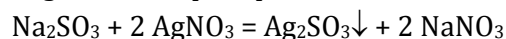


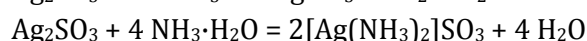
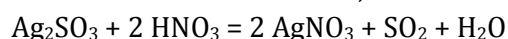
The goal of the Exercise 7 is to analyze a solution that may contain a mixture of the following anions:  $\text{SO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{BO}_2^-$  and  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ . These anions form white precipitates with  $\text{AgNO}_3$  which are soluble in diluted  $\text{HNO}_3$  acid.  $\text{BaCl}_2$  also forms white precipitates hardly soluble in water and soluble in  $\text{HNO}_3$ . Some of the analytical reactions of  $\text{SO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{BO}_2^-$  and  $\text{C}_4\text{H}_4\text{O}_6^{2-}$  ions and methods of their identification in solution are given below.

### Analytical reactions of sulfite(IV) ions $\text{SO}_3^{2-}$

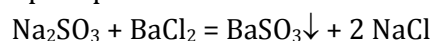
1.  $\text{AgNO}_3$  gives white precipitate of silver sulfite:



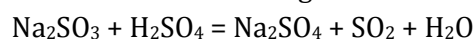
which dissolves in mineral acids, acetic acid and ammonia.



2.  $\text{BaCl}_2$  precipitates white residue of barium sulfite:



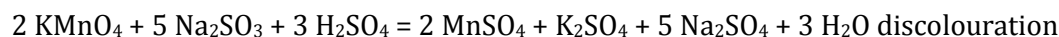
3.  $\text{H}_2\text{SO}_4$  diluted causes the degradation of  $\text{SO}_3^{2-}$  according to the reaction:



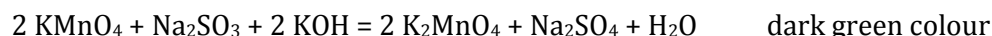
The reaction runs more vigorously when  $\text{H}_2\text{SO}_4$  is concentrated.

4.  $\text{KMnO}_4$

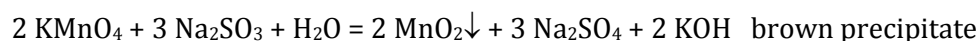
a) in acidic solution:



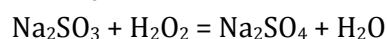
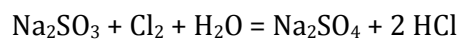
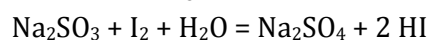
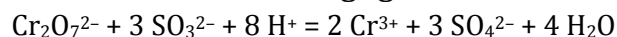
b) in basic solution:



c) in neutral solution:

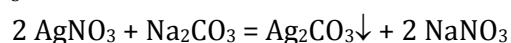


5. Other reactions with oxidizing agents:

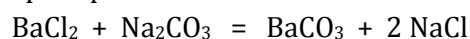


### Analytical reactions of carbonate ions $\text{CO}_3^{2-}$

1.  $\text{AgNO}_3$  gives white precipitate of silver carbonate which dissolves easily in diluted  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$  and  $\text{NH}_3$ :



2.  $\text{BaCl}_2$  precipitates as white residue of  $\text{BaCO}_3$  which dissolves in mineral acids beside  $\text{H}_2\text{SO}_4$

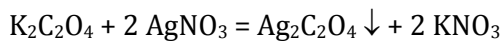


**3. H<sub>2</sub>SO<sub>4</sub>(VI)** diluted and other acids (even CH<sub>3</sub>COOH) decompose carbonate salts, releasing carbon dioxide gas, visible as gas bubbles:



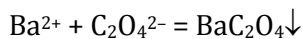
#### Analytical reactions of oxalate ions C<sub>2</sub>O<sub>4</sub><sup>2-</sup>

**1. AgNO<sub>3</sub>** precipitates as white precipitate of calcium oxalate:



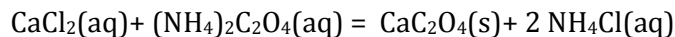
soluble in diluted HNO<sub>3</sub> and ammonia

**2. BaCl<sub>2</sub>** also precipitates as white residue of barium oxalate:

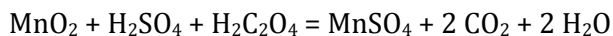


soluble in diluted HNO<sub>3</sub> and boiling acetic acid

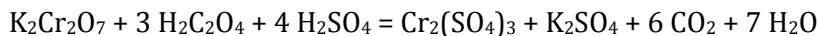
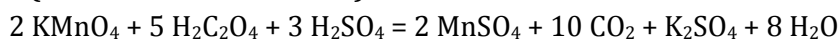
**3. CaCl<sub>2</sub>** gives white precipitate of calcium oxalate CaC<sub>2</sub>O<sub>4</sub> almost insoluble in water and acetic acid, but it dissolves in mineral acids



**4. MnO<sub>2</sub>** in the presence of hot and diluted H<sub>2</sub>SO<sub>4</sub> acid:

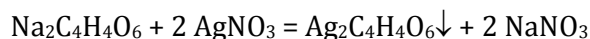


**6. KMnO<sub>4</sub> (and dichromate Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>)** oxidizes acidic solution of oxalates into carbon dioxide:

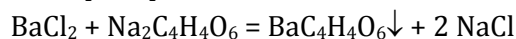


#### Analytical reactions of tartrate ions C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>

**1. AgNO<sub>3</sub>** precipitates as white silver tartrate which is soluble in diluted HNO<sub>3</sub> and ammonia:



**2. BaCl<sub>2</sub>** also precipitates as white barium tartrate:



This precipitate dissolves in diluted HNO<sub>3</sub> acid, hardly in acetic acid

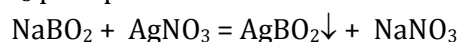
**3. CaCl<sub>2</sub>** gives white precipitate of calcium tartrate CaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> but only when the tartrate anions are in excess in analysed solution. CaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> dissolves in acetic acid, in contrast to calcium oxalate CaC<sub>2</sub>O<sub>4</sub> which does not dissolve in acetic acid.

**4. H<sub>2</sub>SO<sub>4</sub> diluted** does not cause any changes, but concentrated H<sub>2</sub>SO<sub>4</sub> char tartrate anions and CO, CO<sub>2</sub>, SO<sub>2</sub> and other products of degradation are formed. As a result, the colour of analysed solution turns into dark brown and the smell of burnt sugar occurs.

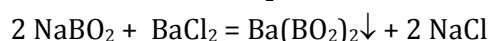
**5. KMnO<sub>4</sub>** slowly reduces tartrate anions in the presence of sulphuric acid. The reaction runs faster when the solution is warmed.

**Analytical reactions of borate ions  $\text{BO}_2^-$** 

1.  $\text{AgNO}_3$  precipitates as white silver borate which is soluble in diluted  $\text{HNO}_3$

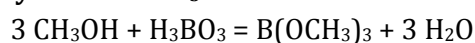


2.  $\text{BaCl}_2$  also precipitates as white barium borate which dissolves in mineral acid and acetic acid, as well as in the excess of  $\text{BaCl}_2$



3.  $\text{H}_2\text{SO}_4$  diluted and concentrated does not cause any changes.

4. Methyl alcohol  $\text{CH}_3\text{OH}$  forms ester of trimethyl borate:



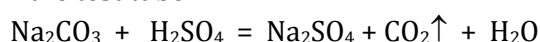
It is a colourless liquid that burns with a green flame

**Identification of III Group anions in analyzed mixture**

As a first step check the pH of analyzed solution with indicator paper. Basic pH may suggest the presence of  $\text{CO}_3^{2-}$  ions in the solution. Their presence can be confirmed with a very simple test:

**Test for  $\text{CO}_3^{2-}$  ions:**

Add a few drops of diluted  $\text{H}_2\text{SO}_4$  (or  $\text{HCl}$ ) solution to the analyzed solution and observe whether gas bubbles start to form in the test tube:

**Test for  $\text{SO}_3^{2-}$  ions:**

The presence of  $\text{SO}_3^{2-}$  ions can be verified in the reaction with  $\text{KMnO}_4$  in acidic solution, because  $\text{SO}_3^{2-}$  oxidize permanganate anions into  $\text{Mn}^{2+}$  and the violet colour disappears simultaneously.

Test: take small amount of analyzed solution, add some of diluted  $\text{H}_2\text{SO}_4$  and add one drop of  $\text{KMnO}_4$ . The immediate discoloration of  $\text{KMnO}_4$  drop proves that  $\text{SO}_3^{2-}$  anions are present in the solution. If the color does not changes it means that  $\text{SO}_3^{2-}$  ions are absent in analyzed solution.

**NOTE!**

$\text{C}_2\text{O}_4^{2-}$  and  $\text{C}_4\text{H}_4\text{O}_6^{2-}$  ions also oxidize  $\text{KMnO}_4$  but these reactions are significantly slower.

**Test for  $\text{C}_2\text{O}_4^{2-}$  ions:**

$\text{C}_2\text{O}_4^{2-}$  ions form white precipitate in reaction with  $\text{CaCl}_2$  and obtained  $\text{CaC}_2\text{O}_4$  does not dissolve in acetic acid. To run the test, take fresh part of analysed solution and acidify it with ca 5 ml of diluted acetic acid. Then add 1 ml of calcium chloride solution and shake the test tube. If white precipitate remains in the test tube it means, that oxalate anions are present in the sample.

### **Test for $\text{C}_4\text{H}_4\text{O}_6^{2-}$ and $\text{BO}_2^-$ ions in one evaporating dish:**

**NOTE!** This test must be performed in the fume hood.

As a first  $\text{BO}_2^-$  ions are verified. For this purpose take a porcelain dish, pour about 3 ml of the mixture and add some drops of conc. sulphuric acid followed by 1 ml of methyl alcohol. Heat the dish and set it alight with matches. The  $\text{BO}_2^-$  ions are confirmed when green flame is observed. Continue the heating of the porcelain until the solution will evaporate. If tartrate anions are present, the obtained residue will turn into dark-brown mixture and the smell of burnt sugar will be noticeable.

*The end ☺*