



## Sample Analysis. Precipitates and Complexes of Silver Ion

### Data for Determining Formulas

Solutions containing  $\text{NH}_3$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ , 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.

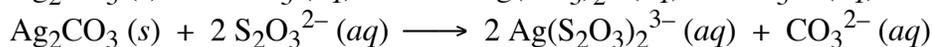
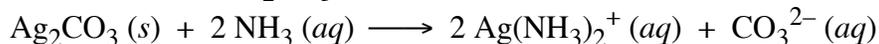
$\text{AgNO}_3$ (aq) by itself	Colorless solution
$\text{AgNO}_3$ (aq) with $\text{NH}_3$ (aq)	Colorless solution
$\text{AgNO}_3$ (aq) with $\text{Na}_2\text{CO}_3$ (aq)	Pale yellow precipitate
$\text{AgNO}_3$ (aq) with $\text{NaCl}$ (aq)	White precipitate
$\text{AgNO}_3$ (aq) with $\text{NaI}$ (aq)	Yellow precipitate
$\text{AgNO}_3$ (aq) with $\text{Na}_3\text{PO}_4$ (aq)	Yellow precipitate
$\text{AgNO}_3$ (aq) with $\text{Na}_2\text{S}_2\text{O}_3$ (aq)	Colorless solution

### Formulas of Silver Complexes and Precipitates

$\text{Ag}^+$  ions formed precipitates with  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ , and  $\text{PO}_4^{3-}$  ions. Solids are electrically neutral; the charges of all their ions add up to zero. Therefore, the formulas of these precipitates are:  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgCl}$ ,  $\text{AgI}$ , and  $\text{Ag}_3\text{PO}_4$ .

It is not obvious from these observations that  $\text{Ag}^+$  ions formed soluble complex ions with  $\text{NH}_3$  and  $\text{S}_2\text{O}_3^{2-}$  ions. However, data on the next page shows that solutions containing  $\text{NH}_3$  and  $\text{S}_2\text{O}_3^{2-}$  ions were able to convert the pale yellow precipitate  $\text{Ag}_2\text{CO}_3$  into colorless solutions. Thus, complex ions more stable than  $\text{Ag}_2\text{CO}_3$  must have formed.  $\text{Ag}^+$  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  $\text{NH}_3$  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  $\text{NH}_3$  (aq) and  $\text{Na}_2\text{S}_2\text{O}_3$  (aq) solutions were added to  $\text{Ag}_2\text{CO}_3$  (s) were:



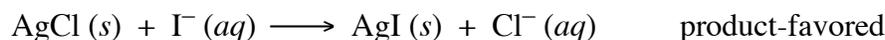
$\text{Ag}(\text{H}_2\text{O})_2^+$ (aq)	Colorless solution
$\text{Ag}(\text{NH}_3)_2^+$ (aq)	Colorless solution
$\text{Ag}_2\text{CO}_3$ (s)	Pale yellow precipitate
$\text{AgCl}$ (s)	White precipitate
$\text{AgI}$ (s)	Yellow precipitate
$\text{Ag}_3\text{PO}_4$ (s)	Yellow precipitate
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$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

### Data for Determining Relative Stabilities

In order to rank the observed precipitates and complex ions in order of stability, solutions containing  $\text{NH}_3$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ , 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  $\text{NH}_3$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ , or  $\text{S}_2\text{O}_3^{2-}$  ions was added.

Added 2 <sup>nd</sup> Added 1 <sup>st</sup>	$\text{NH}_3$	$\text{CO}_3^{2-}$	$\text{Cl}^-$	$\text{I}^-$	$\text{PO}_4^{3-}$	$\text{S}_2\text{O}_3^{2-}$
$\text{NH}_3$	X	No change cpx w/ $\text{NH}_3$ more stable	Change to white ppt ppt w/ $\text{Cl}^-$ more stable	Change to yellow ppt ppt w/ $\text{I}^-$ more stable	Change to yellow ppt ppt w/ $\text{PO}_4^{3-}$ more stable	No observed change
$\text{CO}_3^{2-}$	Change to colorless soln cpx w/ $\text{NH}_3$ more stable	X	Change to white ppt ppt w/ $\text{Cl}^-$ more stable	Change to yellow ppt ppt w/ $\text{I}^-$ more stable	Change to yellow ppt ppt w/ $\text{PO}_4^{3-}$ more stable	Change to colorless soln cpx w/ $\text{S}_2\text{O}_3^{2-}$ more stable
$\text{Cl}^-$	No change ppt w/ $\text{Cl}^-$ more stable	No change ppt w/ $\text{Cl}^-$ more stable	X	Change to yellow ppt ppt w/ $\text{I}^-$ more stable	No change ppt w/ $\text{Cl}^-$ more stable	Change to colorless soln cpx w/ $\text{S}_2\text{O}_3^{2-}$ more stable
$\text{I}^-$	No change ppt w/ $\text{I}^-$ more stable	No change ppt w/ $\text{I}^-$ more stable	No change ppt w/ $\text{I}^-$ more stable	X	No observed change	No change ppt w/ $\text{I}^-$ more stable
$\text{PO}_4^{3-}$	No change ppt w/ $\text{PO}_4^{3-}$ more stable	No change ppt w/ $\text{PO}_4^{3-}$ more stable	Change to white ppt ppt w/ $\text{Cl}^-$ 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/ $\text{I}^-$ 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.

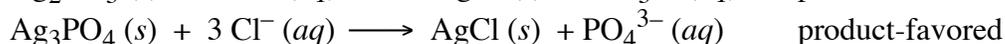
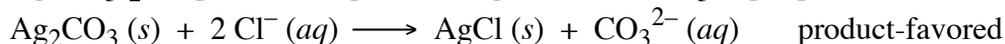
In two cases, the pairwise tests did not immediately show which species is more stable.  $\text{AgI} (s)$  and  $\text{Ag}_3\text{PO}_4 (s)$  are both yellow precipitates, so further analysis of the data is necessary to determine which is more stable. Similarly,  $\text{Ag}(\text{NH}_3)_2^+ (aq)$  and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

$\text{Cl}^-$  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:



$\text{Cl}^-$  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.  $\text{I}^-$  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  $\text{Cl}^-$  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 $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$***

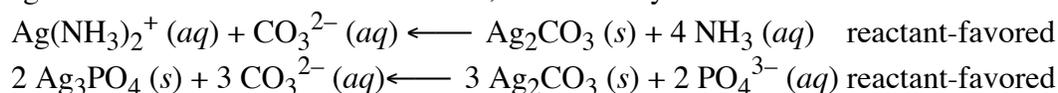
$\text{AgI} (s)$  is more stable than  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$  because  $\text{I}^-$  ions were able to change  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} (aq)$  into the yellow precipitate  $\text{AgI} (s)$ . The following product-favored reaction was observed:



### 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.  $\text{CO}_3^{2-}$  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  
 $\text{CO}_3^{2-}$  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  $\text{PO}_4^{3-}$  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