

## Chemistry 132 NT

**If you ever drop your keys into a river of molten lava, let 'em go, because, man, they're gone.**

Jack Handey

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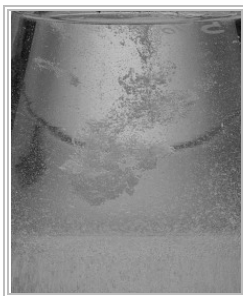
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Chem 132 NT

### Solubility and Complex-ion Equilibria

#### Module 2

- Complex-Ion Equilibria
  - Complex-Ion Formation
  - Complex-Ions and Solubility
  - Qualitative Analysis of Metal Ions



Reaction of zinc metal with hydrochloric acid.

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## Review

- ✎ Writing solubility product expressions
- ✎ Calculating  $K_{sp}$  from the solubility, or vice versa.
- ✎ Calculating the solubility of a slightly soluble salt in a solution of a common ion.
- ✎ Predicting whether precipitation will occur
- ✎ Determining the qualitative effect of pH on solubility

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## Complex-Ion Equilibria

Many metal ions, especially transition metals, form **coordinate covalent bonds** with molecules or anions having a lone pair of electrons.

- This type of bond formation is essentially a Lewis acid-base reaction (Acid-base chapter).

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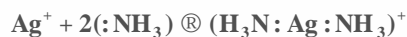
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## Complex-Ion Equilibria

Many metal ions, especially transition metals, form **coordinate covalent bonds** with molecules or anions having a lone pair of electrons.

- For example, the silver ion,  $\text{Ag}^+$ , can react with ammonia to form the  $\text{Ag}(\text{NH}_3)_2^+$  ion.



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## Complex-Ion Equilibria

A **complex ion** is an ion formed from a metal ion with a Lewis base attached to it by a coordinate covalent bond.

- A **complex** is defined as a compound containing complex ions.
- A **ligand** is a Lewis base (an electron pair donor) that bonds to a metal ion to form a complex ion.

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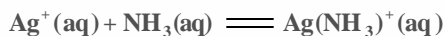
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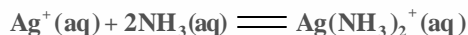
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## Complex-Ion Formation

- ⚡ The aqueous silver ion forms a **complex ion** with ammonia in steps.



- ⚡ When you add these equations, you get the overall equation for the formation of  $\text{Ag}(\text{NH}_3)_2^+$ .



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## Complex-Ion Formation

- ⚡ The **formation constant,  $K_f$** , is the equilibrium constant for the formation of a complex ion from the aqueous metal ion and the ligands.

- ⚡ The formation constant for  $\text{Ag}(\text{NH}_3)_2^+$  is:

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

- ⚡ The value of  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

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## Complex-Ion Formation

- ⚡ The **formation constant,  $K_f$** , is the equilibrium constant for the formation of a complex ion from the aqueous metal ion and the ligands.

- ⚡ The large value means that **the complex ion is quite stable**.

- ⚡ When a large amount of  $\text{NH}_3$  is added to a solution of  $\text{Ag}^+$ , you expect most of the  $\text{Ag}^+$  ion to react to form the complex ion.

- ⚡ A table in your text lists formation constants of some complex ions.

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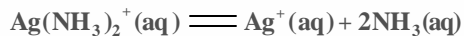
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## Complex-Ion Formation

✎ The **dissociation constant,  $K_d$** , is the reciprocal, or inverse, value of  $K_f$ .

• The equation for the dissociation of  $\text{Ag}(\text{NH}_3)_2^+$  is



• The equilibrium constant equation is

$$K_d = \frac{1}{K_f} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

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## Equilibrium Calculations with $K_f$

✎ What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

• In 1.0 L of solution, you initially have 0.010 mol  $\text{Ag}^+(\text{aq})$  from  $\text{AgNO}_3$ .

• This reacts to give 0.010 mol  $\text{Ag}(\text{NH}_3)_2^+$ , leaving  $(1.00 - (2 \times 0.010)) = 0.98$  mol  $\text{NH}_3$ .

• You now look at the dissociation of  $\text{Ag}(\text{NH}_3)_2^+$ .

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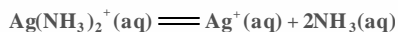
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## Equilibrium Calculations with $K_f$

✎ What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

• The following table summarizes.



Starting	0.010
Change	-x
Equilibrium	0.010-x

0	0.98
+x	+2x
x	0.98+2x

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### Equilibrium Calculations with $K_f$

What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

The dissociation constant equation is:

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = K_d = \frac{1}{K_f}$$

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### Equilibrium Calculations with $K_f$

What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

Substituting into this equation gives:

$$\frac{(x)(0.98 + 2x)^2}{(0.010 - x)} = \frac{1}{1.7 \times 10^7}$$

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### Equilibrium Calculations with $K_f$

What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

If we assume  $x$  is small compared with 0.010 and 0.98, then

$$\frac{(x)(0.98)^2}{(0.010)} @ 5.9 \times 10^{-8}$$

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## Equilibrium Calculations with $K_f$

What is the concentration of  $\text{Ag}^+(\text{aq})$  ion in 0.010 M  $\text{AgNO}_3$  that is also 1.00 M  $\text{NH}_3$ ?  
The  $K_f$  for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ .

• and

$$x @ 5.9 \times 10^{-8} \cdot (0.010) / (0.98)^2 = 6.1 \times 10^{-10}$$

• The silver ion concentration is  $6.1 \times 10^{-10}$  M.

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## Amphoteric Hydroxides

An **amphoteric hydroxide** is a metal hydroxide that reacts with both acids and bases.

• For example, zinc hydroxide,  $\text{Zn}(\text{OH})_2$ , reacts with a strong acid and the metal hydroxide dissolves.



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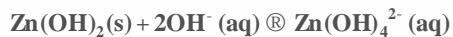
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## Amphoteric Hydroxides

An **amphoteric hydroxide** is a metal hydroxide that reacts with both acids and bases.

• With a base however,  $\text{Zn}(\text{OH})_2$  reacts to form the complex ion  $\text{Zn}(\text{OH})_4^{2-}$ .



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## Amphoteric Hydroxides

☛ An **amphoteric hydroxide** is a metal hydroxide that reacts with both acids and bases.

- ◆ When a strong base is slowly added to a solution of  $\text{ZnCl}_2$ , a white precipitate of  $\text{Zn(OH)}_2$  first forms.



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## Amphoteric Hydroxides

☛ An **amphoteric hydroxide** is a metal hydroxide that reacts with both acids and bases.

- ◆ But as more base is added, the white precipitate dissolves, forming the complex ion  $\text{Zn(OH)}_4^{2-}$ .
- ◆ Other common amphoteric hydroxides are those of aluminum, chromium(III), lead(II), tin(II), and tin(IV).

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## Complex Ions and Solubility

☛ An example worked out previously in this module demonstrates that the formation of the complex ion  $\text{Ag(NH}_3)_2^+$  **reduces the concentration of silver ion**,  $\text{Ag}^+(\text{aq})$  in solution.

- ◆ The solution was initially 0.010 M  $\text{Ag}^+(\text{aq})$ .
- ◆ When the solution was made 1.0 M in  $\text{NH}_3$ , the  $\text{Ag}^+(\text{aq})$  concentration decreases to  $6.1 \times 10^{-10}$  M.
- ◆ This implies that a slightly soluble silver salt might not precipitate in a solution containing ammonia, whereas it otherwise would.

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## Complex Ions and Solubility

✎ An example worked out previously in this module demonstrates that the formation of the complex ion  $\text{Ag}(\text{NH}_3)_2^+$  **reduces the concentration of silver ion**,  $\text{Ag}^+(\text{aq})$  in solution.

◆ Let's take a look at an example where the formation of a complex reduces the ion product,  $Q_c$ , for a slightly soluble salt, to below its  $K_{sp}$ .

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## A Problem To Consider

✎ a) Will silver chloride precipitate from a solution that is 0.0100 M  $\text{AgNO}_3$  and 0.010 M  $\text{NaCl}$ ?

b) Will silver chloride precipitate from this solution if it is also 1.0 M  $\text{NH}_3$ ?

◆ Part (a) is a simple precipitation problem in which we **compare the  $Q_c$  with  $K_c$** .

◆ To determine whether a precipitate will form, we must calculate the  $Q_c$  and compare it with the  $K_{sp}$  for  $\text{AgCl}$  ( $1.8 \times 10^{-10}$ ).

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## A Problem To Consider

✎ a) Will silver chloride precipitate from a solution that is 0.0100 M  $\text{AgNO}_3$  and 0.010 M  $\text{NaCl}$ ?

b) Will silver chloride precipitate from this solution if it is also 1.0 M  $\text{NH}_3$ ?

$$Q_c = [\text{Ag}^+]_i [\text{Cl}^-]_i = (0.010)(0.010) \\ = 1.0 \times 10^{-4}$$

◆ This is greater than the  $K_{sp} = 1.8 \times 10^{-10}$ . So a **precipitate should form**.

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## A Problem To Consider

☛ a) Will silver chloride precipitate from a solution that is 0.0100 M AgNO<sub>3</sub> and 0.010 M NaCl?

b) Will silver chloride precipitate from this solution if it is also 1.0 M NH<sub>3</sub>?

◆ For part (b), we **must calculate the concentration of Ag<sup>+</sup>(aq) in a solution containing 1.0 M NH<sub>3</sub>.**

◆ We did this in a previous example and found [Ag<sup>+</sup>] equals 6.1 x 10<sup>-10</sup>.

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## A Problem To Consider

☛ a) Will silver chloride precipitate from a solution that is 0.0100 M AgNO<sub>3</sub> and 0.010 M NaCl?

b) Will silver chloride precipitate from this solution if it is also 1.0 M NH<sub>3</sub>?

◆ This time, the Q<sub>c</sub> is:

$$Q_c = [Ag^+]_i [Cl^-]_i = (6.1 \times 10^{-10})(0.010) \\ = 6.1 \times 10^{-12}$$

◆ Because the Q<sub>c</sub> is less than the K<sub>sp</sub> = 1.8 x 10<sup>-10</sup>. So **no precipitate should form.**

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## Qualitative Analysis

☛ **Qualitative analysis** involves the determination of the identity of substances present in a mixture.

◆ In the qualitative analysis scheme for metal ions, a cation is usually detected by the **presence of a characteristic precipitate.**

◆ The figure on the next slide summarizes how metal ions in an aqueous solution are separated into five analytical groups.

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