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The goal of the Exercise 6 is to analyze a solution that may contain a mixture of the following anions: NO_2^-, CH_3COO^-, NO_3^- and MnO_4^-. The first two anions belong to 2nd group, whereas NO_3^- and MnO_4^- are from 5th group anions and they react variously with $AgNO_3$ and $BaCl_2$ groups reagents. But first some analytical reactions of NO_2^-, CH_3COO^-, NO_3^- and MnO_4^- were summarized and the most important among them are given below.

Reactions with $AgNO_3$

$AgNO_3 + KNO_2 \rightarrow AgNO_2\downarrow + KNO_3$ (*reaction 1*)
$AgNO_3 + CH_3COONa \rightarrow CH_3COOAg\downarrow + NaNO_3$ (*reaction 2*)

NOTE: Both CH_3COO^- and NO_2^- ions precipitate as silver salt when their concentration is high in analyzed solution. The concentration of all anions in mixtures indicated for Student analysis are standard but not high enough to obtain CH_3COOAg and $AgNO_2$ salts as precipitates.

NO_3^- and MnO_4^- anions do not precipitate when $AgNO_3$ is added to the analyzing solution.

Reactions with $BaCl_2$

All NO_2^-, CH_3COO^-, NO_3^- and MnO_4^- ions do not form precipitates with $BaCl_2$

Reactions with H_2SO_4

Diluted and concentrated H_2SO_4 causes the degradation of NO_2^- ions into NO_2 (brown vapors) even at low temperature

$2\ NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HNO_2$ (*reaction 3*)
HNO_2 acid decomposes at: $3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$ (*reaction 4*)
$2\ NO + O_2 \rightarrow 2\ NO_2$ (*reaction 5*)

H_2SO_4 as a strong acid displaces weak acetic acid from its salt solutions

$CH_3COONa + H_2SO_4 \rightarrow 2\ CH_3COOH + Na_2SO_4$ (*reaction 6*)

Diluted H_2SO_4 does not react visibly with NO_3^- and MnO_4^- solutions, as opposed to concentrated sulfuric acid:

$2\ NaNO_3 + H_2SO_{4\ concentrated} \rightarrow Na_2SO_4 + 2\ HNO_3$ (*reaction 7*)
$2\ HNO_3 \rightarrow H_2O + 2\ NO_2\uparrow + ½\ O_2\uparrow$

Concentrated sulfuric acid reacts with $KMnO_4$ giving dark green oil of Mn_2O_7, which can be explosive after initiation by striking the sample or by its exposure to oxidizable organic compounds (the products are MnO_2 and O_2).

$2\ KMnO_4 + 2\ H_2SO_4 \rightarrow Mn_2O_7 + H_2O + 2\ KHSO_4$ (*reaction 8*)

Reactions with Fe(II) salts

$2\,NaNO_2 + 2\,FeSO_4 + 2\,H_2SO_{4\ diluted} \rightarrow Fe_2(SO_4)_3 + 2\,NO + Na_2SO_4 + 2\,H_2O$ (*reaction 9*)

Nitrogen oxide forms brown $Fe(NO)^{2+}$ ions with the excess of Fe^{2+} ions visible as brown ring in the analyzed solution:

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O \quad (\textit{reaction 10})$$

Identical reaction occurs for NO_3^- ions.

$2\,NaNO_3 + 6\,FeSO_4 + 4\,H_2SO_{4}$ concentrated $\rightarrow 3\,Fe_2(SO_4)_3 + 2\,NO + Na_2SO_4 + H_2O$ (*reaction 11*)

Reactions with Fe(III) salts

$FeCl_3 + 3\,CH_3COONa \rightarrow (CH_3COO)_3Fe + 3\,NaCl$ red-brown color of the solution (*reaction 12*)

Reactions with KI

NO_2^- ions oxidize I^- ions into I_2 in acetic solution and the solution color changes into yellow and brown-red as a result of the conversion into I_2:

$2\,KI + 2\,KNO_2 + 4\,CH_3COOH \rightarrow 4\,CH_3COOK + I_2 + 2\,NO + 2\,H_2O$ (*reaction 13*)

The reaction of MnO_4^- with I^- requires the presence of H_2SO_4 solution:

$2\,KMnO_4 + 10\,KI + 8\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5\,I_2 + 6\,K_2SO_4 + 8\,H_2O$ (*reaction 14*)

Reactions with $KMnO_4$ and $K_2Cr_2O_7$

$5\,HNO_2 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow 5\,HNO_3 + 2\,MnSO_4 + K_2SO_4 + 3\,H_2O$ (*reaction 15*)

$3\,KNO_2 + K_2Cr_2O_7 + 4\,H_2SO_4 \rightarrow 3\,KNO_3 + Cr_2(SO_4)_3 + K_2SO_4 + 4\,H_2O$ (*reaction 16*)

Reactions with other reducing agents:

NO_2^- (*reactions 17-24*)

$2\,KNO_2 + H_2S + H_2SO_4 \rightarrow 2\,NO + 2\,H_2O + S + K_2SO_4$

$2\,NaNO_2 + Cu + 2\,H_2SO_4 \rightarrow Na_2SO_4 + CuSO_4 + 2\,NO + 2\,H_2O$

$2\,NaNO_2 + SO_2 \rightarrow Na_2SO_4 + 2\,NO$

$2\,NaNO_2 + SnCl_2 + 4\,HCl \rightarrow SnCl_4 + 2\,NO + NaCl + 2\,H_2O$

$NaNO_2 + NH_4Cl \rightarrow NaCl + N_2 + 2\,H_2O$

Urea $CO(NH_2)_2 + 2\,HNO_2 \rightarrow 2\,N_2 + CO_2 + 3\,H_2O$

Thiourea $CS(NH_2)_2 + HNO_2 \rightarrow N_2 + HSCN + 2\,H_2O$

$NaN_3 + NaNO_2 + 2\,CH_3COOH \rightarrow N_2 + N_2O + 2\,CH_3COONa + H_2O$

MnO_4^- (*reactions 25-33*)

a) in acidic solution:

$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + K_2SO_4 + 8\,H_2O$

$2\,KMnO_4 + 5\,H_2S + 3\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5\,S + K_2SO_4 + 8\,H_2O$

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$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + 10\ CO_2 + K_2SO_4 + 8\ H_2O$
$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + 5\ O_2 + K_2SO_4 + 8\ H_2O$

b) in neutral solution:

$2\ KMnO_4 + 3\ H_2O_2 \rightarrow 2\ MnO_2 + 3\ O_2 + 2\ KOH + 2\ H_2O$
$2\ KMnO_4 + 3\ C_2H_5OH \rightarrow 2\ MnO_2 + 3\ CH_3COOH + 2\ KOH + 2\ H_2O$
$2\ KMnO_4 + 3\ Na_2SO_3 + H_2O \rightarrow 2\ MnO_2 + 3\ Na_2SO_4 + 2\ KOH$

c) in basic solution:

$2\ KMnO_4 + Na_2SO_3 + 2\ KOH \rightarrow 2\ K_2MnO_4 + Na_2SO_4 + H_2O$

After adding some CH_3COOH solution changes its color from dark green into violet again
$3\ K_2MnO_4 + 4\ CH_3COOH \rightarrow 2\ KMnO_4 + MnO_2 + 4\ CH_3COOK + 2\ H_2O$

Reactions with Zn, Al metal or Devarda's alloy: (*reactions 34-38*)

a) in basic solution: $NaNO_2 + 2\ Al + NaOH + 5\ H_2O \rightarrow NH_3\uparrow + 2\ Na[Al(OH)_4]$
$3\ NaNO_3 + 8\ Al + 5\ NaOH + 18\ H_2O \rightarrow 3\ NH_3\uparrow + 8\ Na[Al(OH)_4]$

b) in acidic solution: $6\ Zn + 2\ NaNO_2 + 8\ H_2SO_4 \rightarrow (NH_4)_2SO_4 + 6\ ZnSO_4 + Na_2SO_4 + 4\ H_2O$
$Zn + NaNO_3 + 2\ CH_3COOH \rightarrow NaNO_2 + Zn(CH_3COO)_2 + H_2O$

c) in neutral solution: $5\ H_2O + KNO_2 + 3\ Zn \rightarrow NH_3 + KOH + 3\ Zn(OH)_2$

Identification of II and V Group anions

USEFUL HINTS:

1. If an analyzed sample is colorless it does not contain MnO_4^- ions and consequently dark-violet color suggest the presence of MnO_4^- ions
2. NO_2^- ions cannot be present in a sample together with MnO_4^- ions because NO_2^- undergoes oxidation into NO_3^- ions in acidic solution (see reactions above)
3. $NO_2^-$and NO_3^- both form ammonia with hot Al powder in $NaOH_{(aq)}$ solution and gives 'brown ring' test that's why the additional procedures must be taken for proper identification of both anions.
4. NO_2^- can be identified in a simple test in the absence of MnO_4^- ions (below)

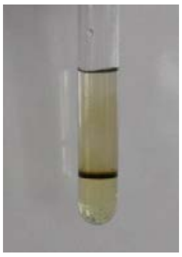
First, if the sample contains MnO_4^- ions, they must be removed. For this purpose, take some of the initial sample, add some of H_2O_2 solution into it and wait 2 minutes (*reaction 30*). The resulted brown precipitate of MnO_2 must be filtered and the filtrate must be colorless. If not, add some H_2O_2 solution again and repeat the filtration. The colorless final solution may contain CH_3COO^-, NO_2^- and NO_3^-.
CH_3COO^- ions can be identified in the reaction with H_2SO_4 (*reaction 6*) and characteristic smell of vinegar should be detected.

Next NO_2^- can be determined in two ways. First and the simplest test is discoloration of $KMnO_4$ in acidic solution. In order to do this, take small amount of investigated sample, add some H_2SO_4 solution and then add two drops of $KMnO_4$ solution and observe the solution. The disappearance of the violet color denotes the presence of NO_2^- ions in analyzed solution (*reaction 15*). NO_2^- ions can be also identified with the brown ring test which is described below. It also follows, therefore, that if NO_2^- ions are absent, the brown ring test can be followed for NO_3^- without additional activities.

Analyze the solution for the presence of NO_2^- and NO_3^- - the brown ring test

As a first NO_2^- are identified according to the procedure:

1. Take clean test tube and prepare a concentrated solution of **Mohr's Salt** - inorganic compound with the formula $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ – **SOLUTION 1**
2. Take second clean test tube and pour some of your analyzing sample and add small amount (few drops are enough) of diluted H_2SO_4 – **SOLUTION 2**
3. Pour gently the Solution 1 into test tube containing Solution 2 and observe whether deep brown ring occurs at the junction of the two liquid layers (see the picture). If so, NO_2^- ions are present in analyzed sample.



This deep brown ring is in fact the complex with the formula of $[Fe(H_2O)_5NO]^{2+}$ (reactions 9,10)

The identification of NO_3^- ions requires the removal of the NO_2^- ions from the solution, if they are present. For this purpose, pour some of the initial sample into a beaker and add some of amidosulfonic acid H_3NSO_3 and boil it for 5 minutes. Te reaction runs vigorously due to the emission of gaseous N_2: $NaNO_2 + H_3NSO_3 \rightarrow NaHSO_4 + N_2\uparrow + H_2O$. Then take some of the solution and cool in the stream of running water before further investigations (**Solution 3**). Next, take some **Mohr's Salt** into clean test-tube and introduce about 0.5 mL of concentrated H_2SO_4. Cool the solution in the stream of running water <u>without shaking</u> (**Test tube 1**). Then, pour gently some of the Solution 3 into Test tube 1 by allowing it to flow down the side of the tilted test tube and allow the solution to sit undisturbed. The formation of a brown color at the edges of solid and solution constitutes a positive test for NO_3^- ions.

The end ☺