Задания II (практического) тура по химии.
The second (experimental) tour on chemistry.
Problems
**Bromatometric determination of antimony**

Bromatometric method is one of the basic approaches in redox titremetry. In this method oxidation by \( \text{BrO}_3^- \) is used in acidic conditions:

\[
\text{BrO}_3^- + 6\text{H}^+ + 6e \rightarrow \text{Br}^- + 3\text{H}_2\text{O}
\]

Potassium bromate \( \text{KBrO}_3 \) is a powerful oxidizing reagent \( (E^0 = +1.45\text{B}) \), by the way, the rate of the reaction is quite low. So, heating and presence of acid must be the reaction conditions.

During the reaction \( \text{Br}^- \) ions immediately react with \( \text{BrO}_3^- \) ions to form bromine, that change color of the solution to pale-yellow:

\[
\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}
\]

In this method acid-base indicators are usually used - like methyl orange or methyl red. Methyl orange oxidation is irreversible process so extra addition of indicator is required.

Bromatometric method is the most useful for arsenic (III) and antimony (III) determination.

**Determination of antimony (III)**

During the titremetry the following reactions are occurred in the solution:

\[
\text{KBrO}_3 + 3\text{SbCl}_3 + 6\text{HCl} \rightarrow \text{KBr} + 3\text{SbCl}_5 + 3\text{H}_2\text{O}
\]

\[
\text{BrO}_3^- + 6\text{H}^+ + 6e \rightarrow \text{Br}^- + 3\text{H}_2\text{O}
\]

\[
\text{Sb}^{3+} - 2e \rightarrow \text{Sb}^{5+}
\]

\( M_r = \frac{121.75 \times 2}{60.88} = 40.44 \)

**Task**

1. On your bench you got the test-tubes with \( \text{HCl} \ (\text{q}=15\%) \), \( \text{SbCl}_3 \), \( \text{BaCl}_2 \), \( \text{ZnSO}_4 \), \( \text{NaOH} \), \( \text{Na}_2\text{S}_2\text{O}_3 \), \( \text{AgNO}_3 \). Using only this solutions identify each solution. Write chemical equations for each reaction.
2. Determine antimony concentration in the given solution by bromatometric method.
3. Confirm the nature of the antimony acid by chemical reactions.

**Reagents:** \( \text{KBrO}_3 \ (c = 0.1 \text{ M}) \), concentrated \( \text{HCl} \ (\rho = 1.19 \text{ g/cm}^3) \), methyl orange, distilled water.
**Equipment:** chemical tripod, burette, vessel, test tubes, pipette, glass, heater.

**Method**

1. Qualitative determination

<table>
<thead>
<tr>
<th></th>
<th>HCl</th>
<th>SbCl₅</th>
<th>BaCl₂</th>
<th>ZnSO₄</th>
<th>NaOH</th>
<th>Na₂S₂O₇</th>
<th>AgNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td></td>
<td>H[HSbCl₅]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>SO₂↑, S⁴</td>
<td>AgCl↓</td>
</tr>
<tr>
<td>SbCl₅</td>
<td>H[HSbCl₅]</td>
<td>-</td>
<td>-</td>
<td>(Sb₂O₅)₂SO₄</td>
<td>Sb₂O₃↓ white</td>
<td>Sb₂O₃↓ red</td>
<td>AgCl↓</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>-</td>
<td>-</td>
<td>BaSO₄↓</td>
<td>-</td>
<td>BaSO₄↓</td>
<td>-</td>
<td>AgCl↓</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>(Sb₂O₅)SO₄</td>
<td>BaSO₄↓</td>
<td>-</td>
<td>*Zn(OH)₂↓ or Na₂[Zn(OH)₆]</td>
<td>*Zn(OH)₂↓ or Na₂[Zn(OH)₆]</td>
<td>*Zn(OH)₂↓ or Na₂[Zn(OH)₆]</td>
<td>Ag₂SO₄↓</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sb₂O₃↓ white</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ag₂O↓ black</td>
<td>-</td>
<td>Ag₂O↓ black</td>
</tr>
<tr>
<td>Na₂S₂O₇</td>
<td>SO₂↑, S⁴</td>
<td>Sb₂O₃↓ red</td>
<td>BaSO₄↓</td>
<td>Na₂[Zn(OH)₆]</td>
<td>Na₂[Zn(OH)₆]</td>
<td>-</td>
<td>Ag₂S₂O₇↓ ***</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>AgCl↓</td>
<td>AgCl↓</td>
<td>AgCl↓</td>
<td>Ag₂SO₄↓</td>
<td>Ag₂O↓ black</td>
<td>Ag₂S₂O₇↓ ***</td>
<td>-</td>
</tr>
</tbody>
</table>

* depends on procedure

**white solid which rapidly becomes black on standing

** using excess of the reagent Na₂[Ag(S₂O₄)₂] is formed

**** during heating precipitate dissolves

***** SO₂↑, S⁴ in excess of acid

2. Buretometric determination of antimony

A solution of antimony chloride (III) SbCl₃ is placed in flask (100 ml), solution of diluted HCl is added. The hydrolysis reaction occurs rapidly but reversible:

SbCl₃ + H₂O ↔ Sb(OH)₃ + 3HCl

20,00 ml of the solution dissolve to 100 ml in a measure flask, then 10-12 ml of concentrated HCl solution is added (d = 1.19 g/cm³), finally heat till 70°C. After addition of 2-3 drops of methyl red, titrate the solution with KBrO₃. At the end of titration add extra more indicator, when colour becomes too pale. Titrate until sharp change in color occurs.

During second titration less amount of KBrO₃ (than in the first time) must be added. Heat the solution till 70 °C and after that, add the indicator, and then start titration until formation of colorless solution.

**Calculations**

\[
M(SbCl₃) = 228 \text{ g/mol} \\
M_{\text{KBrO₃}} = 114 \text{ g}
\]

\[
C(I/zX) = \frac{(m×1000) / (M×V)}{C(I/zX) - C(I/zX)×V(X) = C(I/zX) - V(Y)}
\]

\[
C(I/zX) = \frac{C(I/zX) - V(Y) / V(X)}{T/a/b = (C(I/zX) A M(B))/1000}
\]

**Compounds determination – 7 scores**

**Chemical equations – 7 scores**

**Method – 6 scores**

**Experiment and experimental results – 10 scores**

**TOTAL: 30 scores**