} is related to solubility s by means the following formula

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

As the solubility product of $\text{Ba}(\text{OH})_2$ 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

$$[\text{Ba}^{2+}] = s$$

$$[\text{OH}^-] = 2s$$

Hence we have that the PH is directly related to solubility

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

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 $\text{Ba}(\text{OH})_2$ 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 $1.3 \times 10^{-5} \text{M}$ 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 $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$. In order to do this, we will first display the solubility equilibrium of the salt



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

$$[\text{Ag}^+] = s$$

$$[\text{Cl}^-] = 0.1 + s$$

Solving for s we have:

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

that leads to a polynomial

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

1.6 Predicting precipitation from mixtures and solutions

Imagine we have a clear solution with any sign of precipitate. Now we add a second solution knowing that the mixture will produce a precipitate. The question here is when would the precipitate form. Some precipitates will form after adding just a few drops. Other would require a larger amount of reagents. Where is the limit for precipitation when we mix two reagents? As you can see is crucial to predict at what point of the addition will a precipitate form.

Mixing ion solutions can lead to precipitation. This section addresses how to predict the precipitation of an insoluble compound from mixtures containing different ions and mixtures of solutions.

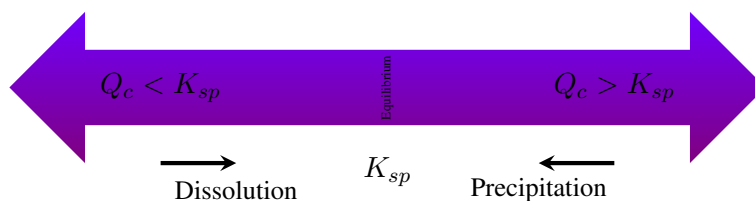
Predicting precipitation from mixtures Let us analyze a situation in which we dissolve in water an insoluble compound such as lead(II) fluoride. The solubility products constant K_{sp} is just an equilibrium constant that described the process of solubility. K_{sp} depends on the equilibrium concentration of the ions in solution. For example, K_{sp} for lead(II) fluoride is 3.3×10^{-8} and its mathematical expression is presented below



In the expression above, $[\text{Pb}^{2+}]$ represents the equilibrium concentration of ions Lead(II) and $[\text{F}^{-}]$ 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} :

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

By comparing the calculated concentration product and the solubility product constant we can predict if a precipitate will appear or not. A precipitate will appear only for Q_c values larger than K_{sp} . In other words, mixtures of solutions more concentrated than the compound solubility will precipitate, whereas less concentrated mixtures in comparison with solubility will not precipitate.



As a side note the difference between the concentration in K_{sp} and Q_c is based on the fact that K_{sp} include *equilibrium* concentration resulting of the slow dissolution of an insoluble compound, whereas Q_c include *nonequilibrium* concentrations resulting of artificially preparing and 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:

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

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:

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

Sample Problem 6

Predict if a precipitate will form in any of the following mixtures: (a) $[\text{Cu}^{+}] = 10^{-6}\text{M}$ and $[\text{I}^{-}] = 10^{-7}\text{M}$ given that $K_{sp}(\text{CuI}) = 1.27 \times 10^{-12}\text{M}$ (b) $[\text{Cd}^{2+}] = 0.5\text{M}$ and $[\text{F}^{-}] = 0.5\text{M}$ given that $K_{sp}(\text{CdF}_2) = 6.44 \times 10^{-3}\text{M}$

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:

$$Q_c(\text{CuI}) = [\text{Cu}^+]_{\text{noneq}} \cdot [\text{I}^-]_{\text{noneq}} = (10^{-6}) \cdot (10^{-7}) = 10^{-13} < K_{sp}(\text{CuI})$$

Therefore in the first mixture no precipitate will form. For the second mixture:

$$Q_c(\text{CdF}_2) = [\text{Cd}^{2+}]_{\text{noneq}} \cdot [\text{F}^-]_{\text{noneq}}^2 = (0.5) \cdot (0.5)^2 = 3.1 \times 10^{-2} > K_{sp}(\text{CdF}_2)$$

Therefore in the second mixture a precipitate will form.

◆ STUDY CHECK

Predict if a precipitate will form in a mixture of $[\text{Li}^+] = 10^{-1}\text{M}$ and $[\text{CO}_3^{2-}] = 10^{-1}\text{M}$ given that $K_{sp}(\text{Li}_2\text{CO}_3) = 8.15 \times 10^{-4}\text{M}$

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 $\text{Pb}(\text{NO}_3)_2$ 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 $\text{Pb}(\text{NO}_3)_2$, given that the salt dissociates giving one lead cation and two nitrate anions:

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

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

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

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

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

Based on this comparison, we can predict that after mixing the two solutions PbF_2 will precipitate.

Sample Problem 7

Predict if a $\text{Cu}_3(\text{AsO}_4)_2$ 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 $K_{sp}(\text{Cu}_3(\text{AsO}_4)_2) = 8 \times 10^{-36}$.

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:

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

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:

$$[\text{AsO}_4^{3-}] = \frac{10^{-9}\text{M} \cdot 10\text{mL}}{20\text{mL}} = 5 \times 10^{-10}\text{M}$$

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

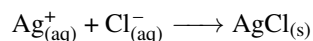
$$\begin{aligned} Q_c &= [\text{Cu}^{2+}]_{\text{noneq}}^3 \cdot [\text{AsO}_4^{3-}]_{\text{noneq}}^2 = (5 \times 10^{-11})^3 \cdot (5 \times 10^{-10})^2 = \\ &= 3.3 \times 10^{-50} < K_{sp} = 8 \times 10^{-36} \text{ hence } (\downarrow) \end{aligned}$$

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 $K_{sp}(\text{FeCO}_3) = 3 \times 10^{-11}$.

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 leftovers. We will leave aside the spectator ions knowing that they will remain in solution. 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:



Second, 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 mmol:

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

We will now calculate the number of moles of chloride:

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

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

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

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

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

When AgCl forms at the same time there will be silver(I) 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 and we assume liquid volumes can be added:

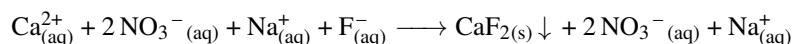
$$[\text{Ag}^+] = \frac{n_{\text{Ag}^+}^{\text{left}}}{V} = \frac{2 \times 10^{-2} \text{ mmol}}{(5 + 6) \text{ mL}} = 1.8 \times 10^{-3} \text{ M}$$

Sample Problem 8

A mixture is prepared by adding 100mL of 0.01M-CaNO₃ with 50mL of 0.02M-NaF. Calculate the number of moles of CaF₂ that precipitate—CaF₂ is insoluble—and the concentration of the leftover ion in solution.

SOLUTION

Given that CaF₂ precipitates, we will have the following ions in the solution:



The spectators will be NO₃[−] and Na⁺, whereas Ca²⁺ and F[−] are involved in the precipitation reaction. We will first calculate the number of moles the ions involved in the precipitation

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

to then identify the limiting reagent, calculating the number of moles needed to react with 1mmol of Ca²⁺

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

As we will need 2-mmol of F[−] but we only have 1-mmol, F[−] will limit the precipitation whereas Ca²⁺ will be in excess. We will base our calculations on F[−] to predict the moles of precipitate formed

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

and the leftover moles of Ca²⁺, given that we have 1mmol of Ca²⁺ and we need

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

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

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

STUDY CHECK

A mixture is prepared by adding 50mL of 0.03M-GaCl₃ 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; $2 \times 10^{-3} \text{ M}$

CHAPTER 1

SOLUBILITY EQUILIBRIUM

1.1 Write down the solubility equilibrium for the following chemicals: (a) CuCl (b) Iron(II) sulfide (c) CuS

1.2 Write down the solubility equilibrium for the following chemicals: (a) Mercury(II) sulfide (b) AlPO₄ (c) Manganese(II) sulfide

1.3 Write down the solubility equilibrium for the following chemicals: (a) Beryllium hydroxide (b) Ba(BrO₃)₂ (c) Lead(II) iodide

1.4 Write down the solubility equilibrium for the following chemicals: (a) SrSO₄ (b) Silver(I) chromate (c) Sr(IO₃)₂

SOLUBILITY PRODUCT

1.5 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) CuCl (b) FeS (c) MnS

1.6 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) MgCO₃ (b) PbCrO₄ (c) TlBr

1.7 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) ScF₃ (b) NiS (c) HgI₂

1.8 Write down the solubility product in terms of the molarities of the ions in solution for the following chemicals: (a) Cu₂O (b) Co₃(PO₄)₂ (c) Fe(OH)₃

PREDICTING PRECIPITATION

1.9 Predict whether CdF₂ will precipitate in the following mixtures given that $K_{sp} = 6.44 \times 10^{-3}$: (a) A mixture containing $[Cd^{2+}] = 1 \times 10^{-1}M$ and $[F^-] = 1 \times 10^{-1}M$ (b) A mixture containing $[Cd^{2+}] = 1 \times 10^{-1}M$ and $[F^-] = 1 \times 10^{-2}M$ (c) A mixture containing $[Cd^{2+}] = 1 \times 10^{-2}M$ and $[F^-] = 1 \times 10^{-2}M$

1.10 Predict whether CuCl will precipitate in the following mixtures given that $K_{sp} = 1.7 \times 10^{-7}$: (a) A mixture containing $[Cu^+] = 1 \times 10^{-3}M$ and $[Cl^-] = 1 \times 10^{-3}M$ (b) A mixture containing $[Cu^+] = 1 \times 10^{-4}M$ and $[Cl^-] = 1 \times 10^{-4}M$ (c) A mixture containing $[Cu^+] = 1 \times 10^{-4}M$ and $[Cl^-] = 1 \times 10^{-3}M$

1.11 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for Ni(IO₃)₂ is 4.7×10^{-5} : (a) 10mL of a 0.1M-NiCl solution and 10mL of a 0.1M-NaIO₃ solution (b) 10mL of a 0.1M-NiCl solution and 20mL of a 0.1M-NaIO₃ solution (c) 10mL of a 0.01M-NiCl solution and 20mL of a 0.01M-NaIO₃ solution

1.12 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for FeF₂ is 2.4×10^{-6} : (a) 1mL of a 0.1M-Fe(NO₃)₂ solution and 1mL of a 0.1M-NaF solution (b) 1mL of a 0.01M-Fe(NO₃)₂ solution and 1mL of a 0.1M-NaF solution (c) 1mL of a 0.01M-Fe(NO₃)₂ solution and 1mL of a 0.01M-NaF solution

Answers