



KTH Information and
Communication Technology

IM2665 Chemistry of Nanomaterials

Solubility and Solubility Products

Nanomaterials Fabrication by Precipitation

Assoc. Prof. Muhammet Toprak

Functional Materials
KTH Royal Institute of Technology

11/09/14

1

Objectives:

- Learning about precipitation reactions
- Learning about the solubility constant expression K_{sp} and how to use it
- Learning about the solubilities of various classes of ionic solids and how to use that knowledge to analyze for the presence of unknown ions in solution
- Nanomaterials synthesis

11/09/14

2



Synthesis, magnetic and electrical characteristics of poly(2-thiophen-3-yl-malonic acid)/Fe₃O₄ nanocomposite

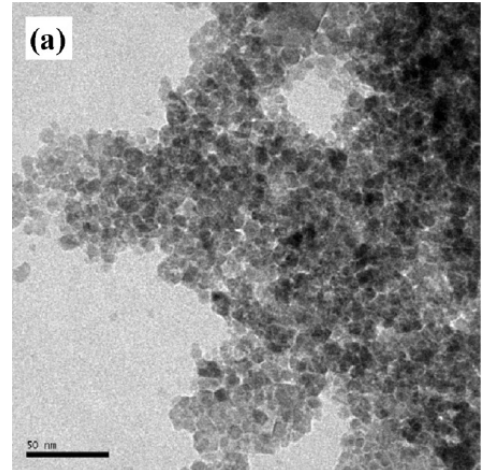
M. Aydın^a, B. Ünal^{b,c}, B. Esat^{d,*}, A. Baykal^{c,d}, E. Karaoğlu^d, M.S. Toprak^e, H. Sözeri^f

2.1. Materials

2-Thiophen-3-yl-malonic acid (T3MA), anhydrous iron (III) chloride (98%) (FeCl₃), ammonium hydroxide (NH₄OH), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98%), iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 98%), concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl), sodium hydroxide (NaOH) were all of analytical purity (obtained from Merck and Sigma–Aldrich) and used as-received, without any purification.

2.4. Synthesis of PT3MA/Fe₃O₄ nanocomposite

Stoichiometric amounts of Fe(III) and Fe(II) chloride salts (with a molar ratio of 2:1) and 50 mg of PT3MA were dissolved in 100 ml distilled water under vigorous stirring. Then a 2 M aqueous NaOH solution was added very slowly until the pH was raised to ~11 and a black suspension was formed. This suspension was then refluxed at 90°C for 12 h, under vigorous stirring and Ar gas. Magnetic particles were separated from the aqueous solution by magnetic decantation, washed with distilled water several times and then dried in an oven overnight.



11/09/14

3

Types of Solutions

✓ Saturated

✓ Unsaturated

✓ Supersaturated



11/09/14

4

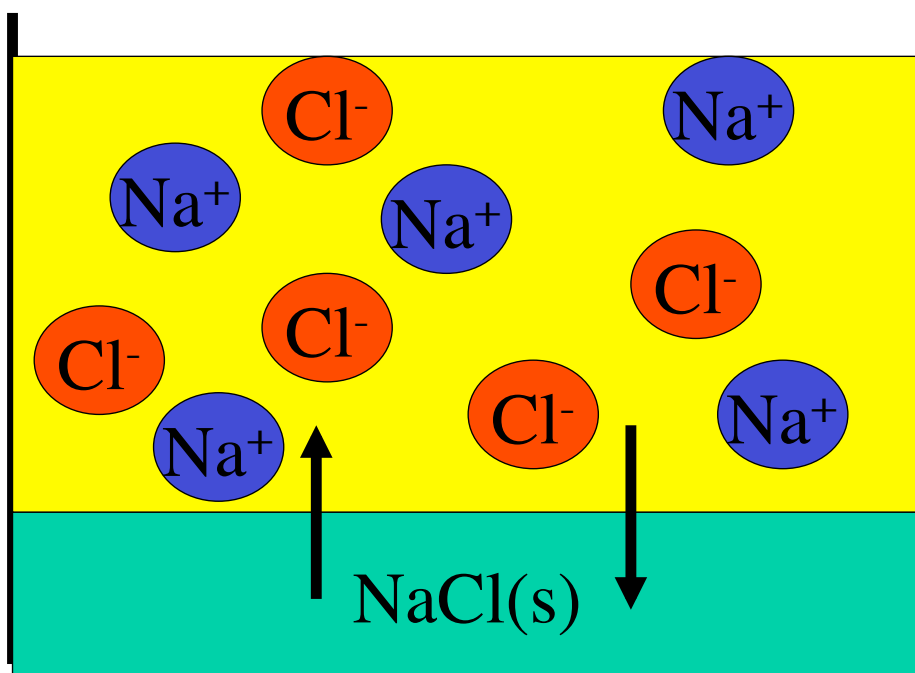
Solubility Equilibria

- Acid and base equilibria involve homogenous systems
 - Same phase
- **Saturated solution**
 - The solution is in contact with undissolved solute.
 - Heterogeneous equilibria system

11/09/14

5

Solution Equilibrium



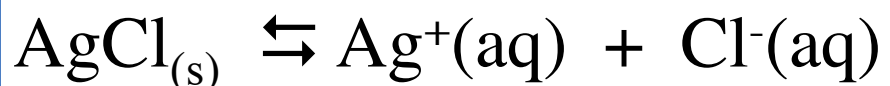
11/09/14

6

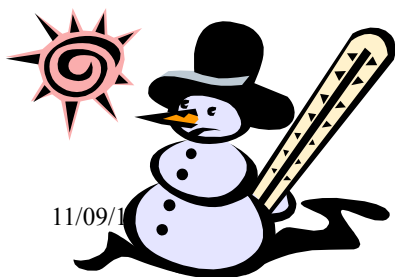
Degrees of Solubility



soluble



insoluble

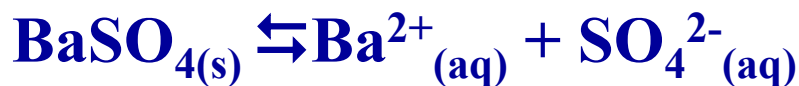


slightly soluble

11/09/1

7

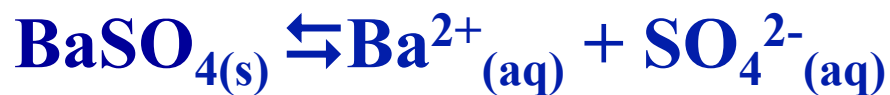
- To write an equilibrium product constant for a heterogeneous system, ignore the concentrations of pure solids or pure liquids.



- The K_c depends only on the molar conc. of species in solution.
- **Solubility-Product constant (K_{sp})**

11/09/14

8



- Even though $[\text{BaSO}_4]$ is not included in the K_{sp} , some must be present for the system to be at equilibrium.

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

11/09/14

9

- **K_{sp}** is the equilibrium constant between an ionic solute and its ions in a saturated solution.
- A very small K_{sp} indicates that only a small amount of solid will dissolve in water.

11/09/14

10

Some Values For Solubility Product Constants (K_{sp}) At 25 °C

TABLE 16.1 Some Solubility Product Constants at 25 °C

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	1.3×10^{-33}
Barium carbonate	$\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	5.1×10^{-9}
Barium sulfate	$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	1.1×10^{-10}
Calcium carbonate	$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	2.8×10^{-9}
Calcium fluoride	$\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$	5.3×10^{-9}
Calcium sulfate	$\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	9.1×10^{-6}
Calcium oxalate	$\text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq})$	2.7×10^{-9}
Chromium(III) hydroxide	$\text{Cr}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	6.3×10^{-31}
Copper(II) sulfide	$\text{CuS}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	8.7×10^{-36}
Iron(III) hydroxide	$\text{Fe}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	4×10^{-38}
Lead(II) chloride	$\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$	1.6×10^{-5}
Lead(II) chromate	$\text{PbCrO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$	2.8×10^{-13}
Lead(II) iodide	$\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$	7.1×10^{-9}
Magnesium carbonate	$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	3.5×10^{-8}
Magnesium fluoride	$\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$	3.7×10^{-8}
Magnesium hydroxide	$\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$	1.8×10^{-11}
Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3 \text{Mg}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$	1×10^{-25}
Mercury(I) chloride	$\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$	1.3×10^{-18}
Mercury(II) sulfide	$\text{HgS}(\text{s}) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	2×10^{-53}
Silver bromide	$\text{AgBr}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Br}^{-}(\text{aq})$	5.0×10^{-13}
Silver chloride	$\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$	1.8×10^{-10}
Silver iodide	$\text{AgI}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{I}^{-}(\text{aq})$	8.5×10^{-17}

Links for solubility products

http://www.solubilityofthings.com/water/ions_solubility/ksp_chart.php

<http://dbhs.wvusd.k12.ca.us/webdocs/Equations/Solubility-Table.html>

Solubility Chart

Soluble	Insoluble
Group I and NH_4^+ compounds	carbonates (except Group I, NH_4^+ and uranyl compounds)
nitrates	sulfites (except Group I and NH_4^+ compounds)
acetates (ethanoates) (except Ag^+ compounds)	phosphates (except Group I and NH_4^+ compounds)
chlorides, bromides and iodides (except Ag^+ , Pb^{2+} , Cu^+ and Hg_2^{2+})	hydroxides and oxides (except Group I, NH_4^+ , Ba^{2+} , Sr^{2+} and Tl^+)
sulfates (except Ag^+ , Pb^{2+} , Ba^{2+} , Sr^{2+} and Ca^{2+})	sulfides (except Group I, Group II and NH_4^+ compounds)

11/09/14

13

[http://phet.colorado.edu/simulations/sims.php?sim=Salts and Solubility](http://phet.colorado.edu/simulations/sims.php?sim=Salts%20and%20Solubility)

	Bromide Br^-	Carbonate CO_3^{2-}	Chloride Cl^-	Hydroxide OH^-	Nitrate NO_3^-	Oxide O^{2-}	Phosphate PO_4^{3-}	Sulfate SO_4^{2-}	Dichromate $\text{Cr}_2\text{O}_7^{2-}$
Aluminium Al^{3+}	S	X	S	I	S	I	I	S	I
Ammonium NH_4^+	S	S	S	S	S	X	S	S	S
Calcium Ca^{2+}	S	I	S	I	S	sS	I	sS	I
Copper(II) Cu^{2+}	S	X	S	I	S	I	I	S	I
Iron(II) Fe^{2+}	S	I	S	I	S	I	I	S	I
Iron(III) Fe^{3+}	S	X	S	I	S	I	I	sS	I
Magnesium Mg^{2+}	S	I	S	I	S	I	I	S	I
Potassium K^+	S	S	S	S	S	S	S	S	S
Silver Ag^+	I	I	I	X	S	I	I	sS	I
Sodium Na^+	S	S	S	S	S	S	S	S	S
Zinc Zn^{2+}	S	I	S	I	S	I	I	S	I

Key:

S	soluble
I	insoluble
sS	slightly soluble
X	other

[http://en.wikipedia.org/wiki/Solubility chart](http://en.wikipedia.org/wiki/Solubility_chart)

14

Rules for Writing K_{sp}

- K_{sp} is equal to the product of the concentration of the ions in the equilibrium, each raised to the power of its coefficient in the equation.

11/09/14

15

The Solubility Product Constant

K_{sp}

Example:

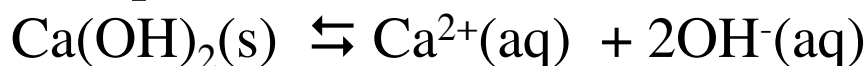


$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

11/09/14

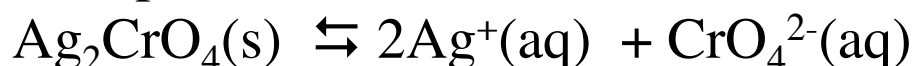
16

Example:



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$

Example:



$$K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{CrO}_4^{2-}]$$

11/09/14

17

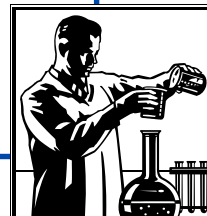
Your Turn

- Give the K_{sp} expressions for
 - a) Barium carbonate
 - b) Silver sulfate
 - c) Calcium fluoride

11/09/14

18

Solubility and K_{sp}



**Solubility = grams of solute
liter of solution**

**Molar = moles of solute
solubility liter of saturated solution**

K_{sp} is the equilibrium constant between the ionic solid and saturated solution.

11/09/14

19

- The solubility of a substance can change as concentrations of other solutes change.
 - $Mg(OH)_2$ solubility is dependent on pH as well as concentration of Mg^{2+}
- K_{sp} has only one value at any specific temperature.

11/09/14

20

Calculating K_{sp} from Solubility Data

Step 1: Use data to determine molar solubility.

Step 2: Use molar solubility and stoichiometry of dissociation to determine concentrations of cations and anions.

Step 3: Write equilibrium expression, calculate K_{sp} .

A saturated solution of AgCl in contact with undissolved solid is prepared at 25°C. The concentration of Ag⁺ ions in the solution is found to be 1.35×10^{-5} M. Assuming that AgCl dissociates completely in water and that there are no other simultaneous equilibria involving the Ag⁺ or Cl⁻ ions in the solution, calculate K_{sp} for this compound.

Your Turn

- The molar solubility of silver sulfate is 1.5×10^{-2} mol/L. Calculate the solubility product of the salt.

Calculating solubility from K_{sp}

Step 1: Use equilibrium expression & K_{sp} value to determine concentrations of cations and anions.

Step 2: Use ion concentrations to determine molar solubility.

Step 3: convert molar solubility to solubility (grams solute/liter).

Calculate the solubility of copper (II) hydroxide in g/L.

$$K_{sp} = 2.2 \times 10^{-20}$$

Molar mass $\text{Cu}(\text{OH})_2 = 97.57 \text{ g/mol}$



Initial		0.00	0.00
Change		+x	+2x
Equil.		x	2x

11/09/14

25

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

$$2.2 \times 10^{-20} = (x)(2x)^2$$

$$x^3 = \frac{2.2 \times 10^{-20}}{4} \quad x = 1.8 \times 10^{-7} \text{ M}$$

$$\text{Solubility Cu}(\text{OH})_2 = \frac{1.8 \times 10^{-7} \text{ mol}}{\text{L}} \times \frac{97.57 \text{ g}}{\text{mol}}$$

$$= 1.8 \times 10^{-5} \text{ g/L}$$

11/09/14

26

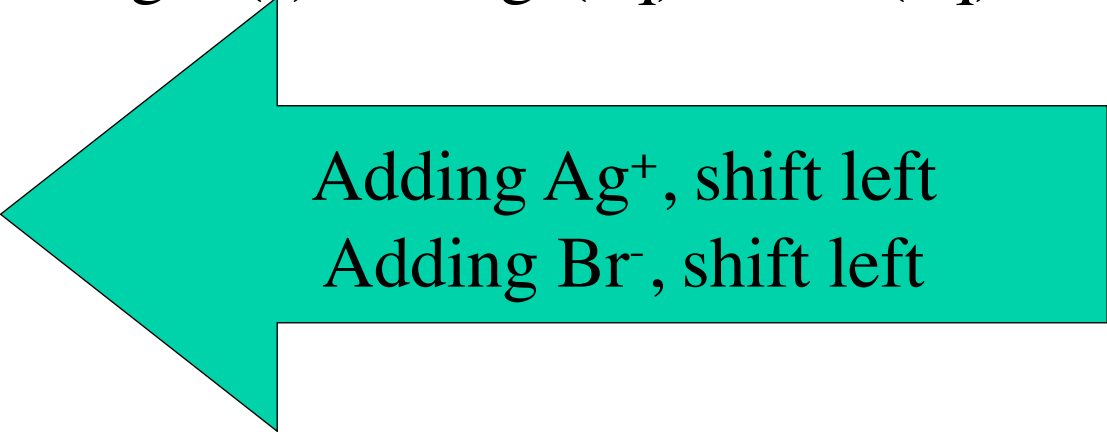
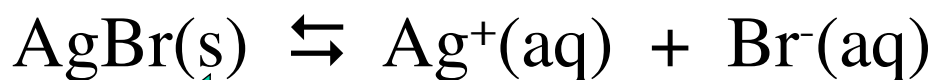
Solubility Factors

- 1) Common-ion effect
- 2) pH
- 3) Complex ion formation
- 4) Amphoterism

Common-ion effect & Solubility

- In general, the solubility of a slightly soluble salt is decreased by the presence of a second solute that supplies a common ion.
- **K_{sp} is unchanged by additional solutes.**

The common ion effect decreases the solubility of the salt.



Adding Ag^+ , shift left
Adding Br^- , shift left

11/09/14

29

- The K_{sp} for manganese(II) hydroxide is 1.6×10^{-13} . Calculate the molar solubility of manganese (II) hydroxide in a solution that contains 0.020 M NaOH.



11/09/14

30



Initial	_____	0.00	0.020
Change	___-x___	+x	2x
Equil.	_____	+ x	0.020+2x

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

11/09/14

31

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

$$1.6 \times 10^{-13} = (x)(0.020 + x)^2$$

- The solubility of Mn(OH)_2 is very small compared to the 0.020M NaOH

$$1.6 \times 10^{-13} = (x)(4.0 \times 10^{-4})$$

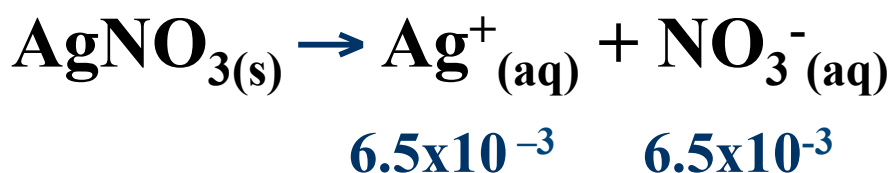
$$x = 4.0 \times 10^{-10} \text{ M}$$

11/09/14

32

Calculate the solubility of silver chloride (g/L) in a 6.5×10^{-3} M silver nitrate solution.

$$K_{sp} \text{ AgCl} = 1.6 \times 10^{-10}$$

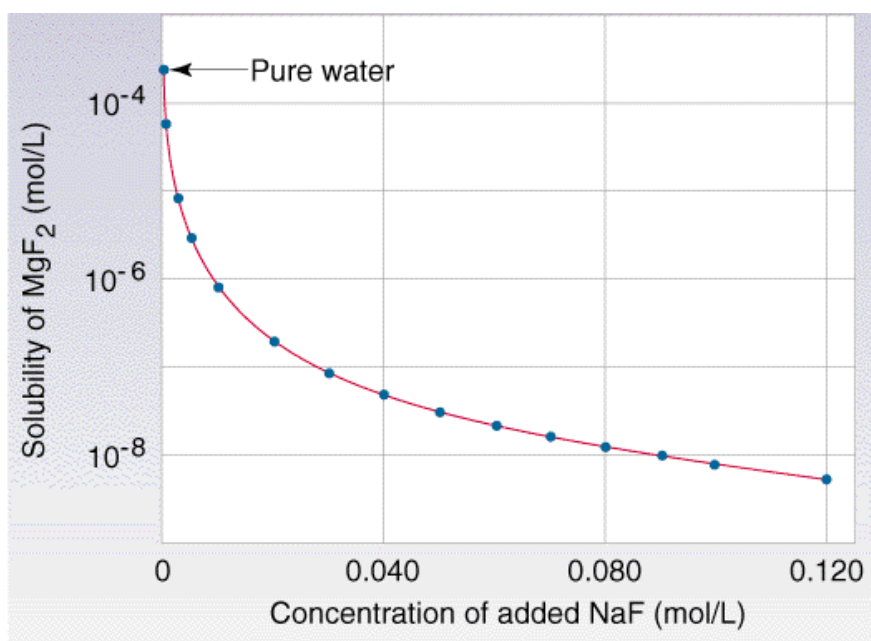


11/09/14

33

The Common Ion Effect on Solubility

The solubility of MgF_2 in pure water is 2.6×10^{-4} mol/L. What happens to the solubility if we dissolve the MgF_2 in a solution of NaF, instead of pure water?



11/09/14

34

Explaining the Common Ion Effect

The presence of a common ion in a solution will lower the solubility of a salt.

- LeChatelier's Principle:

The addition of the common ion will shift the solubility equilibrium backwards. This means that there is more solid salt in the solution and therefore the solubility is lower!

Solubility & pH

- The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic.
- The solubility of slightly soluble salts containing basic anions increases as $[H^+]$ (pH ↓).

pH Can Change Solubility



High pH,
shift left

Low pH,
shift right

11/09/14

37

At 25°C the molar solubility of Mg(OH)_2 in pure water is $1.4 \times 10^{-4} \text{M}$. Calculate its molar solubility in a buffer medium whose pH is :

$$K_{sp} = 1.2 \times 10^{-11}$$

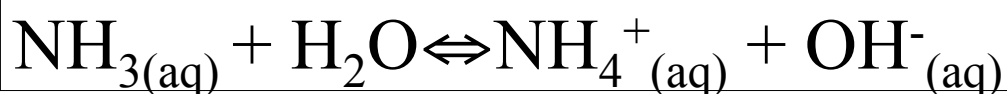
a.) 12.00 b.) 11.00



11/09/14

38

- Calculate the concentration of aqueous ammonia necessary to initiate the precipitation of iron(II) hydroxide from a 0.0030 M solution of FeCl₂.
- K_{sp} of Fe(OH)₂ = 1.6×10^{-14}
- K_b of NH₃ = 1.8×10^{-5}



11/09/14

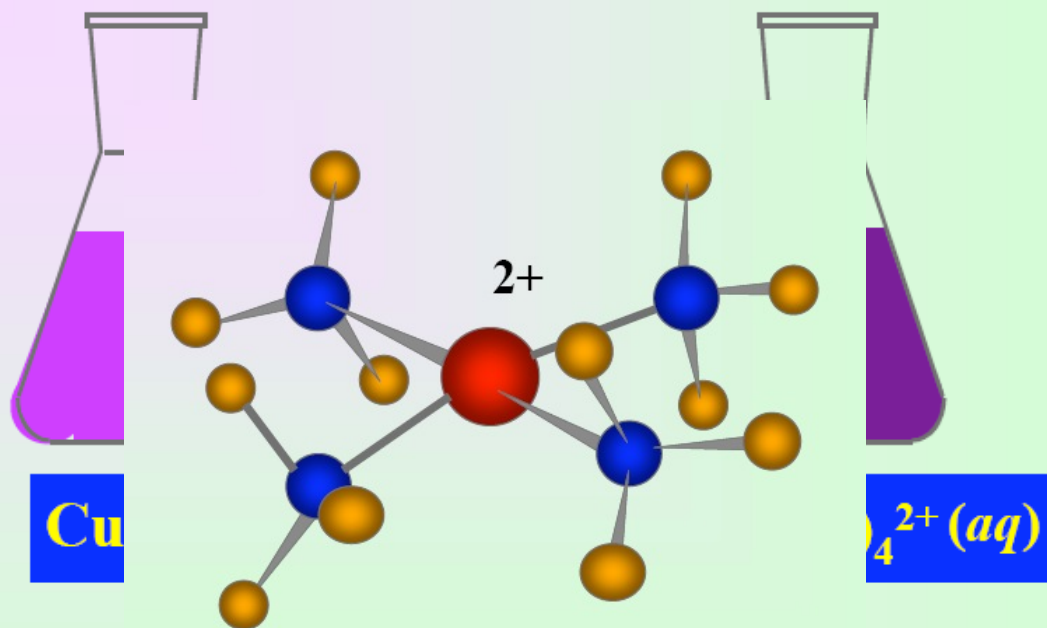
39

Formation of Complex Ions

- Metal ions have the ability to act as Lewis acids (electron pair acceptors) toward water molecules, which act as Lewis bases.
- Lewis bases other than water also interact with metal ions (particularly transition metals)

11/09/14

40



$$K_f = \frac{1}{[\text{Cu}^{2+}] [\text{NH}_3]^4} = 5.0 \times 10^{13}$$

11/09/14

41

- a complex ion is formed by Lewis acid-Lewis base reaction;

- metal ion is the Lewis acid

- the neutral molecule or ion that acts as the Lewis base is called a **Ligand**

- the number of ligands attached to the metal ion is called the **coordination number**

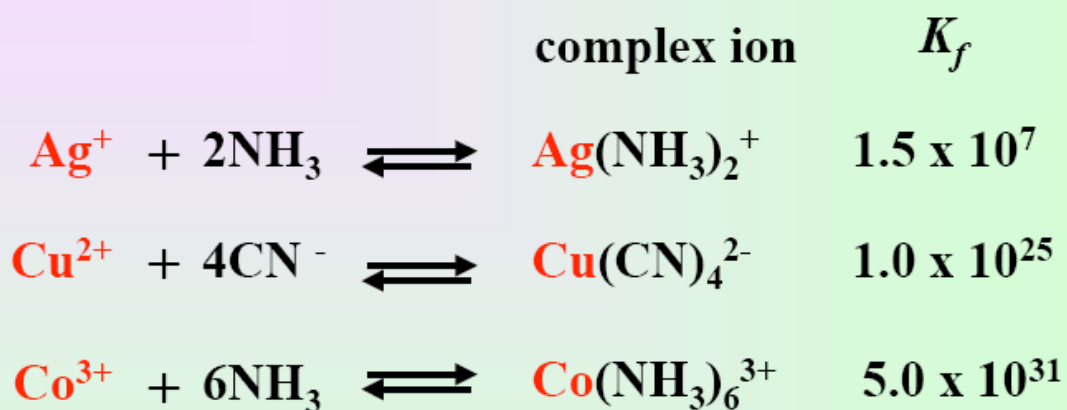
- the bond between the Lewis acid and Lewis base is covalent

- a complex ion is characterized by the formation constant (K_f)

11/09/14

42

Some typical complex ions



11/09/14

43

Some typical coordination numbers

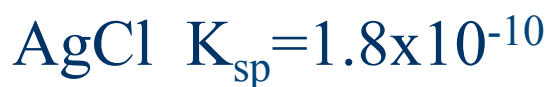
<i>Coordination numbers</i>		<i>Coordination numbers</i>		<i>Coordination numbers</i>	
Ag^+	2	Mn^{2+}	4,6	Co^{3+}	6
Cu^+	2,4	Fe^{2+}	6	Cr^{3+}	6
Au^+	2,4	Co^{2+}	4,6	Au^{3+}	4
		Ni^{2+}	4,6	Sc^{3+}	6
		Cu^{2+}	4,6		
		Zn^{2+}	4,6		

Some common ligands

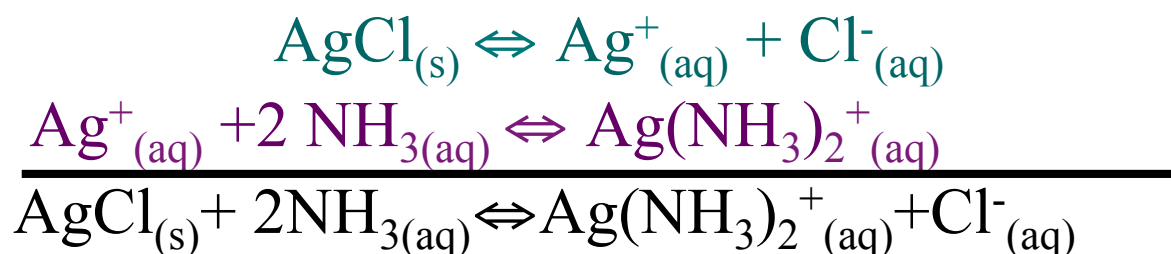
H_2O	SCN^-
CO	CN^-
NO	I^-
NH_3	F^-
CH_3NH_2	Cl^-
	44Br^-

11/09/14

44



- In the presence of aqueous ammonia AgCl will dissolve.



Presence of NH_3 drives the top reaction to the right
(\uparrow solubility of AgCl).

11/09/14

45

Complex Ions

an ion made up of the metal ion with one or more molecules or ions (Lewis bases) bonded to it.

Examples:



11/09/14

46

- The stability of a complex ion in aqueous solution is dependent upon the size of the equilibrium constant for its formation (K_f).

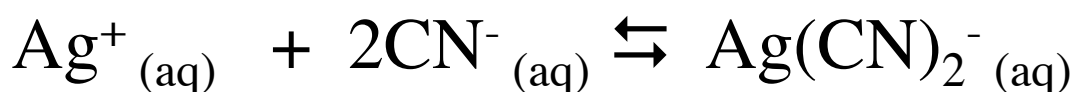


$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7$$

11/09/14

47

Stable or Unstable?



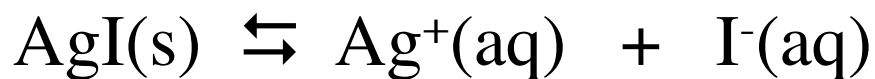
$$K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = 1.0 \times 10^{21}$$

The larger the K_f the more stable the ion.

11/09/14

48

The formation of a complex ion has a strong affect on the solubility of a metal salt.

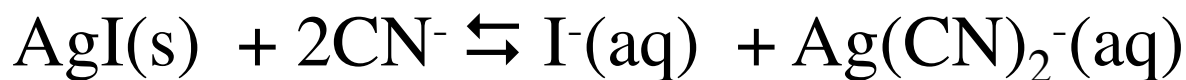
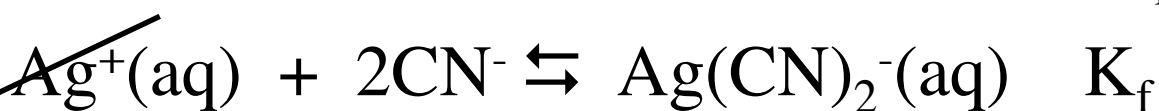
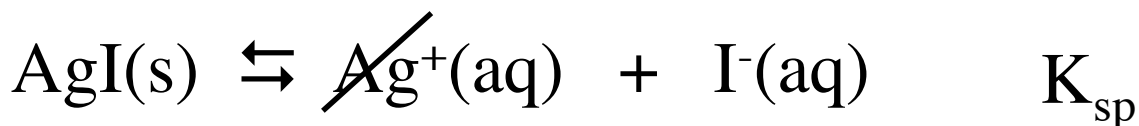


Adding CN^- shift right



11/09/14

49



$$K = K_{\text{sp}} K_{\text{f}}$$

$$= (8.3 \times 10^{-17})(1.0 \times 10^{21})$$

$$= 8.3 \times 10^4$$

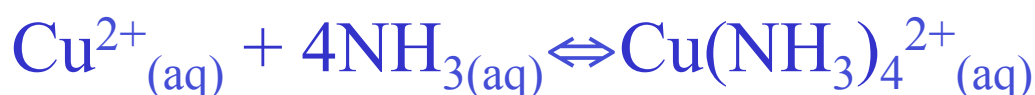
Solubility has increased!

11/09/14

50

A 0.20 mole quantity of CuSO_4 is added to a liter of 1.20 M NH_3 solution. What is the concentration of Cu^{2+} ions at equilibrium?

$$K_f \text{ for } \text{Cu}(\text{NH}_3)_4^{2+} = 5.0 \times 10^{13}$$



11/09/14

51



K_f is very large.

Assume that all of the Cu^{2+} added ends up as complex.

NH_3 consumed is $4(0.20\text{mol}) = 0.80 \text{ mol}$

$[\text{NH}_3]$ at equilibrium is $1.20 - 0.80$, or **0.40M**

$[\text{Cu}(\text{NH}_3)_4^{2+}]$ at equilibrium is **0.20M**

11/09/14

52

$$K_f = \frac{[Cu(NH_3)_4^{+2}]}{[Cu^{2+}][NH_3]^4} = 5.0 \times 10^{13}$$

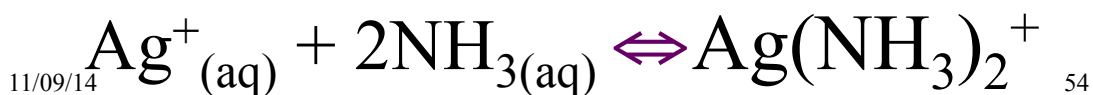
$$\frac{0.20}{x(0.40)^4} = 5.0 \times 10^{13}$$

$$X = [Cu^{2+}] = 1.6 \times 10^{-13} \text{ M}$$

11/09/14

53

- Calculate the molar solubility of silver chloride in a 1.0 M NH_3 solution.
- $K_{sp} \text{ AgCl} = 1.6 \times 10^{-10}$
- $K_f \text{ Ag}(NH_3)_2^+ = 1.5 \times 10^7$



11/09/14

54

Overall Equation



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.5 \times 10^7$$

$$K = K_{sp}(K_f) = \frac{[\cancel{\text{Ag}^+}][\cancel{\text{Cl}^-}]}{[\cancel{\text{Ag}^+}][\text{NH}_3]^2} \times \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\cancel{\text{Ag}^+}][\text{NH}_3]^2}$$

11/09/14

55



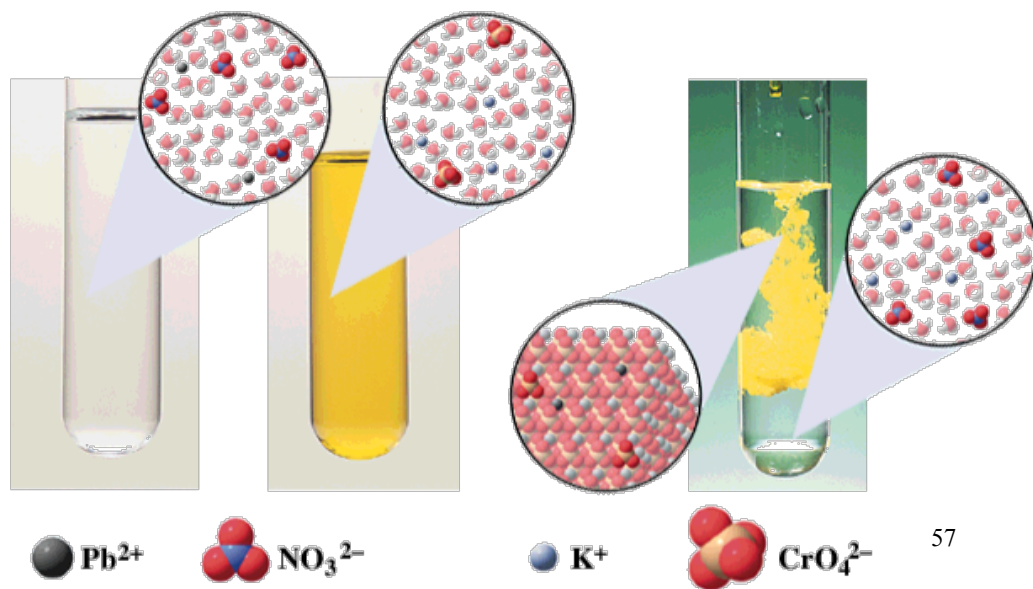
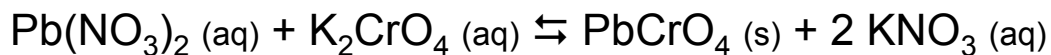
Initial	1.0	0.0	0.0
Change	-2x	+x	+x
Equil.	1.0-2x	x	x

$$K = \frac{x^2}{(1.0 - 2x)^2} = 2.4 \times 10^{-3}$$

11/09/14 0.049 mol of AgCl dis. in 1L of 1MNH₃ 56

Mixing Solutions - Will a Precipitate Form?

If 15 mL of 0.024-M lead nitrate is mixed with 30 mL of 0.030-M potassium chromate - will a precipitate form?



Precipitation & Separation

Ion Product (Q) - the value obtained from the equilibrium expression using initial concentrations.

For BaSO_4 :

$$Q = [\text{Ba}^{+2}][\text{SO}_4^{2-}]$$

Reaction quotient (Q) can be used to determine the direction a reaction will proceed in order to reach equilibrium.

Compare Q to K_{sp}

$Q = K_{sp}$ $Q < K_{sp}$ $Q > K_{sp}$
saturated unsaturated supersaturated

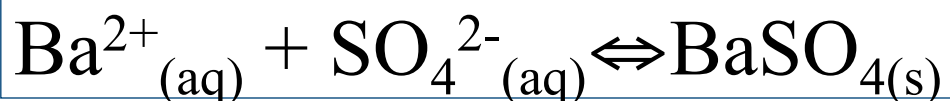
11/09/14

59

Exactly 200.0mL of 0.0040M $BaCl_2$ are added to 600.0mL of 0.0080M K_2SO_4 . Will a precipitate form?

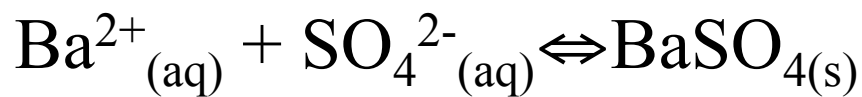
$K_{sp} BaSO_4 = 1.1 \times 10^{-10}$

According to solubility rules the only precipitate that might form is $BaSO_4$.



11/09/14

60



- How many moles of Ba^{2+} are present in original?
- Concentration of Ba^{2+} in final solution?
- Moles of SO_4^{2-} in original?
- Concentration of SO_4^{2-} in final volume?

11/09/14

61

A) $1.0 \times 10^{-3} \text{ M Ba}^{2+}$

B) $6.0 \times 10^{-3} \text{ M SO}_4^{2-}$

$$Q = [\text{Ba}][\text{SO}_4]$$

$$Q = 1.0 \times 10^{-3} (6.0 \times 10^{-3}) = 6.0 \times 10^{-6}$$

$$K_{\text{sp}} \text{ BaSO}_4 = 1.1 \times 10^{-10}$$

$Q > K_{\text{sp}}$ therefore BaSO_4 will precipitate.

11/09/14

62

Fractional Precipitation

Selective Precipitation

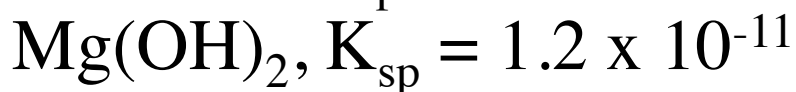
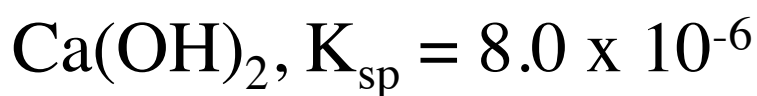
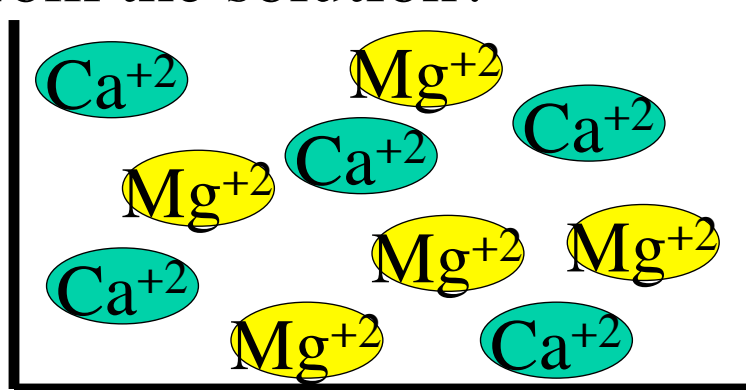
Ions in a solution can be separated from each other on the basis of the different solubilities of their salts.

➤ Add HCl to a solution containing Ag^+ and Cu^{2+} and only the AgCl precipitates out.

11/09/14

63

What could be added to separate these ions from the solution?



11/09/14

64

$$K_{sp} = [Ca^{2+}][OH^{-}]^2 \quad K_{sp} = [Mg^{2+}][OH^{-}]^2$$

$$[OH^{-}]^2 = \frac{K_{sp}}{[Ca^{2+}]}$$

$$[OH^{-}]^2 = \frac{K_{sp}}{[Mg^{2+}]}$$

If the Ca^{2+} and Mg^{2+} concentrations are known, you can calculate the OH^{-} concentration above which the salt will precipitate.

11/09/14

65

Silver nitrate is slowly added to a solution that is 0.020M in Cl^{-} ions and 0.020M Br^{-} ions. Calculate the concentration of Ag^{+} ions (in mol/L) needed to:

$$K_{sp} AgBr = 7.7 \times 10^{-13} \quad K_{sp} AgCl = 1.6 \times 10^{-10}$$

- The precipitation of AgBr.
- The precipitation of AgCl.

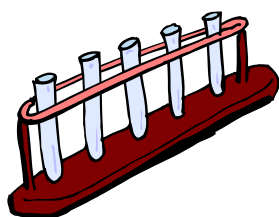
11/09/14

66

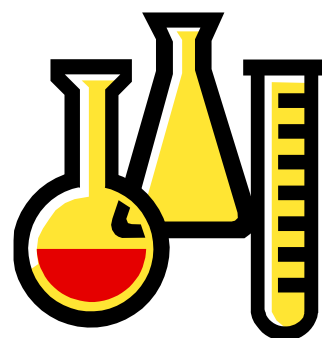
Qualitative Analysis



Determining the types of ions present in a solution.



11/09/14



67

Qualitative Analysis of Metallic Elements

- Scheme that is in common use divides *common cations* into 5 groups.
- The order of addition of reagents is important, the most selective separations are carried out first.

11/09/14

68

1) Insoluble Chlorides

- a. Ag^+ , Hg^{2+} , and Pb^{2+}
- b. Add dilute HCl only these ppt.

2) Acid insoluble sulfides (b/c excess H^+)

- a. After any insoluble chlorides have been removed, treat solution with H_2S .
- b. Only the most insoluble sulfides ppt. b/c only small amts HS^- and S^{2-} available
- c. (Le Chat: $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+ \rightleftharpoons \text{S}^{2-} + 2\text{H}^+$)
- d. CuS , Bi_2S_3 , CdS , PbS , HgS , As_2S_3 , Sb_2S_3 , SnS_2

11/09/14

69

3.) Base insoluble Sulfides and hydroxides.

- a.) Filter and remove any insoluble sulfides.
- b.) Make slightly basic add small amts of OH^- , then add $(\text{NH}_4)_2\text{S}$. (more S^{2-} avail.)

K_{sp} values are exceeded, ppt occurs

Zn^{+2} , Ni^{2+} , Co^{2+} , Mn^{+2}

Al^{3+} , Cr^{3+} , Fe^{3+} (form insol. OH)

11/09/14

70

4) Insoluble phosphates

- a) Addition of $(\text{NH}_4)_2\text{HPO}_4$ to the solution precipitates the group 2A metals (Mg, Ca, Sr, and Ba).

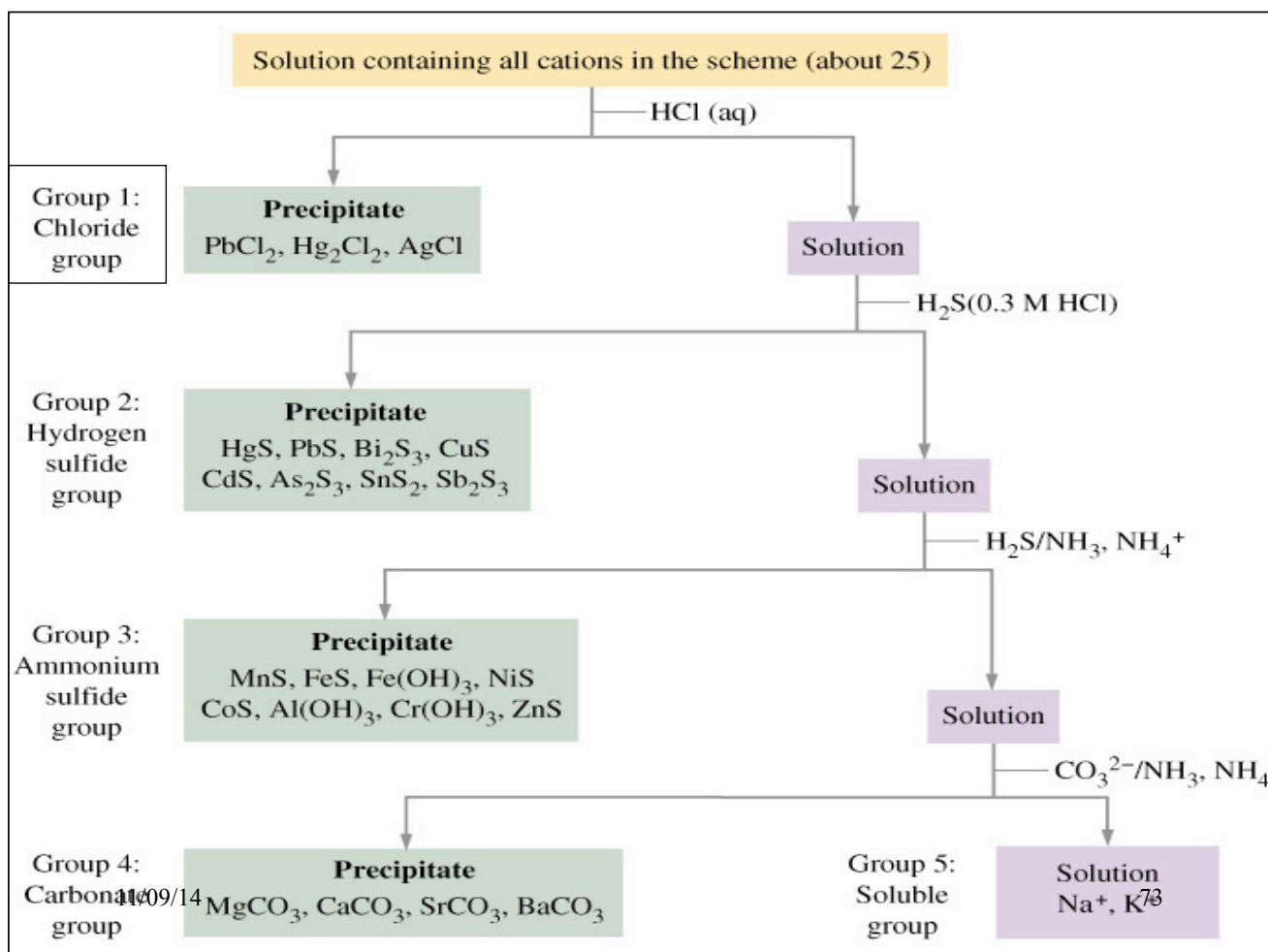
5) Formation of complex ions:

Add excess conc. NH_3 or CN^- or OH^- to see if ppt redissolves.

i.e. Excess NH_3 will cause AgCl to redissolve.

Qualitative Inorganic Analysis

- Acid-base chemistry, precipitation reactions, oxidation-reduction, and complex-ion formation all come into sharp focus in an area of analytical chemistry called *classical qualitative inorganic analysis*.
- “Qualitative” signifies that the interest is in determining what is present, not how much is present.
- Although classical qualitative analysis is not as widely used today as instrumental methods, it is still a good vehicle for applying all the basic concepts of equilibria in aqueous solutions.



Summary:

- Precipitation reactions
- Solubility constant expression K_{sp} and its use
- Solubility of various classes of ionic solids and how to use that knowledge to analyze for the presence of unknown ions in solution
- Nanomaterials synthesis