

## Complex Ion Equilibria

*A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts and comprise central metal atoms or ions acting as Lewis acids bonded to molecules or ions called ligands that act as Lewis bases. The equilibrium constant for the reaction between a metal ion and ligands produces a complex ion called a formation constant; for the reverse reaction, it is called a dissociation constant.*

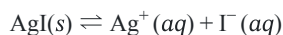
### Learning Objectives

By the end of this section, you will be able to:

- Explain the common ion effect
- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

### 31.0.1 Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le Châtelier's principle. Consider the dissolution of silver iodide:



This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved  $\text{Ag}^+$  and  $\text{I}^-$ . In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

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

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

## LINK TO LEARNING

View this [simulation](#) to explore various aspects of the common ion effect.

## EXAMPLE 31.0.2

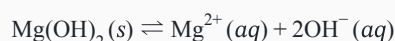
### Common Ion Effect on Solubility

What is the effect on the amount of solid  $\text{Mg}(\text{OH})_2$  and the concentrations of  $\text{Mg}^{2+}$  and  $\text{OH}^-$  when each of the following are added to a saturated solution of  $\text{Mg}(\text{OH})_2$ ?

- (a)  $\text{MgCl}_2$
- (b)  $\text{KOH}$
- (c)  $\text{NaNO}_3$
- (d)  $\text{Mg}(\text{OH})_2$

### Solution

The solubility equilibrium is



- (a) Adding a common ion,  $\text{Mg}^{2+}$ , will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.
- (b) Adding a common ion,  $\text{OH}^-$ , will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.
- (c) The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.
- (d) Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of  $Q$ , and no shift is required to restore  $Q$  to the value of the equilibrium constant.

### Check Your Learning

What is the effect on the amount of solid  $\text{NiCO}_3$  and the concentrations of  $\text{Ni}^{2+}$  and



when each of the following are added to a saturated solution of  $\text{NiCO}_3$

- (a)  $\text{Ni}(\text{NO}_3)_2$
- (b)  $\text{KClO}_4$

(c)  $\text{NiCO}_3$

(d)  $\text{K}_2\text{CO}_3$

### ✓ Answer

(a) mass of  $\text{NiCO}_3(s)$  increases,  $[\text{Ni}^{2+}]$  increases,

$[\text{CO}_3^{2-}]$

decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid  $\text{NiCO}_3$ ; (d) mass of  $\text{NiCO}_3(s)$  increases,  $[\text{Ni}^{2+}]$  decreases,

$[\text{CO}_3^{2-}]$

increases;

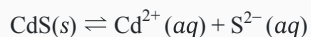
### EXAMPLE 31.0.3

#### Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide (CdBr<sub>2</sub>). The  $K_{sp}$  of CdS is  $1.0 \times 10^{-28}$ .

#### Solution

This calculation can be performed using the ICE approach:



	$\text{CdS}(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)$		
Initial concentration ( <i>M</i> )		0.010	0
Change ( <i>M</i> )		+ <i>x</i>	+ <i>x</i>
Equilibrium concentration ( <i>M</i> )		0.010 + <i>x</i>	<i>x</i>

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because  $K_{sp}$  is very small, assume  $x \ll 0.010$  and solve the simplified equation for  $x$ :

$$(0.010)(x) = 1.0 \times 10^{-28}$$

$$x = 1.0 \times 10^{-26} \text{ M}$$

The molar solubility of CdS in this solution is  $1.0 \times 10^{-26} \text{ M}$ .

#### Check Your Learning

Calculate the molar solubility of aluminum hydroxide, Al(OH)<sub>3</sub>, in a 0.015-*M* solution of aluminum nitrate, Al(NO<sub>3</sub>)<sub>3</sub>. The  $K_{sp}$  of Al(OH)<sub>3</sub> is  $2 \times 10^{-32}$ .

#### ✓ Answer

4

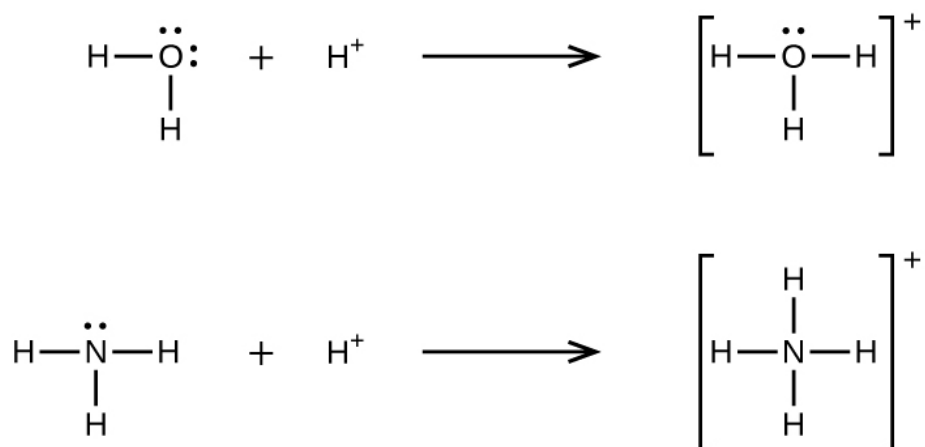
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$10^{-11} \text{ M}$

## 31.1 Lewis Acids and Bases

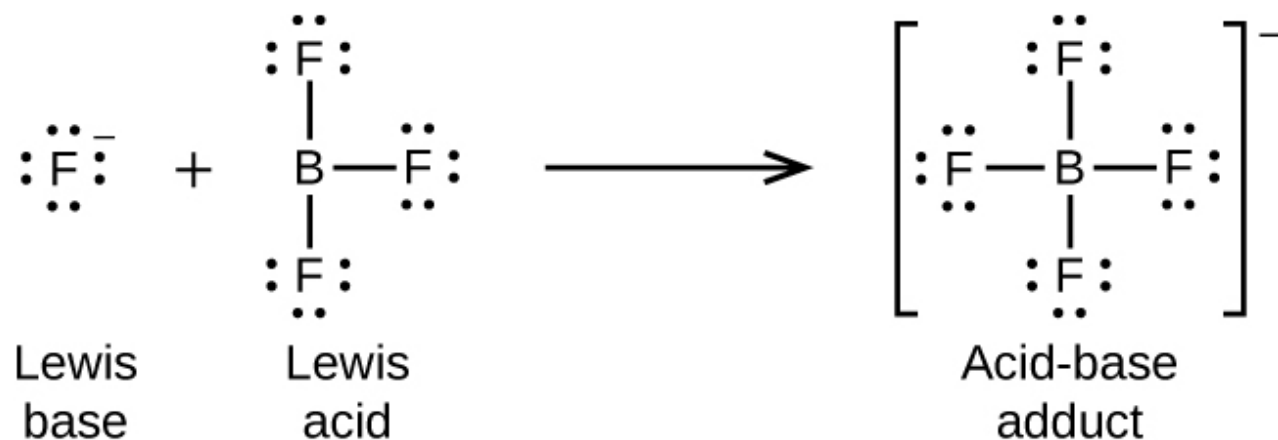
In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

A coordinate covalent bond (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.

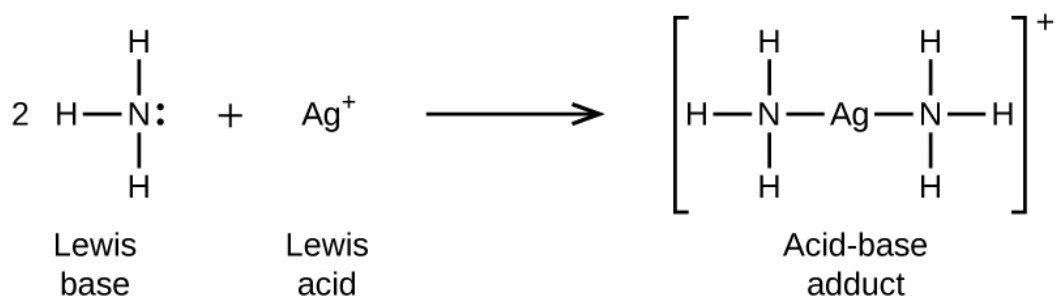


Reactions involving the formation of coordinate covalent bonds are classified as Lewis acid-base chemistry. The species donating the electron pair that compose the bond is a Lewis base, the species accepting the electron pair is a Lewis acid, and the product of the reaction is a Lewis acid-base adduct. As the two examples above illustrate, Brønsted-Lowry acid-base reactions represent a subcategory of Lewis acid reactions, specifically, those in which the acid species is  $\text{H}^+$ . A few examples involving other Lewis acids and bases are described below.

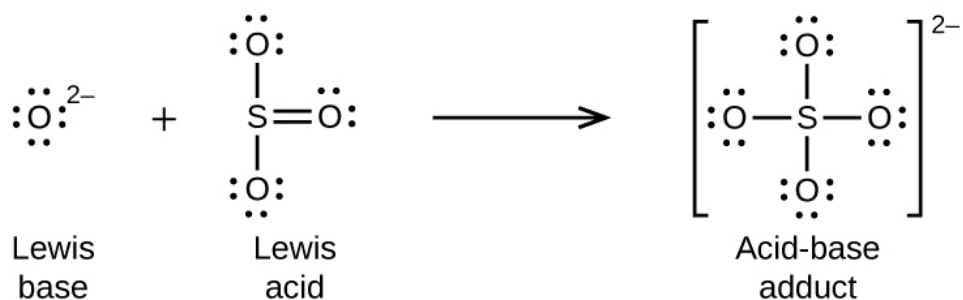
The boron atom in boron trifluoride,  $\text{BF}_3$ , has only six electrons in its valence shell. Being short of the preferred octet,  $\text{BF}_3$  is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



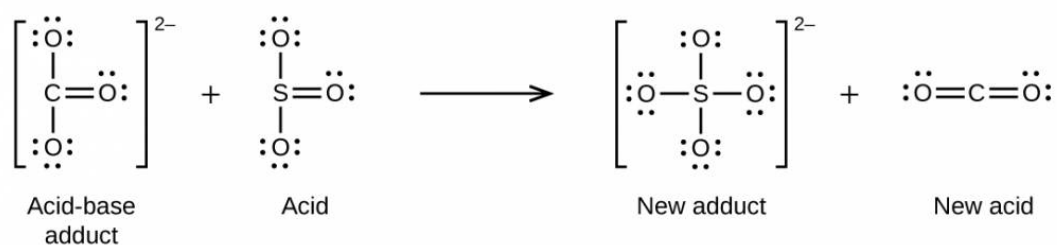
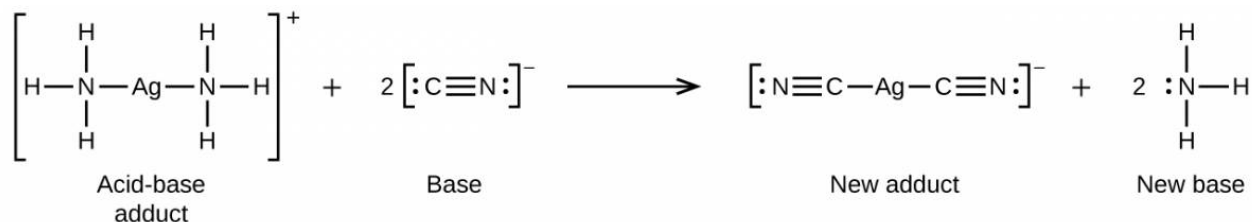
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:



Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:

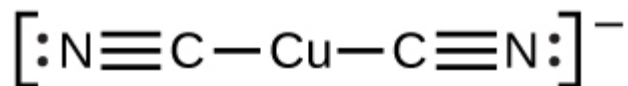


Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:

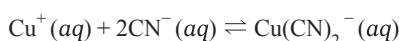


Another type of Lewis acid-base chemistry involves the formation of a complex ion (or a coordination complex) comprising a central atom, typically a transition metal cation, surrounded by ions or molecules called ligands. These ligands can be neutral molecules like H<sub>2</sub>O or NH<sub>3</sub>, or ions such as CN<sup>−</sup> or OH<sup>−</sup>. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. These types of Lewis acid-base reactions are examples of a broad subdiscipline called *coordination chemistry*—the topic of another chapter in this text.

The equilibrium constant for the reaction of a metal ion with one or more ligands to form a coordination complex is called a formation constant ( $K_f$ ) (sometimes called a stability constant). For example, the complex ion



is produced by the reaction

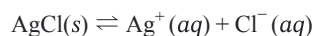


The formation constant for this reaction is

$$K_f = \frac{[\text{Cu}(\text{CN})_2^-]}{[\text{Cu}^+][\text{CN}^-]^2}$$

Alternatively, the reverse reaction (decomposition of the complex ion) can be considered, in which case the equilibrium constant is a dissociation constant ( $K_d$ ). Per the relation between equilibrium constants for reciprocal reactions described, the dissociation constant is the mathematical inverse of the formation constant,  $K_d = K_f^{-1}$ . A tabulation of formation constants is provided in [Appendix K](#).

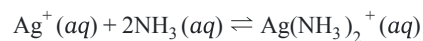
As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of  $\text{Ag}^+$  ( $[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}$ ):



However, if  $\text{NH}_3$  is present in the water, the complex ion,



can form according to the equation:



with

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

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of  $\text{AgCl}$  combine with  $\text{NH}_3$  to form





As a consequence, the concentration of silver ions,  $[\text{Ag}^+]$ , is reduced, and the reaction quotient for the dissolution of silver chloride,  $[\text{Ag}^+][\text{Cl}^-]$ , falls below the solubility product of AgCl:

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

More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

## EXAMPLE 31.1.1

### Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to



### Solution

Applying the standard ICE approach to this reaction yields the following:

	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$		
Initial concentration ( <i>M</i> )	0	0	0.10
Change ( <i>M</i> )	+ <i>x</i>	+2 <i>x</i>	− <i>x</i>
Equilibrium concentration ( <i>M</i> )	<i>x</i>	2 <i>x</i>	0.10 − <i>x</i>

Substituting these equilibrium concentration terms into the  $K_f$  expression gives

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

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

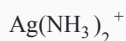
The very large equilibrium constant means the amount of the complex ion that will dissociate, *x*, will be very small. Assuming  $x \ll 0.1$  permits simplifying the above equation:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$

$$x^3 = \frac{0.10}{4(1.7 \times 10^7)} = 1.5 \times 10^{-9}$$

$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3}$$

Because only 1.1% of the



dissociates into  $\text{Ag}^+$  and  $\text{NH}_3$ , the assumption that  $x$  is small is justified.

Using this value of  $x$  and the relations in the above ICE table allows calculation of all species' equilibrium concentrations:

$$[\text{Ag}^+] = 0 + x = 1.1 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3] = 0 + 2x = 2.2 \times 10^{-3} \text{ M}$$

$$[\text{Ag}(\text{NH}_3)_2^+] = 0.10 - x = 0.10 - 0.0011 = 0.099$$

The concentration of free silver ion in the solution is  $0.0011 \text{ M}$ .

### Check Your Learning

Calculate the silver ion concentration,  $[\text{Ag}^+]$ , of a solution prepared by dissolving  $1.00 \text{ g}$  of  $\text{AgNO}_3$  and  $10.0 \text{ g}$  of  $\text{KCN}$  in sufficient water to make  $1.00 \text{ L}$  of solution. (Hint: Because  $K_f$  is very large, assume the reaction goes to completion then calculate the  $[\text{Ag}^+]$  produced by dissociation of the complex.)

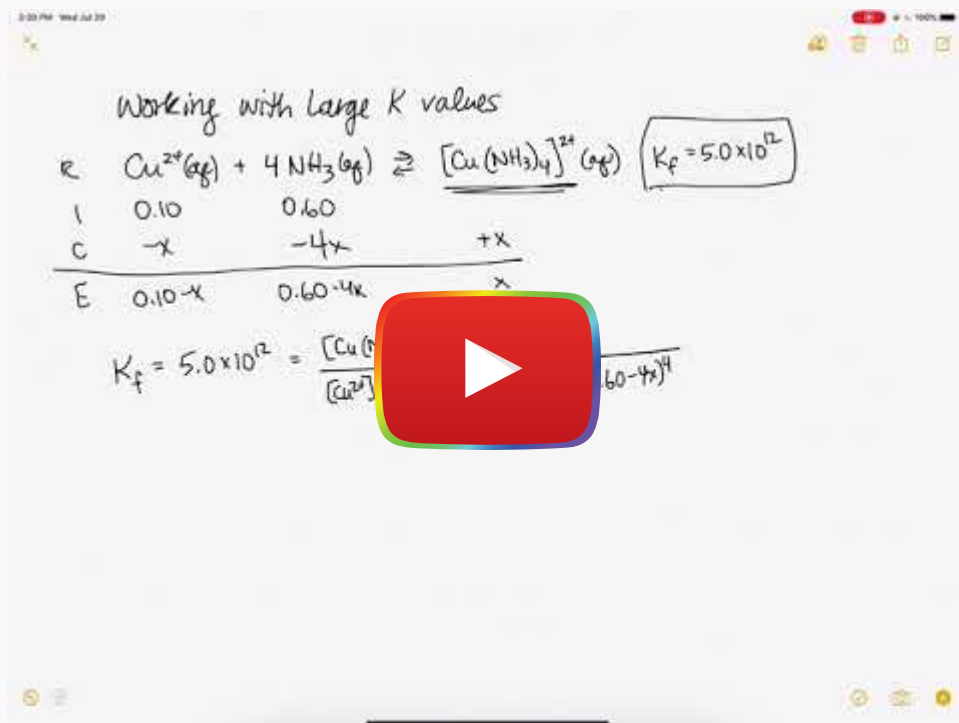
#### ✓ Answer

2.9

×

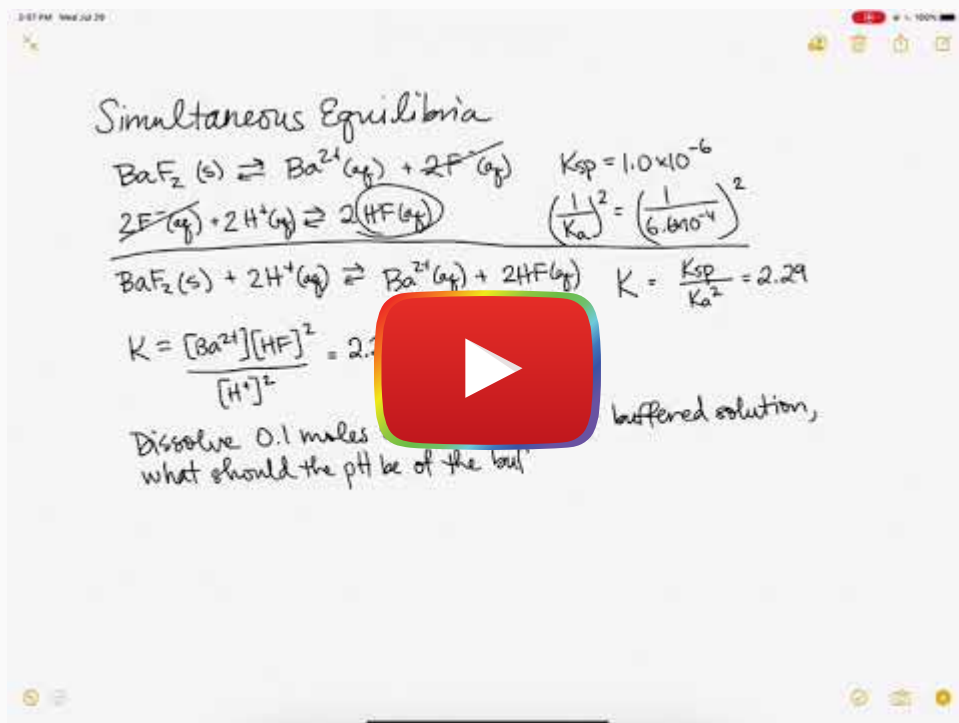
$10^{-22} \text{ M}$

### 31.1.2 Working with Large K Values



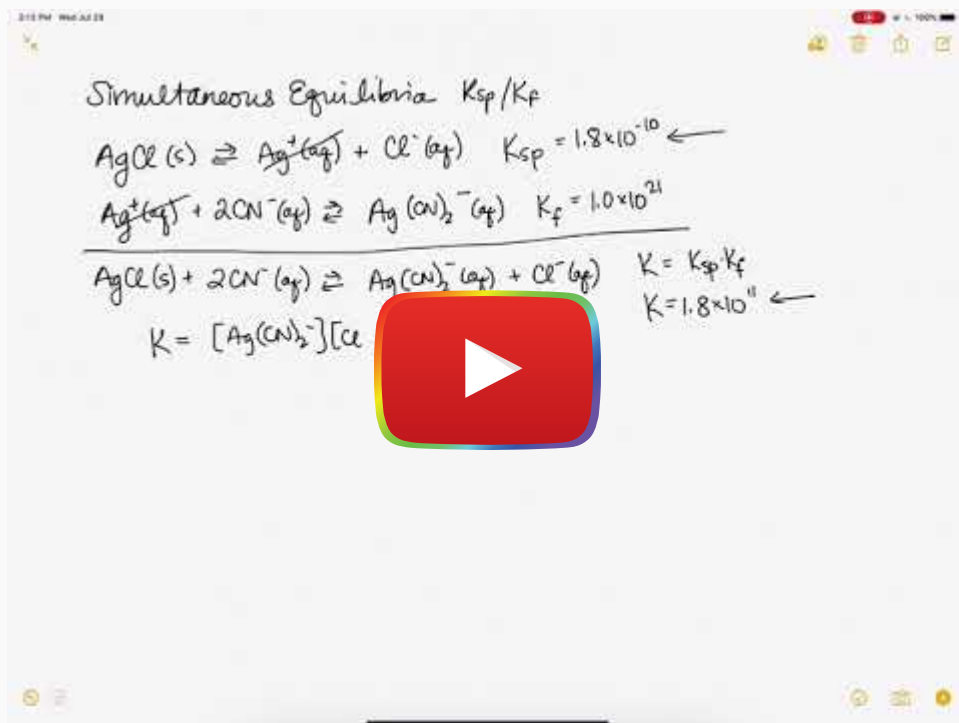
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### 31.1.3 Simultaneous Equilibria K<sub>sp</sub>/K<sub>a</sub>



[Watch on YouTube](#)

### 31.1.4 Simultaneous Equilibria $K_{sp}/K_f$



[Watch on YouTube](#)

### 31.1.5 Simultaneous Equilibria $K_{sp}/K_f$ Part 2

Calculate the molar solubility of  $\text{AgCl}$  in pure water and in  $0.25 \text{ M KCN}$ .

$K_{sp}$  for  $\text{AgCl}$  is  $1.8 \times 10^{-10}$

\*  $K_f$  for  $\text{Ag}(\text{CN})_2^-$  is  $1.0 \times 10^{21}$

R	$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	$1.8 \times 10^{-10}$
I	0	
C	+x      +x	$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
E	x      x	$1.8 \times 10^{-10} = x^2$

$1.3 \times 10^{-5} = x$

molar solubility of  $\text{AgCl}$  in pure water

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