

# The Use of Dilute Nitric Acid in the Qualitative Analysis of Anions



- Aqueous barium nitrate is primarily used in qualitative analysis to test for the presence of sulfate ions.
  - If sulfate ions are present in aqueous solution, then when aqueous barium nitrate is added, a white precipitate of barium sulfate will form.

#### $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$

 Solubility rules – all sulfates are soluble except barium sulfate, calcium sulfate and lead(II) sulfate.



 Aqueous silver nitrate is primarily used in qualitative analysis to test for the presence of chloride ions.

• If chloride ions are present in aqueous solution, then when aqueous silver nitrate is added, a white precipitate of silver chloride will form.

 $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ 

 Solubility rules – all chlorides are soluble except lead(II) chloride and silver chloride.



• When aqueous barium nitrate is added to the aqueous solution of an unknown salt, several different precipitates could be produced *e.g.* 

Barium Carbonate – BaCO<sub>3</sub>(s)

$$\begin{split} \mathsf{Ba}(\mathsf{NO}_3)_2(\mathsf{aq}) \ + \ \mathsf{Na}_2\mathsf{CO}_3(\mathsf{aq}) \ \to \ \mathsf{Ba}\mathsf{CO}_3(\mathsf{s}) \ + \ \mathbf{2}\mathsf{Na}\mathsf{NO}_3(\mathsf{aq}) \\ \\ \mathsf{Ba}^{2+}(\mathsf{aq}) \ + \ \mathsf{CO}_3^{2-}(\mathsf{aq}) \ \to \ \mathsf{Ba}\mathsf{CO}_3(\mathsf{s}) \end{split}$$

• Barium Sulfate – BaSO<sub>4</sub>(s)

$$\begin{split} \mathsf{Ba}(\mathsf{NO}_3)_2(\mathsf{aq}) \ + \ \mathsf{Na}_2\mathsf{SO}_4(\mathsf{aq}) \ \to \ \mathsf{Ba}\mathsf{SO}_4(\mathsf{s}) \ + \ \mathbf{2}\mathsf{Na}\mathsf{NO}_3(\mathsf{aq}) \\ \\ \mathsf{Ba}^{2+}(\mathsf{aq}) \ + \ \mathsf{SO}_4^{2-}(\mathsf{aq}) \ \to \ \mathsf{Ba}\mathsf{SO}_4(\mathsf{s}) \end{split}$$



• A similar problem is encountered when adding aqueous silver nitrate to the aqueous solution of an unknown salt:

• Silver Carbonate  $-Ag_2CO_3(s)$ 

 $\begin{array}{rl} 2 \mbox{AgNO}_3(aq) \ + \ \mbox{Na}_2 \mbox{CO}_3(aq) \ \rightarrow \ \mbox{Ag}_2 \mbox{CO}_3(s) \ + \ \mbox{2NaNO}_3(aq) \\ & 2 \mbox{Ag}^+(aq) \ + \ \mbox{CO}_3^{2-}(aq) \ \rightarrow \ \mbox{Ag}_2 \mbox{CO}_3(s) \end{array}$ 

• Silver Chloride – AgCl(s)

$$\begin{split} &\mathsf{AgNO}_3(\mathsf{aq}) \, + \, \mathsf{NaC}l(\mathsf{aq}) \, \to \, \mathsf{AgC}l(\mathsf{s}) \, + \, \mathsf{NaNO}_3(\mathsf{aq}) \\ & \mathsf{Ag}^+(\mathsf{aq}) \, + \, \mathsf{C}l^-(\mathsf{aq}) \, \to \, \mathsf{AgC}l(\mathsf{s}) \end{split}$$

Silver Hydroxide – AgOH(s)

 $AgNO_3(aq) + NaOH(aq) \rightarrow AgOH(s) + NaNO_3(aq)$ 



 $Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s)$ 

 So how can aqueous barium nitrate be used confidently to test for sulfate ions when precipitates other than barium sulfate can form?

 And how can aqueous silver nitrate be used confidently to test for chloride ions when precipitates other than silver chloride can form?



• The solution is quite simple. Adding dilute nitric acid to the solution that is being tested will remove any carbonate ions and / or hydroxide ions from the solution.

• Nitric acid removes carbonate ions from solution:  $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$  $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$ 

• Nitric acid removes hydroxide ions from solution:  $HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ 



 After adding dilute nitric acid to the solution being tested (and therefore removing carbonate ions and hydroxide ions from the solution) a student can be confident that any white precipitate that is formed after adding aqueous barium nitrate is the precipitate of barium sulfate *only*, confirming the presence of sulfate ions in solution:

• Barium Sulfate –  $BaSO_4(s)$ 



• Likewise, after adding dilute nitric acid to the solution being tested (and therefore removing carbonate ions and hydroxide ions from the solution) a student can be confident that any white precipitate that is formed after adding aqueous silver nitrate is the precipitate of silver chloride *only*, confirming the presence of chloride ions in solution:

• Silver Chloride – AgC*l*(s)

$$\begin{split} &\mathsf{AgNO}_3(\mathsf{aq}) \, + \, \mathsf{NaC}l(\mathsf{aq}) \, \to \, \mathsf{AgC}l(\mathsf{s}) \, + \, \mathsf{NaNO}_3(\mathsf{aq}) \\ & \mathsf{Ag}^+(\mathsf{aq}) \, + \, \mathsf{C}l^-(\mathsf{aq}) \, \to \, \mathsf{AgC}l(\mathsf{s}) \end{split}$$



#### Why add dilute nitric acid and not hydrochloric acid or sulfuric acid?

• Adding dilute nitric acid to the aqueous solution of the unknown salt is desirable, as any new salt that is formed will be a nitrate, and all nitrates are soluble.

 Logically, there is no point in using dilute hydrochloric acid to acidify the unknown solution, and then adding aqueous silver nitrate to test for chloride ions – of course a white precipitate of silver chloride will form.

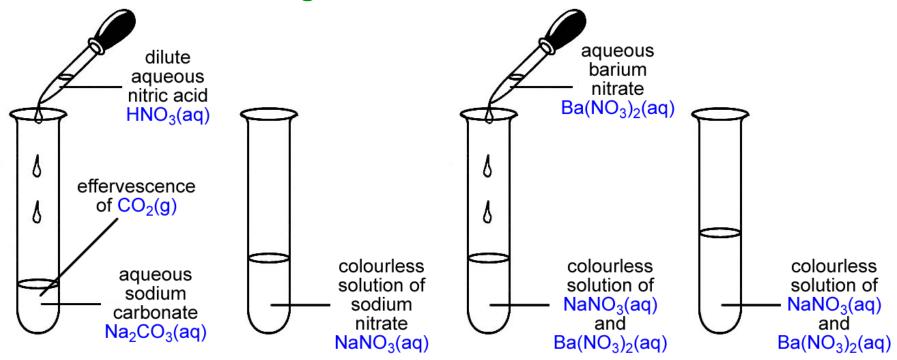
 Likewise, there is no point in using dilute sulfuric acid to acidify the unknown solution, and then adding aqueous barium nitrate to test for sulfate ions – of course a white precipitate of barium sulfate will form. A Comparison of Reactions The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Carbonate

Adding HNO<sub>3</sub>(aq) then Ba(NO<sub>3</sub>)<sub>2</sub>(aq)

Adding Ba(NO<sub>3</sub>)<sub>2</sub>(aq) then HNO<sub>3</sub>(aq)



#### The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Carbonate Adding Dilute Nitric Acid First



• Nitric acid reacts with carbonate ions, removing them from solution:  $2HNO_3(aq) + Na_2CO_3(s) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$ 

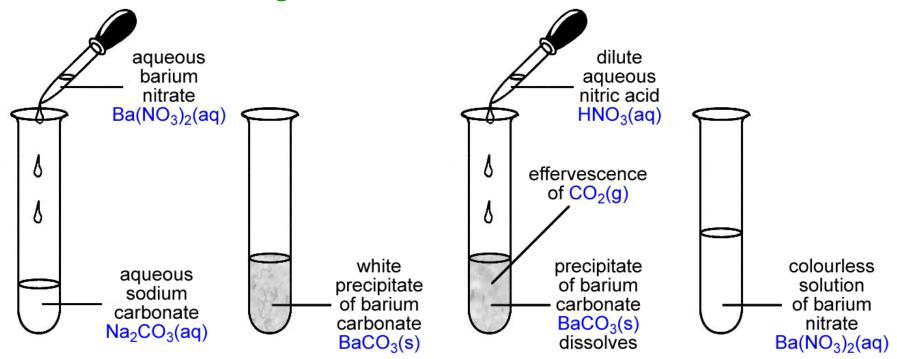


 There are no carbonate ions in aqueous solution by the time the aqueous barium nitrate is added. Consequently, a white precipitate of barium carbonate is not observed. The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Carbonate Generalisations

 Adding dilute nitric acid as the first reagent removes carbonate ions from aqueous solution, so no white precipitate is observed when aqueous barium nitrate is added as the second reagent. The student will not observe a white precipitate and will not conclude that sulfate ions are present in the solution of the unknown salt.



#### The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Carbonate Adding Dilute Nitric Acid Second



• White precipitate of barium carbonate forms:

 $Ba(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow BaCO_3(s) + 2NaNO_3(aq)$ 

• White precipitate dissolves in nitric acid to give a colourless solution:  $2HNO_3(aq) + BaCO_3(s) \rightarrow Ba(NO_3)_2(aq) + H_2O(l) + CO_2(g)$ 



#### The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Carbonate Generalisations

 Adding aqueous barium nitrate as the first reagent causes a white precipitate of barium carbonate to form. A student observing this may incorrectly conclude that the white precipitate is barium sulfate, and that sulfate ions are present in the solution of the unknown salt.

 However, when dilute nitric acid is added as the second reagent, the white precipitate dissolves to produce
effervescence and a colourless solution. The student should now be able to correctly conclude that sulfate ions are absent from the solution of the unknown salt.

 The student should now proceed to carry out the qualitative test for carbonate ions.



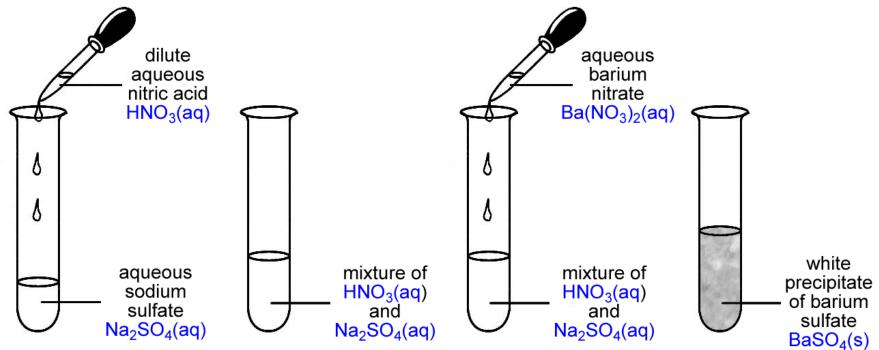
A Comparison of Reactions The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Sulfate

Adding HNO<sub>3</sub>(aq) then Ba(NO<sub>3</sub>)<sub>2</sub>(aq)

Adding Ba(NO<sub>3</sub>)<sub>2</sub>(aq) then HNO<sub>3</sub>(aq)



#### The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Sulfate Adding Dilute Nitric Acid First



- White precipitate of barium sulfate forms, even in acidic solution:  $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$
- The formation of a white precipitate, even in acidic solution, confirms the presence of  $SO_4^{2-}(aq)$  and rules out the possibility of  $CO_3^{2-}(aq)$ .

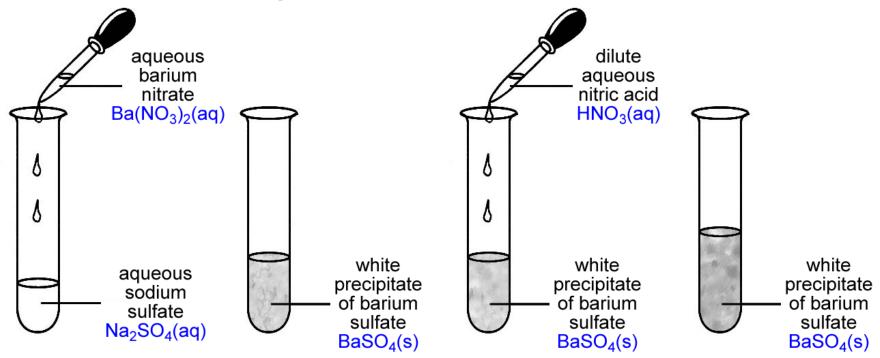
The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Sulfate Generalisations

• Adding dilute nitric acid to the solution of the unknown salt will remove any carbonate ions if they are present.

• When a student adds aqueous barium nitrate as the second reagent, a white precipitate is formed. The student can correctly conclude that sulfate ions are present in the solution of the unknown salt, confident that carbonate ions have been removed by the reaction with the dilute nitric acid.



#### The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Sulfate Adding Dilute Nitric Acid Second



• White precipitate of barium sulfate forms:  $Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$ 



• The white precipitate of barium sulfate is insoluble in dilute nitric acid. This confirms the presence of  $SO_4^{2-}(aq)$ .

The Reaction Between Aqueous Barium Nitrate and Aqueous Sodium Sulfate Generalisations

 Adding aqueous barium nitrate to the solution of the unknown salt results in the formation of a white precipitate. It is incorrect to immediately conclude that the white precipitate is barium sulfate, it could also be a white precipitate of barium carbonate.

 When dilute nitric acid is added as the second reagent, there is no observed reaction, the white precipitate does not dissolve. The student is now able to conclude that the white precipitate is barium sulfate, as a white precipitate of barium carbonate would have dissolved in the dilute nitric acid to produce a colourless solution.



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