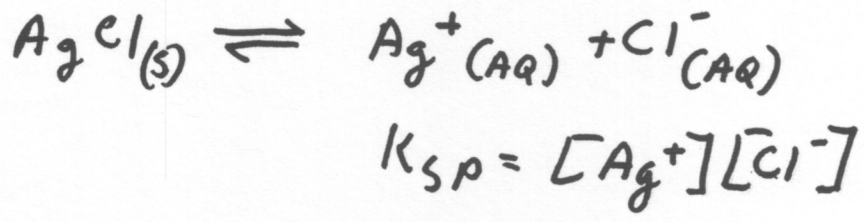
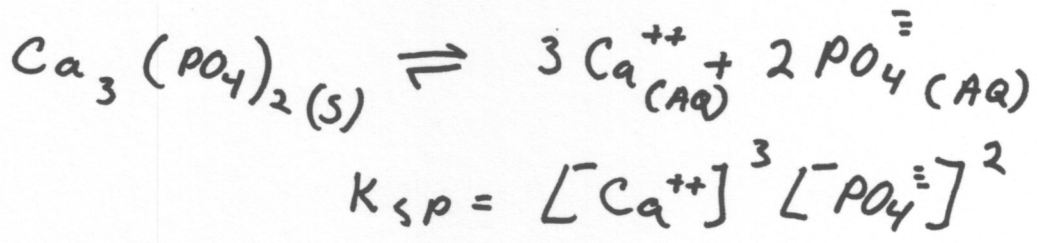
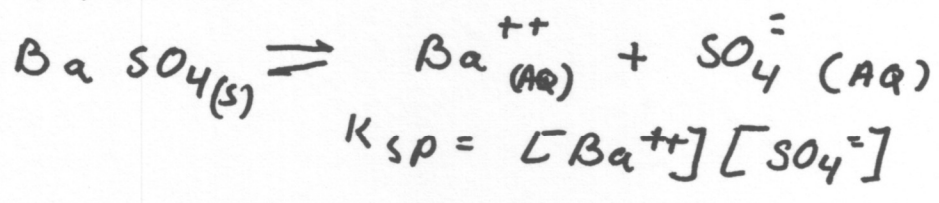


K_{sp} IS DEFINED AS THE PRODUCT OF THE EQUILIBRIUM CONCENTRATIONS OF THE IONS IN THE COMPOUND, EACH CONCENTRATION RAISED TO A POWER EQUAL TO THE NUMBER OF SUCH IONS IN THE FORMULA OF THE COMPOUND.

FOR EXAMPLE



CALCULATING K_{sp}

ONE LITER OF A SOLUTION SATURATED WITH CaC_2O_4 CONTAINS (AFTER EVAPORATION TO DRYNESS) 0.0061g CaC_2O_4 . CALCULATE K_{sp}

1) grams TO moles $0.0061g \times \frac{1}{128g/mole} = 4.8 \times 10^{-5} \text{ MOLES } CaC_2O_4$

2) CONCENTRATION TABLE

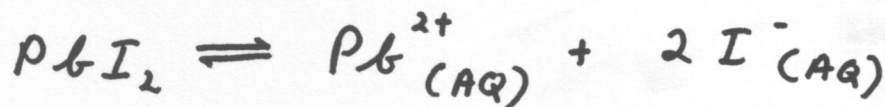
	CaC_2O_4	\rightleftharpoons	Ca^{2+}	+	$C_2O_4^{2-}$
INITIAL			0		0
CHANGE			$+ 4.8 \times 10^{-5}$		$+ 4.8 \times 10^{-5}$
FINAL			4.8×10^{-5}		4.8×10^{-5}

$$\text{IF } [\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] = 4.8 \times 10^{-5} \text{ M} \quad (3)$$

$$\text{THEN } K_{SP} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (4.8 \times 10^{-5})^2 = 2.3 \times 10^{-9}$$

ANOTHER EXAMPLE

1.2×10^{-3} moles OF PbI_2 DISSOLVES IN 1 L H_2O
WHAT IS K_{SP} ?



THERE ARE TWO CONSEQUENCES OF THE FACT THAT THIS COMPOUND HAS 2 I^{-} IONS

- 1) EACH MOLE OF PbI_2 PRODUCES 2 MOLES I^{-}
- 2) THE $[\text{I}^{-}]$ TERM WILL BE SQUARED $[\text{I}^{-}]^2$

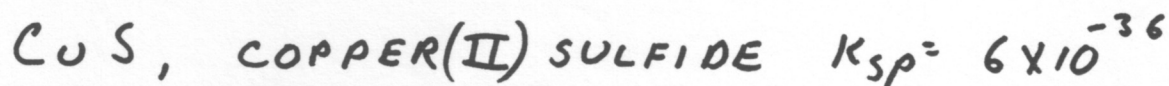
CONCENTRATION TABLE

	$\text{PbI}_2(\text{s})$	\rightleftharpoons	$\text{Pb}^{2+}(\text{AQ})$	+	2I^{-}
INITIAL			0		0
CHANGE			1.2×10^{-3}		$2 \times (1.2 \times 10^{-3})$
FINAL			1.2×10^{-3}		2.4×10^{-3}

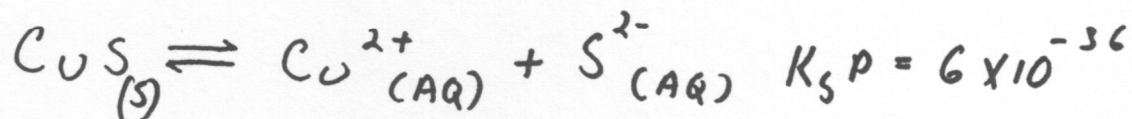
NOW SUBSTITUTE INTO K_{SP} EXPRESSION

$$K_{SP} = [\text{Pb}][\text{I}^{-}]^2 = 1.2 \times 10^{-3} \times (2.4 \times 10^{-3})^2 = 6.9 \times 10^{-9}$$

THE PROBLEM CAN BE LOOKED AT IN THE OPPOSITE WAY, GIVE K_{SP} CALCULATE MOLAR ION CONCENTRATIONS
EXAMPLE



CALCULATE THE SOLUBILITY OF CuS IN 1 LITER H_2O



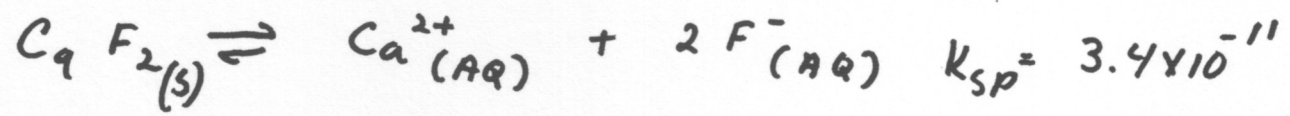
CONCENTRATION TABLE

	$CuS \rightleftharpoons$	Cu^{2+}	+	S^{2-}
INITIAL		0		0
CHANGE		+x		+x
FINAL		x		x

$$K_{sp} = [Cu^{2+}][S^{2-}] = 6 \times 10^{-36}$$

$$x^2 = 6 \times 10^{-36} \quad x = 2.4 \times 10^{-18} M$$

A MORE COMPLICATED EXAMPLE



AGAIN, THE FACT THAT ONE MOLE CaF_2 MAKES 2 MOLES F^{-} HAS TWO CONSEQUENCES

CONCENTRATION TABLE

	$CaF_2 \rightleftharpoons$	Ca^{2+}	+	$2F^{-}$
INITIAL		0		0
CHANGE		+x		+2x
FINAL		x		2x

SUBSTITUTE INTO EQUILIBRIUM EXPRESSION

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

$$x (2x)^2 = 3.4 \times 10^{-11}$$

$$x \times 4x^2 = 3.4 \times 10^{-11}$$

$$4x^3 = 3.4 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{3.4 \times 10^{-11}}{4}}$$

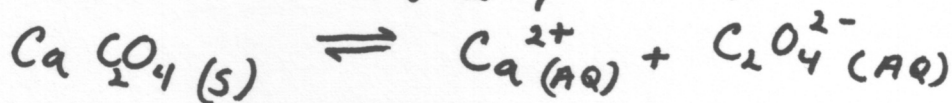
$$x = \sqrt[3]{8.5 \times 10^{-12}} = 2 \times 10^{-4} M$$

SOLUBILITY AND THE COMMON-ION EFFECT

A VERY STRAIGHT FORWARD APPLICATION OF LECHATELIER'S PRINCIPLE IS OFTEN USEFUL IN IONIC EQUILIBRIA IF ANOTHER SOURCE OF ONE OF THE IONS IN THE EQUILIBRIUM IS FOUND, THE EQUILIBRIUM MUST REACT TO PRODUCE MORE SOLID

FOR EXAMPLE

SUPPOSE YOU HAD A SATURATED SOLUTION OF CALCIUM OXALATE CaC_2O_4 $K_{sp} = 2.3 \times 10^{-9}$



1) CALCULATE $[\text{Ca}^{2+}]$

$$x^2 = 2.3 \times 10^{-9} \quad x = 4.8 \times 10^{-5} \text{ M}$$

NOW SUPPOSE WE ADD SOME Ca^{2+} IN THE FORM OF A SOLUBLE SALT SUCH AS CaCl_2 .

WHICH DIRECTION WILL THE EQUILIBRIUM GO?

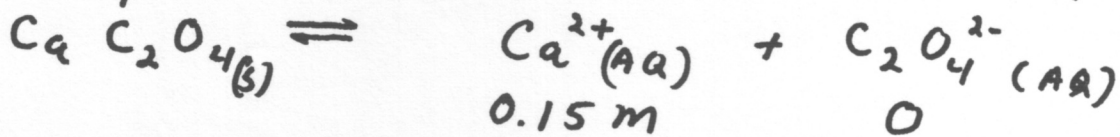
TO THE LEFT, OF COURSE, SO MORE SOLID WILL BE PRODUCED.

IN OTHER WORDS, CaC_2O_4 IS LESS SOLUBLE IN THE PRESENCE OF Ca^{2+} THAN IT IS IN PURE WATER

NOW CALCULATE THE SOLUBILITY OF CaC_2O_4 IN AN AQUEOUS SOLUTION THAT CONTAINS $0.15 \text{ M } \text{Ca}^{++}$

(6)

SOLUBILITY OF CaC_2O_4 IN 0.15 M CaCl_2



INITIAL

0.15 M

0

CHANGE

+x

+x

FINAL

0.15 + x

x

NOW SUBSTITUTE INTO K_{sp}

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.15 + x)x = 2.3 \times 10^{-9}$$

REARRANGING,

$$x = \frac{2.3 \times 10^{-9}}{0.15 + x}$$

ASSUMING x IS SMALL

$$x = \frac{2.3 \times 10^{-9}}{0.15}$$

$$x = 15 \times 10^{-9} \text{ or } 1.5 \times 10^{-8}$$

SO, THE SOLUBILITY OF CaC_2O_4 IN H_2O IS $4.8 \times 10^{-5}\text{ M}$

AND, THE SOLUBILITY OF CaC_2O_4 IN 0.15 M CaCl_2 IS 1.5×10^{-8}

A FACTOR OF 3000 LESS SOLUBLE

PREDICTING PRECIPITATION REACTIONS

WE WILL ASK "WILL PRECIPITATION OCCUR" FOR GIVEN INITIAL IONIC CONCENTRATIONS

WE WILL ANSWER YES IF THE PRODUCT OF THE IONIC CONCENTRATIONS EXCEEDS K_{sp}

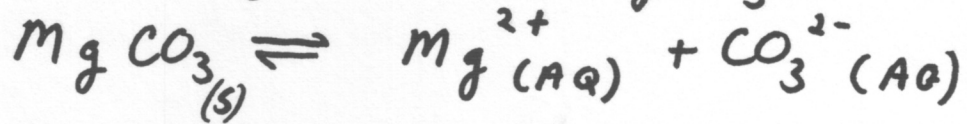
(7)

PREDICTING PRECIPITATIONS

THESE PROBLEMS REQUIRE EVALUATING THE REACTION QUOTIENT FOR A GIVEN REACTION AND A GIVEN CONCENTRATION OF IONS. THIS PARTICULAR REACTION QUOTIENT IS CALLED THE ION-PRODUCT.

AN EXAMPLE

A SOLUTION IS PREPARED TO BE 0.05 M Mg^{2+} AND 0.02 M CO_3^{2-} . WILL $MgCO_3$ PRECIPITATE?



$$K_{sp} = [Mg^{2+}][CO_3^{2-}] = 1 \times 10^{-5}$$

$$Q_c = [Mg^{2+}][CO_3^{2-}] = 0.05 \times 0.02 = 1 \times 10^{-3}$$

$$1 \times 10^{-3} > 1 \times 10^{-5}$$

$$Q_c > K_{sp}$$

SO, YES THERE WILL BE A PRECIPITATE OF MAGNESIUM CARBONATE

IF THE SAME SOLUTION HAD $[Mg^{2+}] = .001 M$
 $[CO_3^{2-}] = .002 M$

$$Q_c = 1 \times 10^{-3} \times 2 \times 10^{-3} = 2 \times 10^{-6}$$

$$2 \times 10^{-6} < 1 \times 10^{-5}$$

$$Q_c < K_{sp}$$

SO, NO PRECIPITATE

COMPLETENESS OF PRECIPITATION

IN QUANTITATIVE ANALYSIS, IT IS OFTEN NECESSARY TO CALCULATE THE CONCENTRATION OF AN ION REMAINING AFTER PRECIPITATION AND THE PERCENTAGE OF THE ION THAT WAS NOT PRECIPITATED

EXAMPLE

SULFATE (SO_4^{2-}) IS DETERMINED BY PRECIPITATION AS $BaSO_4$ BY ADDITION OF EXCESS Ba^{2+} (BARIUM) ION. BEFORE PRECIPITATION, $[Ba^{2+}] = 5.0 \times 10^{-4} M$ AND $[SO_4^{2-}] = 5.0 \times 10^{-5} M$. CALCULATE $[SO_4^{2-}]$ AFTER $BaSO_4$ PRECIPITATES. WHAT PERCENTAGE SO_4^{2-} IS NOT PRECIPITATED?

STEP 1 STOICHIOMETRY CALCULATION ASSUMING NEARLY 100% COMPLETION OF THE REACTION

	$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightleftharpoons BaSO_4(s) \quad K_{sp} = 1.1 \times 10^{-10}$	
	$[Ba]$	$[SO_4]$
INITIAL	.00050	.00005
CHANGE	-.00005	-.00005
FINAL	.00045 M	0

STEP 2 EQUILIBRIUM CALCULATION $K_{sp} = 1.1 \times 10^{-10}$

	$[Ba]$	$[SO_4]$	
INITIAL	.00045	0	
CHANGE	+x	+x	$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$
	.00045+x	x	$(.00045+x)(x) = 1.1 \times 10^{-10}$

$$x = \frac{1.1 \times 10^{-10}}{.00045} = 2.4 \times 10^{-7}$$

$$[SO_4^{2-}] = 2.4 \times 10^{-7}$$

ASSUMING x IS SMALL

COMPLETENESS OF PRECIPITATION

9

IF $[SO_4^{2-}] = 2.4 \times 10^{-7} M$ AND THE INITIAL $[SO_4^{2-}] = 5.0 \times 10^{-5} M$
THE PERCENTAGE REMAINING IS

$$\frac{2.4 \times 10^{-7}}{5.0 \times 10^{-5}} \times 100 = 0.48 \%$$

FRACTIONAL PRECIPITATION

USES THE DIFFERENCE IN TWO K_{SP} VALUES TO
SEPARATE 2 IONS

FOR EXAMPLE, A SOLUTION IS $0.10 M Ba^{2+}$ AND $0.10 M Sr^{2+}$
BY ADDING A SOLUTION OF K_2CrO_4 (SOLUBLE CrO_4^{2-})
BOTH IONS CAN BE PRECIPITATED SEQUENTIALLY

$$K_{SP} BaCrO_4 = 1.2 \times 10^{-10}$$

$$K_{SP} SrCrO_4 = 3.5 \times 10^{-5}$$

CALCULATE THE CrO_4 CONCENTRATION REQUIRED TO
BEGIN PRECIPITATING EACH ION. SUBSTITUTE THE
INITIAL Ba^{2+} CONCENTRATION INTO THE K_{SP} EQUATION

$$[Ba^{2+}][CrO_4^{2-}] = K_{SP} = 1.2 \times 10^{-10}$$

$$0.10 M [CrO_4^{2-}] = 1.2 \times 10^{-10}$$

$$[CrO_4^{2-}] = 1.2 \times 10^{-9} M$$

SIMILARLY FOR Sr^{2+}

$$[Sr^{2+}][CrO_4^{2-}] = K_{SP} = 3.5 \times 10^{-5}$$

$$0.10 [CrO_4^{2-}] = 3.5 \times 10^{-5}$$

$$[CrO_4^{2-}] = 3.5 \times 10^{-4} M$$

CLEARLY, Ba^{2+} PRECIPITATES FIRST. NOW WE ASK ABOUT
THE COMPLETENESS OF Ba^{2+} PRECIPITATION OR THE
COMPLETENESS OF THE FRACTIONAL PRECIPITATION

COMPLETENESS OF PRECIPITATION

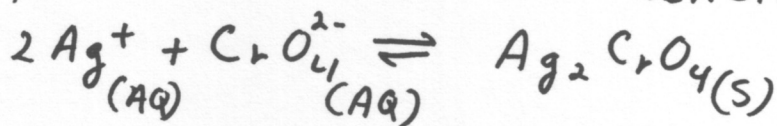
EXAMPLE 2

(10)

HOW MUCH Ag^+ ION REMAINS WHEN 25.0 ML AgNO_3 AT 0.10M IS ADDED TO 25.0 ML OF 0.10M K_2CrO_4 ?

K_{sp} FOR Ag_2CrO_4 IS 1.1×10^{-12}

1) STOICHIOMETRY (ASSUME COMPLETE REACTION)



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

$$\text{MOLES Ag} = 0.025\text{L} \times 0.1\text{M/L} = 0.0025 \text{ moles}$$

$$\text{MOLES CrO}_4 = 0.025\text{L} \times 0.1\text{M/L} = 0.0025 \text{ moles}$$

SINCE 2 MOLES Ag^+ ARE REQUIRED TO REACT 1 MOLE CrO_4^{2-} ,

$$\text{MOLES CrO}_4 \text{ REMAINING} = 0.00250$$

$$- 0.00125$$

$$0.00125 \text{ MOLES CrO}_4 \text{ IN } 0.05\text{L}$$

$$[\text{CrO}_4] = \frac{0.00125}{0.05} = 0.025\text{M}$$

2) EQUILIBRIUM

$$[\text{Ag}^+] \quad [\text{CrO}_4]$$

INITIAL

0

0.025

CHANGE

+2x

+x

FINAL

2x

0.025 + x

SUBSTITUTE

$$K_{sp} = 1.1 \times 10^{-12} = [\text{Ag}^+]^2 [\text{CrO}_4] \quad \text{ASSUME } x \text{ IS SMALL}$$

$$1.1 \times 10^{-12} = [2x]^2 [0.025]$$

$$\frac{1.1 \times 10^{-12}}{0.025} = 4x^2 \rightarrow \frac{1.1 \times 10^{-12}}{0.1} = x^2$$

$$x = \sqrt{11 \times 10^{-12}} = 3.3 \times 10^{-6}$$

$$2x = 6.6 \times 10^{-6} \text{ M } [\text{Ag}^+]$$

COMPLETENESS OF Ba²⁺ PRECIPITATION

WHAT IS [Ba²⁺] WHEN Sr²⁺ JUST BEGINS TO PPT?

Sr²⁺ BEGINS TO PRECIPITATE WHEN [ClO₄²⁻] = 3.5 x 10⁻⁴ M

SUBSTITUTE INTO K_{sp} EXPRESSION

$$[Ba^{2+}][ClO_4^{2-}] = K_{sp} = 1.2 \times 10^{-10}$$

$$[Ba^{2+}](3.5 \times 10^{-4}) = 1.2 \times 10^{-10}$$

$$[Ba^{2+}] = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = 0.34 \times 10^{-6} \text{ OR } 3.4 \times 10^{-7} \text{ M}$$

COMPARED TO THE INITIAL CONCENTRATION (0.10 M)

$$\frac{3.4 \times 10^{-7} \text{ M}}{0.10 \text{ M}} \times 100\% = 0.00034\%$$

THE EFFECT OF pH ON SOLUBILITY

IF THE ANION OF A SLIGHTLY SOLUBLE SALT IS ALSO

THE CONJUGATE BASE OF A WEAK ACID, THAT ANION

ALSO PARTICIPATES IN THE ACID-BASE EQUILIBRIUM

AND ITS SOLUBILITY IS AFFECTED BY pH.

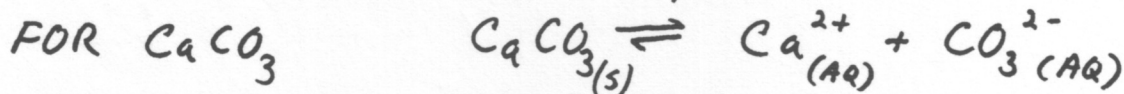
CONSIDER TWO SLIGHTLY SOLUBLE SALTS, CaCO₃

AND CaSO₄. WHICH OF THESE WOULD HAVE ITS

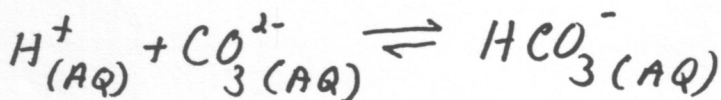
SOLUBILITY MORE AFFECTED BY THE ADDITION OF H⁺?

WOULD THE SOLUBILITY OF THE SALT INCREASE OR DECREASE?

THE H⁺ IONS OF THE ACID MAY REACT WITH THE ANION



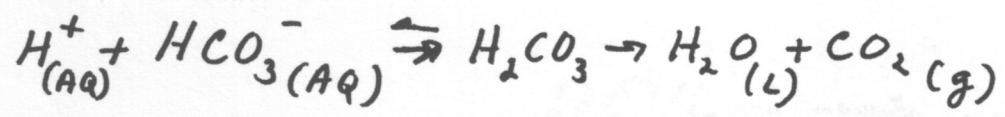
IN THE PRESENCE OF H⁺,



AS CARBONATE IS REMOVED BY THIS REACTION, CaCO₃

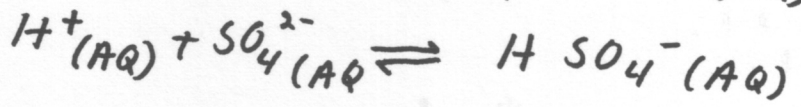
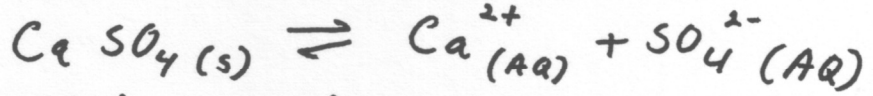
DISSOLVES

IN ADDITION, THE HCO_3^- (BICARBONATE) REACTS IF MORE H^+ IS ADDED:



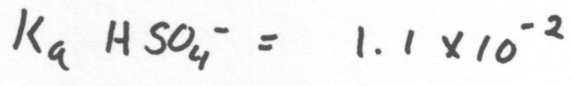
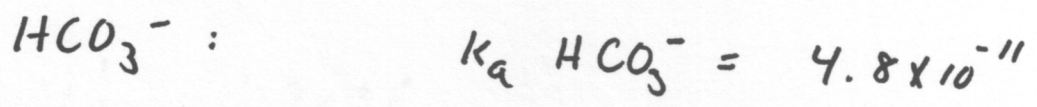
SO, INCREASING $[\text{H}^+]$ CAUSES THE SOLUBILITY OF CaCO_3 TO INCREASE

FOR CaSO_4 , THE EQUILIBRIA ARE:



AGAIN, THE ANION OF THE INSOLUBLE SALT IS REMOVED BY REACTION WITH H^+

HOWEVER, HSO_4^- IS A MUCH STRONGER ACID THAN



SO CALCIUM CARBONATE IS MUCH MORE SOLUBLE IN ACIDIC SOLUTION, WHILE CALCIUM SULFATE IS ONLY SLIGHTLY MORE SOLUBLE.

COMPLEX IONS

MANY METAL IONS FORM COMPLEX IONS WHICH ARE METAL IONS WITH ADDITIONAL BONDS FORMED BETWEEN THE METAL AND A LEWIS BASE

THE BOND BETWEEN THE METAL AND THE LIGAND IS CALLED A COORDINATE COVALENT BOND

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

(14)

SUBSTITUTE EQUILIBRIUM VALUES

$$\frac{(0.010 - x)}{x \times (0.98)^2} = 1.7 \times 10^7$$

ASSUME x WILL BE SMALL

$$\frac{0.010}{0.96x} = 1.7 \times 10^7$$

SOLVE FOR x

$$x = 6.1 \times 10^{-10} \text{ M } Ag^+$$

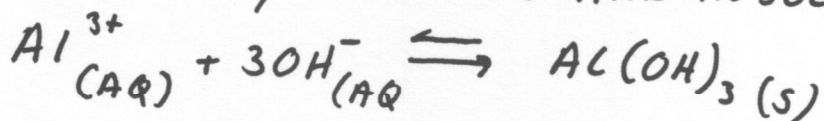
AMPHOTERIC HYDROXIDES

ARE A SPECIAL CASE OF COMPLEX IONS

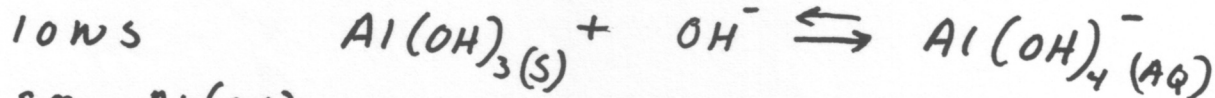
THEY ARE METAL HYDROXIDES WHICH REACT WITH

BOTH ACIDS AND BASES

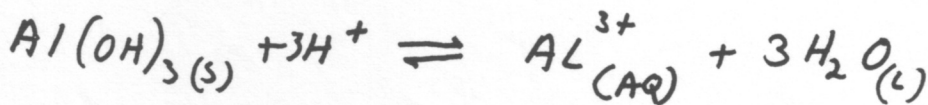
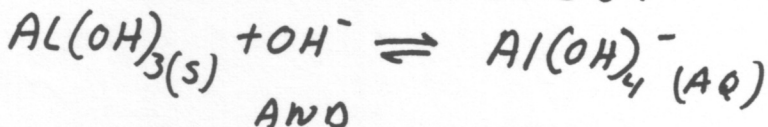
MOST METAL HYDROXIDES ARE INSOLUBLE



BUT SOME (Zn, Al, Cu, Pb, Sn, Cr) FORM COMPLEX



SO, $Al(OH)_3$ IS AN AMPHOTERIC SPECIES:



COMPLEX ION EQUILIBRIUM EXAMPLE

PREDICT WHETHER CADMIUM OXALATE CdC_2O_4 WILL PRECIPITATE FROM A SOLUTION THAT IS $0.0020 M Cd(NO_3)_2$ AND $0.01 M Na_2C_2O_4$ AND $0.10 M NH_3$

$$K_{sp} CdC_2O_4 = 1.5 \times 10^{-8}$$

$$K_F Cd(NH_3)_4^{2+} = 1.0 \times 10^7$$

STOICHIOMETRY $K_F = \frac{[Cd(NH_3)_4^{2+}]}{[Cd][NH_3]^4} = 1 \times 10^7$ ASSUME COMPLETION

$0.0020 M Cd$ WILL CONSUME $0.008 M NH_3$
LEAVING $[NH_3] = 0.092 M$

EQUILIBRIUM

$$K_F = \frac{(0.002)}{(0.092)^4} \gamma = 1 \times 10^7$$

$$\frac{1}{\gamma} = \frac{1 \times 10^7 (0.092)^4}{0.002}$$

$$\gamma = \frac{0.002}{1 \times 10^7 (0.092)^4}$$

$$\gamma = \frac{0.002}{7.2 \times 10^2} = 2.8 \times 10^{-6}$$

NOW USE K_{sp}

$$[Cd^{2+}] = 2.8 \times 10^{-6} M$$

$$[C_2O_4] = 0.01 M$$

$$K_{sp} = 1.5 \times 10^{-8}$$

PPT

$$Q = 2.8 \times 10^{-8} \text{ SO, WILL PPT}$$