SECTION 19.3. Slightly Soluble Ionic Compounds

A very soluble ionic salt (*e.g.,* NaCl) dissolves and completely dissociates into Na^+ (aq) and Cl^- (aq). However, some salts are only slightly soluble, and an equilibrium exists between dissolved and undissolved compound. Consider the addition of $PbSO_4$ (s) to water.

$$PbSO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

If the reaction hasn't reached equilibrium, the reaction quotient Q_c is

$$Q_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

The concentration of a solid (= its density) is a constant $\therefore$ combine it with Q_c.

$$Q_c\,[PbSO_4] = Q_{sp} = [Pb^{2+}][SO_4^{2-}]$$

Q_{sp} = "ion-product expression". At equilibrium, $Q_{sp} = K_{sp}$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

K_{sp} = "Solubility Product Constant" or just "Solubility Product"

K_{sp}, like other equilibrium constants, only depends on temperature.

For any salt $M_pX_q\,(s) \rightleftharpoons pM^{n+}\,(aq) + qX^{z-}\,(aq)$

$$\boxed{K_{sp} = [M^{n+}]^p[X^{z-}]^q}$$

Examples:

$Cu(OH)_2\ (s) \rightleftharpoons Cu^{2+}\ (aq) + 2\ OH^-\ (aq)$ $K_{sp} = [Cu^{2+}][OH^-]^2$

$CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$ $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3\ Ca^{2+}\ (aq) + 2\ PO_4^{3-}\ (aq)$ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Special case of metal sulfides: The S^{2-} (aq) anion, a weak base (but one of the strongest weak bases) is very unstable in water and undergoes (~100%) a base-dissociation reaction to give HS^- (aq) and OH^- (aq).

$$S^{2-}\ (aq) + H_2O\ (l) \rightarrow HS^-\ (aq) + OH^-\ (aq)$$

∴ the solubility equilibrium when MnS (s) is dissolved in water is

$$MnS\ (s) + H_2O\ (l) \rightleftharpoons Mn^{2+}\ (aq) + HS^-\ (aq) + OH^-\ (aq)$$

$$\therefore K_{sp} = [Mn^{2+}][HS^-][OH^-]$$

**** Now, the greater is K_{sp}, the more soluble the substance is. ****

e.g.,	$PbSO_4$	$K_{sp} = 1.6 \times 10^{-8}$	insoluble
	$CoCO_3$	$K_{sp} = 1.0 \times 10^{-10}$	more insoluble (or less soluble)
	$Fe(OH)_2$	$K_{sp} = 4.1 \times 10^{-15}$	most insoluble (or least soluble)

Table 19.2

Table 19.2 Solubility-Product Constants (K_{sp}) of Selected Ionic Compounds at 25°C

Name, Formula	K_{sp}
Aluminum hydroxide, $Al(OH)_3$	3×10^{-34}
Cobalt(II) carbonate, $CoCO_3$	1.0×10^{-10}
Iron(II) hydroxide, $Fe(OH)_2$	4.1×10^{-15}
Lead(II) fluoride, PbF_2	3.6×10^{-8}
Lead(II) sulfate, $PbSO_4$	1.6×10^{-8}
Mercury(I) iodide, Hg_2I_2	4.7×10^{-29}
Silver sulfide, Ag_2S	8×10^{-48}
Zinc iodate, $Zn(IO_3)_2$	3.9×10^{-6}

Table 19.3 Relationship Between K_{sp} and Solubility at 25°C

No. of Ions	Formula	Cation/Anion	K_{sp}	Solubility (*M*)
2	$MgCO_3$	1/1	$3.5x10^{-8}$	$1.9x10^{-4}$
2	$PbSO_4$	1/1	$1.6x10^{-8}$	$1.3x10^{-4}$
2	$BaCrO_4$	1/1	$2.1x10^{-10}$	$1.4x10^{-5}$
3	$Ca(OH)_2$	1/2	$6.5x10^{-6}$	$1.2x10^{-2}$
3	BaF_2	1/2	$1.5x10^{-6}$	$7.2x10^{-3}$
3	CaF_2	1/2	$3.2x10^{-11}$	$2.0x10^{-4}$
3	Ag_2CrO_4	2/1	$2.6x10^{-12}$	$8.7x10^{-5}$

**** The *higher* the K_{sp} value, the *greater* the solubility, as long as we compare compounds that have the *same total number of ions* in their formulas. ****

Calculations Involving Solubility Products

Two types: Use K_{sp} to find concs of dissolved ions
Use concs to find K_{sp}.

Example: The solubility of Ag_2CO_3 is 0.032 M at 20 °C. What is its K_{sp}?

A common type of question - note that we are told the molar solubility of Ag_2CO_3, but of course it will dissociate into ions. Therefore,

	Ag_2CO_3 (s)	→	2 Ag^+ (aq)	+	CO_3^{2-} (aq)
[init]	(solid)		0		0
[change]	-0.032 M		+0.064		+0.032
[equil]	(solid)		0.064 M		0.032 M

$$K_{sp} = [Ag^+]^2[CO_3] = (0.064)^2(0.032)$$

$$\boxed{K_{sp} = 1.3 \times 10^{-4}}$$

Example: The solubility of Zn (oxalate) is 7.9×10^{-3} M at 18 °C. What is its K_{sp}?

	Zn (ox)	⇌	Zn^{2+} (aq)	+	ox^{2-} (aq)
[init]	(solid)	-			
[change]	-7.9×10^{-3} M		$+7.9 \times 10^{-3}$		$+7.9 \times 10^{-3}$
[equil]	(solid)		7.9×10^{-3} M		7.9×10^{-3} M

$$K_{sp} = [Zn^{2+}][ox] = (7.9 \times 10^{-3})^2 \qquad \boxed{K_{sp} = 6.2 \times 10^{-5}}$$

Example: What is the molar solubility of $SrCO_3$? ($K_{sp} = 5.4 \times 10^{-10}$)

	$SrCO_3$ (s)	$\rightleftharpoons$ Sr^{2+} (aq)	+ CO_3^{2-} (aq)
[init]	(solid)	0	0
change	-x	+x	+x
[equil]	(solid)	x	x

$K_{sp} = x^2$ ∴ $x =$ ∴ $x = 2.3 \times 10^{-5}$ M

∴ Solubility of $SrCO_3$ is 2.3×10^{-5} M

Example: What is the molar solubility of $Ca(OH)_2$? ($K_{sp} = 6.5 \times 10^{-6}$).

	$Ca(OH)_2$ (s)	$\rightleftharpoons$ Ca^{2+} (aq)	+ 2 OH^- (aq)
[init]	(solid)	0	0
change	-x	+x	+2x
[equil]	(solid)	x	2x

$K_{sp} = 6.5 \times 10^{-6} = x(2x)^2 = 4x^3$ (careful!)

∴ Solubility of $Ca(OH)_2 = 1.2 \times 10^{-2}$ M

To obtain the $\sqrt[x]{\ }$ of a number, learn to use the $\sqrt[x]{\ }$ button on your calculator, **or** take the log, divide by x, then antilog.

The Effect of a Common Ion on Solubility

Addition of a common ion decreases solubility - due to Le Chatelier's principle.

$$PbCrO_4\ (s) \rightleftharpoons Pb^{2+}\ (aq) + CrO_4^{2-}\ (aq)$$

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.3 \times 10^{-13}$$

Consider this $PbCrO_4$ system at equilibrium. If we dissolve some Na_2CrO_4 (s) (very soluble) in the solution, what will happen? $[CrO_4^{2-}]$ will increase, because the Na_2CrO_4 will dissociate to give more CrO_4^{2-}.

$$Na_2CrO_4\ (s) \xrightarrow{100\%} 2\ Na^{+}\ (aq) + CrO_4^{2-}\ (aq)$$

The K_{sp} for $PbCrO_4$ tells us that $[Pb^{2+}][CrO_4^{2-}]$ is a constant ∴ if $[CrO_4^{2-}]$ increases, $[Pb^{2+}]$ must decrease. How can that happen? Some $PbCrO_4$ (s) precipitates from solution, *i.e.*, **the equilibrium shifts to the left.**

$$PbCrO_4\ (s) \rightleftharpoons Pb^{2+}\ (aq) + CrO_4^{2-}\ (aq)$$

$$\overset{\textstyle\longleftarrow}{\text{Shift}} \qquad \text{add } CrO_4^{2-}$$

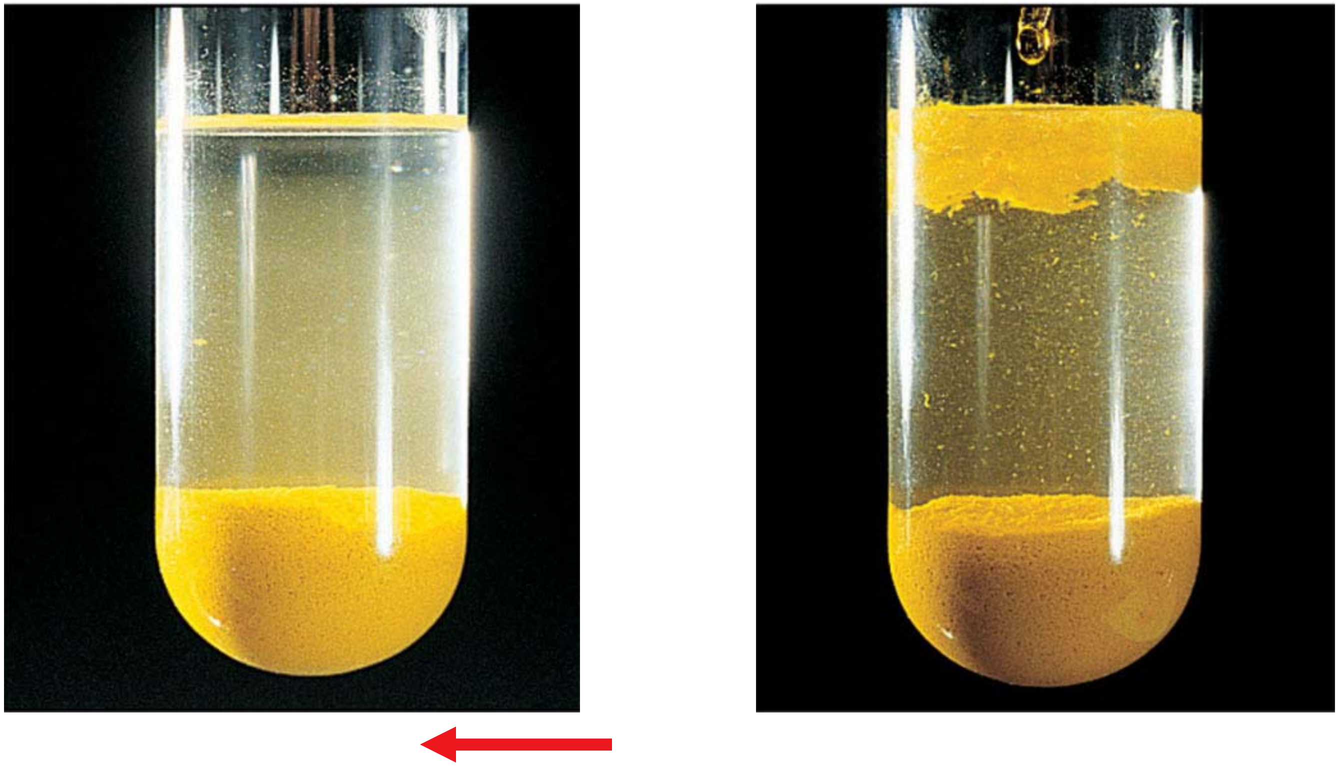
The equilibrium will shift to the left (*i.e.*, more $PbCrO_4$ (s) will form) until $[Pb^{2+}]_{new}[CrO_4^{2-}]_{new} = K_{sp} = 2.3 \times 10^{-13}$.

**** i.e. $PbCrO_4$ is less soluble in aqueous Na_2CrO_4 solution than in pure water. ****

Similarly, addition of a soluble source of Pb^{2+} (*e.g.*, $Pb(NO_3)_2$) to a solution of $PbCrO_4$ will increase $[Pb^{2+}]$ and cause $PbCrO_4$ (s) to precipitate from solution.

Fig 19.12

Figure 19.12 The effect of a common ion on solubility.



$$\boxed{PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)}$$

If Na_2CrO_4 solution is added to a saturated solution of $PbCrO_4$, it provides the ***common ion*** CrO_4^{2-}, causing the equilibrium to shift to the left. Solubility ***decreases*** and solid $PbCrO_4$ precipitates.

To understand this, let's make up an example that will use more convenient numbers. Imagine a solid MX with K_{sp} = 100.

$$MX\ (s) \rightleftharpoons M^+\ (aq) + X^-\ (aq)$$

at equilibrium, $[M^+] = 10.0$ M $[X^-] = 10.0$ M $\therefore K_{sp} = 10.0 \times 10.0 = 100$

(i.e MX(s) will dissolve until $[M^+]=[X^-] = 10.0$M because $K_{sp} = [M^+][X^-]=100$)

Now, let's add enough very soluble NaX to make new $[X^-] = 20$ M, *i.e.,* we double $[X^-]$.

now $[M^+][X^-] = 10.0 \times 20.0 = 200 = Q_{sp} \neq K_{sp}$.

Reaction no longer at equilibrium ∴ shifts to the left until it returns to equilibrium ∴ more MX (s) forms, decreasing $[M^+]$ and $[X^-]$.

When	$[M^+] = 10$M	$[X^-] = 20$M	$Q_{sp} = 200 \neq K_{sp}$
	$[M^+] = 9$M	$[X^-] = 19$M	$Q_{sp} = 171 \neq K_{sp}$
	$[M^+] = 8$M	$[X^-] = 18$M	$Q_{sp} = 144 \neq K_{sp}$
	$[M^+] = 7$M	$[X^-] = 17$M	$Q_{sp} = 119 \neq K_{sp}$
	$[M^+] = 6.5$M	$[X^-] = 16.5$M	$Q_{sp} = 107 \neq K_{sp}$
	$[M^+] = 6.2$M	$[X^-] = 16.2$ M	$Q_{sp} = 100 = K_{sp}$

∴ reaction at equilibrium again with new $[M^+] = 6.2$ M, new $[X^-] = 16.2$ M

Compare with old $[M^+] = 10.0$ M, new $[X^-] = 10.0$ M

$$Q_{sp} = [M^+][X^-] = (6.2)(16.2) = 100 = K_{sp}.$$

Remember: Le Chatelier's principle tells us that if we perturb a reaction at equilibrium, it will shift in a direction that allows it to reach equilibrium again.

Effect of pH on Solubility

Similar to the previous section, if a compound contains the anion of a weak acid, addition of H_3O^+ (from a strong acid) increases its solubility.

Why? Le Chatelier's principle again.

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

Addition of H_3O^+ causes the $[CO_3^{2-}]$ to decrease.

$$CO_3^{2-}\,(aq) + H_3O^+\,(aq) \rightarrow HCO_3^-\,(aq) + H_2O$$

$$\therefore CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

$$\xrightarrow[\text{Shift}]{} \qquad \text{if } [CO_3^{2-}] \text{ decreases}$$

i.e., when we decrease $[CO_3^{2-}]$ (by adding H_3O^+), reaction will shift to the right to make more CO_3^{2-} and restore equilibrium.

Figure 19.13 Test for the presence of a carbonate.

When a carbonate mineral is treated with HCl, bubbles of CO_2 form

$$HCO_3^- (aq) + H_3O^+ (aq) \rightarrow H_2CO_3 (aq) + H_2O$$

$$H_2CO_3 (aq) \rightarrow CO_2 (g) + H_2O.$$

Predicting the Formation of a Precipitate: $Q_{sp} = K_{sp}$

Three possibilities:

(a) If $Q_{sp} = K_{sp}$, reaction at equilibrium, no change.

(b) If $Q_{sp} > K_{sp}$, reaction not at equilibrium

$\therefore$ [ ] of ions in solution too high

$\therefore$ solid (precipitate) forms until $Q_{sp} = K_{sp}$

(c) If $Q_{sp} < K_{sp}$, reaction not at equilibrium

$\therefore$ [ ] of ions in solution too low

$\therefore$ no solid (precipitate) forms, i.e. nothing happens

Example: Will a precipitate form if 0.100 L of 0.30 M $Ca(NO_3)_2$ is mixed with 0.200 L of 0.060 M NaF?

Method: Calculate Q_{sp} and compare with K_{sp}.

First: What is the sparingly soluble salt? $NaNO_3$, like all Na^+ and NO_3^- salts, is very soluble in water ∴ it must be CaF_2.

$$\therefore\ CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

$$K_{sp} = [Ca^{2+}][F^-]^2 \quad \therefore \text{ need } [Ca^{2+}] \text{ and } [F^-].$$

(a) We start with 0.30 M $Ca(NO_3)_2$ = 0.30 M $[Ca^{2+}]$ (~100% dissociation)
(b) We start with 0.060 M NaF = 0.060 M $[F^-]$ (~100% dissociation)

-- but we are mixing two solutions, therefore both will be diluted.

Remember: $M_iV_i = M_fV_f$ (i = initial, f = final)

$$\therefore [Ca^{2+}]_f = \frac{[Ca^{2+}]_i V_i}{V_f} = \frac{(0.30\,M)(0.100\,L)}{(0.200\,L + 0.100\,L)} \qquad \therefore \mathbf{[Ca^{2+}]_f = 0.10\ M}$$

$$[F^-]_f = \frac{[F^-]_i V_i}{V_f} = \frac{(0.060\,M)(0.200\,L)}{(0.300\,L)} \qquad \therefore \mathbf{[F^-]_f = 0.040\ M}$$

$Q_{sp} = [Ca^{2+}][F^-]^2 = (0.10)(0.040)^2 = 1.6 \times 10^{-4}$
$K_{sp} = 3.2 \times 10^{-11}$ ∴ $Q_{sp} > K_{sp}$

∴ CaF_2 (s) precipitates until $Q_{sp} = K_{sp}$

Section 19.4 Solubility Equilibria involving Complex Ions

AgCl (s) is only slightly soluble, and it does NOT become more soluble if we lower the pH (because Cl^- is the conjugate base of a strong acid and therefore does not bind the added H^+)

BUT, AgCl (s) becomes much more soluble if we add NH_3 to the solution. Why? - because the NH_3 reacts with the Ag^+ (aq) (Lewis acid/Lewis base reaction) to give a complex ion $[Ag(NH_3)_2]^+$. Consider what happens as two steps:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \qquad K_{sp} = 1.8 \times 10^{-10} \text{ (v. small)}$$

$$Ag^+\,(aq) + 2\,NH_3\,(aq) \rightleftharpoons [Ag(NH_3)_2]^+ \qquad K = K_{form} = 1.6 \times 10^{7}$$

**** The equilibrium constant of a reaction which is the formation of a complex ion is called the "formation constant", K_{form} or K_f ****

So, the overall reaction that occurs when AgCl is dissolved in water with NH_3 also present is

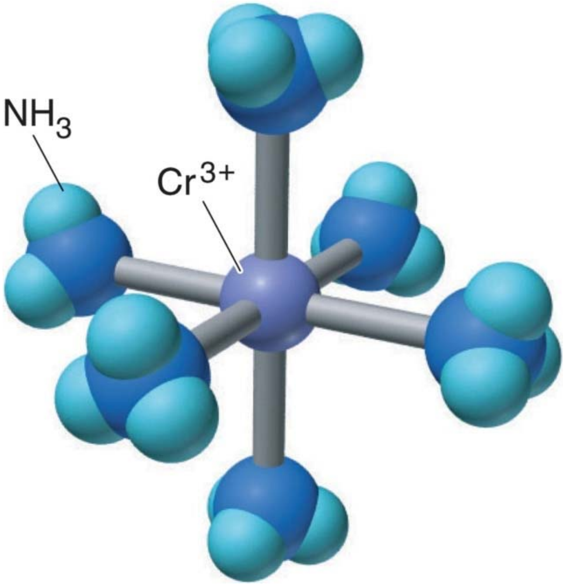
$$AgCl\,(s) + 2\,NH_3\,(aq) \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-\,(aq) \qquad (K_{net})$$

The net K_c for this (K_{net}) is the product of the K_{sp} and K_{form} i.e. the K's of the individual two steps.

$$\therefore K_{net} = K_{sp} \times K_f = (1.8 \times 10^{-10})(1.6 \times 10^{7}) = 2.9 \times 10^{-3}$$

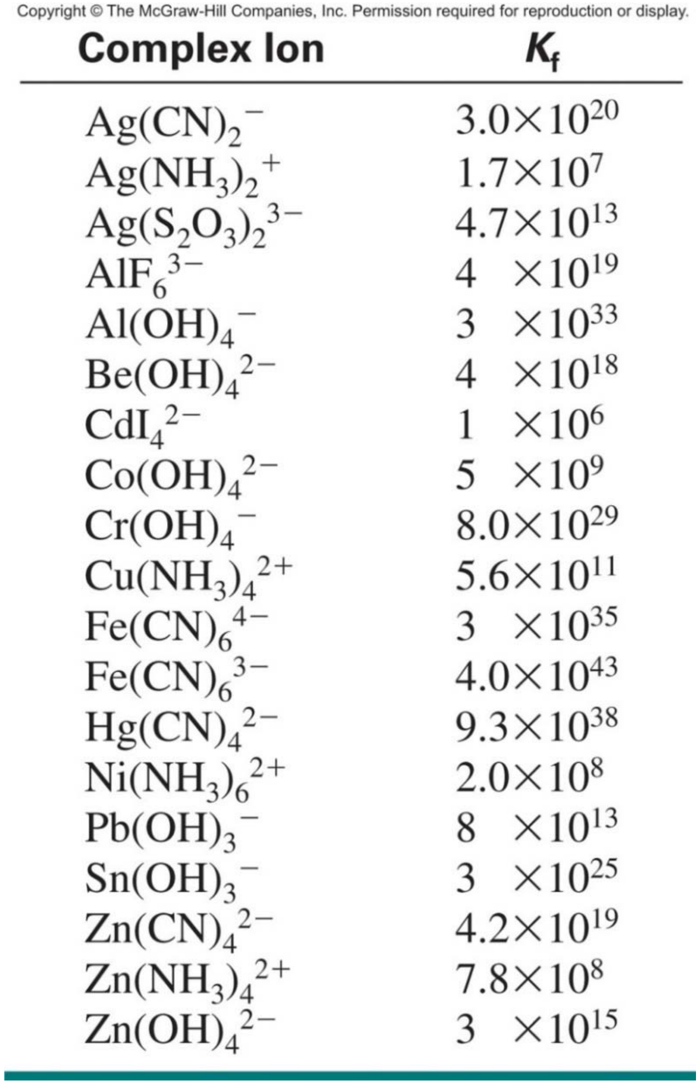
$\therefore$ therefore the solubility of the AgCl (s) is indeed much greater when NH_3 is also present, since $K_{net} >> K_{sp}$ (by 10 million times !)

Figure 19.15 $Cr(NH_3)_6^{3+}$, a typical complex ion.



A ***complex ion*** consists of a central metal ion covalently bonded to two or more anions or molecules, called ***ligands***.

Table 19.4 Formation Constants (K_f) of Some Complex Ions at 25°C



Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Ag(NH_3)_2^+$	1.7×10^{7}
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}
AlF_6^{3-}	4×10^{19}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
CdI_4^{2-}	1×10^{6}
$Co(OH)_4^{2-}$	5×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Fe(CN)_6^{4-}$	3×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(CN)_4^{2-}$	4.2×10^{19}
$Zn(NH_3)_4^{2+}$	7.8×10^{8}
$Zn(OH)_4^{2-}$	3×10^{15}