Chemistry – Matter and Its Changes 4/e
Brady • Senese

Chapter 19:

Solubility and Simultaneous Equilibria

Reference: Chapter 15 in "*Chemistry*" 6/e
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19.1 An insoluble salt is in equilibrium with the solution around it

For solids dissolving to form aqueous solutions

例如 $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

$K_{sp} =$

K_{sp} = solubility product constant

The is the product of the molar concentrations of the dissolved ions of the solute.

- **effect (共同離子效應)**: The shift in equilibrium that occurs because of the addition of an ion already involved in the equilibrium reaction.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$\xleftarrow[\text{adding NaCl}(aq)\text{ shifts equilibrium position}]{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

- K_{sp} can be used to determine if a precipitation will occur:
  - If the ion product K_{sp}, the solution is *supersaturated* and a precipitate will form.
  - If the ion product K_{sp}, the solution is *saturated* and no precipitate will form.
  - If the ion product K_{sp}, the solution is *unsaturated* and no precipitate will form.

- **Solubility (s) vs. solubility product (K_{sp})**

K_{sp} is (at a given temperature)

s is (especially with a common ion present)

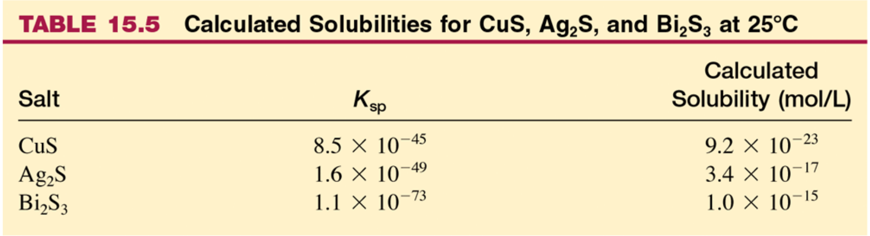


TABLE 15.5 Calculated Solubilities for CuS, Ag_2S, and Bi_2S_3 at 25°C

Salt	K_{sp}	Calculated Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

Precipitation of bismuth sulfide (Bi_2S_3).

- K_{sp} can be calculated by determining the molar solubility or *the number of moles of salt dissolved in one liter of the solution.*

➢Example: The molar solubility of PbF_2 in a 0.10 *M* $Pb(NO_3)_2$ solution at 25°C is 3.1×10^{-4} mol L^{-1}. What is K_{sp} for PbF_2?

SOLUTION:

$$PbF_2(s) \rightleftarrows Pb^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Pb^{2+}][F^-]^2$$

I	0.10	0	$= (0.10 + x)(2x)^2$
C	$+x$	$+2x$	
E	$0.10 + x$	$2x$	

but x is the molar solubility so that

$$K_{sp} = (0.10 + x)(2x)^2 = (0.10 + 3.1\times10^{-4})(2\times3.1\times10^{-4})^2$$

$$= 3.9\times10^{-8} \quad \text{(the value from Table 19.1 is } 3.6\times10^{-8}\text{)}$$

- Molar solubility can be calculated from K_{sp}.

- Example: What is the molar solubility of PbI_2 in 0.10 *M* NaI?

SOLUTION:

$$PbI_2(aq) \rightleftarrows Pb^{2+}(aq) + 2I^-(aq) \qquad K_{sp} = [Pb^{2+}][I^-]^2$$

$$= 7.9\times10^{-9}$$

$$\text{(from Table 19.1)}$$

I

C

E

Example 19.1 ~ 19.8

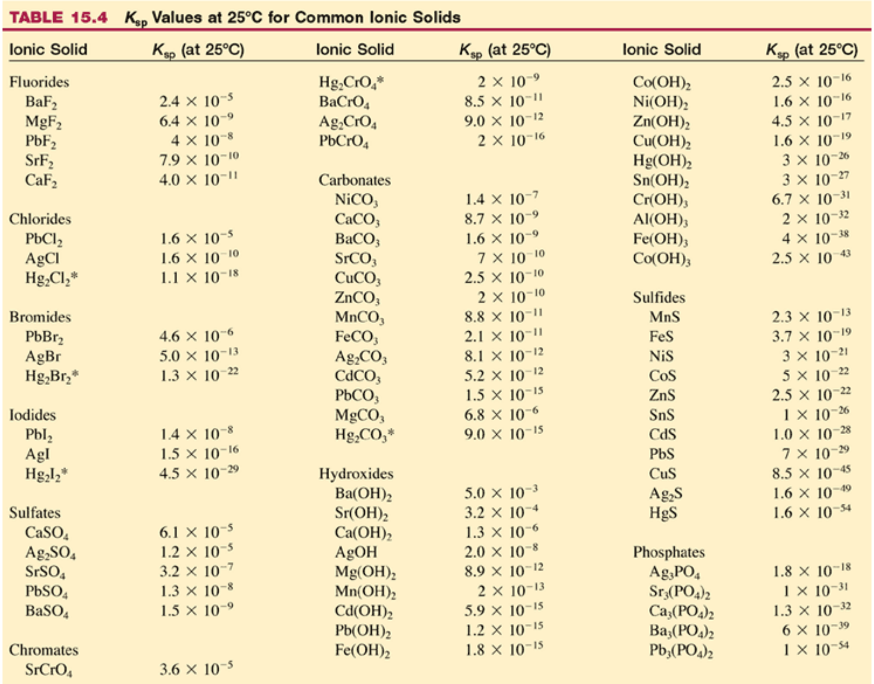


TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		Hg_2CrO_4*	2×10^{-9}	$Co(OH)_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	$BaCrO_4$	8.5×10^{-11}	$Ni(OH)_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$Zn(OH)_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	$PbCrO_4$	2×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$Hg(OH)_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	Carbonates		$Sn(OH)_2$	3×10^{-27}
		$NiCO_3$	1.4×10^{-7}	$Cr(OH)_3$	6.7×10^{-31}
Chlorides		$CaCO_3$	8.7×10^{-9}	$Al(OH)_3$	2×10^{-32}
$PbCl_2$	1.6×10^{-5}	$BaCO_3$	1.6×10^{-9}	$Fe(OH)_3$	4×10^{-38}
$AgCl$	1.6×10^{-10}	$SrCO_3$	7×10^{-10}	$Co(OH)_3$	2.5×10^{-43}
Hg_2Cl_2*	1.1×10^{-18}	$CuCO_3$	2.5×10^{-10}		
		$ZnCO_3$	2×10^{-10}	Sulfides	
Bromides		$MnCO_3$	8.8×10^{-11}	MnS	2.3×10^{-13}
$PbBr_2$	4.6×10^{-6}	$FeCO_3$	2.1×10^{-11}	FeS	3.7×10^{-19}
$AgBr$	5.0×10^{-13}	Ag_2CO_3	8.1×10^{-12}	NiS	3×10^{-21}
Hg_2Br_2*	1.3×10^{-22}	$CdCO_3$	5.2×10^{-12}	CoS	5×10^{-22}
		$PbCO_3$	1.5×10^{-15}	ZnS	2.5×10^{-22}
Iodides		$MgCO_3$	6.8×10^{-6}	SnS	1×10^{-26}
PbI_2	1.4×10^{-8}	Hg_2CO_3*	9.0×10^{-15}	CdS	1.0×10^{-28}
AgI	1.5×10^{-16}			PbS	7×10^{-29}
Hg_2I_2*	4.5×10^{-29}	Hydroxides		CuS	8.5×10^{-45}
		$Ba(OH)_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
Sulfates		$Sr(OH)_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
$CaSO_4$	6.1×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}		
Ag_2SO_4	1.2×10^{-5}	$AgOH$	2.0×10^{-8}	Phosphates	
$SrSO_4$	3.2×10^{-7}	$Mg(OH)_2$	8.9×10^{-12}	Ag_3PO_4	1.8×10^{-18}
$PbSO_4$	1.3×10^{-8}	$Mn(OH)_2$	2×10^{-13}	$Sr_3(PO_4)_2$	1×10^{-31}
$BaSO_4$	1.5×10^{-9}	$Cd(OH)_2$	5.9×10^{-15}	$Ca_3(PO_4)_2$	1.3×10^{-32}
		$Pb(OH)_2$	1.2×10^{-15}	$Ba_3(PO_4)_2$	6×10^{-39}
Chromates		$Fe(OH)_2$	1.8×10^{-15}	$Pb_3(PO_4)_2$	1×10^{-54}
$SrCrO_4$	3.6×10^{-5}				

19.2 Solubility equilibria of metal oxides and sulfides involve reactions with water

- Some metal oxides dissolve in water by reacting with H_2O.

  例如:
- Most water-insoluble metal oxides dissolve in acid.

  例如:
- Water-insoluble metal oxides can form in basic solution.

  例如:

Metal sulfides are similar to metal oxides.

- Some sulfides dissolve by reacting with water

  例如: $Na_2S(s)+H_2O \rightarrow 2Na^+(aq)+HS^-(aq)+OH^-(aq)$
- Some metal ions are so reactive that they react with H_2S directly. These active ions include Cu^{2+}, Pb^{2+}, and Ni^{2+}.

  例如: $Cu^{2+}(aq)+H_2S(aq) \rightleftarrows CuS(s)+2H^+(aq) \quad K=1.7\times10^{15}$

- The solubility of CuS in water is describe by:

$$CuS(s) \rightleftarrows Cu^{2+}(aq) + S^{2-}(aq)$$

But the S^{2-} *reacts* with water so that

$$CuS(s) + H_2O \rightleftarrows Cu^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq)$$

the ion product is now $[Cu^{2+}][HS^{-}][OH^{-}]$ and

$$K_{sp} = [Cu^{2+}][HS^{-}][OH^{-}]$$

- Both OH^- and HS^- would react (to form H_2O and H_2S) in acidic solutions ⇒ a modification to the ion product.

$$CuS(s) + H_2O + 2H^{+}(aq) \rightleftarrows Cu^{2+}(aq) + H_2S(aq) + H_2O$$

removing water

$$CuS(s) + 2H^{+}(aq) \rightleftarrows Cu^{2+}(aq) + H_2S(aq)$$

which is described by the acid solubility product, K_{spa}

$$K_{spa} = \frac{[Cu^{2+}][H_2S]}{[H^{+}]^2}$$

- The metal sulfides can be collected into two groups:
  - The *acid-insoluble* sulfides, which dissolve in neither acidic nor basic solution.
  - The *acid-soluble* or base-insoluble sulfides that dissolve in acidic, but not basic, solutions.

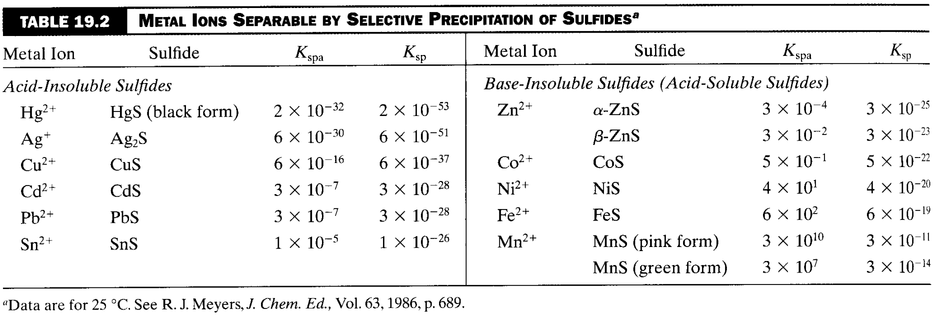
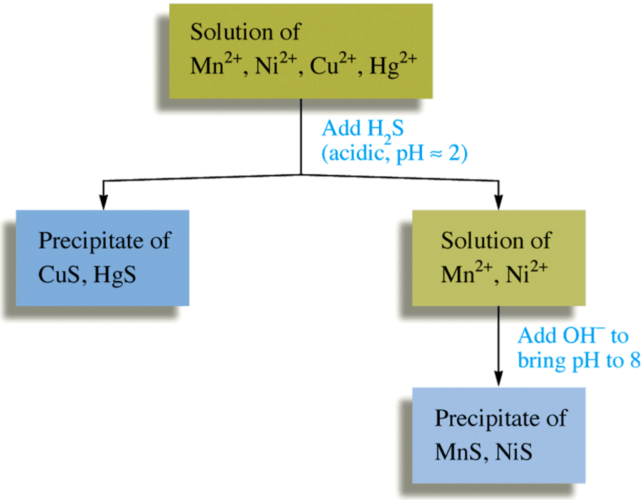


TABLE 19.2 **METAL IONS SEPARABLE BY SELECTIVE PRECIPITATION OF SULFIDES**[a]

Metal Ion	Sulfide	K_{spa}	K_{sp}	Metal Ion	Sulfide	K_{spa}	K_{sp}
Acid-Insoluble Sulfides				*Base-Insoluble Sulfides (Acid-Soluble Sulfides)*			
Hg^{2+}	HgS (black form)	2×10^{-32}	2×10^{-53}	Zn^{2+}	α-ZnS	3×10^{-4}	3×10^{-25}
Ag^{+}	Ag_2S	6×10^{-30}	6×10^{-51}		β-ZnS	3×10^{-2}	3×10^{-23}
Cu^{2+}	CuS	6×10^{-16}	6×10^{-37}	Co^{2+}	CoS	5×10^{-1}	5×10^{-22}
Cd^{2+}	CdS	3×10^{-7}	3×10^{-28}	Ni^{2+}	NiS	4×10^{1}	4×10^{-20}
Pb^{2+}	PbS	3×10^{-7}	3×10^{-28}	Fe^{2+}	FeS	6×10^{2}	6×10^{-19}
Sn^{2+}	SnS	1×10^{-5}	1×10^{-26}	Mn^{2+}	MnS (pink form)	3×10^{10}	3×10^{-11}
					MnS (green form)	3×10^{7}	3×10^{-14}

[a] Data are for 25 °C. See R. J. Meyers, *J. Chem. Ed.*, Vol. 63, 1986, p. 689.

Fig. 15.11: The separation of Cu^{2+} and Hg^{2+} from Ni^{2+} and Mn^{2+} using H_2S.



Solution of Mn^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}

Add H_2S (acidic, pH ≈ 2)

Precipitate of CuS, HgS

Solution of Mn^{2+}, Ni^{2+}

Add OH^- to bring pH to 8

Precipitate of MnS, NiS

19.3 Metal ions can be separated by selective precipitation

- Selective precipitation means causing one metal ion to precipitate while holding the other in solution.
- Selective precipitation by control of pH applies to any system where the anion comes from a weak acid
- Consider the solubility of metal carbonates
  - The amount of $[CO_3^{2-}]$ depends on $[H^+]$:

$$H_2CO_3(aq) \rightleftarrows HCO_3^-(aq) + H^+(aq) \quad K_{a1} = 4.3\times10^{-7}$$
$$HCO_3^-(aq) \rightleftarrows CO_3^{2-}(aq) + H^+(aq) \quad K_{a2} = 4.7\times10^{-11}$$

  - Thus, the $[CO_3^{2-}]$:
    - as pH increases (because $[H^+]$ ↓)
    - as pH decreases (because $[H^+]$ ↑)

Example 19.10

Example 19.9

- Example: Over what range of pH is it possible to selectively precipitate Cu^{2+} and Ni^{2+} as their sulfides from a solution initially 0.010*M* in both ions? ($[H_2S]=0.1M$ in a saturated solution.)

ANALYSIS: Cu^{2+} is an acid-insoluble sulfide ($K_{spa}=6\times10^{-16}$) and Ni^{2+} is a base-insuble sulfide ($K_{spa}=4\times10^{1}$). Thus NiS will dissolve in acidic solution while CuS will not. The pH limits for the precipitation of both sulfides in saturates H_2S must be calculated.

SOLUTION:

Consider CuS first

$$CuS(s) + 2H^+(\text{aq}) \rightleftarrows Cu^{2+}(aq) + H_2S(aq) \quad K_{spa} = \frac{[Cu^{2+}][H_2S]}{[H^+]^2}$$

The Cu^{2+} will stay in solution only if $[H^+]$ is *above*

$$[H^+] = \sqrt{\frac{[Cu^{2+}][H_2S]}{K_{spa}}} = \sqrt{\frac{(0.010)(0.1)}{6\times10^{-16}}} = 1\times10^{6}\,M$$

this $[H^+]$ could never be reached so Cu^{2+} precipitates no matter how acidic the solution is.

Now consider Ni^{2+}

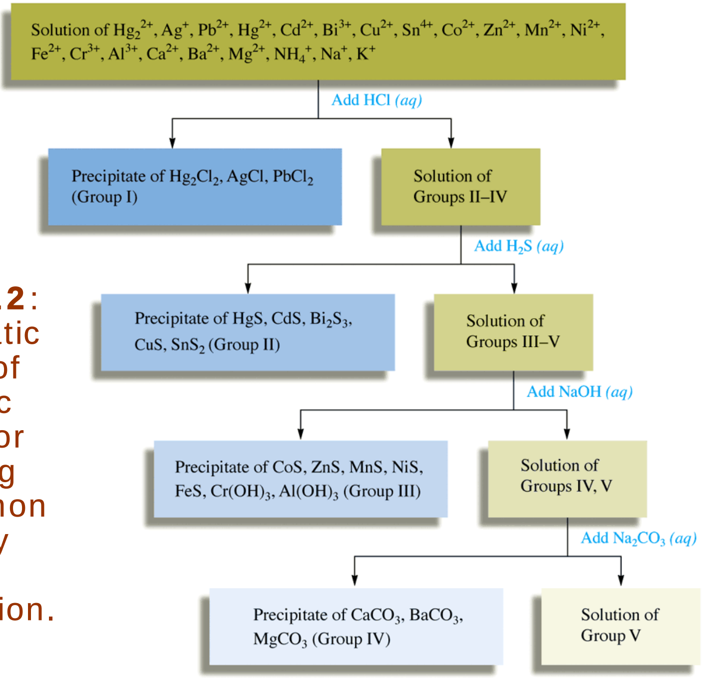
$$NiS(s) + 2H^+(\text{aq}) \rightleftarrows Ni^{2+}(aq) + H_2S(aq) \quad K_{spa} = \frac{[Ni^{2+}][H_2S]}{[H^+]^2}$$

The Ni^{2+} precipitate from solution when $[H^+]$ is *below*

$$[H^+] = \sqrt{\frac{[Ni^{2+}][H_2S]}{K_{spa}}} = \sqrt{\frac{(0.010)(0.1)}{4\times10^{1}}} = 0.005M$$

or a pH > 2.3

Thus, if we maintain the pH of the solution of 0.010 M Cu^{2+} and 0.010 M Ni^{2+} at pH ≤ 2.3, as we make the solution saturated in H_2S, virtually all the Cu^{2+} will precipitate as CuS, but all the Ni^{2+} will stay in solution.



Solution of Hg_2^{2+}, Ag^+, Pb^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, Sn^{4+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}, Cr^{3+}, Al^{3+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+, Na^+, K^+

Add HCl *(aq)*

Precipitate of Hg_2Cl_2, AgCl, $PbCl_2$ (Group I)

Solution of Groups II–IV

Add H_2S *(aq)*

Precipitate of HgS, CdS, Bi_2S_3, CuS, SnS_2 (Group II)

Solution of Groups III–V

Add NaOH *(aq)*

Precipitate of CoS, ZnS, MnS, NiS, FeS, $Cr(OH)_3$, $Al(OH)_3$ (Group III)

Solution of Groups IV, V

Add Na_2CO_3 *(aq)*

Precipitate of $CaCO_3$, $BaCO_3$, $MgCO_3$ (Group IV)

Solution of Group V

Fig. 15.12: A schematic diagram of the classic method for separating the common cations by selective precipitation.

19.4 Complex ions participate in equilibria in aqueous solutions

- **Complex Ion (錯合離子)**: A charged species consisting of a metal ion (Lewis acids) surrounded by ligands (Lewis bases).

  例如: $Cu^{2+} + 4H_2O \rightleftarrows Cu(H_2O)_4^{2+}$

- **Coordination compounds (配位化合物):** Compounds that contain complex ions are called and the complex itself is sometimes called a **coordination complex.**

- **Coordination Number (配位數):** Number of ligands attached to a metal ion. (Most common are)

- **Formation (Stability) Constants:** The equilibrium constants characterizing the stepwise addition of ligands to metal ions. The inverse of the formation constant is called the *instability constant*, K_{inst}.

  例如：

$$Cu(NH_3)_4^{2+}(aq) \rightleftarrows Cu^{2+}(aq) + 4NH_3(aq)$$

$$K_{form} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.1\times10^{13}$$

$$K_{inst} = \frac{1}{K_{form}} = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} = 9.1\times10^{-14}$$

- The solubility of a slightly soluble salt increases when one of its ions can be changed into soluble complex ion.

(left) Aqueous ammonia is added to silver chloride (white). (right) Silver chloride, insoluble in water, dissolves to form $Ag(NH_3)_2^+(aq)$ and $Cl^-(aq)$.

$$AgCl_{(s)} + 2\,NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$$2H^+{}_{(aq)} + Ag(NH_3)_2^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow 2NH_4^+{}_{(aq)} + AgCl_{(s)}$$

- Example: Calculate the solubility of silver chloride in 0.10 *M* NH_3.

SOLUTION:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftarrows Ag(NH_3)_2^+$$

$$K_{form} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.6\times10^7,\ \text{combining}$$

$$AgCl(s) + 2NH_3(aq) \rightleftarrows Ag(NH_3)_2^+ + Cl^-(aq)$$

$$K_c = K_{sp}K_{form} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = 2.9\times10^{-3}$$

$$
\begin{array}{lcccc}
 & AgCl(s)+2NH_3(aq) & \rightleftarrows & Ag(NH_3)_2^+ & +\,Cl^-(aq)\\
\text{I} & 0.10 & & 0 & 0\\
\text{C} & -2x & & +x & +x\\
\text{E} & 0.10\text{-}2x & & x & x
\end{array}
$$

$$K_c=\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}=\frac{x^2}{(0.10-x)^2}=2.9\times10^{-3}$$

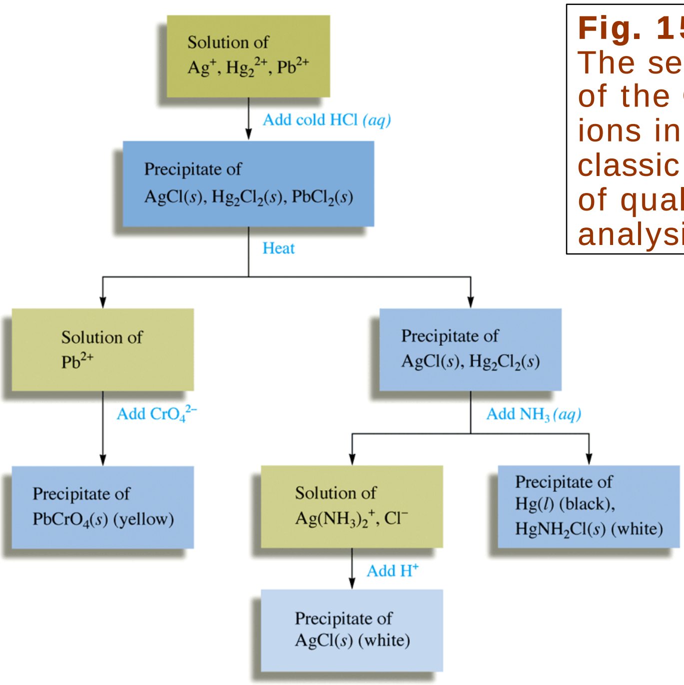
$$\frac{x}{0.10-x}=\sqrt{K_c}=0.054 \text{ or } x=5.1\times10^{-3}M$$

The solubility of AgCl in pure water is $\sqrt{K_{sp}}=1.3\times10^{-5}M$

thus, the solubility is a factor of

$$\frac{5.1\times10^{-3}}{1.3\times10^{-5}}=392 \text{ times larger in } 0.10M \text{ NH}_3$$

Example 19.11



Solution of Ag^+, Hg_2^{2+}, Pb^{2+}

Add cold HCl *(aq)*

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$, $PbCl_2(s)$

Heat

Solution of Pb^{2+}

Add CrO_4^{2-}

Precipitate of $PbCrO_4(s)$ (yellow)

Precipitate of $AgCl(s)$, $Hg_2Cl_2(s)$

Add $NH_3(aq)$

Solution of $Ag(NH_3)_2^+$, Cl^-

Add H^+

Precipitate of $AgCl(s)$ (white)

Precipitate of $Hg(l)$ (black), $HgNH_2Cl(s)$ (white)

Fig. 15.13: The separation of the Group I ions in the classic scheme of qualitative analysis.