14.11: The Solubility Product

In the section on precipitation reactions, we saw that there are some salts which dissolve in water to only a very limited extent. For example, if $BaSO_4$ crystals are shaken with water, so little dissolves that it is impossible to see that anything has happened, as you will see in the video below. Nevertheless, the few Ba^{2+}(*aq*) and $SO_4{}^{2-}$(*aq*) ions that do go into solution increase the conductivity of the water, allowing us to measure their concentration. The video below shows the creation of Barium Sulfate in a precipitation reaction between barium chloride and sodium sulfate. Notice the white precipitate that forms, which is barium sulfate.

We find that at 25°C

$$[\mathrm{Ba}^{2+}] = 0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1} = [\mathrm{SO}_4^{2-}] \tag{14.11.1}$$

that we would describe the solubility of $BaSO_4$ as 0.97 × 10^{-5} mol L^{-1} at this temperature. The solid salt and its ions are in dynamic equilibrium, and so we can write the equation

$$\mathrm{BaSO}_4(s) \rightleftharpoons \mathrm{Ba}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) \tag{14.11.2}$$

As in other dynamic equilibria we have discussed, a particular Ba^{2+} ion will sometimes find itself part of a crystal and at other times find itself hydrated and in solution.

Since the concentration of $BaSO_4$ has a constant value, it can be incorporated into K_c for Equation 14.11.2 This gives a special equilibrium constant called the **solubility product K_{sp}**:

$$K_{sp} = K_c[\mathrm{BaSO}_4] = [\mathrm{Ba}^{2+}][\mathrm{SO}_4^{2-}] \tag{14.11.3}$$

For $BaSO_4$, K_{sp} is easily calculated from the solubility by substituting Equation 14.11.1into 14.11.3:

$$K_{sp} = (0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1})(0.97 \times 10^{-5}\ \mathrm{mol\ L}^{-1}) \tag{14.11.4}$$

$$= 0.94 \times 10^{-10}\ \mathrm{mol}^2\ \mathrm{L}^{-2} \tag{14.11.5}$$

In the general case of an ionic compound whose formula is A_xB_y, the equilibrium can be written

$$\mathrm{A}_x\mathrm{B}_y(s) \rightleftharpoons x\mathrm{A}^{m+}(aq) + y\mathrm{A}^{n+}(aq)$$

The solubility product is then

$$\mathrm{K}_{sp} = [\mathrm{A}^{m+}]^x[\mathrm{B}^{n+}]^y$$

Solubility products for some of the more common sparingly soluble compounds are given in the table below.

Table 14.11.1 Solubility Product Constants for Some Inorganic Compounds at 25 °C1

Substance	K_s	Substance	K_{sp}
Aluminum Compounds		*Barium Compounds*	
$AlAsO_4$	1.6 × 10^{-16}	$Ba_3(AsO_4)_2$	8.0 × 10^{-15}

Substance	K_s	Substance	K_{sp}
$Al(OH)_3$ amorphous	1.3×10^{-33}	$BaCO_3$	5.1×10^{-9}
$AlPO_4$	6.3×10^{-19}	BaC_2O_4	1.6×10^{-7}
Bismuth Compounds		$BaCrO_4$	1.2×10^{-10}
$BiAsO_4$	4.4×10^{-10}	BaF_2	1.0×10^{-6}
$BiOCl^2$	7.0×10^{-9}	$Ba(OH)_2$	5×10^{-3}
$BiO(OH)$	4×10^{-10}	$Ba_3(PO_4)_2$	3.4×10^{-23}
$Bi(OH)_3$	4×10^{-31}	$BaSeO_4$	3.5×10^{-8}
Bil_3	8.1×10^{-19}	$BaSO_4$	1.1×10^{-10}
$BiPO_4$	1.3×10^{-23}	$BaSO_3$	8×10^{-7}
Cadmium Compounds		BaS_2O_3	1.6×10^{-5}
$Cd_3(AsO_4)_2$	2.2×10^{-33}	*Calcium Compounds*	
$CdCO_3$	5.2×10^{-12}	$Ca_3(AsO_4)_2$	6.8×10^{-19}
$Cd(CN)_2$	1.0×10^{-8}	$CaCO_3$	2.8×10^{-9}
$Cd_2[Fe(CN)_6]$	3.2×10^{-17}	$CaCrO_4$	7.1×10^{-4}
$Cd(OH)_2$ fresh	2.5×10^{-14}	$CaC_2O_4 \cdot H_2O^3$	4×10^{-9}
Chromium Compounds		CaF_2	5.3×10^{-9}
$CrAsO_4$	7.7×10^{-21}	$Ca(OH)_2$	5.5×10^{-6}
$Cr(OH)_2$	2×10^{-16}	$CaHPO_4$	1×10^{-7}
$Cr(OH)_3$	6.3×10^{-31}	$Ca_3(PO_4)_2$	2.0×10^{-29}
$CrPO_4 \cdot 4H_2O$ green	2.4×10^{-23}	$CaSeO_4$	8.1×10^{-4}
$CrPO_4 \cdot 4H_2O$ violet	1.0 × 10-17	$CaSO_4$	9.1×10^{-6}
Cobalt Compounds		$CaSO_3$	6.8×10^{-8}
$Co_3(AsO_4)_2$	7.6×10^{-29}	*Copper Compounds*	
$CoCO_3$	1.4×10^{-13}	$CuBr$	5.3×10^{-9}
$Co(OH)_2$ fresh	1.6×10^{-15}	$CuCl$	1.2×10^{-6}
$Co(OH)_3$	1.6×10^{-44}	$CuCN$	3.2×10^{-20}
$CoHPO_4$	2×10^{-7}	CuI	1.1×10^{-12}
$CO_3(PO_4)_2$	2×10^{-35}	$CuOH$	1×10^{-14}
Gold Compounds		$CuSCN$	4.8×10^{-15}
$AuCl$	2.0×10^{-13}	$Cu_3(AsO_4)_2$	7.6×10^{-36}
AuI	1.6×10^{-23}	$CuCO_3$	1.4×10^{-10}
$AuCl_3$	3.2×10^{-25}	$Cu_2[Fe(CN)_6]$	1.3×10^{-16}
$Au(OH)_3$	5.5×10^{-46}	$Cu(OH)_2$	2.2×10^{-20}
AuI_3	1×10^{-46}	$Cu_3(PO_4)_2$	1.3×10^{-37}

Substance	K_s	Substance	K_{sp}
Iron Compounds		*Lead Compounds*	
$FeCO_3$	3.2×10^{-11}	$Pb_3(AsO_4)_2$	4.0×10^{-36}
$Fe(OH)_2$	8.0×10^{-16}	$PbBr_2$	4.0×10^{-5}
$FeC_2O_4 \cdot 2H_2O^3$	3.2×10^{-7}	$PbCO_3$	7.4×10^{-14}
$FeAsO_4$	5.7×10^{-21}	$PbCl_2$	1.6×10^{-5}
$Fe_4[Fe(CN)_6]_3$	3.3×10^{-41}	$PbCrO_4$	2.8×10^{-13}
$Fe(OH)_3$	4×10^{-38}	PbF_2	2.7×10^{-8}
$FePO_4$	1.3×10^{-22}	$Pb(OH)_2$	1.2×10^{-15}
Magnesium Compounds		PbI_2	7.1×10^{-9}
$Mg_3(AsO_4)_2$	2.1×10^{-20}	PbC_2O_4	4.8×10^{-10}
$MgCO_3$	3.5×10^{-8}	$PbHPO_4$	1.3×10^{-10}
$MgCO_3 \cdot 3H_2O^3$	2.1×10^{-5}	$Pb_3(PO_4)_2$	8.0×10^{-43}
$MgC_2O_4 \cdot 2H_2O^3$	1×10^{-8}	$PbSeO_4$	1.4×10^{-7}
MgF_2	6.5×10^{-9}	$PbSO_4$	1.6×10^{-8}
$Mg(OH)_2$	1.8×10^{-11}	$Pb(SCN)_2$	2.0×10^{-5}
$Mg_3(PO_4)_2$	10^{-23} to 10^{-27}	*Manganese Compounds*	
$MgSeO_3$	1.3×10^{-5}	$Mn_3(AsO_4)_2$	1.9×10^{-29}
$MgSO_3$	3.2×10^{-3}	$MnCO_3$	1.8×10^{-11}
$MgNH_4PO_4$	2.5×10^{-13}	$Mn_2[Fe(CN)_6]$	8.0×10^{-13}
Mercury Compounds		$Mn(OH)_2$	1.9×10^{-13}
Hg_2Br_2	5.6×10^{-23}	$MnC_2O_4 \cdot 2H_2O^3$	1.1×10^{-15}
Hg_2CO_3	8.9×10^{-17}	*Nickel Compounds*	
$Hg_2(CN)_2$	5×10^{-40}	$Ni_3(AsO_4)_2$	3.1×10^{-26}
Hg_2Cl_2	1.3×10^{-18}	$NiCO_3$	6.6×10^{-9}
Hg_2CrO_4	2.0×10^{-9}	$2\ Ni(CN)_2 \rightarrow Ni^{2+} + Ni(CN)_4^{2-}$	1.7×10^{-9}
$Hg_2(OH)_2$	2.0×10^{-24}	$Ni_2[Fe(CN)_6]$	1.3×10^{-15}
Hg_2I_2	4.5×10^{-29}	$Ni(OH)_2$ fresh	2.0×10^{-15}
Hg_2SO_4	7.4×10^{-7}	NiC_2O_4	4×10^{-10}
Hg_2SO_3	1.0×10^{-27}	$Ni_3(PO_4)_2$	5×10^{-31}
$Hg(OH)_2$	3.0×10^{-26}	*Silver Compounds*	
Strontium Compounds		Ag_3AsO_4	1.0×10^{-22}
$Sr_3(AsO_4)_2$	8.1×10^{-19}	$AgBr$	5.0×10^{-13}
$SrCO_3$	1.1×10^{-10}	Ag_2CO_3	8.1×10^{-12}
$SrCrO_4$	2.2×10^{-5}	$AgCl$	1.8×10^{-10}

Substance	K_s	Substance	K_{sp}
$SrC_2O_4 \cdot H_2O$[3]	1.6×10^{-7}	Ag_2CrO_4	1.1×10^{-12}
$Sr_3(PO_4)_2$	4.0×10^{-28}	AgCN	1.2×10^{-16}
$SrSO_3$	4×10^{-8}	$Ag_2Cr_2O_7$	2.0×10^{-7}
$SrSO_4$	3.2×10^{-7}	$Ag_4[Fe(CN)_6]$	1.6×10^{-41}
Tin Compounds		AgOH	2.0×10^{-8}
$Sn(OH)_2$	1.4×10^{-28}	AgI	8.3×10^{-17}
$Sn(OH)_4$	1×10^{-56}	Ag_3PO_4	1.4×10^{-16}
Zinc Compounds		Ag_2SO_4	1.4×10^{-5}
$Zn_3(AsO_4)_2$	1.3×10^{-28}	Ag_2SO_3	1.5×10^{-14}
$ZnCO_3$	1.4×10^{-11}	AgSCN	1.0×10^{-12}
$Zn_2[Fe(CN)_6]$	4.0×10^{-16}		
$Zn(OH)_2$	1.2×10^{-17}		
ZnC_2O_4	2.7×10^{-8}		
$Zn_3(PO_4)_2$	9.0×10^{-33}		

1. Taken from Patnaik, Pradyot, Dean's Analytical Chemistry Handbook, 2nd ed., New York: McGraw-Hill, 2004, Table 4.2 (published on the Web by Knovel, http://www.knovel.com).

2. Taken from Meites, L. ed., Handbook of Analytical Chemistry, 1st ed., New York: McGraw-Hill, 1963.

3. Because $[H_2O]$ does not appear in equilibrium constants for equilibria in aqueous solution in general, it does not appear in the K_{sp} expressions for hydrated solids.

No metal sulfides are listed in this table because sulfide ion is such a strong base that the usual solubility product equilibrium equation does not apply. See Myers, R. J. *Journal of Chemical Education*, Vol. 63, 1986; pp. 687-690.

Example 14.11.1: Equilibrium

When crystals of $PbCl_2$ are shaken with water at 25°C, it is found that 1.62×10^{-2} mol $PbCl_2$ dissolves per cubic decimeter of solution. Find the value of K_{sp} at this temperature.

Solution

We first write out the equation for the equilibrium:

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) = 2\mathrm{Cl^-}(aq)$$

so that

$$\mathrm{K}_{sp}\mathrm{PbCl_2} = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2$$

Since 1.62×10^{-2} mol $PbCl_2$ dissolves per cubic decimeter, we have

$$[\mathrm{Pb^{2+}}] = 1.62 \times 10^{-2} \mathrm{mol\ L^{-1}}$$

while

$$[\mathrm{Cl^-}] = 2 \times 1.62 \times 10^{-2} \mathrm{mol\ L^{-1}}$$

since 2 mol Cl^- ions are produced for each mol $PbCl_2$ which dissolves. Thus

$$K_{sp} = (1.62 \times 10^{-2}\text{mol L}^{-1})(2 \times 1.62 \times 10^{-2}\text{mol L}^{-1})^{2} \tag{14.11.6}$$

$$= 1.70 \times 10^{-5} \text{ mol}^3\text{L}^{-3} \tag{14.11.7}$$

Example 14.11.2: Solubility

The solubility product of silver chromate, Ag_2CrO_4, is 1.0×10^{-12} mol^3 L^{-3}. Find the solubility of this salt.

Solution

Again we start by writing the equation

$$\text{Ag}_2\text{CrO}\ (s) \rightleftharpoons 2\text{Ag}^{2+}(aq) + \text{CrO}_4^{2-}(aq)$$

from which

$$K_{sp}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 1.0 \times 10^{-12}\text{mol}^3\text{L}^{-3}$$

Let the solubility be x mol L^{-1}. Then

$$[\text{CrO}_4^{2-}] = x \text{ mol L}^{-1}$$

and

$$[\text{Ag}^+] = 2x\text{mol L}^{-1}$$

Thus

$$K_{sp} = (2x \text{ mol L}^{-1})^2 x \text{ mol L}^{-1} \tag{14.11.8}$$

$$= (2x)^2 x \text{ mol}^3 \text{ L}^{-3} = 1.0 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3} \tag{14.11.9}$$

or

$$4x^3 = 1.0 \text{ x } 10^{-12}$$

and

$$x^3 = \frac{1.0}{4} \times 10^{12} = 2.5 \times 10^{-13} = 250 \times 10^{-15}$$

so that

$$x = \sqrt[3]{250} \times \sqrt[3]{10^{-15}} = 6.30 \times 10^{-5}$$

Thus the solubility is 6.30×10^{-5} mol L^{-1}.