

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 $\text{S}_2\text{O}_3^{2-}$ ions were added to equal proportions of a silver nitrate solution, which contained the complex ion $\text{Ag}(\text{H}_2\text{O})_2^+$. All of the added solutions were also clear and colorless.

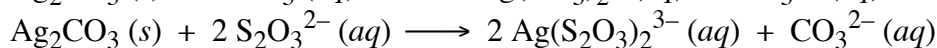
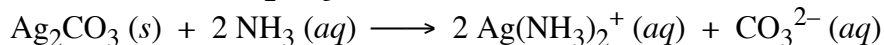
AgNO_3 (aq) by itself	Colorless solution
AgNO_3 (aq) with NH_3 (aq)	Colorless solution
AgNO_3 (aq) with Na_2CO_3 (aq)	Pale yellow precipitate
AgNO_3 (aq) with NaCl (aq)	White precipitate
AgNO_3 (aq) with NaI (aq)	Yellow precipitate
AgNO_3 (aq) with Na_3PO_4 (aq)	Yellow precipitate
AgNO_3 (aq) with $\text{Na}_2\text{S}_2\text{O}_3$ (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 $\text{S}_2\text{O}_3^{2-}$ ions. However, data on the next page shows that solutions containing NH_3 and $\text{S}_2\text{O}_3^{2-}$ 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 $\text{S}_2\text{O}_3^{2-}$ are therefore: $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$.

The product-favored reactions that occurred when NH_3 (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq) solutions were added to Ag_2CO_3 (s) were:



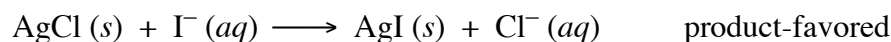
$\text{Ag}(\text{H}_2\text{O})_2^+$ (aq)	Colorless solution
$\text{Ag}(\text{NH}_3)_2^+$ (aq)	Colorless solution
Ag_2CO_3 (s)	Pale yellow precipitate
AgCl (s)	White precipitate
AgI (s)	Yellow precipitate
Ag_3PO_4 (s)	Yellow precipitate
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ (aq)	Colorless solution

Data for Determining Relative Stabilities

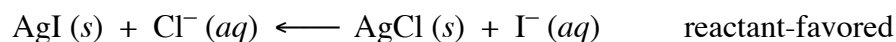
In order to rank the observed precipitates and complex ions in order of stability, solutions containing NH_3 , CO_3^{2-} , Cl^- , I^- , PO_4^{3-} , and $\text{S}_2\text{O}_3^{2-}$ ions were again added to equal proportions of a silver nitrate solution. Then a third portion of a second solution, also containing NH_3 , CO_3^{2-} , Cl^- , I^- , PO_4^{3-} , or $\text{S}_2\text{O}_3^{2-}$ ions was added.

Added 2 nd / Added 1 st	NH_3	CO_3^{2-}	Cl^-	I^-	PO_4^{3-}	$\text{S}_2\text{O}_3^{2-}$
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/ $\text{S}_2\text{O}_3^{2-}$ 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/ $\text{S}_2\text{O}_3^{2-}$ 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/ $\text{S}_2\text{O}_3^{2-}$ more stable
$\text{S}_2\text{O}_3^{2-}$	No observed change	No change cpx w/ $\text{S}_2\text{O}_3^{2-}$ more stable	No change cpx w/ $\text{S}_2\text{O}_3^{2-}$ more stable	Change to yellow ppt ppt w/ I^- more stable	No change cpx w/ $\text{S}_2\text{O}_3^{2-}$ more stable	X

The above tests were repeated as necessary until all the observations were consistent. For example, adding $\text{NaCl} (aq)$ to $\text{AgNO}_3 (aq)$ produced a white precipitate, $\text{AgCl} (s)$. When $\text{NaI} (aq)$ was added to this precipitate, it changed into the yellow precipitate, $\text{AgI} (s)$. So, the following reaction is product-favored, indicating that $\text{AgI} (s)$ is more stable than $\text{AgCl} (s)$.



In a second test, adding $\text{NaI} (aq)$ to $\text{AgNO}_3 (aq)$ produced a yellow precipitate, $\text{AgI} (s)$. When $\text{NaCl} (aq)$ was added to this precipitate, it did not change. The reverse reaction is therefore reactant-favored, again indicating that $\text{AgI} (s)$ is more stable than $\text{AgCl} (s)$.



The two tests are thus consistent with each other.

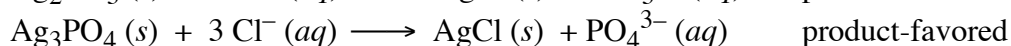
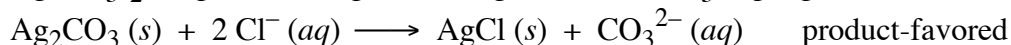
In two cases, the pairwise tests did not immediately show which species is more stable. $\text{AgI} (s)$ and $\text{Ag}_3\text{PO}_4 (s)$ are both yellow precipitates, so further analysis of the data is necessary to determine which is more stable. Similarly, $\text{Ag}(\text{NH}_3)_2^+ (aq)$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$ are both colorless solutions, and further data analysis is needed.

Deducing the Relative Stabilities

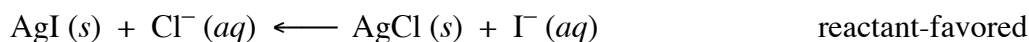
1. Reactions of $\text{AgCl} (s)$

To rank all the species in order of stability, we will arbitrarily start with the reactions involving $\text{AgCl} (s)$, 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 $\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$, $\text{Ag}(\text{NH}_3)_2^+ (aq)$, $\text{Ag}_2\text{CO}_3 (s)$, and $\text{Ag}_3\text{PO}_4 (s)$ into the white solid $\text{AgCl} (s)$. This means that $\text{AgCl} (s)$ is more stable than each of those species. The following product-favored reactions were observed:



Cl^- ions were not able to change $\text{AgI} (s)$ or $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$ into $\text{AgCl} (s)$. This means that $\text{AgCl} (s)$ is less stable than those species. The following reactions must be reactant-favored, because they were not observed:



To summarize what we have deduced so far:

$\text{AgI} (s)$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$	More stable
$\text{AgCl} (s)$	
$\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$, $\text{Ag}(\text{NH}_3)_2^+ (aq)$, $\text{Ag}_2\text{CO}_3 (s)$, and $\text{Ag}_3\text{PO}_4 (s)$	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 $\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$, $\text{Ag}(\text{NH}_3)_2^+ (aq)$, and $\text{Ag}_2\text{CO}_3 (s)$ into the yellow solid $\text{AgI} (s)$. $\text{S}_2\text{O}_3^{2-}$ ions were indeed able to change the less stable $\text{Ag}_2\text{CO}_3 (s)$ and $\text{Ag}_3\text{PO}_4 (s)$ into the colorless and soluble complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$.

The reactions with Cl^- ions show indirectly that the yellow precipitate $\text{AgI} (s)$ is more stable than the other yellow precipitate $\text{Ag}_3\text{PO}_4 (s)$. They also show indirectly that the colorless complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$ is more stable than the other colorless complex ions, $\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$ and $\text{Ag}(\text{NH}_3)_2^+ (aq)$.

2. $\text{AgI} (s)$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$

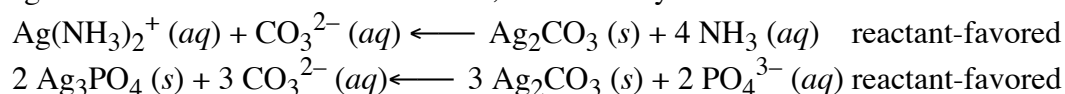
$\text{AgI} (s)$ is more stable than $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$ because I^- ions were able to change $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$ into the yellow precipitate $\text{AgI} (s)$. The following product-favored reaction was observed:



3. Reactions of $\text{Ag}_2\text{CO}_3 (s)$

Next, we consider reactions involving $\text{Ag}_2\text{CO}_3 (s)$, which has a distinctive pale yellow color. CO_3^{2-} ions were able to change $\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$ in the $\text{AgNO}_3 (aq)$ solution into the pale yellow precipitate $\text{Ag}_2\text{CO}_3 (s)$, so $\text{Ag}_2\text{CO}_3 (s)$ is more stable than $\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$. The following product-favored reaction was observed:

$2 \text{Ag}(\text{H}_2\text{O})_2^+ (aq) + \text{CO}_3^{2-} (aq) \longrightarrow \text{Ag}_2\text{CO}_3 (s) + 4 \text{H}_2\text{O} (l)$ product-favored
 CO_3^{2-} ions were not able to change either $\text{Ag}(\text{NH}_3)_2^+ (aq)$ or $\text{Ag}_3\text{PO}_4 (s)$ into the pale yellow precipitate $\text{Ag}_2\text{CO}_3 (s)$, so $\text{Ag}_2\text{CO}_3 (s)$ is less stable than those species. The following reactions must be reactant-favored, because they were not observed:



4. $\text{Ag}_3\text{PO}_4 (s)$ and $\text{Ag}(\text{NH}_3)_2^+ (aq)$

Finally, $\text{Ag}_3\text{PO}_4 (s)$ is more stable than $\text{Ag}(\text{NH}_3)_2^+ (aq)$ because PO_4^{3-} ions were able to change $\text{Ag}(\text{NH}_3)_2^+ (aq)$ into the yellow solid $\text{Ag}_3\text{PO}_4 (s)$. The following product-favored reaction was observed:



Results: Relative Stabilities of Precipitates and Complexes of Silver Ion

$\text{AgI} (s)$	Yellow precipitate	Most stable
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$	Colorless solution	
$\text{AgCl} (s)$	White precipitate	
$\text{Ag}_3\text{PO}_4 (s)$	Yellow precipitate	
$\text{Ag}(\text{NH}_3)_2^+ (aq)$	Colorless solution	
$\text{Ag}_2\text{CO}_3 (s)$	Pale yellow precipitate	
$\text{Ag}(\text{H}_2\text{O})_2^+ (aq)$	Colorless solution	Least stable