Chapter 18: Aqueous Ionic Equilibria III

Solubility equilibria

Chem 102
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Solubility equilibria

- **Solubility:** amount of a solid (usually an ionic compound – a salt) that dissolves in solution. Molar solubility uses mol/L unit.
- **Dynamic equilibrium** between the solid and the solute.
- **Solubility product:** K_{sp} describes the equilibrium, e.g.:

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

$$K_{sp} = [Ca^{2+}][F^-]^2$$

Small K_{sp}: low solubility; Large K_{sp}: high solubility.

Solubility

Even “insoluble” compounds establish a dynamic equilibrium with the ions in solution.

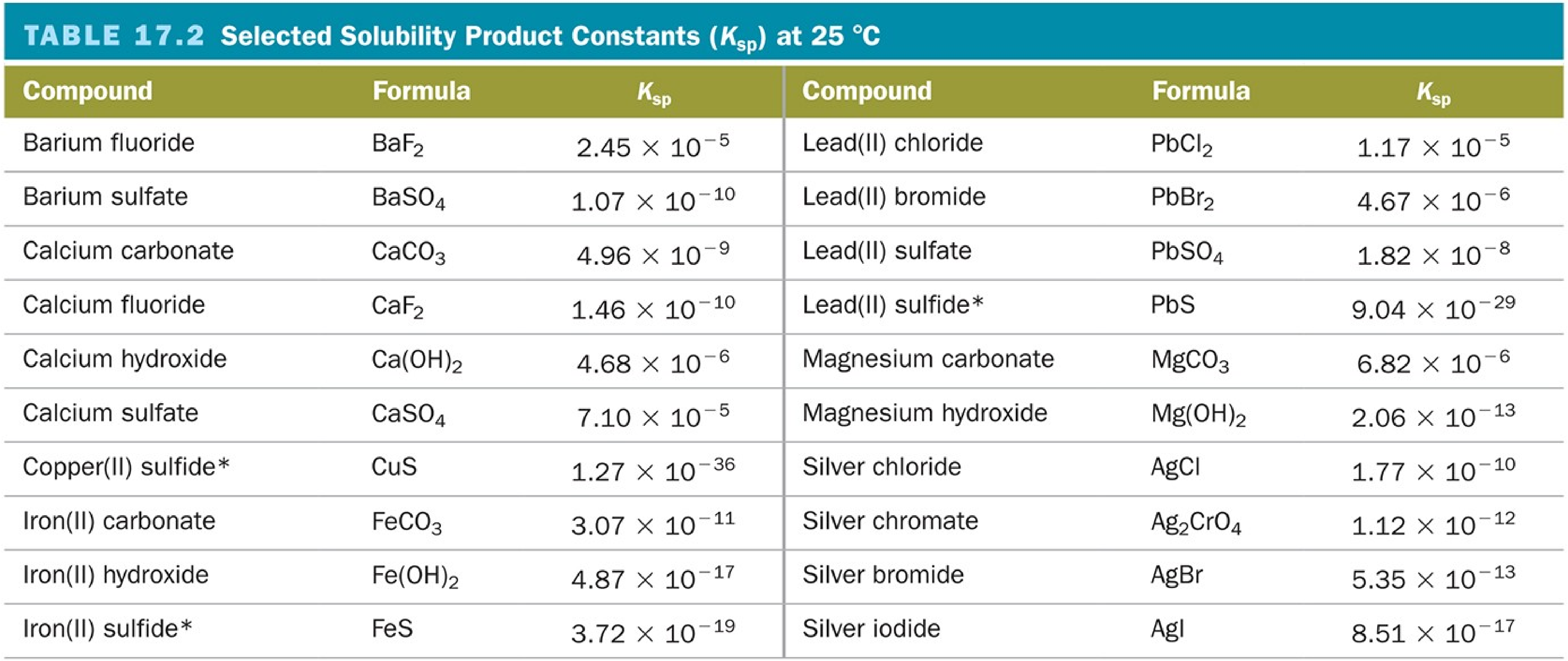


TABLE 17.2 Selected Solubility Product Constants (K_{sp}) at 25 °C

Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	$PbCl_2$	1.17×10^{-5}
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	$PbBr_2$	4.67×10^{-6}
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide*	PbS	9.04×10^{-29}
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
Copper(II) sulfide*	CuS	1.27×10^{-36}	Silver chloride	$AgCl$	1.77×10^{-10}
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	$AgBr$	5.35×10^{-13}
Iron(II) sulfide*	FeS	3.72×10^{-19}	Silver iodide	AgI	8.51×10^{-17}

*Sulfide equilibrium is of the type: $MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$

If $K_{sp} << 1$, the compound is only slightly soluble or insoluble.

If $K_{sp} > 1$, the compound is soluble.

Calculating molar solubility

Set up an ICE chart. *Pure solids don't enter!*

Example. Calculate the molar solubility of AgCl(*s*) in a saturated solution.

	$\mathrm{AgCl(s)}$	$\rightleftharpoons$	$\mathrm{Ag^+(aq)} +$	$\mathrm{Cl^-(aq)}$
I	--		0	0
C	--		+S	+S
E	--		S	S

$$K_{sp} = [Ag^+][Cl^-] = S^2 = 1.77 \times 10^{-10}$$

$$S = 1.33 \times 10^{-5}\ M$$

Calculating molar solubility

Example. What is the molar solubility of lead chloride $PbCl_2$ (K_{sp} = 1.17×10^{-5})?

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

Since this is an equilibrium problem, we'll write an ICE table.

Don't include $PbCl_2$ in the table because it is a solid and won't enter into expression for K_{sp}.

Calculating molar solubility

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

Writing an ICE table:

	$Pb^{2+}(aq)$	$Cl^{-}(aq)$
Initial	0.00	0.00
Change	$+S$	$+2\cdot S$
Equilibrium	S	$2\cdot S$

We’ll use S (for molar solubility) rather than x

Calculating molar solubility

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

Insert into expression for K_{sp}:

$$\begin{aligned} K_{sp} &= [Pb^{2+}]\cdot[Cl^-]^2 \\ 1.17\text{x}10^{-5} &= S\cdot(2\cdot S)^2 \\ &= S\cdot(4\cdot S^2) \\ &= 4\cdot S^3 \end{aligned}$$

$$S = \sqrt[3]{\frac{1.17\text{x}10^{-5}}{4}} = 1.43\text{x}10^{-2}$$

Careful!

Molar solubility = $1.43\text{x}10^{-2}$ mol/L

K_{sp} and Relative Molar Solubility

Care must be taken when comparing K_{sp} values:

		K_{sp}	Molar solubility
3 mol	$Mg(OH)_2$	$2.06\text{x}10^{-13}$	$3.72\text{x}10^{-5}$ M
2 mol	$FeCO_3$	$3.07\text{x}10^{-11}$	$5.54\text{x}10^{-6}$ M

The relationship between K_{sp} and molar solubility depends on the number of moles of ions it produces in water.

K_{sp}’s can only be compared if the same number of moles of ions are made otherwise compare molar solubility.

The common ion effect

If one of the ions from a solid is already in the solution, it will drive the equilibrium left, **reducing** the solubility.

Example. What is the solubility of AgCl in a 0.10 M solution of NaCl?

Equilibrium shifts left

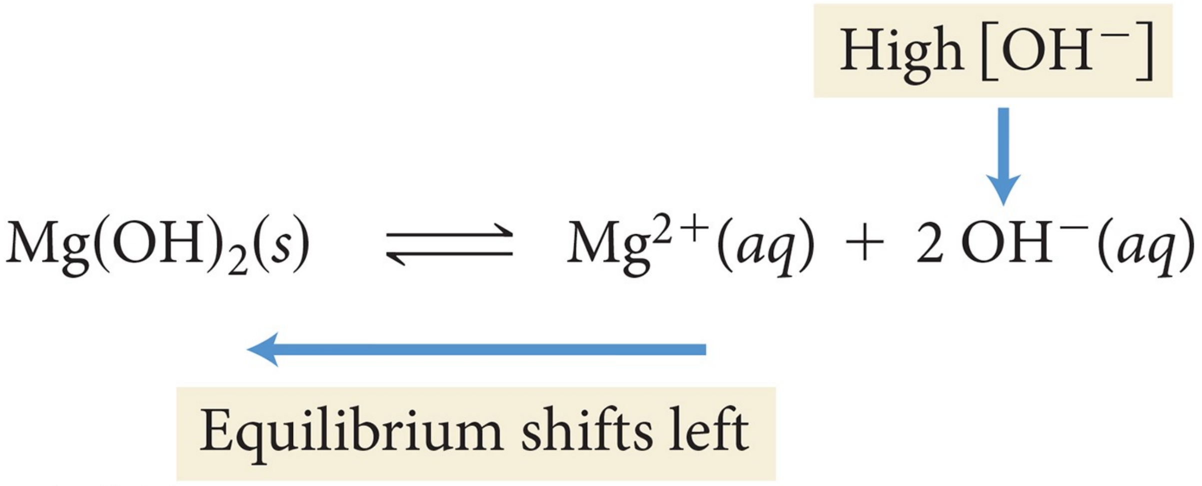
	$\mathrm{AgCl(s)}$	$\rightleftharpoons$	$\mathrm{Ag^+(aq)} +$	$\mathrm{Cl^-(aq)}$
I	--		0	0.10
C	--		+S	+S
E	--		S	0.10+S

$$K_{sp} = [Ag^+][Cl^-] = S(0.10 + S) \approx 0.10S$$

$$S = 1.77 \times 10^{-9}\ M$$

Reduced from 1.33×10^{-5} M

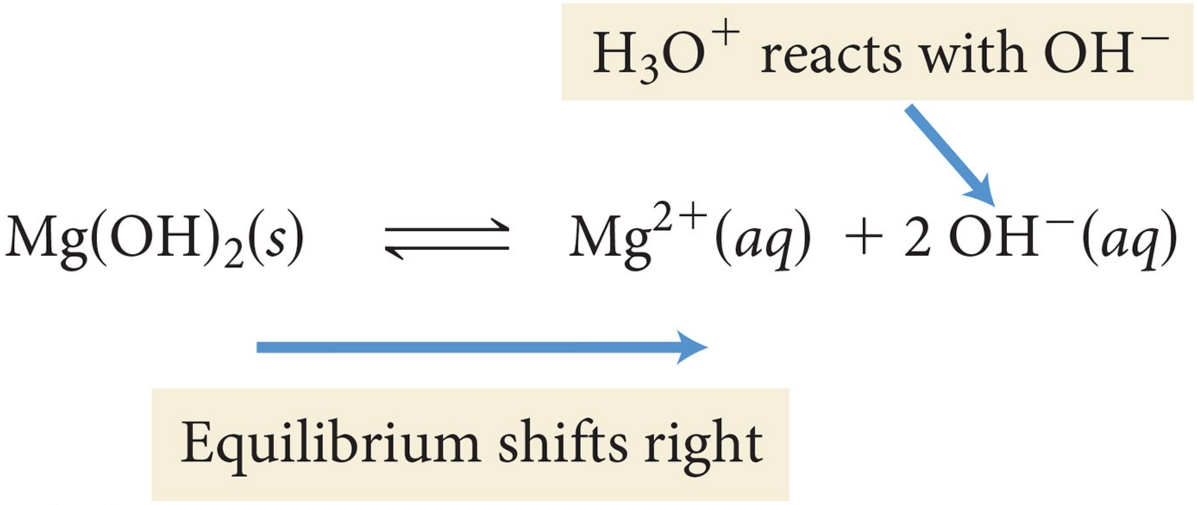
Effect of pH on solubility



High $[OH^-]$

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Equilibrium shifts left



H_3O^+ reacts with OH^-

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Equilibrium shifts right

Solubility of $Mg(OH)_2$ would decrease in a basic solution, but increase in an acid. *Le Chatelier's principle!*

Precipitation

- **Saturated solution**: Concentration of ions in solution is equal to the concentration expected from K_{sp}: $Q = K_{sp}$.
- If more ions are added to a saturated solution, an equilibrium is established between the solid and the ions and some solid remains will remain.
- If $Q < K_{sp}$, the solution is **unsaturated**, and more ions could be added to the solution (i.e., added solid would dissolve).
- Sometimes, the ion concentration can become greater than simply expected from $K_{sp.}$ In this case the solution is **super-saturated** and a *precipitate* would form as soon as a *crystallization seed* is provided.

Precipitation summary

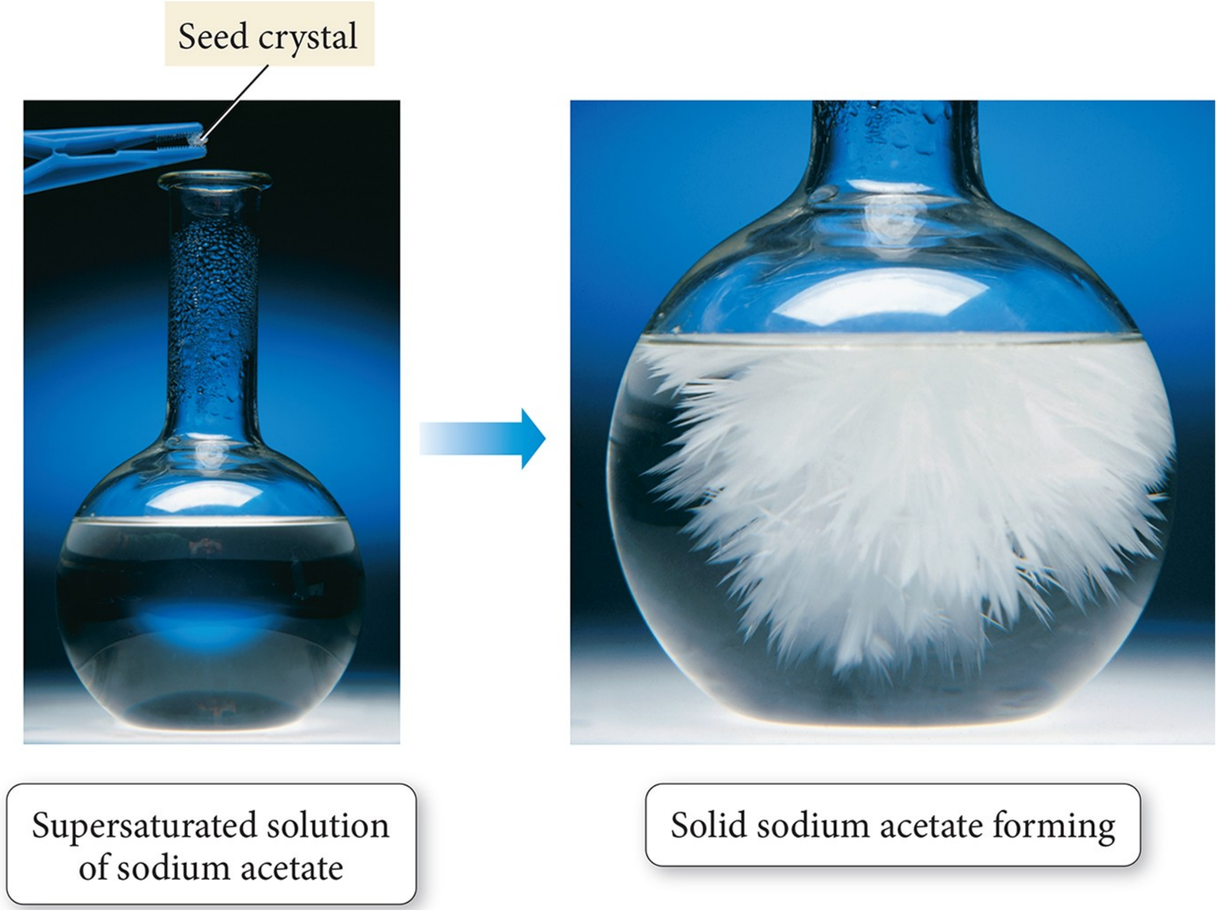
- $Q < K_{sp}$: **Unsaturated**, more solute could go into solution
- $Q = K_{sp}$: **Saturated**, at equilibrium with the solid
- $Q > K_{sp}$: **Supersaturated**, a precipitate is expected to form

(This is the same K & Q comparison we did earlier)

Supersaturation

Note: Sometimes a solution can become supersaturated and a precipitate will not form because there is a kinetic barrier to precipitate forming. Here $Q > K_{sp}$!

A seed crystal or a scratch on the side of the beaker can cause precipitation to occur.



Precipitation reactions

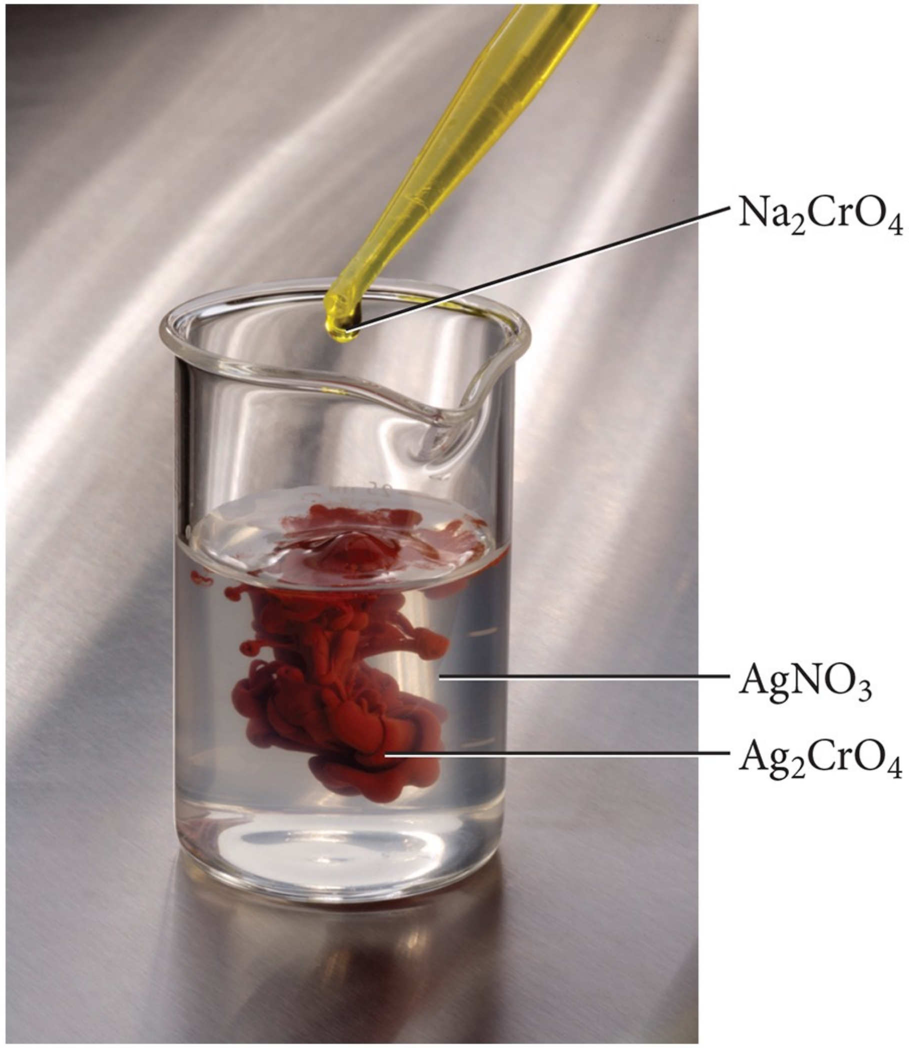
Precipitation can be used to remove ions from solution.

Example:

1. $Na_2CrO_4\,(aq) = 2Na^+(aq) + CrO_4^{2-}(aq)$
2. $AgNO_3(aq) = Ag^+(aq) + NO_3^-(aq)$
3. $\mathbf{Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)}$

$$Q = [Ag^+]^2[CrO_4^{2-}]$$

- If $Q < K_{sp}$, no precipitate.
- If $Q = K_{sp}$, precipitate begins to form.
- If $Q > K_{sp}$, precipitate forms.



Precipitation reactions

Example. Does a solution of 0.020 M $Ca(CH_3CO_2)_2(aq)$ mixed with 0.004 M $Na_2SO_4(aq)$ produce a precipitate of $CaSO_4(s)$ ($K_{sp} = 7.10 \times 10^{-5}$)?

First identify the the participant ion concentrations:

$$Ca(CH_3CO_2)_2(s) \rightarrow Ca^{2+}(aq) + 2\ CH_3CO_2^-(aq)$$

Full dissociation: $[Ca^{2+}] = 0.020$ M

$$Na_2SO_4(s) \rightarrow 2\ Na^+(aq) + SO_4^{2-}(aq)$$

Full dissociation: $[SO_4^{2-}] = 0.004$ M

Precipitation reactions

Write down the reaction that could form the precipitate:

$$CaSO_4(s) \rightleftarrows Ca^{2+}(aq) + SO_4^{2-}(aq)$$

Solve the solubility problem as described previously:

$$\begin{aligned} Q &= [Ca^{2+}] \cdot [SO_4^{2-}] \\ &= 0.020 \times 0.004 \\ &= 8x10^{-5} \end{aligned}$$

$$K_{sp} = 7.10x10^{-5}$$

Since $Q > K_{sp}$, we have exceeded the solubility and a small amount of $CaSO_4(s)$ should precipitate.

Precipitation reactions

Exercise. A solution containing potassium bromide is mixed with another containing lead(II)acetate to form a solution that is 0.013 M in KBr and 0.0035 M in $Pb(C_2H_3O_2)_2$. Does a precipitate form in the mixed solution at 20 ^oC? If so, identify the precipitate.

Task: Identify pairs of ions that form the least soluble compound and then check whether soluble using its K_{sp}. You can find K_{sp} values online at: https://en.wikipedia.org/wiki/Solubility_table

Selective precipitation

If a solution contains more than one ion, you might be able to remove one by selective precipitation.

Add a reagent that precipitates one ion, but not the others.

Example. Sea water contains both Mg^{2+} and Ca^{2+}. Could they be separated by adding KOH?

$Ca(OH)_2$: $K_{sp} = 4.68 \times 10^{-6}$

$Mg(OH)_2$: $K_{sp} = 2.06 \times 10^{-13}$

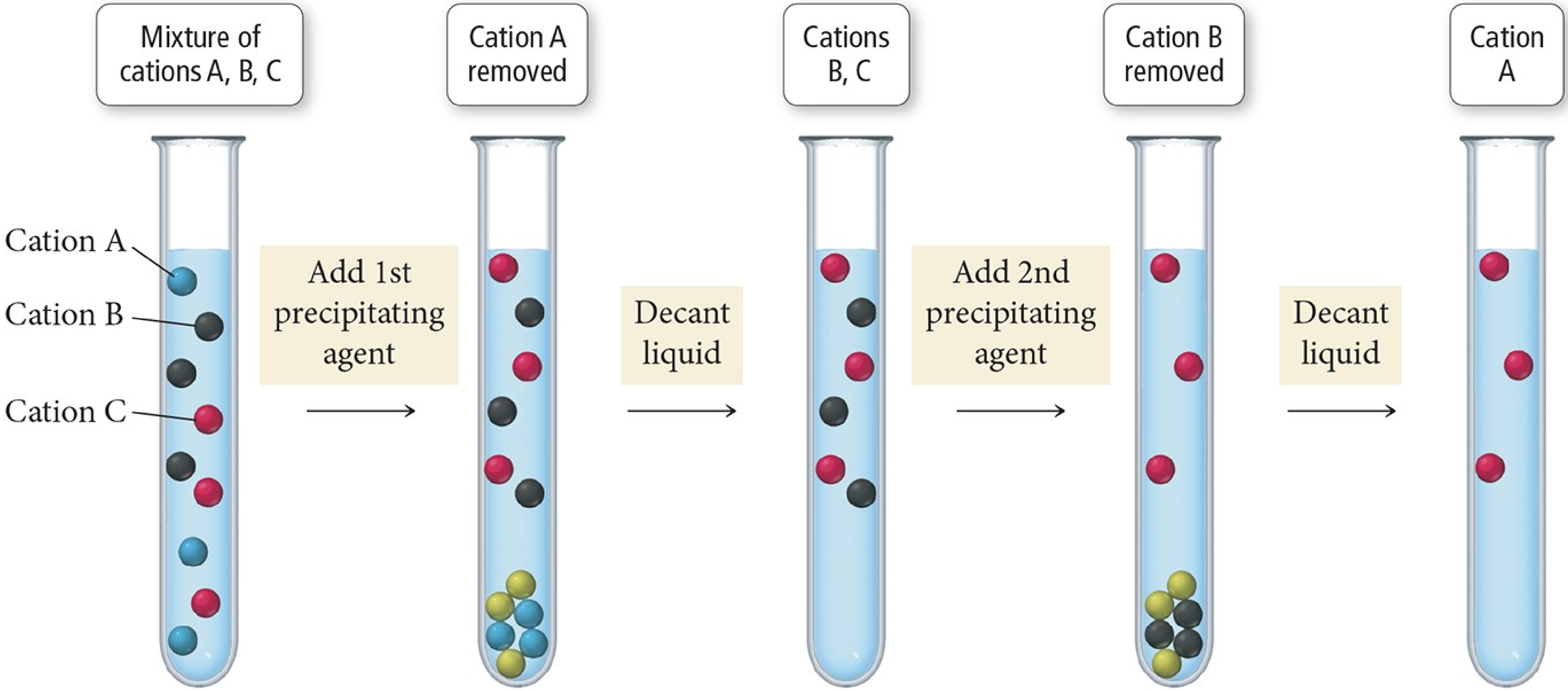
Yes, large difference between solubilities!

(both hydroxides are rather insoluble in water)

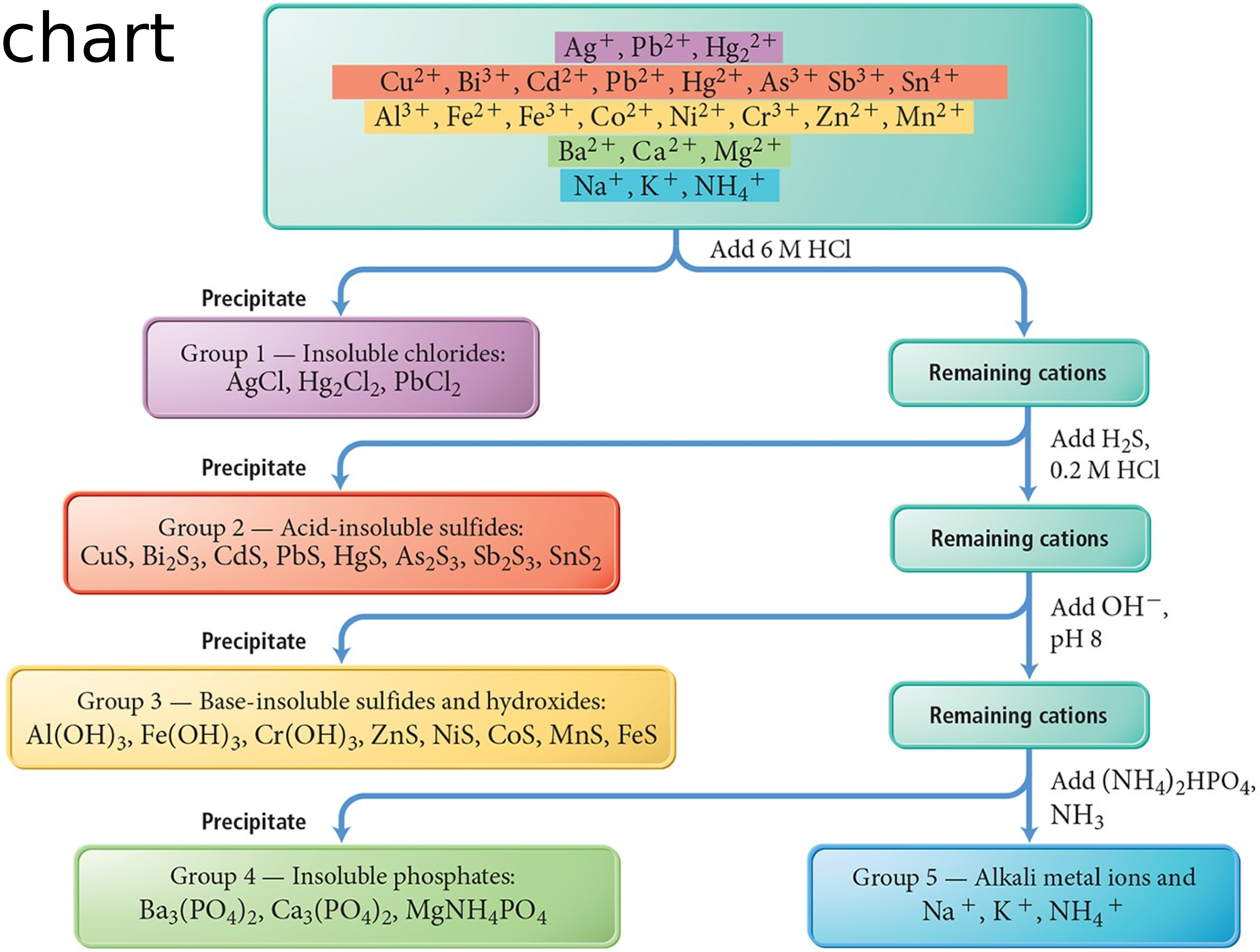
Application: qualitative analysis

- Non-quantitative determination of the ions in an unknown solution.
- Add certain regents to see if a precipitate forms, then determine what the precipitate could be.
- “Flow charts” can be used to do such studies systematically.

Application: qualitative analysis



Flowchart



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

Add 6 M HCl

Precipitate

Group 1 — Insoluble chlorides:
$AgCl, Hg_2Cl_2, PbCl_2$

Remaining cations

Add H_2S,
0.2 M HCl

Precipitate

Group 2 — Acid-insoluble sulfides:
$CuS, Bi_2S_3, CdS, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2$

Remaining cations

Add OH^-,
pH 8

Precipitate

Group 3 — Base-insoluble sulfides and hydroxides:
$Al(OH)_3, Fe(OH)_3, Cr(OH)_3, ZnS, NiS, CoS, MnS, FeS$

Remaining cations

Add $(NH_4)_2HPO_4$,
NH_3

Precipitate

Group 4 — Insoluble phosphates:
$Ba_3(PO_4)_2, Ca_3(PO_4)_2, MgNH_4PO_4$

Group 5 — Alkali metal ions and
Na^+, K^+, NH_4^+

Complex ion equilibria

- Transition metals can generally act as Lewis acids to form a “complex ion”.
- Central metal ion surrounded by a neutral molecule or ion that acts as a Lewis base.

Example. $\mathrm{Ag^+\,(aq) + 2\ H_2O(\ell) \rightleftharpoons Ag(H_2O)_2{}^+\,(aq)}$

- Even though we write the ion as Ag^+(*aq*), it is understood that it might be hydrated in aqueous solution.

Complex ion equilibria

The water can be displaced by something else in the solution:

$$\mathrm{Ag^{+}\,(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^{+}\,(aq)}$$

really $\mathrm{Ag(H_2O)_2{}^{+}\,(aq)}$

This complex has a “formation constant”:

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

K_f values are usually large

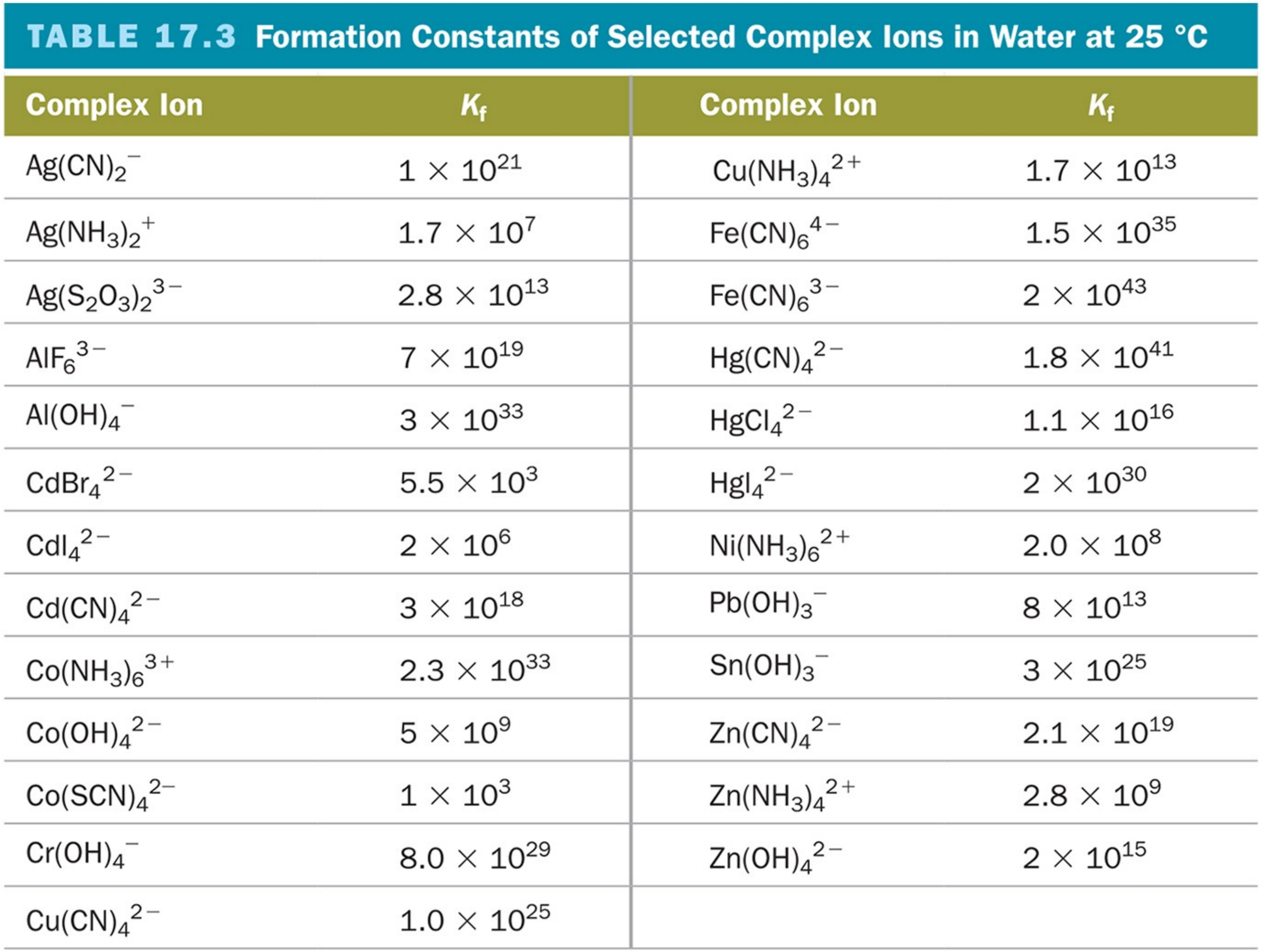


TABLE 17.3 Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	K_f	Complex Ion	K_f
$Ag(CN)_2^-$	1×10^{21}	$Cu(NH_3)_4^{2+}$	1.7×10^{13}
$Ag(NH_3)_2^+$	1.7×10^{7}	$Fe(CN)_6^{4-}$	1.5×10^{35}
$Ag(S_2O_3)_2^{3-}$	2.8×10^{13}	$Fe(CN)_6^{3-}$	2×10^{43}
AlF_6^{3-}	7×10^{19}	$Hg(CN)_4^{2-}$	1.8×10^{41}
$Al(OH)_4^-$	3×10^{33}	$HgCl_4^{2-}$	1.1×10^{16}
$CdBr_4^{2-}$	5.5×10^{3}	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^{6}	$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Cd(CN)_4^{2-}$	3×10^{18}	$Pb(OH)_3^-$	8×10^{13}
$Co(NH_3)_6^{3+}$	2.3×10^{33}	$Sn(OH)_3^-$	3×10^{25}
$Co(OH)_4^{2-}$	5×10^{9}	$Zn(CN)_4^{2-}$	2.1×10^{19}
$Co(SCN)_4^{2-}$	1×10^{3}	$Zn(NH_3)_4^{2+}$	2.8×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}	$Zn(OH)_4^{2-}$	2×10^{15}
$Cu(CN)_4^{2-}$	1.0×10^{25}		

Effect of complex ions on solubility

Formation of complex ions can increase the solubility of a salt that normally is not very soluble. For example:

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^{+}(aq)} + \mathrm{Cl^{-}(aq)} \quad K_{sp} = 1.77 \times 10^{-10}$$

$$\mathrm{Ag^{+}\,(aq)} + 2\mathrm{NH_3(aq)} \rightleftharpoons \mathrm{Ag(NH_3)_2{}^{+}(aq)} \quad K_f = 1.7 \times 10^{7}$$

$$\mathrm{AgCl(s)} + 2\,\mathrm{NH_3(aq)} \rightleftharpoons \mathrm{Ag(NH_3)_2{}^{+}(aq)} + \mathrm{Cl^{-}(aq)}$$

$$K = K_{sp} \times K_f = 3.0 \times 10^{-3}$$

This is much larger than the original K_{sp} value ($1.77\text{x}10^{-10}$).

Tips for this section

- Be able to write a solubility expression for K_{sp}
- Write the balanced reactions
- Calculate molar solubility (or mass solubility) from a given K_{sp}
- Calculate K_{sp} from solubility data
- Common ion effect
- Identify a potential precipitate in a reaction
- Identify whether or not a precipitate forms