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Solubility equilibria and complex ions

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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 $Ca_5(PO_4)_3OH$ 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.

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

1.1 Solubility equilibrium and solubility product

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-bases solutions at 298K–remember equilibrium constants are temperature and solvent dependent.

> 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.

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}

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 $Pb(IO_3)_2$, 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: $Co_3(PO_4)_{2(s)} \rightleftharpoons 3\,Co^{2+}_{(aq)} + 2\,{PO_4}^{3-}{}_{(aq)}$;
$CuCN_{(s)} \rightleftharpoons Cu^{+}_{(aq)} + CN^{-}_{(aq)}$

Solubility product, 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*:

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

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:

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

The solubility product is related to the solubility of the chemical. However, the relation is not one-on-one. For example, K_{sp} for $PbBr_2$ is6.6×10^{-3}M, and K_{sp} for $MgCO_3$ is 4.0×10^{-5}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, $Mg(OH)_2$, and $MgCO_3$.

SOLUTION

The solubility equilibrium for first compound, silver sulfate, is

$$Ag_2SO_{4(s)} \rightleftharpoons 2\,Ag^{+}_{(aq)} + {SO_4}^{2-}{}_{(aq)} \qquad K_{sp} = \left[Ag^{+}\right]^2 \cdot \left[{SO_4}^{2-}\right]$$

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

magnesium hydroxide:

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

Finally, for magnesium carbonate:

$$MgCO_{3(s)} \rightleftharpoons Mg^{2+}_{(aq)} + {CO_3}^{2-}{}_{(aq)} \qquad K_{sp} = \left[Mg^{2+}\right] \cdot \left[{CO_3}^{2-}\right]$$

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

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}:

$$CuI_{(s)} \rightleftharpoons Cu^{+}_{(aq)} + I^{-}_{(aq)} \qquad K_{sp} = \left[Cu^{+}\right] \cdot \left[I^{-}\right] = 1.27 \times 10^{-12}$$

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

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

We have that $\left[I^-\right] = 1.27 \times 10^{-11}$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 asume 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:

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

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

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

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

1.2 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 $\overline{s}$ 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:

$$\boxed{\overline{s} = s \cdot MW} \tag{1.1}$$

where:

$\overline{s}$ 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=1.33×10^{-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=2.41×10^{-12}M. The molar mass of is ScF_3 101.9g/mol.

4081mL

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:

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

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:

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

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

$$\mathrm{Nd_2(CO_3)_{3(s)}} \rightleftharpoons 2\,\mathrm{Nd^{3+}_{(aq)}} + 3\,\mathrm{{CO_3}^{2-}{}_{(aq)}} \qquad K_{sp} = \left[\mathrm{Nd^{3+}}\right]^2 \cdot \left[\mathrm{{CO_3}^{2-}}\right]^3$$

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 $\mathrm{A}_x\mathrm{B}_y$, we have that K_{sp} is related to s by means of a general formula:

$$\boxed{K_{sp} = a \cdot s^b} \tag{1.2}$$

where:

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

For example, for $\mathrm{Ba_1F_2}$ 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: $\mathrm{Co_3(PO_4)_2}$ and HgS.

SOLUTION

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

$$K_{sp}(\mathrm{Co_3(PO_4)_2}) = (3^3 \cdot 2^2) \cdot s^{3+2} = 108 \cdot s^5$$

For the second salt:

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

STUDY CHECK

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

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 $\mathrm{A}_x\mathrm{B}_y$, we have:

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

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 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_3PO_4	K_{sp}=2×10^{-4}	$s = 7 \times 10^{-2}$
Li_2CO_3	K_{sp}=8×10^{-4}	$s = 6 \times 10^{-2}$

then an increase in K_{sp} do not necesarily 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

1.3 Solubility and K_{sp}

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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

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

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 $K_{sp}(\mathrm{AgCl}) = 1.8 \times 10^{-10}$. In order to do this, we will first display the solubility equilibriu of the salt

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad K_{sp} = \left[Ag^+\right] \cdot \left[Cl^-\right] = 1.8 \times 10^{-10}$$

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

$$\left[Ag^+\right] = s \qquad \left[Cl^-\right] = 0.1 + s$$

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 polynomia

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

1.4 Predicting precipitation from mixtures and solutions

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.

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.

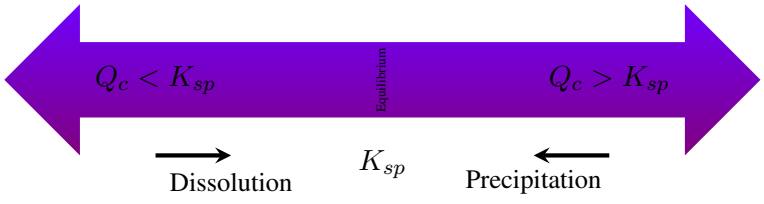
Predicting precipitation from mixtures Let us analyze a situation in which we dissolve in water an insoluble compound such as lead(II) fluoride. The solubility products constant K_{sp} is just an equilibrium constant that described the process of solubility. K_{sp} depends on the equilibrium concentration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

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

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}:

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

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 that 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:

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

$$Q_c = \left[\mathrm{Pb}^{2+}\right]_{noneq} \cdot \left[\mathrm{F}^{-}\right]^2_{noneq} = 10^{-3} \cdot (10^{-3})^2 = 10^{-9} < K_{sp} = 3.3 \times 10^{-8}$$
hence ($\not\downarrow$)

Sample Problem 6

Predict if a precipitate will form in any of the following mixtures: (a) $\left[\mathrm{Cu}^{+}\right]$=$10^{-6}$M and $\left[\mathrm{I}^{-}\right]$=$10^{-7}$M given that $K_{sp}(\mathrm{CuI}) = 1.27 \times 10^{-12}$M (b) $\left[\mathrm{Cd}^{2+}\right]$=0.5M and $\left[\mathrm{F}^{-}\right]$=0.5M given that $K_{sp}(\mathrm{CdF_2}) = 6.44 \times 10^{-3}$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:

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

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

$$Q_c(\mathrm{CdF_2}) = \left[\mathrm{Cd}^{2+}\right]_{noneq} \cdot \left[\mathrm{F}^{-}\right]^2_{noneq} = (0.5) \cdot (0.5)^2 = 3.1 \times 10^{-2} > K_{sp}(\mathrm{CdF_2})$$

Therefore in the second mixture a precipitate will form.

STUDY CHECK

Predict if a precipitate will form in a mixtures of $\left[\mathrm{Li}^{+}\right]$=$10^{-1}$M and $\left[{\mathrm{CO_3}}^{2-}\right]$=$10^{-1}$M given that $K_{sp}(\mathrm{Li_2CO_3}) = 8.15 \times 10^{-4}$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 $Pb(NO_3)_2$ 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 $Pb(NO_3)_2$, given that the salt dissociates giving one lead cation and two nitrate anions:

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

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

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

With these two concentrations, we can compute the ion product Q_c and compare it with

K_{sp}:

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

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

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 $K_{sp}(Cu_3(AsO_4)_2)$=8×10^{-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:

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

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:

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

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

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

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 $K_{sp}(FeCO_3)$=3×10^{-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:

$$\mathrm{Ag^+_{(aq)}} + \mathrm{Cl^-_{(aq)}} \longrightarrow \mathrm{AgCl_{(s)}}$$

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:

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

We will now calculate the number of moles of cloride:

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

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

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

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

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

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 voluments and we asume liquid volumes can be added:

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

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:

$$\mathrm{Ca}^{2+}_{(aq)} + 2\,\mathrm{NO_3}^-{}_{(aq)} + \mathrm{Na}^+_{(aq)} + \mathrm{F}^-_{(aq)} \longrightarrow \mathrm{CaF_{2(s)}}\downarrow + 2\,\mathrm{NO_3}^-{}_{(aq)} + \mathrm{Na}^+_{(aq)}$$

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

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

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

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

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

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

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

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

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

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

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

CHAPTER 1

PREDICTING PRECIPITATION

1.1 Predict whether CdF_2 will precipitate in the following mixtures given that $K_{sp} = 6.44 \times 10^{-3}$: (a) A mixture containing $\left[Cd^{2+}\right] = 1 \times 10^{-1}$M and $\left[F^{-}\right] = 1 \times 10^{-1}$M (b) A mixture containing $\left[Cd^{2+}\right] = 1 \times 10^{-1}$M and $\left[F^{-}\right] = 1 \times 10^{-2}$M (c) A mixture containing $\left[Cd^{2+}\right] = 1 \times 10^{-2}$M and $\left[F^{-}\right] = 1 \times 10^{-2}$M

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

1.3 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for $Ni(IO_3)_2$ is 4.7×10^{-5}: (a) 10mL of a 0.1M-NiCl solution and 10mL of a 0.1M-$NaIO_3$ solution (b) 10mL of a 0.1M-NiCl solution and 20mL of a 0.1M-$NaIO_3$ solution (c) 10mL of a 0.01M-NiCl solution and 20mL of a 0.01M-$NaIO_3$ solution

1.4 Indicate whether a precipitation will form when mixing the following solutions given that K_{sp} for FeF_2 is 2.4×10^{-6}: (a) 1mL of a 0.1M-$Fe(NO_3)_2$ solution and 1mL of a 0.1M-NaF solution (b) 1mL of a 0.01M-$Fe(NO_3)_2$ solution and 1mL of a 0.1M-NaF solution (c) 1mL of a 0.01M-$Fe(NO_3)_2$ solution and 1mL of a 0.01M-NaF solution

Answers