Sample Analysis. Precipitates and Complexes of Silver Ion

Data for Determining Formulas

Solutions containing NH_3, CO_3^{2-}, Cl^-, I^-, PO_4^{3-}, and $S_2O_3^{2-}$ ions were added to equal proportions of a silver nitrate solution, which contained the complex ion $Ag(H_2O)_2^+$. All of the added solutions were also clear and colorless.

$AgNO_3$ (*aq*) by itself	Colorless solution
$AgNO_3$ (*aq*) with NH_3 (*aq*)	Colorless solution
$AgNO_3$ (*aq*) with Na_2CO_3 (*aq*)	Pale yellow precipitate
$AgNO_3$ (*aq*) with NaCl (*aq*)	White precipitate
$AgNO_3$ (*aq*) with NaI (*aq*)	Yellow precipitate
$AgNO_3$ (*aq*) with Na_3PO_4 (*aq*)	Yellow precipitate
$AgNO_3$ (*aq*) with $Na_2S_2O_3$ (*aq*)	Colorless solution

Formulas of Silver Complexes and Precipitates

Ag^+ ions formed precipitates with CO_3^{2-}, Cl^-, I^-, and PO_4^{3-} ions. Solids are electrically neutral; the charges of all their ions add up to zero. Therefore, the formulas of these precipitates are: Ag_2CO_3, AgCl, AgI, and Ag_3PO_4.

It is not obvious from these observations that Ag^+ ions formed soluble complex ions with NH_3 and $S_2O_3^{2-}$ ions. However, data on the next page shows that solutions containing NH_3 and $S_2O_3^{2-}$ ions were able to convert the pale yellow precipitate Ag_2CO_3 into colorless solutions. Thus, complex ions more stable than Ag_2CO_3 must have formed. Ag^+ has a coordination number of 2, so it binds to two ligands when it forms complex ions. The formulas of the complex ions formed with NH_3 and $S_2O_3^{2-}$ are therefore: $Ag(NH_3)_2^+$ and $Ag(S_2O_3)_2^{3-}$.

The product-favored reactions that occurred when NH_3 (*aq*) and $Na_2S_2O_3$ (*aq*) solutions were added to Ag_2CO_3 (*s*) were:

$$Ag_2CO_3\ (s)\ +\ 2\ NH_3\ (aq) \longrightarrow 2\ Ag(NH_3)_2^+\ (aq)\ +\ CO_3^{2-}\ (aq)$$

$$Ag_2CO_3\ (s)\ +\ 2\ S_2O_3^{2-}\ (aq) \longrightarrow 2\ Ag(S_2O_3)_2^{3-}\ (aq)\ +\ CO_3^{2-}\ (aq)$$

$Ag(H_2O)_2^+$ (*aq*)	Colorless solution
$Ag(NH_3)_2^+$ (*aq*)	Colorless solution
Ag_2CO_3 (*s*)	Pale yellow precipitate
AgCl (*s*)	White precipitate
AgI (*s*)	Yellow precipitate
Ag_3PO_4 (*s*)	Yellow precipitate
$Ag(S_2O_3)_2^{3-}$ (*aq*)	Colorless solution

Data for Determining Relative Stabilities

In order to rank the observed precipitates and complex ions in order of stability, solutions containing NH_3, CO_3^{2-}, Cl^-, I^-, PO_4^{3-}, and $S_2O_3^{2-}$ ions were again added to equal proportions of a silver nitrate solution. Then a third portion of a second solution, also containing NH_3, CO_3^{2-}, Cl^-, I^-, PO_4^{3-}, or $S_2O_3^{2-}$ ions was added.

Added 2nd / Added 1st	NH_3	CO_3^{2-}	Cl^-	I^-	PO_4^{3-}	$S_2O_3^{2-}$
NH_3	X	No change cpx w/NH_3 more stable	Change to white ppt ppt w/Cl^- more stable	Change to yellow ppt ppt w/I^- more stable	Change to yellow ppt ppt w/PO_4^{3-} more stable	No observed change
CO_3^{2-}	Change to colorless soln cpx w/NH_3 more stable	X	Change to white ppt ppt w/Cl^- more stable	Change to yellow ppt ppt w/I^- more stable	Change to yellow ppt ppt w/PO_4^{3-} more stable	Change to colorless soln cpx w/$S_2O_3^{2-}$ more stable
Cl^-	No change ppt w/Cl^- more stable	No change ppt w/Cl^- more stable	X	Change to yellow ppt ppt w/I^- more stable	No change ppt w/Cl^- more stable	Change to colorless soln cpx w/$S_2O_3^{2-}$ more stable
I^-	No change ppt w/I^- more stable	No change ppt w/I^- more stable	No change ppt w/I^- more stable	X	No observed change	No change ppt w/I^- more stable
PO_4^{3-}	No change ppt w/PO_4^{3-} more stable	No change ppt w/PO_4^{3-} more stable	Change to white ppt ppt w/Cl^- more stable	No observed change	X	Change to colorless soln cpx w/$S_2O_3^{2-}$ more stable
$S_2O_3^{2-}$	No observed change	No change cpx w/$S_2O_3^{2-}$ more stable	No change cpx w/$S_2O_3^{2-}$ more stable	Change to yellow ppt ppt w/I^- more stable	No change cpx w/$S_2O_3^{2-}$ more stable	X

The above tests were repeated as necessary until all the observations were consistent. For example, adding NaCl (*aq*) to $AgNO_3$ (*aq*) produced a white precipitate, AgCl (*s*). When NaI (*aq*) was added to this precipitate, it changed into the yellow precipitate, AgI (*s*). So, the following reaction is product-favored, indicating that AgI (*s*) is more stable than AgCl (*s*).

$$AgCl\,(s) + I^-\,(aq) \longrightarrow AgI\,(s) + Cl^-\,(aq) \qquad \text{product-favored}$$

In a second test, adding NaI (*aq*) to $AgNO_3$ (*aq*) produced a yellow precipitate, AgI (*s*). When NaCl (*aq*) was added to this precipitate, it did not change. The reverse reaction is therefore reactant-favored, again indicating that AgI (*s*) is more stable than AgCl (*s*).

$$AgI\,(s) + Cl^-\,(aq) \longleftarrow AgCl\,(s) + I^-\,(aq) \qquad \text{reactant-favored}$$

The two tests are thus consistent with each other.

In two cases, the pairwise tests did not immediately show which species is more stable. AgI (*s*) and Ag_3PO_4 (*s*) are both yellow precipitates, so further analysis of the data is necessary to determine which is more stable. Similarly, $Ag(NH_3)_2^+$ (*aq*) and $Ag(S_2O_3)_2^{3-}$ (*aq*) are both colorless solutions, and further data analysis is needed.

Deducing the Relative Stabilities

1. Reactions of AgCl (s)

To rank all the species in order of stability, we will arbitrarily start with the reactions involving AgCl (*s*), which has a distinctive white color. Cl^- ions reacted with some of the species in this experiment, but not others.

Cl^- ions were able to change $Ag(H_2O)_2^+$ (*aq*), $Ag(NH_3)_2^+$ (*aq*), Ag_2CO_3 (*s*), and Ag_3PO_4 (*s*) into the white solid AgCl (*s*). This means that AgCl (*s*) is more stable than each of those species. The following product-favored reactions were observed:

$Ag(H_2O)_2^+ (aq) + Cl^- (aq) \longrightarrow AgCl (s) + 2\ H_2O (l)$ product-favored

$Ag(NH_3)_2^+ (aq) + Cl^- (aq) \longrightarrow AgCl (s) + 2\ NH_3 (aq)$ product-favored

$Ag_2CO_3 (s) + 2\ Cl^- (aq) \longrightarrow AgCl (s) + CO_3^{2-} (aq)$ product-favored

$Ag_3PO_4 (s) + 3\ Cl^- (aq) \longrightarrow AgCl (s) + PO_4^{3-} (aq)$ product-favored

Cl^- ions were not able to change AgI (*s*) or $Ag(S_2O_3)_2^{3-}$ (*aq*) into AgCl (*s*). This means that AgCl (*s*) is less stable than those species. The following reactions must be reactant-favored, because they were not observed:

$AgI (s) + Cl^- (aq) \longleftarrow AgCl (s) + I^- (aq)$ reactant-favored

$Ag(S_2O_3)_2^{3-} (aq) + Cl^- (aq) \longleftarrow AgCl (s) + 2\ S_2O_3^{2-} (aq)$ reactant-favored

To summarize what we have deduced so far:

AgI (*s*) and $Ag(S_2O_3)_2^{3-}$ (*aq*)	More stable
AgCl (*s*)	
$Ag(H_2O)_2^+$ (*aq*), $Ag(NH_3)_2^+$ (*aq*), Ag_2CO_3 (*s*), and Ag_3PO_4 (*s*)	Less stable

Our deductions can be checked for consistency by looking back at the table of observations. I^- ions were indeed able to change the less stable $Ag(H_2O)_2^+$ (*aq*), $Ag(NH_3)_2^+$ (*aq*), and Ag_2CO_3 (*s*) into the yellow solid AgI (*s*). $S_2O_3^{2-}$ ions were indeed able to change the less stable Ag_2CO_3 (*s*) and Ag_3PO_4 (*s*) into the colorless and soluble complex ion $Ag(S_2O_3)_2^{3-}$ (*aq*).

The reactions with Cl^- ions show indirectly that the yellow precipitate AgI (*s*) is more stable than the other yellow precipitate Ag_3PO_4 (*s*). They also show indirectly that the colorless complex ion $Ag(S_2O_3)_2^{3-}$ (*aq*) is more stable than the other colorless complex ions, $Ag(H_2O)_2^+$ (*aq*) and $Ag(NH_3)_2^+$ (*aq*).

2. AgI (s) and $Ag(S_2O_3)_2^{3-}$ (aq)

AgI (*s*) is more stable than $Ag(S_2O_3)_2^{3-}$ (*aq*) because I^- ions were able to change $Ag(S_2O_3)_2^{3-}$ (*aq*) into the yellow precipitate AgI (s). The following product-favored reaction was observed:

$$Ag(S_2O_3)_2^{3-}\ (aq) + I^-\ (aq) \longrightarrow AgI\ (s) + 2\ S_2O_3^{2-}\ (aq) \quad \text{product-favored}$$

3. Reactions of Ag_2CO_3 (s)

Next, we consider reactions involving Ag_2CO_3 (*s*), which has a distinctive pale yellow color. CO_3^{2-} ions were able to change $Ag(H_2O)_2^+$ (*aq*) in the $AgNO_3$ (*aq*) solution into the pale yellow precipitate Ag_2CO_3 (*s*), so Ag_2CO_3 (*s*) is more stable than $Ag(H_2O)_2^+$ (*aq*). The following product-favored reaction was observed:

$$2\ Ag(H_2O)_2^+\ (aq) + CO_3^{2-}\ (aq) \longrightarrow Ag_2CO_3\ (s) + 4\ H_2O\ (l) \quad \text{product-favored}$$

CO_3^{2-} ions were not able to change either $Ag(NH_3)_2^+$ (*aq*) or Ag_3PO_4 (*s*) into the pale yellow precipitate Ag_2CO_3 (*s*), so Ag_2CO_3 (*s*) is less stable than those species. The following reactions must be reactant-favored, because they were not observed:

$$Ag(NH_3)_2^+\ (aq) + CO_3^{2-}\ (aq) \longleftarrow Ag_2CO_3\ (s) + 4\ NH_3\ (aq) \quad \text{reactant-favored}$$

$$2\ Ag_3PO_4\ (s) + 3\ CO_3^{2-}\ (aq) \longleftarrow 3\ Ag_2CO_3\ (s) + 2\ PO_4^{3-}\ (aq) \quad \text{reactant-favored}$$

4. Ag_3PO_4 (s) and $Ag(NH_3)_2^+$ (aq)

Finally, Ag_3PO_4 (*s*) is more stable than $Ag(NH_3)_2^+$ (*aq*) because PO_4^{3-} ions were able to change $Ag(NH_3)_2^+$ (*aq*) into the yellow solid Ag_3PO_4 (*s*). The following product-favored reaction was observed:

$$3\ Ag(NH_3)_2^+\ (aq) + PO_4^{3-}\ (aq) \longrightarrow Ag_3PO_4\ (s) + 6\ NH_3\ (aq) \quad \text{product-favored}$$

Results: Relative Stabilities of Precipitates and Complexes of Silver Ion

AgI (*s*)	Yellow precipitate	Most stable
$Ag(S_2O_3)_2^{3-}$ (*aq*)	Colorless solution	
AgCl (*s*)	White precipitate	
Ag_3PO_4 (*s*)	Yellow precipitate	
$Ag(NH_3)_2^+$ (*aq*)	Colorless solution	
Ag_2CO_3 (*s*)	Pale yellow precipitate	
$Ag(H_2O)_2^+$ (*aq*)	Colorless solution	Least stable