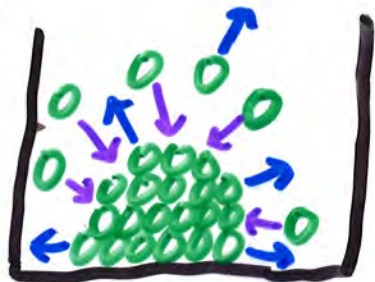


IV) Solubility Equilibria

50 g NaCl in 100 g H₂O



14 g solid remains



A soln. in **equilibrium** w.

un dissolved solute is

Saturated

Solubility

conc. (amt.) of solute in a saturated soln.

g solute / 100 g solvent

Solubility of NaCl at 20°C,

$$\frac{36.0 \text{ g NaCl}}{100 \text{ g H}_2\text{O}} \approx \frac{36.0 \text{ g NaCl}}{100 \text{ mL H}_2\text{O}}$$

Molar solubility

moles solute
L soln

in a
sat. soln

$$\frac{\text{g}}{\text{L}} \leftrightarrow \frac{\text{mol}}{\text{L}}$$

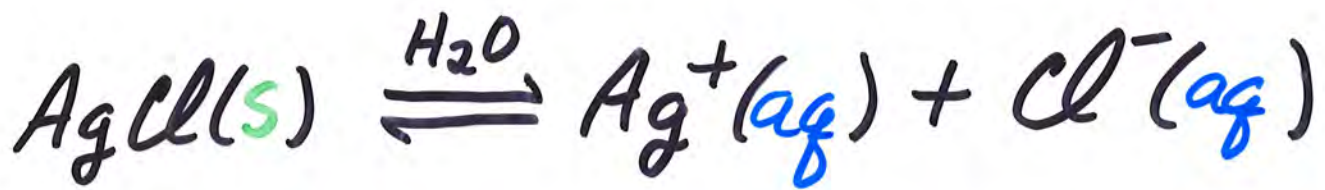
use molar mass

1) Ex: The solubility of CaF_2 is 0.016 g CaF_2 in 1.0 L of H_2O . What is the molarity?

2) Ex: If the water contains
0.010 M $\text{Ca}(\text{NO}_3)_2$ only
0.0024 g of CaF_2 dissolves
in 1.0 L H_2O ($3.1 \times 10^{-5} \text{ M}$).
It's 85% less soluble. Why?



A) Solubility-Product Constant, K_{sp}



heterogeneous equil.

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

eq. constant for equil.
between solid ionic solute
& its ions in a sat. soln.

B) Solubility & K_{sp}

Solubility changes as conc. of other solutes change

K_{sp} is constant

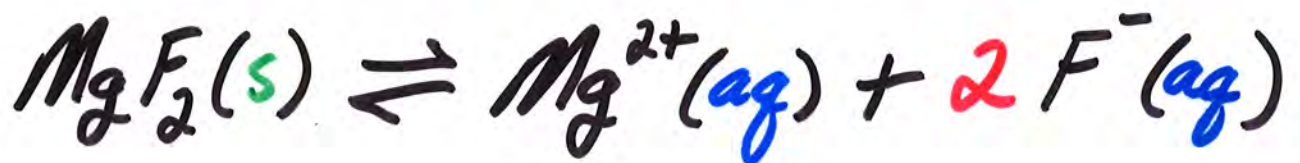
(at a given Temp.)

lower solubility \Rightarrow smaller K_{sp}

Note: can't simply compare K_{sp} 's like K_a 's & K_b 's bec. form of eqn. diff. for diff. substances

1) Ex : Calc. K_{sp} for MgF_2 .
Solub. of MgF_2 is 7.6×10^{-2} g/L at $25^\circ C$.

a) Write equil. eqn.



b) Determine equil. conc.

$$[Mg^{2+}] = \frac{\text{mol } Mg^{2+}}{L} =$$

$$[F^-] =$$

c) Write K_{sp} expression & solve

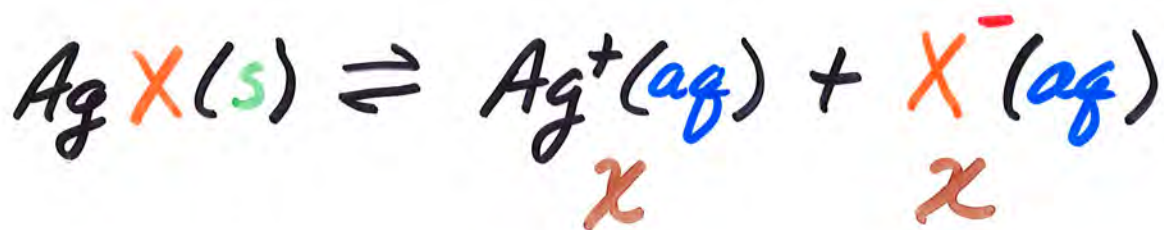
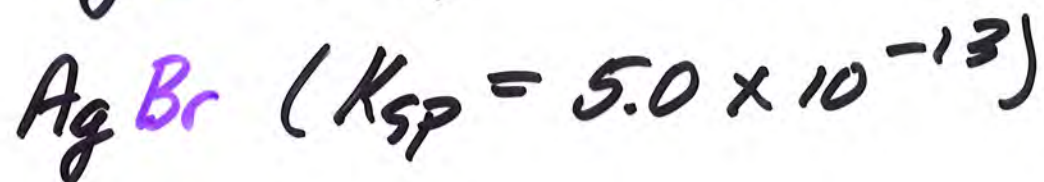
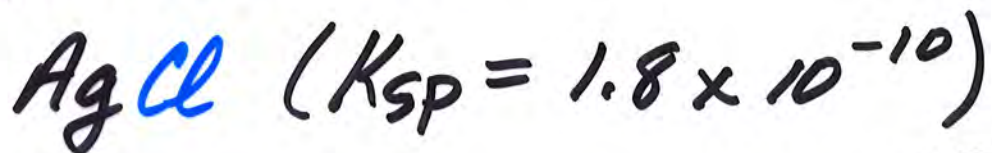
$$K_{sp} =$$

2) Ex : Calc. molar solubility
of $Al(OH)_3$. $K_{sp} = 4.6 \times 10^{-33}$

a) Write equil. eqn.



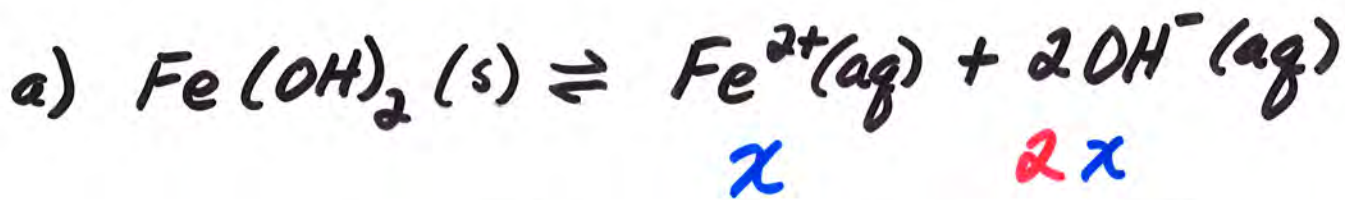
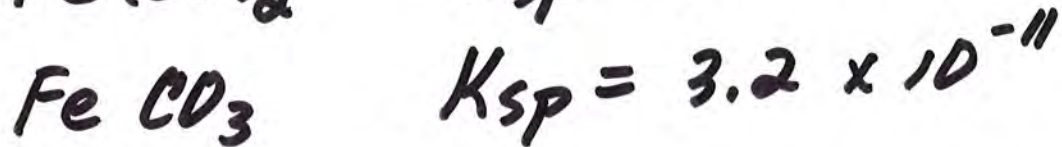
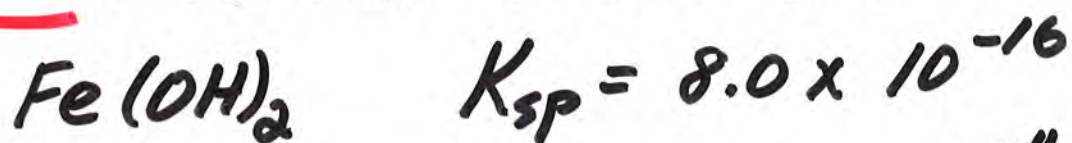
3) Ex : w/o calc., which is more soluble:



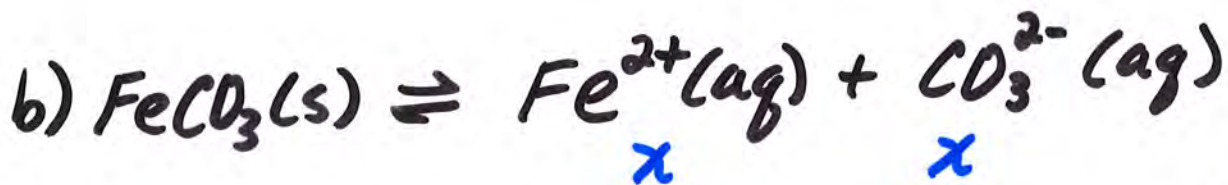
$$K_{sp} = [\text{Ag}^+][\text{X}^-] = x^2$$

$$x = \sqrt{K_{sp}}$$

4) Ex : Which is more soluble?



$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 8.0 \times 10^{-16}$$



$$K_{sp} = [\text{Fe}^{2+}][\text{CO}_3^{2-}] = 3.2 \times 10^{-11}$$

V) Factors Affecting Solubility

A) Common-Ion Effect



Addition of Mg^{2+} or F^{-}
shifts equil.



reduces solubility

solubility dec. upon
addition of a common-ion

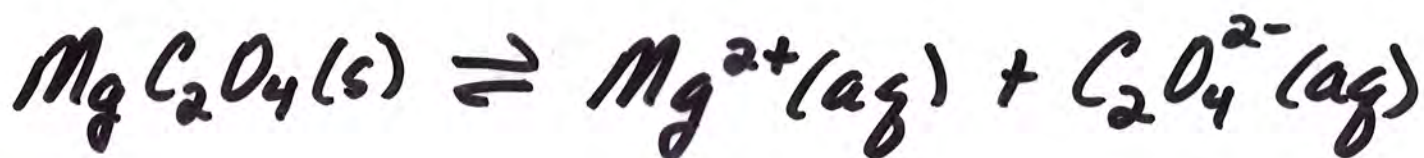
1) Ex : What is molar solub. of MgF_2 in $0.10 M NaF$

$$K_{sp} = 7.3 \times 10^{-9}$$



init.
chg.
equil.

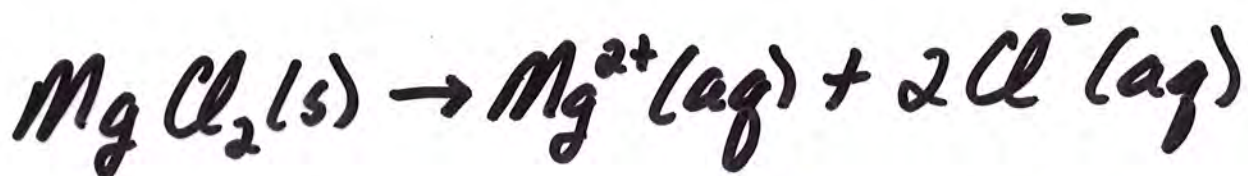
2) Ex : What is solub. in g/L of MgC_2O_4 in 0.020 M $Na_2C_2O_4$?



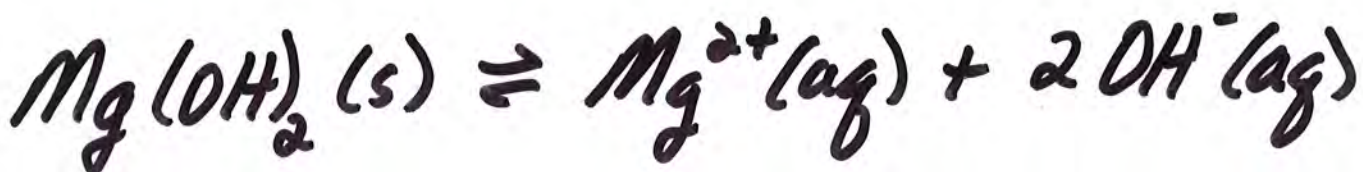
init.		0	0.020
chg	-x	+x	+x
equil		x	0.020 + x

Method of successive approx.

3) Ex : Mix 1 M $MgCl_2$ +
1 M NH_3 . A ppt forms.
What is it?



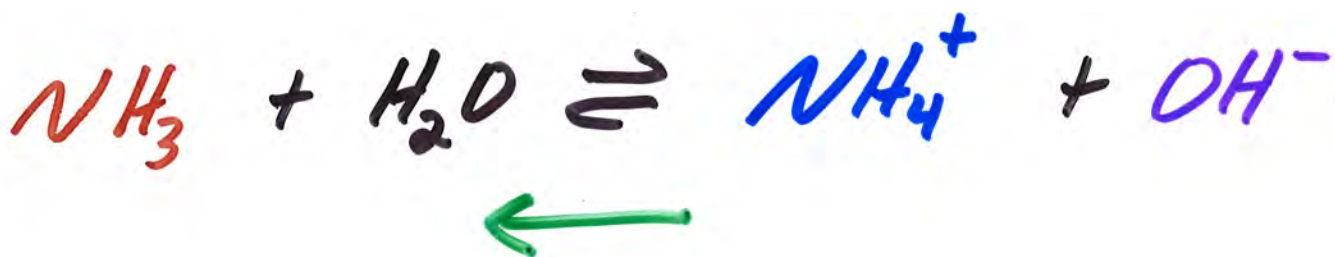
Exceeded solub. of $Mg(OH)_2$



$$K_{sp} = 1.8 \times 10^{-11}$$

What happens if we add $\text{NH}_4\text{Cl}(s)$?

Common-Ion, NH_4^+



$[\text{OH}^-]$ dec.



shifts right to replace OH^-

$\text{Mg}(\text{OH})_2$ dissolves

solubility inc.

B) Solubility & pH

Solubility of slightly soluble salts containing basic anions affected by changes in pH

inc. as $[H^+]$ inc.
(pH dec)

dec. as $[H^+]$ dec.
(pH inc.)

1) Ex : What is the molar solubility of $Mg(OH)_2$ in $0.10 M NaOH$?

$$K_{sp} = 1.8 \times 10^{-11}$$

2) Ex : What is the molar solubility of $Mg(OH)_2$ in a soln. buffered at pH 10.0 ?

3) Ex : What happens when HCl is added to a soln. of $Mg(OH)_2$?

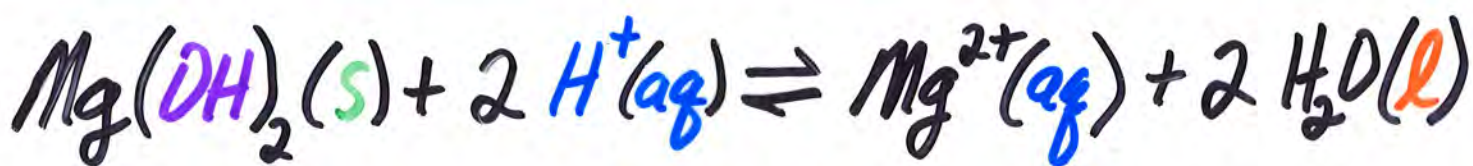


K_{sp}

Add H^{+}

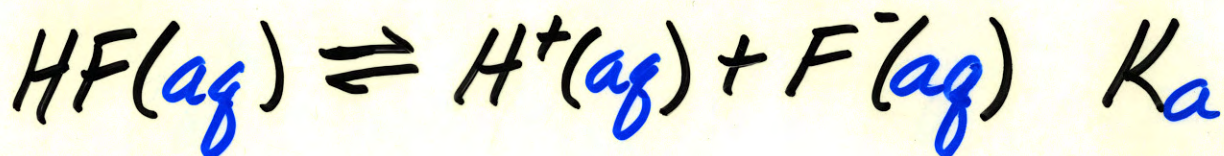
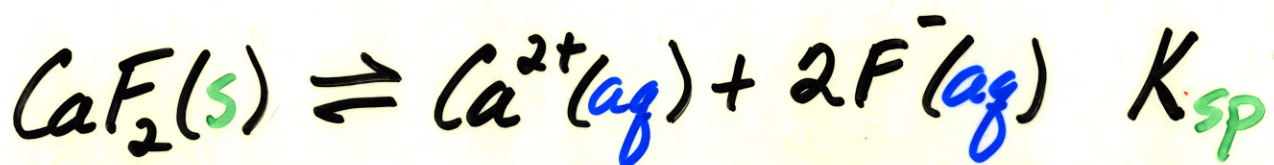


K_w^{-2}



solubility inc

4) Ex : What happens when 1.0M HCl is added to a soln. of CaF_2 ?



C) Complex-Ion Formation

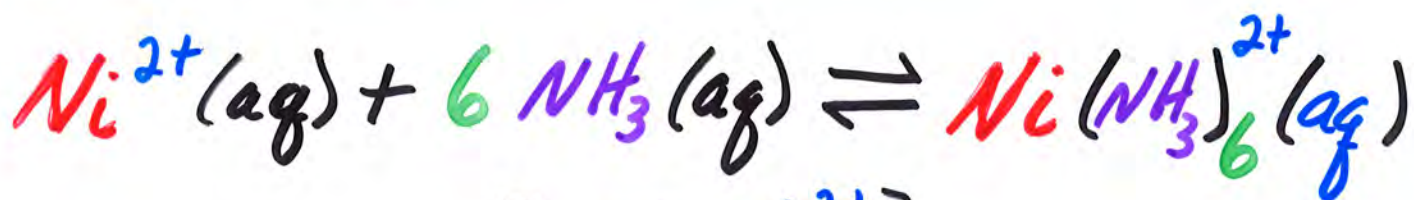
Ion consisting of a central **metal cation** (Lewis acid) bound to ligands (Lewis base)

Ligands

NH_3 , CN^- , OH^- , SCN^- ,
 $\text{S}_2\text{O}_3^{2-}$, Cl^- , Br^-



Formation Constant, K_f



$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6} = 1.2 \times 10^9$$

K_f values **LARGE**

Complex-Ion Dissociation



$$K_d = \frac{[\text{Ni}^{2+}][\text{NH}_3]^6}{[\text{Ni}(\text{NH}_3)_6^{2+}]} = \frac{1}{K_f} = 8.3 \times 10^{-10}$$

K_d values **SMALL**

1) Ex : What is $[Cu^{2+}]$ in a
soln of 0.050 M $Cu(NO_3)_2$
+ 3.0 M NH_3 ?

$$K_f = 1.1 \times 10^{13} \text{ for } [Cu(NH_3)_4]^{2+}$$

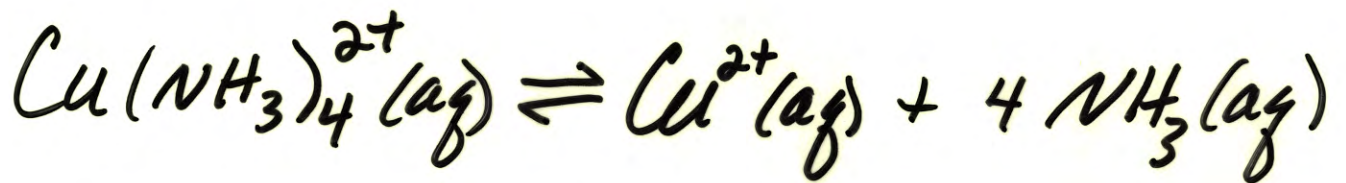
Assume **all** Cu^{2+} complexes



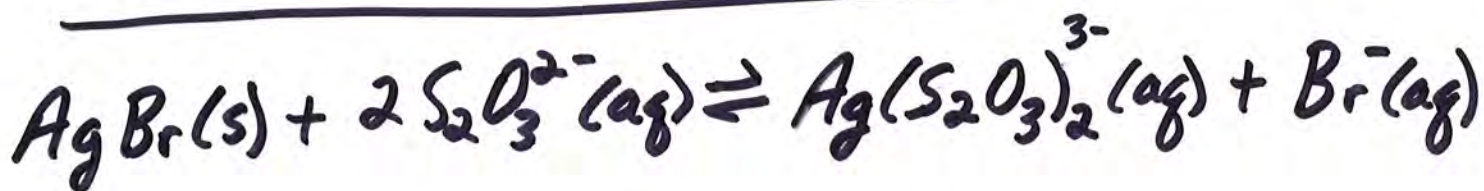
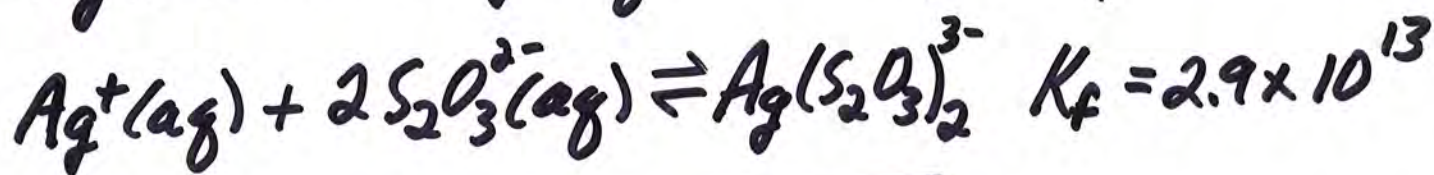
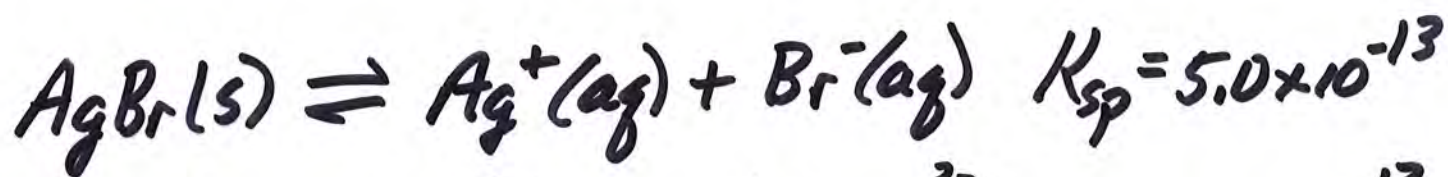
Initial Conc

$$[\text{Cu}(\text{NH}_3)_4^{2+}] =$$

$$[\text{NH}_3] =$$



2) Ex : Molar solb. of AgBr is 7.1×10^{-7} . What is molar solb. of AgBr in $2.0\text{M Na}_2\text{S}_2\text{O}_3$?



$$K = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}][\text{Br}^-]}{[\text{S}_2\text{O}_3^{2-}]^2} = K_{sp} \cdot K_f$$

$$= 14.5$$



D) Amphoterism

Capable of behaving as either
acid or base

- oxides & hydroxides

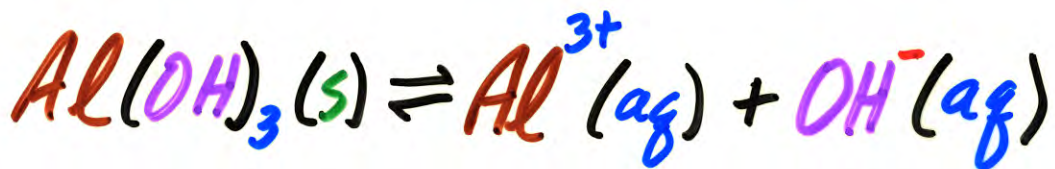
Anion in ppt & complexing
ligand are the same

Dissolve in both strongly
acidic & basic solns.

Occurs w. only a few metals



1) Ex : Add OH^- to a soln. of Al^{3+}



$$K_{\text{sp}} = 4.6 \times 10^{-33}$$

Add OH^- to Al^{3+} soln.

a) get ppt first



$$K = \frac{1}{K_{\text{sp}}} = 2.2 \times 10^{32}$$

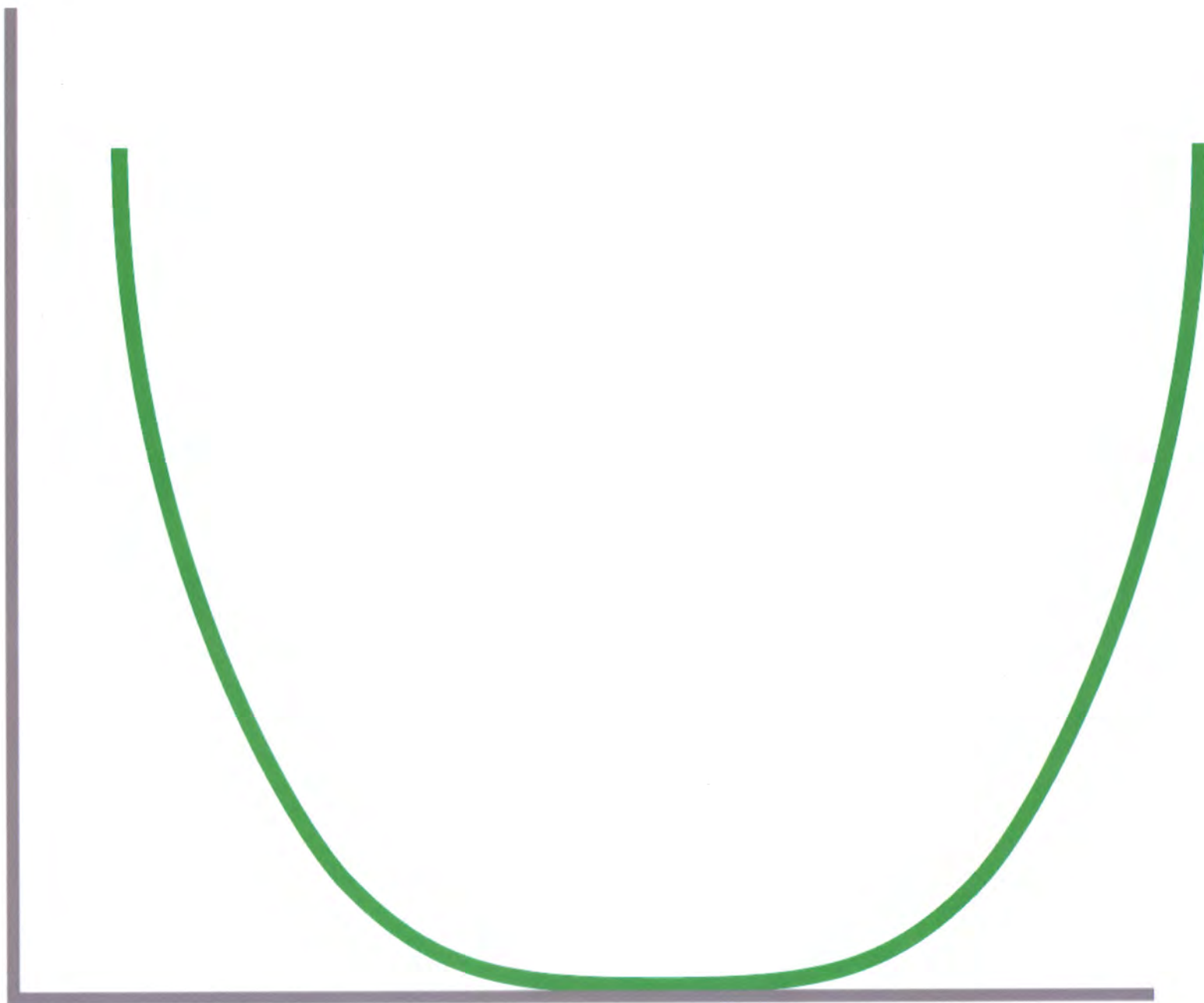
reacts w. acid

b) Add OH^- ppt dissolves



$$K_{\text{f}} = 1.1 \times 10^{33}$$

Solubility



pH

2) Ex : What is the molar solb.
of $Al(OH)_3$ in a soln. w
a $pH = 13.00$?

VI) Precipitation & Separation of Ions

K_{sp} tells **max conc.** of **ions** which can exist in soln.
- equil. in a **saturated** soln.

Can reach **equil.** from either direction

- if only **ions** present in soln. precipitation is possible

A) Will a Precipitate Form

Use Q Ion Product



$Q > K_{sp}$ ppt forms
- rxn shifts left
until $Q = K_{sp}$

$Q = K_{sp}$ equilibrium
(saturated soln)

$Q < K_{sp}$ solid dissolves
- rxn shifts right
until $Q = K_{sp}$

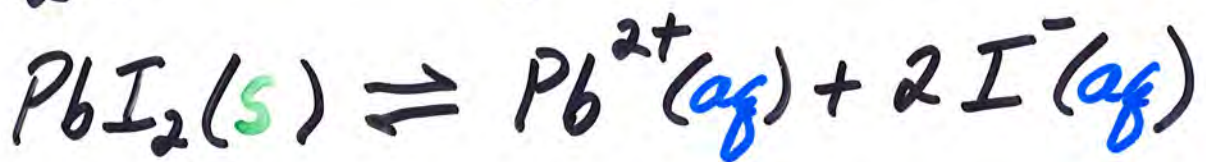
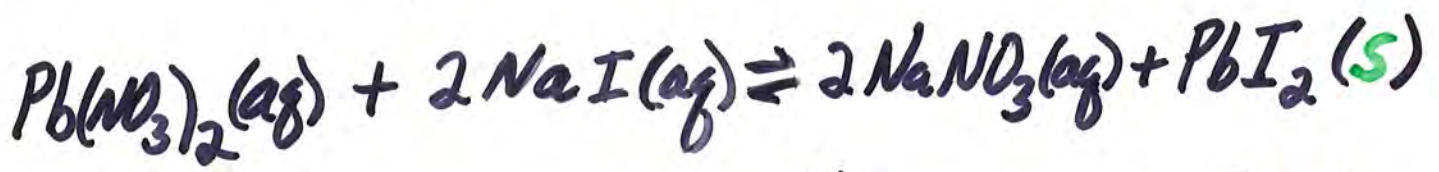
1) Ex : Precipitation ex.

A 25.0 mL sample of 0.020 M $Pb(NO_3)_2$ is added to 40.0 mL of 0.0054 M NaI.

Will a ppt form?

(Assume vol. are additive)

$$K_{sp}(PbI_2) = 8.7 \times 10^{-9}$$



$$Q = [Pb^{2+}][I^{-}]^2$$

a) Calc. moles

b) Calc molarities at mixing

c) Calc. Q & compare to K

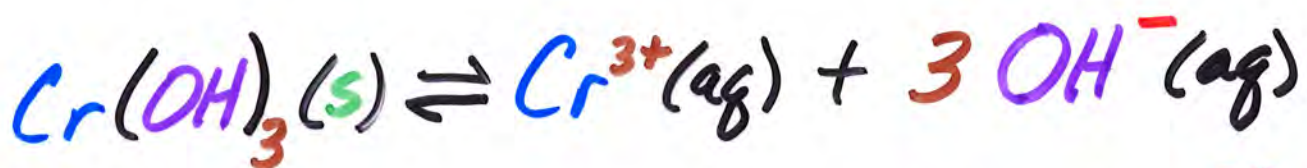
B) Selective Precipitation

Use *diff.* in solubility of salts which have *diff.* K_{sp} values.

1) Similar Formulas & K_{sp} Expressions

Compd	K_{sp}
AgCl	1.8×10^{-10}
AgBr	3.3×10^{-13}
AgI	1.5×10^{-16}

2) Ex : What conc. of OH^- is req. to achieve max. separation of Cr^{3+} & Sn^{2+} from a soln. where both are 0.10M?



$$K_{sp} = 1.6 \times 10^{-30}$$



$$K_{sp} = 5.4 \times 10^{-27}$$

Can **not** tell which will ppt. first based on K_{sp} unless form of eqn. is same & conc. are same

a) Calc $[OH^-]$ req. to
ppt. each cation

b) Which cation ppt first?

c) What is $\text{max } [\text{OH}^-]$ which
can be added w/o ppt $\text{Cr}(\text{OH})_3$?

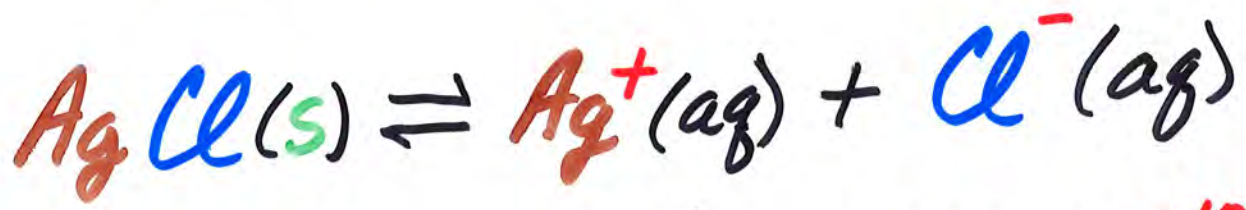
d) What is $[\text{Sn}^{2+}]$ when
 $\text{Cr}(\text{OH})_3$ starts to ppt?

e) How Effective is
the Separation?

What % Sn^{2+} remains?

% Sn^{2+}

3) Ex : What happens when 0.10M AgNO_3 is gradually added to a soln. of 0.050M NaCl + 0.050M Na_2CrO_4 ?



$$K_{sp} = 1.8 \times 10^{-10}$$



$$K_{sp} = 1.1 \times 10^{-12}$$

a) Calc $[Ag^+]$ req. to
ppt. each anion

b) Which anion ppt first?

c) What is $\max [Ag^+]$ which
can be added w/o ppt Ag_2CrO_4 ?

d) What is $[Cl^-]$ when
 Ag_2CrO_4 starts to ppt?

e) How Effective is
the Separation?

What % Cl^- remains?

% Cl^-

C) Solubility of Metal Sulfides

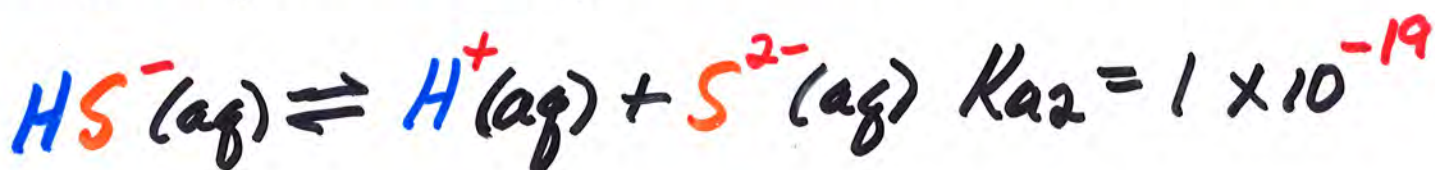
Might think rxn is:



NOT the case

S^{2-} strong base

- does **not** exist in soln



1) Derive MS Equil. Expression

for metal sulfides ONLY

K_{sp} rxn is:



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

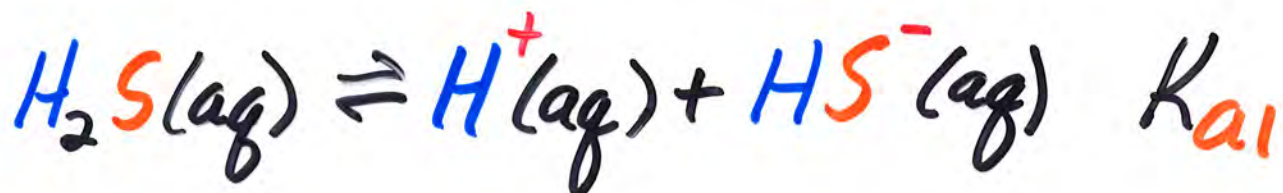
How do we get

HS^- & OH^- ?

a) HS⁻

saturate soln. w. H₂S

- 0.10 M H₂S



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$[\text{HS}^-] = \frac{K_{a1} [\text{H}_2\text{S}]}{[\text{H}^+]}$$

b) OH⁻



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

For a specific problem
solve for $[\text{HS}^-] + [\text{OH}^-]$
& substitute into
expression for Q &
compare to K_{sp}

c) Alternatively

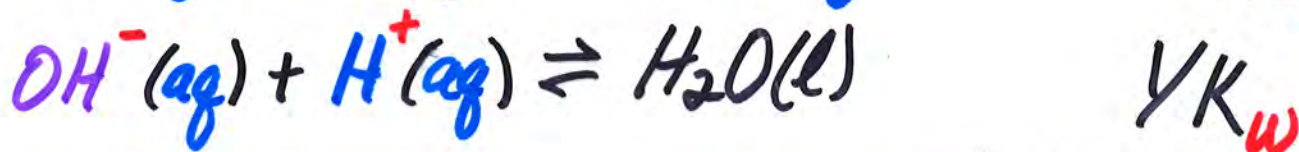
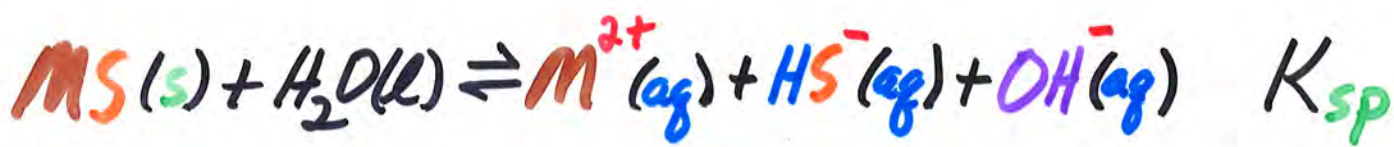
substitute expressions
for $[HS^-]$ & $[OH^-]$
into K_{sp}

$$K_{sp} = [M^{2+}] \left\{ \frac{K_{a1} [H_2S]}{[H^+]} \right\} \left\{ \frac{K_w}{[H^+]} \right\}$$

$$= \frac{[M^{2+}] [H_2S]}{[H^+]^2} (K_{a1} K_w)$$

$$\frac{K_{sp}}{K_{a1} K_w} = \frac{[M^{2+}] [H_2S]}{[H^+]^2}$$

Actually K for following rxn:



$$K = \frac{K_{sp}}{K_{a1} K_w}$$

Use to determine $[H^+]$
+ pH at which ppt forms

$$[H^+] = \left\{ \frac{[M^{2+}][H_2S] K_{a1} K_w}{K_{sp}} \right\}^{1/2}$$

d) Ex : A soln. contains
0.010 M Pb^{2+} & 0.010 M Fe^{2+} .
Will PbS &/or FeS ppt
when the soln is made to
be 0.10 M H_2S & 0.30 M
 HNO_3 is added?

$$K_{sp}(PbS) = 3 \times 10^{-28}$$

$$K_{sp}(FeS) = 6 \times 10^{-19}$$

1) Calc. $[HS^-]$

2) Calc $[OH^-]$

3) Calc Q

e) Ex : A soln contains
0.010 M Pb^{2+} & 0.010 M Fe^{2+} .
What pH will give the
maximum separation.

$$[H^+] = \left\{ \frac{[M^{2+}][H_2S]K_{a1}K_w}{K_{sp}} \right\}^{1/2}$$

