The Complex Formation of Antimony(III) in Perchloric Acid and Nitric Acid Solutions. A Solubility Study

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The hydrolysis of antimony(III) in perchloric and nitric acid solutions has been investigated by solubility measurements at an ionic strength $I = 5.00$ M and a temperature of $25.0\, ^\circ\text{C}$. In perchloric acid solutions the complexes $\text{Sb(OH)}_2^{3+}$ and $\text{Sb}_4(\text{OH})_4^{4+}$ exist in equilibrium with orthorhombic and cubic $\text{Sb}_2\text{O}_4$. The oxides are metastable for acidities over 0.26 M and 0.68 M, respectively, where $\text{Sb}_2\text{O}_4(\text{OH})\text{ClO}_4 -4\text{H}_2\text{O}$ is the stable phase. The monomer $\text{Sb(OH)}_2^{3+}$, but not the dimer $\text{Sb}_2(\text{OH})_4^{4+}$, is also found in equilibrium with this phase.

The only solid phase in equilibrium with nitric acid solutions of an acidity below 5.00 M is the oxide nitrate $\text{Sb}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_2$. Besides the complex $\text{Sb(OH)}_2^{3+}$ also found in the perchloric acid solutions, the monomer $\text{Sb(OH)}_2^{3+}$ appears to be present.

On account of the strongly acidic properties of antimony(III), its chemistry in aqueous solution is very much dominated by hydrolytic reactions which have to be taken into account in all studies of its complex formation. Unfortunately, the course of the hydrolysis has not yet been clarified, not even in those instances where the anions present in the medium show little affinity for antimony(III) and therefore do not bring about any extensive formation of mixed complexes. Weakly complexing media should be provided by, e.g., the perchlorate and nitrate ions, while the halide ions certainly form quite strong complexes. This investigation concerns the hydrolytic reactions taking place in solutions of the weakly complexing anions mentioned above.

The hydrolysis of antimony(III) has been previously studied, mostly by the use of solubility measurements. Schuhmann concluded from a study of the solubility of orthorhombic $\text{Sb}_2\text{O}_4$ in perchloric acid of molality between 0.231 and 1.133 that the species present in solution is $\text{SbO}^+$ and he calculated the constant for the corresponding equilibrium $\text{Sb}_2\text{O}_4(s) + \text{H}^+ \rightleftharpoons \text{SbO}^+ + \text{H}_2\text{O}$ (Table 7). Gayer and Garrett found that the same equilibrium is established in hydrochloric acid of molality up to 0.1. Furthermore the value of the equilibrium constant is comparable for the two media (Table 7). Fridman et al. verified Schuhmann's result from solubility measurements in perchloric acid. They also investigated the solubility of $\text{SbOCl}$ in solutions of $\text{HClO}_4$ and $\text{NaCl}$ at $25\, ^\circ\text{C}$ and constant ionic strength $I = 6$ M (regulated by means of $\text{NaClO}_4$) and found the complexes $\text{SbCl}_4^{3-}$, $\text{SbCl}_4^{2-}$ and $\text{SbOHCl}_4^{2-}$. Jander and Hartmann found from diffusion measurements that only monomeric $\text{SbO}^+$ and possibly small amounts of $\text{Sb}^{2+}$ are present in perchloric acid solutions up to $C_H = 6$ M when the concentration of $\text{Sb(III)}$ is $\leq 1\, \text{mM}$.

The present investigation started as a study of the solubility of the orthorhombic and cubic modifications of $\text{Sb}_2\text{O}_4$ in perchloric and nitric acid solutions of constant ionic strength, $I = 5.00$ M, maintained by sodium perchlorate and sodium nitrate, respectively. At the temperature of the measurements ($25.0\, ^\circ\text{C}$) the orthorhombic modification, $\text{Sb}_2\text{O}_4(\text{or})$, is metastable but the transition into the stable cubic modification, $\text{Sb}_2\text{O}_4(\text{cr})$, does not take place in aqueous solution. In practice, the transition is conveniently effected in the solid state at $550\, ^\circ\text{C}$; cf. below. Above $570\, ^\circ\text{C}$, $\text{Sb}_2\text{O}_4(\text{or})$ is the stable modification.

Though no conversion takes place between
the oxide modifications, phase transitions are nevertheless observed. In perchloric acid, Sb₂O₅ (or) is in fact stable only up to C_H = 0.3 M and Sb₂O₅(c) up to C_H = 0.7 M at the present total perchlorate concentration of 5.00 M. Both survive long enough, however, for metastable equilibria to be established even at acid concentrations up to C_H = 4.0 and 4.5 M, respectively. The stable phase formed at the transition is an oxide perchlorate Sb₄O₄(OH)ClO₄•H₂O. A structure determination of this compound has been performed by Bovin and has confirmed the above composition. At the highest acid concentrations used, C_H = 4.50 and 5.00 M, another perchlorate can be obtained as an intermediary metastable phase. Its empirical formula is 3Sb₂O₃•2Cl₂O₇•6H₂O, thus, as expected, corresponding to a less strongly hydrolyzed state of antimony(III) than in the former compound. This is immediately evident from the mol ratios perchlorate/antimony, Q_P, which are Q_P = 1/4 and 2/3 for the two phases, respectively, while a completely unhydrolyzed perchlorate would have Q_P = 3. The more hydrolyzed phase will, in the following, be denoted by Sbop(70) and the less hydrolyzed one by Sbop(55), the notation deriving from the antimony content (≈70% and ≈55%, respectively). The phase Sbop(70) can also exist in metastable equilibrium at lower values of C_H, where the oxides are the stable phases.

In order to investigate whether further transitions occur at higher acidities, resulting in compounds of even lower degrees of hydrolysis of antimony(III), the measurements have been extended to include concentrated perchloric acid, C_H = 11.75 M. In this higher acidity range a constant medium could not be maintained, so that identification of the species present in the solutions has not been possible. Further phase transitions have been observed, however. Besides Sbop(55), which only seems to exist as a metastable intermediate around C_H = 5.00 M, at least two more oxide perchlorates have been firmly identified. Thus, between C_H = 6.7 M and concentrated acid, Sb(OH)₆ClO₄H₂O [denoted Sbop(44)], with Q_P = 1, is the stable phase. In concentrated acid, an undoubted even less hydrolyzed phase is stable. On account of the latter’s extreme sensitivity to moisture, it has so far not been possible to determine its composition. The structures of these relatively little hydrolysed compounds might have features of relevance to the interpretation of the equilibria existing in solution. Efforts will therefore be made to determine the structures, although this will, particularly in the case of the least hydrolyzed compound, present great experimental difficulties.

In nitric acid at a nitrate concentration of 5.00 M, Sb₂O₅(or) and Sb₂O₅(c) are even less stable than in the perchloric acid solutions discussed above and they are transformed into an oxide nitrate of the composition Sb₂O₅(OH)₄•(NO₃)₅, denoted in the following by Sbn. The transformation is, moreover, so fast that the oxides do not survive as metastable phases for any appreciable length of time. The mol ratio nitrate/antimony of Sbn is Q_P = 1/2, which means a degree of hydrolysis intermediate between Sbop(70) and Sbop(55). No other oxide nitrate has been observed up to C_H = 5.00 M, the highest concentration employed in the nitric acid measurements. The phase Sbn can also exist in metastable equilibrium with solutions of quite low acidity, at least down to C_H = 0.005 M. The crystal structure of Sb₂O₅(OH)₄(NO₃)₅ has been determined by Bovin and has confirmed the composition.

NOTATIONS AND CALCULATIONS

Notations. The following symbols are used

S = total concentration of Sb(III)
C_H = total concentrations of hydrogen ions
S₁ = concentration of the complex
Sb(OH)₆(α⁺β⁻)⁺
Kᵢ = the calculated exponent in the polynomial
ΣᵢKᵢC_Hᵢ

Kᵢ' = stability constant for complex formation
ΔG° = standard free energy change
μ(B) = chemical potential of the substance B
a(B) = activity, relative activity of substance B
i to q are all integers

Calculation of complex formation. The solid phases considered in the solution equilibria here are Sb₂O₅(or), Sb₂O₅(c), Sb₂O₅(OH)ClO₄•H₂O and Sb₂O₅(OH)₄(NO₃)₅. In order to achieve the simplest formulation possible, the general formula Sb₂O₅(α⁻β⁺)OH(J)Z, with j = 0, 1, 2 and Z = ClO₄⁻.
or \( \text{NO}_2^- \) is employed in the following for these phases. The equilibria can thus be written as

\[
kS_{\text{Br}_2(OH)_2}\text{Z} + m\text{H}^+ = nS_{\text{Br}_2(OH)}\text{Z}^{(2+)} + q\text{H}_2\text{O} + k\text{Z}^-
\]

with \( m = n(3l - p) - kj \) \( (1) \)

and \( 4k = nl \)

Elimination of \( k \) by combination of \( (1) \) and \( (2) \) gives

\[
m/n = 3l - p - lj/4
\]

(3)

Since the activities of \( \text{H}_2\text{O} \) and \( \text{Z}^- \) may be considered as constant in the media employed and since \( [\text{H}^+] \approx C_H \), an equilibrium constant \( K_i' \) can be defined as follows:

\[
K_i' = \frac{[S_{\text{Br}_2(OH)}^{(2+)}]^n}{[\text{H}^+]^m} \approx \frac{(S_i)^n}{C_H^m}
\]

(4)

and hence

\[
S_i = (K_i')^{1/m}C_H^{m/n}
\]

(5)

The total concentration of \( \text{Sb(III)} \) in solution may be written as

\[
S = \sum S_i
\]

(6)

(5) and (6) give:

\[
S = \sum (K_i')^{1/m}C_H^{m/n}
\]

(7)

and

\[
S = \sum K_iC_H^{i/m}
\]

(8)

if

\[
K_i = l_i(K_i')^{1/m}
\]

and

\[
m/n = e_i
\]

(10)

From an experimental determination of \( S \) as a function of \( C_H \) it is clearly possible to derive the exponents \( e_i \) and the coefficients \( K_i \). Each \( e_i \)-value allows several combinations of \( l \) and \( p \) in the complex \( \text{Sb}(OH)_2^{(2+)} \). However, when the solubility \( S \) is measured for different solid phases, as is the case in this investigation, the number of combinations becomes more restricted. The calculation of \( e_i \) and \( K_i \) has been made both graphically and by a computer. When the \( e_i \)-values are known it is possible to compute connected values of \( l \) and \( p \) from (10) and (3), since the value of \( j \) for the solid phase is known.

The graphical treatment was carried out in the following way: From the graph \( S = f(C_H) \)

The Complex Formation of Sb(III) 1091

(cf. Figs. 3, 8) it is obvious that the polynomial (8) must contain a constant term \( K_1 \), i.e. \( e_1 = 0 \). The numerical value of \( K_1 \) was determined by a graphical extrapolation to \( C_H \rightarrow 0 \). This value is not identical with the solubility of the particular solid phase in 5.00 M sodium perchlorate and sodium nitrate solution, the latter being found by direct measurements to be about twice as high (cf. Table 3). For \( C_H < 0.005 \) M other reactions resulting in a higher solubility evidently occur. In the following \( K_1 \) and \( e_i \) are therefore treated as mathematical constants. Eqn. (8) can be written as

\[
S - K_1 = \sum_{i=1}^{\infty} K_iC_H^{e_i-1}
\]

(11)

which for low values of \( C_H \) can be approximated to

\[
S - K_1 \approx K_2C_H^{e_2}
\]

(11')

Hence

\[
\ln (S - K_1) = e_2 \ln C_H + \ln K_2
\]

(11'')

A plot of \( \ln (S - K_1) \) versus \( \ln C_H \) should yield \( e_2 \) as the slope and \( \ln K_2 \) as the intercept of a straight line. When the values of \( e_2 \) and \( K_2 \) are known Eqn. (8) can be written as

\[
S - K_1 - K_2C_H^{e_2} = \sum_{i>3} K_iC_H^{e_i-2}
\]

(12)

or, if terms of \( i > 3 \) are neglected as

\[
S - K_1 - K_2C_H^{e_2} \approx K_3C_H^{e_3}
\]

(12')

It is then possible to determine the constant \( e_2 \) in the same way as \( e_i \). Within the range of \( C_H \) investigated, the polynomial (8) could in fact be fitted with at most three terms.

In the computer treatment, a curve of the form \( S = \sum K_iC_H^{e_i} \) was fitted to the experimental data (\( C_H, S \)) by the least-squares program CURVETFIT. The error square sum

\[
\text{CHISQ} = \sum_i \frac{1}{\sigma S_i^2} (S_{\text{calc},i} - S_i)^2
\]

(13)

was minimized by the subroutine STEPIT, where

\[
S_{\text{calc},i} = \sum_i K_iC_H^{e_i}
\]

(14)

The least-squares treatment was first made with \( e_1 = 0 \) and with \( e_{i-1} \) and \( K_i \) as variables. Because the value of \( e_i \) must be rational, the nearest rational value was then chosen and kept con-

constant in a subsequent refinement cycle which yield the final values of the constants $K_i$.

**EXPERIMENTAL**

*Chemicals.* Orthorhombic antimony(III) oxide \([\text{Sb}_2\text{O}_5\text{(or)}]\) was prepared from \(\text{Sb}_2\text{O}_3\) (Riedel-DeHaen p.a.) as follows. The oxide was dissolved in concentrated hydrochloric acid. After filtration, a sixfold volume of water was added to the solution. After three days in the mother liquor, the crystalline precipitate formed was separated and dissolved in a minimum amount of concentrated hydrochloric acid. This solution was then poured into a boiling solution of sodium carbonate. The \(\text{Sb}_2\text{O}_4\text{(or)}\) obtained was washed free of chloride ions with hot water and then dried at 110 °C. The antimony(III) content was checked (see below; found: 83.3 %, calc. for \(\text{Sb}_2\text{O}_4\): 83.5 %) and a Guinier-Hägg powder photograph was taken to verify the orthorhombic phase.

*Cubic antimony(III) oxide \([\text{Sb}_2\text{O}_5\text{(c)}]\)* was prepared from \(\text{Sb}_2\text{O}_3\text{(or)}\) as follows. A thick-walled glass tube was filled with \(\text{Sb}_2\text{O}_3\text{(or)}\), evacuated and heated to 550 °C. After 24 h the transformation to \(\text{Sb}_2\text{O}_5\text{(c)}\) was complete. The antimony(III) content was checked (found: 83.3 %, calc. 83.5 %) and a Guinier-Hägg powder photograph verified the cubic phase.

During the investigation it was found accidentally that \(\text{Sb}_2\text{O}_5\text{(c)}\) could in fact be prepared at room temperature by washing of the metastable phase SbOp(55) with methanol. On prolonged treatment, all perchlorate is displaced and pure \(\text{Sb}_2\text{O}_5\text{(c)}\) is obtained.

All other chemicals used were *pro analyesi* grade.

*Procedure.* The equilibrium of solid phase and solution was effected in 50 ml polyethylene flasks agitated in a thermostat at 25.0 °C. The agitation time varied between a few hours and more than two hundred days. (cf. below.) Afterwards, the phases were separated within a few seconds by filtration through a membrane filter. Only the solid phases \(\text{Sb}_2\text{O}_3\) (or and c) and SbOp(70) were washed with 5 ml methanol (cf. above) and dried. The other solid phases were only dried. The solution was immediately analysed for antimony(III).

**Analysis.** The solid phases, as well as the perchloric acid solutions with \(C_H \geq 0.250 \text{ M}\), were analysed for antimony(III) titrimetrically. The procedure employed was that described by Belcher, Schulek, and Rózsza and Schulek. This method was not applicable to the nitric acid solutions. In this case, as well as for the perchloric acid solutions with \(C_H \leq 0.250 \text{ M}\), where the concentration of antimony(III) was very low, the analyses were performed spectrophotometrically with a Zeiss Spectrophotometer PMQII at 330 nm, by the method described by Eikind, Gayer and Baltz. It was checked that Beer's law was obeyed (to within \(\pm 3.0 \%\)) for absorbances between 0.2 – 1.5. Both analytical methods were suitable for the measurement of the solubility in 250 mM perchloric acid and gave the same result within the limits of error. At least two samples were equilibrated with each solution. The solubilities could all be reproduced to within \(\pm 3 \%\). The lower limit of \(C_H = 0.0052 \text{ M}\) was chosen for the reason that at lower acidities the solubility becomes too low even for the sensitive spectrophotometric method of analysis. Almost all solid phases were checked after equilibration by Guinier-Hägg X-ray photographs.

The 5.00 M stock solutions of sodium perchlorate and sodium nitrate were analyzed both by cation exchange and by weighing a dried sample, with concurrent result. The \(C_H\) values of all perchloric and nitric acid solutions were checked alkalinometrically.

**MEASUREMENTS AND RESULTS**

*Phase transformation in perchloric acid.* In order to determine the time necessary to establish the various metastable and stable equilibria existing in perchloric acid solutions, \(\text{Sb}_2\text{O}_5\text{(or)}\) was shaken at \(C_H = 3.00 \text{ M}\) and 5.00 M, and \(\text{Sb}_2\text{O}_5\text{(c)}\) at \(C_H = 5.00 \text{ M}\) for a length of time varying from 5 min to more than 200 days (cf. Fig. 1). In 5.00 M acid, \(\text{Sb}_2\text{O}_5\text{(or)}\) never reached equilibrium before a transformation set in. For several hours the solid phase is a mixture of...
of Sb₂O₄(or) and Sbop(55), as evidenced both by determination of the antimony content and by Guinier-Hägg powder photographs. The phase Sbop(55) is then in metastable equilibrium for about 2 days. Transformation to the stable phase Sbop(70) then begins, being complete after a week or more. Transformation of Sb₂O₄(c) to Sbop(55) takes place long before the equilibrium with Sb₂O₄(c) has been attained. In this case, the metastable equilibrium involving Sbop(55) is therefore attained from below saturation (cf. Fig. 1). After another few days, the final transformation into the stable phase Sbop(70) begins. Some fifteen days later the transformation is complete and the solution has attained equilibrium. In 3.00 M acid, Sb₂O₄(or) remains unchanged for at least thirty hours, which is time enough for a metastable equilibrium to be established. The transformation to Sbop(70) then begins and after fourteen days the equilibrium between the stable phase Sbop(70) and the solution has been attained. There is no evidence for a phase transformation from Sb₂O₄(or) via Sb₂O₄(c) to Sbop(70).

Solubility of Sb₂O₄(or) and Sb₂O₄(c) in perchloric acid. The solubilities of Sb₂O₄(or) and Sb₂O₄(c) in perchloric acid of varying concentration are given in Figs. 2 and 3. Between C₉ = 1.00 and 4.50 M, where both oxides are metastable, the agitation time was 24–30 h. Between C₉ = 0.250 and 1.00 M the time could be extended up to eighty days without any transformation. Below C₉ = 0.68 and 0.26 M, respectively, Sb₂O₄(c) and Sb₂O₄(or) are stable relative to Sbop(70). For C₉ > 4.00 M the solubility of Sb₂O₄(or) cannot be determined, because the transformation to Sbop(70), mostly via Sbop(55), is too rapid. The same is true for Sb₂O₄(c) when C₉ > 4.50 M.

From eqn. (14), values of ε₁ = 1.0 and ε₂ = 3.9 were computed for Sb₂O₄(c), and 1.0 and 4.1 for Sb₂O₄(or), by means of the CURVEXFIT program. The least-squares treatment was repeated using the nearest integers ε₁ = 1 and ε₂ = 4. The calculated constants Kᵢ and integer exponents εᵢ are given in Table 1. For both oxides the graphical treatment gives ε₁ = 1.0 as the slope of the function f(ln C₉) = ln (S - K₁) for C₉ < 3.0 M (cf. Fig. 4). In Fig. 5, the function f(ln C₉) = ln (S - K₁ - K₂C₉⁴⁺) is plotted for 1.5 < C₉ < 5.00 M and the slopes of the curves give ε₂ = 4.0 for both oxides. The relative differences between calculated and experimental data are given in Table 2.

As j = 0 for Sb₂O₄(e), eqns. (3) and (10) give εᵢ = m/n = 3l - p, i.e. in this case the values of εᵢ yield directly the charges of the complexes formed, viz. +1 and +4. Explicitly

\[ 1 = 3l - p \]  
\[ 4 = 3l - p \]  

The only mononuclear complex with charge 1+ is Sb(OH)₃⁺, but all polynuclear complexes Sb(OH)₄(Sb(OH)₃)ₙ⁻ also fulfill the condition. No mononuclear complex with the charge 4+ is feasible, but all polynuclear species of the composition Sb₄(OH)₉(Sb(OH)₄)ₙ⁻ do fit. In the simplest case the equilibrium would involve the dinuclear complex Sb₄(OH)₈⁴⁺:

\[ \text{Sb}_2\text{O}_4(\text{or or c}) + 8\text{H}^+ \rightleftharpoons 2\text{Sb}_2\text{O}_4(\text{OH})_4^{4+} + 2\text{H}_2\text{O} \]
Table 1. The factors $K_i$ and exponents $\epsilon_i$ in the polynomial $S_{\text{calc}}$, calculated by a least squares computer program. The standard deviation in $S$ was found to be approximately $S/100$. The numbers in parentheses are the standard deviations calculated by the least-squares program and refer to the last significant digit in each value. The polynomial is: $S_{\text{calc}} = K_1 + K_2 C_H^{\epsilon_2} + K_3 C_H^{\epsilon_3}$.

<table>
<thead>
<tr>
<th>Solid phase factors and exponents</th>
<th>Sb$_2$O$_3$(or)</th>
<th>Sb$_2$O$_3$(c)</th>
<th>Sb$_4$O$_6$(OH)ClO$_4$·$\frac{1}{2}$H$_2$O</th>
<th>Sb$_4$O$_6$(OH)$_3$(NO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>0.705(3) × 10$^{-4}$</td>
<td>0.621(2) × 10$^{-4}$</td>
<td>0.1105(5) × 10$^{-2}$</td>
<td>0.747(8) × 10$^{-4}$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.880(3) × 10$^{-3}$</td>
<td>0.660(2) × 10$^{-3}$</td>
<td>0.541(1) × 10$^{-3}$</td>
<td>0.432(3) × 10$^{-3}$</td>
</tr>
<tr>
<td>$\epsilon_2$</td>
<td>1</td>
<td>1</td>
<td>3/4</td>
<td>1/2</td>
</tr>
<tr>
<td>$K_3$</td>
<td>0.742(8) × 10$^{-5}$</td>
<td>0.278(4) × 10$^{-5}$</td>
<td>–</td>
<td>0.601(9) × 10$^{-4}$</td>
</tr>
<tr>
<td>$\epsilon_3$</td>
<td>4</td>
<td>4</td>
<td>–</td>
<td>3/2</td>
</tr>
</tbody>
</table>

In Table 4, a survey of the complexes compatible with the values of $m/n$ is given.

The solubility of Sb$_4$O$_6$(OH)ClO$_4$·$\frac{1}{2}$H$_2$O [Sbop (70)] in perchloric acid. In Fig. 2 and 3 the solubility of Sbop(70) as a function of $C_H$ is plotted. A complete transformation of Sb$_2$O$_3$(or) into Sbop(70) can be achieved in the range $1.00 < C_H < 5.00$ M, though for the lowest value of $C_H$ a very long agitation time is needed, at least 200 days. The transformation was checked by Guinier-Hägg powder photographs and titrimetric analysis of the solid phase. For $C_H = 0.75$ M, transformation was not complete in all samples even after 290 days, which is understandable as the existence of stability between the two phases is quite small at this value of $C_H$ (cf. Fig. 3). All samples starting with Sb$_2$O$_3$(or) as solid phase reach equilibrium from supersaturation (cf. Fig. 1). In order that the equilibrium should be reached also from below saturation, samples of Sbop(70) were shaken with acid of $C_H$ between 0.250 and 5.00 M for 82 days. Within experimental error, the same values of $S$ were found by both methods. For $C_H < 0.68$ M, Sbop(70) is metastable relative to Sb$_2$O$_3$(c) and for $C_H < 0.26$ M also relative to Sb$_2$O$_3$(or), but no transformation to anhydrous oxides was ever found in these $C_H$ regions. At values of $C_H < 0.250$ M the samples were agitated for 22 and 46 h with results that agreed well. When all data up to $C_H = 5$ M were inserted in eqn. (14), the best fit was obtained for $\epsilon_2 = \epsilon_3 = 0.71$. If only the values for $C_H \leq 3.50$ M

Fig. 4. In $(S - K_1) = f(\ln C_H)$ for $C_H \leq 3.00$ M. The slope of the plot is the $\epsilon_2$-value. The symbols refer to the solid phases: ○ Sb$_2$O$_3$(or), □ Sb$_2$O$_3$(c), ◇ Sbop(70) and ■ Sb$_2$O$_3$(or).

Fig. 5. In $(S - K_1 - K_2 C_H^{\epsilon_2}) = f(\ln C_H)$ for $C_H \geq 2.00$ M. The slope of the lines give the $\epsilon_3$-values. The symbols refer to the solid phases: ○ Sb$_2$O$_3$(or), □ Sb$_2$O$_3$(c) and ■ Sb$_2$O$_3$(or).

Table 2. The relative difference between experimental and calculated solubilities, S is the mean of several experimental values. $S_{\text{calc}}$ is calculated with the polynomial $S_{\text{calc}} = K_1 + K_3 C_H^2 + K_4 C_H^4$.

<table>
<thead>
<tr>
<th>$C_H$</th>
<th>$100(S_{\text{calc}} - S)/S_{\text{calc}}$</th>
<th>$\text{Sb}_2\text{O}_4(\text{OH})\text{ClO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$</th>
<th>$\text{Sb}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>0.12</td>
<td>10.77</td>
<td>3.82</td>
</tr>
<tr>
<td>4.50</td>
<td>0.32</td>
<td>9.22</td>
<td>-0.64</td>
</tr>
<tr>
<td>4.00</td>
<td>-0.12</td>
<td>7.70</td>
<td>-1.81</td>
</tr>
<tr>
<td>3.50</td>
<td>-1.05</td>
<td>5.39</td>
<td>-3.31</td>
</tr>
<tr>
<td>3.00</td>
<td>-1.84</td>
<td>3.62</td>
<td>-3.04</td>
</tr>
<tr>
<td>2.50</td>
<td>0.50</td>
<td>0.77</td>
<td>-1.13</td>
</tr>
<tr>
<td>2.00</td>
<td>1.29</td>
<td>0.07</td>
<td>1.88</td>
</tr>
<tr>
<td>1.50</td>
<td>1.14</td>
<td>-1.68</td>
<td>0.05</td>
</tr>
<tr>
<td>1.00</td>
<td>-1.49</td>
<td>-0.71</td>
<td>3.03</td>
</tr>
<tr>
<td>0.750</td>
<td>-0.13</td>
<td>-0.18</td>
<td>2.10</td>
</tr>
<tr>
<td>0.500</td>
<td>0.03</td>
<td>1.14</td>
<td>0.69</td>
</tr>
<tr>
<td>0.250</td>
<td>0.32</td>
<td>1.92</td>
<td>1.85</td>
</tr>
<tr>
<td>0.1032</td>
<td>-0.95</td>
<td>0.10</td>
<td>-1.53</td>
</tr>
<tr>
<td>0.0516</td>
<td>0.35</td>
<td>-0.83</td>
<td>-3.00</td>
</tr>
<tr>
<td>0.0258</td>
<td>-1.62</td>
<td>-0.58</td>
<td>-1.20</td>
</tr>
<tr>
<td>0.0103</td>
<td>-0.51</td>
<td>-0.14</td>
<td>2.55</td>
</tr>
<tr>
<td>0.0052</td>
<td>-1.28</td>
<td>-0.11</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The solid phase $S_{\text{op}}(70)$ has $j = 1$. Hence, from eqns. (3) and (10), for $e_2 = 3/4$:

$$3/4 = 3l - p - l/4$$  \hspace{1cm} (3\text{IV})

The complex $\text{Sb}_2(\text{OH})_3\text{ClO}_4$ satisfying this condition are listed in Table 4. Only one combination of $l$ and $p$, viz. $l = 1$ and $p = 2$, satisfies the equation system (3\text{I}), (3\text{IV}). This means that of the complexes $\text{Sb}_2(\text{OH})_3(\text{Sb}(\text{OH})_3)_2$ only $\text{Sb}_4(\text{OH})_4$ fits the solubility curves of both the oxides and the oxide perchlorate. The equilibria established are therefore:

$$\text{Sb}_2\text{O}_4(\text{or c}) + 4\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Sb}(\text{OH})_4^+$$

and

$$\text{Sb}_2\text{O}_4(\text{OH})\text{ClO}_4\cdot\frac{1}{2}\text{H}_2\text{O}(s) + 3\text{H}^+ + \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons 4\text{Sb}(\text{OH})_4^+ + \text{ClO}_4^-$$

with the equilibrium constants given in Table 6. The equation system (3\text{IV}), (3\text{III}) is satisfied by $l = 13$ and $p = 35$, i.e. in the series of complexes $\text{Sb}_4(\text{OH})_4(\text{Sb}(\text{OH})_3)_2$ only $\text{Sb}_4(\text{OH})_4^+$ fits the solubility curves of both the oxides and the oxide perchlorate. It is most unlikely, however,
Table 4. Complexes compatible with the ratios $m/n$ determined experimentally for the various solid phases.

<table>
<thead>
<tr>
<th>$\text{Sb}_2\text{O}_4(\text{or, c})$</th>
<th>$\text{Sb}_2\text{O}_4(\text{OH})\text{ClO}_4_4\text{H}_2\text{O}$</th>
<th>$\text{Sb}_2\text{O}_4(\text{OH})_6(\text{NO}_3)_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m/n = 1$</td>
<td></td>
<td>$m/n = 1/2$</td>
</tr>
<tr>
<td>$\text{Sb(OH)}_5^+$</td>
<td>$\text{Sb(OH)}_6^+$</td>
<td>$\text{Sb(OH)}_3^+$</td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_5^+$</td>
<td>$\text{Sb}_2(\text{OH})_6^{2+}$</td>
<td>$\text{Sb}_2(\text{OH})_3^{2+}$</td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_6^{2+}$</td>
<td>$\text{Sb}_2(\text{OH})_7^{3+}$</td>
<td>$\text{Sb}_2(\text{OH})_4^{3+}$</td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_7^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Sb}<em>2(\text{OH})</em>{8-9}^{3+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m/n = 4$</td>
<td>$\text{Sb}_2(\text{OH})_4^{4+}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_5^{4+}$</td>
<td>$\text{Sb}_2(\text{OH})_6^{5+}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_6^{5+}$</td>
<td>$\text{Sb}_2(\text{OH})_7^{6+}$</td>
<td></td>
</tr>
<tr>
<td>$\text{Sb}_2(\text{OH})_7^{6+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Sb}<em>2(\text{OH})</em>{8-9}^{6+}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

that a complex of such high nuclearity would be in equilibrium with Snbop(70) since the concentration of the central ion is very low. On the other hand, the complex $\text{Sb}_2(\text{OH})_4^{4+}$, which is the simplest one compatible with the solubility curves of $\text{Sb}_2\text{O}_4(\text{or})$ and $\text{Sb}_2\text{O}_4(\text{c})$, does not satisfy (3III). As the antimony(III) concentration in equilibrium with the oxides is much higher, it is nevertheless quite possible that the dinuclear complex exists in those solutions in spite of the fact that it is not present in perceptible amount in equilibrium with Snbop(70).

The solubility of $\text{Sb(III)}$ in perchloric acid with $C_H > 5.00$ M. The surveying investigation performed at varying ionic strength for $C_H > 5.00$ M is illustrated in Fig. 6. The solid phase Snbop(70) is stable up to $C_H \approx 6.7$ M. At $C_H = 7.00$ M a phase transformation takes place after three days. The new phase contains 44.6 % Sb. Its composition is very probably $\text{Sb(OH)}_3\text{ClO}_4\cdot \text{H}_2\text{O}$ (calc. 44.3 % Sb). It is most probably identical with the compound earlier formulated as $\text{SbOCl}_4\cdot 2\text{H}_2\text{O}$ by Fichter and Jenny.14 This solid phase is stable up to $C_H \approx 11.75$ M. In concentrated perchloric acid, however, still another phase is formed. As already mentioned, this compound is extremely sensitive to moisture. Thus, if the solution is allowed to take up moisture from the air for a few days, a complete transformation to Snbop(44) takes place. At $C_H = 4.50$ and 5.00 M, Snbop(55) exists as a metastable phase. This compound contains 54.4 % Sb which corresponds very closely to the composition 3$\text{Sb}_2\text{O}_4\cdot 2\text{Cl}_4\text{O}_4\cdot 6\text{H}_2\text{O}$ (calc. 54.2 %). At $C_H = 6.00$ M, however, the solid phase in metastable equilibrium with the solution has neither the Guinier-Hög powder pattern of Snbop(55) nor that of Snbop(44). This new phase has not yet been identified. Like Snbop(55), it evidently does not exist in stable equilibrium with any solution studied here.

Calculation of $\Delta G^\circ$ for $\text{Sb}_2\text{O}_4(\text{or}) \rightarrow \text{Sb}_2\text{O}_4(\text{c})$. The free energy change $\Delta G^\circ$ for the transformation $\text{Sb}_2\text{O}_4(\text{or}) \rightarrow \text{Sb}_2\text{O}_4(\text{c})$ at 25.0 °C can be computed from the present measurements as follows. In perchloric acid solutions of $C_H < 1.00$ M the complex $\text{Sb(OH)}_4^{3+}$ is predominant (cf. Fig. 6).

Fig. 6. The solubility of antimony(III) in perchloric acid solutions up to concentrated acid. For $C_H \leq 5.00$ M the ionic strength is constant at $I = 5.00$ M and for $C_H > 5.00$ M it varies. The different solid phases in equilibria with the solutions are indicated by the symbols: $\bigodot$ Snbop(32), $\square$ Snbop(c), $\bigtriangleup$ Snbop(70) and $\bigtriangledown$ other antimony(III)-oxide-perchlorates.

Table 5. Calculated value of $\Delta G^\circ$ for the phase transformation $\text{Sb}_2\text{O}_3$ (orthorhombic)→$\text{Sb}_2\text{O}_3$ (cubic) at 25°C, (cf. eqn. (20)).

<table>
<thead>
<tr>
<th>$C_H$ (M)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0258</td>
<td>1.2</td>
</tr>
<tr>
<td>0.0516</td>
<td>1.5</td>
</tr>
<tr>
<td>0.1032</td>
<td>1.3</td>
</tr>
<tr>
<td>0.250</td>
<td>1.5</td>
</tr>
<tr>
<td>0.500</td>
<td>1.5</td>
</tr>
<tr>
<td>0.750</td>
<td>1.4</td>
</tr>
<tr>
<td>1.00</td>
<td>1.6</td>
</tr>
</tbody>
</table>

(20)

Fig. 3. The free energy changes on dissolution are therefore:

$$\Delta G_{\text{ar}} = \mu_{\text{ar}}(\text{H}_2\text{O}) + 2\mu_{\text{ar}}(\text{Sb(OH)}_2^{+}) - 2\mu_{\text{ar}}(\text{H}^+) - \mu_{\text{ar}}(\text{Sb}_2\text{O}_3)$$

$$\Delta G_{\text{c}} = \mu_{\text{c}}(\text{H}_2\text{O}) + 2\mu_{\text{c}}(\text{Sb(OH)}_2^{+}) - 2\mu_{\text{c}}(\text{H}^+) - \mu_{\text{c}}(\text{Sb}_2\text{O}_3)$$

where for each species B:

$$\mu(B) = \mu^{\circ}(B) + RT \ln a(B)$$

At equilibrium, i.e. for saturated solutions,

$$\Delta G_{\text{ar}} = \Delta G_{\text{c}} = 0$$

and hence the free energy change of transition

$$\Delta G^\circ = \mu_{\text{c}}(\text{Sb}_2\text{O}_3) - \mu_{\text{ar}}(\text{Sb}_2\text{O}_3)$$

is given by

$$\Delta G^\circ = -2RT \ln \frac{a_{\text{ar}}(\text{Sb(OH)}_2^{+})}{a_{\text{c}}(\text{Sb(OH)}_2^{+})}$$

$$+ 2RT \ln \frac{a_{\text{c}}(\text{H}^+)}{a_{\text{c}}(\text{H}^+)}$$

If it assumed that the activity coefficients for $\text{Sb(OH)}_2^{+}$ and $\text{H}^+$ are constants in the solutions considered, concentrations may be substituted for the activities $a$. Further, if the solubilities of the two phases at the same value of $[\text{H}^+]$≈$C_H$ are considered

$$\Delta G^\circ = -2RT \ln \frac{(S_{\text{ar}} - K_{1,\text{ar}})}{(S_{\text{c}} - K_{1,c})}.$$

Values of $\Delta G^\circ$ calculated for different values of $C_H$ are presented in Table 5. No systematic variation with the acidity can be discerned which shows that the assumptions made are permissible. The mean value is $\Delta G^\circ = -1.4 \pm 0.2$ kJ mol$^{-1}$ at 25°C. Pitman et al.$^{16}$ have earlier reported the value $-7.5$ kJ.

The nitric acid system. It is impossible to measure the solubility of $\text{Sb}_2\text{O}_3$(or) or $\text{Sb}_2\text{O}_3$(c) in nitric acid, as the transformation to the stable oxide nitrate phase $\text{Sb}_2\text{O}_5(\text{OH})_2(\text{NO}_3)_3$ takes place in a few hours, i.e. before the metastable oxide equilibria are established.

The solubility of $\text{Sb}_2\text{O}_5(\text{OH})_2(\text{NO}_3)_3$ in nitric acid is plotted as a function of $C_H$ in Figs. 7 and 8. To make certain that $\text{Sb}_2\text{O}_3$(or) was fully transformed even at the lowest values of $C_H$ used, the samples were agitated for 57 days. In these experiments, the equilibrium was approached from the side of supersaturated solution. To check that the equilibrium had really been established, some experiments were also performed with $\text{SnO}$ as the initial solid phase. No significant difference was found between the final values of $S$ in the two cases. For 0.0031 < $C_H$ < 0.1020 M the experiments were always conducted with $\text{SnO}$ as solid phase.

The best fit to polynomial (14) was achieved with the values $\epsilon_3 = 0.49$ and $\epsilon_3 = 1.49$. The least-squares treatment was repeated with $\epsilon_3 = 1/2$ and $\epsilon_3 = 3/2$ as constants. The resulting constants $K_i$ and the exponents $\epsilon_i$ are given in Table 1. The exponents $\epsilon_3$ and $\epsilon_3$ were also determined graphically by plotting $f(\ln C_H) = \ln (S - K_i)$ for $C_H < 3.0$ M and $f(\ln C_H) = \ln (S - K_i - K_i C_H)$ for 1.5 < $C_H$ < 5.00 M (cf. Figs. 4 and 5). The slopes of the functions give $\epsilon_3 = 0.5$ and $\epsilon_3 = 1.5$. The relative differences between calculated and experimental data are given in Table 2.

The solid phase $\text{SnO}$ has $j = 2$, hence, from eqns. (3) and (10),

$$\frac{1}{2} = 2l - p - 2l/4$$

$$\frac{3}{2} = 2l - p - 2l/4$$

Fig. 7. The solubility of antimony(III) in nitric acid solutions at $I = 0.00$ M. The solid phase in equilibrium with the solutions is $\text{SnO}$. Acta Chem. Scand. A 28 (1974) No. 10
The complexes Sb\(_2\)(OH)\(_p\)\(_{3−p}\) compatible with these conditions are listed in Table 4. The only possible complex of charge +1 is Sb(OH)\(_4\)\(^{2+}\), which thus is the only one of the series Sb(OH)\(_4\)\(^{1−}\) (Sb(OH)\(_3\))\(_{1−}\), indicated by the oxide measurements, which is also compatible with the solubility curve of the oxide nitrate. The following equilibrium is thus established between Sbon and the solution:

\[
\text{Sb}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_4(s) + 2\text{H}^+ + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Sb(OH)}_4^{2+} + 2\text{NO}_3^-
\]

with the equilibrium constant given in Table 6. Among the complexes of charge +4 which may, according to the oxide measurements possibly be present only Sb\(_2\)(OH)\(_{11}\)\(^{4+}\) (with \(m/n = 3/2\)) and Sb\(_2\)(OH)\(_{12}\)\(^{4+}\) (with \(m/n = 1/2\)) are compatible with the oxide nitrate curve (\textit{cf. Table 4}). As the concentrations of antimony(III) in equilibrium with Sbon is very low, complexes of such high nuclearity are not likely to exist. This inference is further strengthened by the fact that none of the complexes mentioned are compatible with the oxide perchlorate curve. A much more plausible species which also satisfies eqn. (3') is Sb(OH)\(_2\)\(^{2+}\). This monomer admitted does not exist in perceptible amounts in any of the perchlorate solutions investigated but it is known from other systems \(^7\) that the formation of mononuclear complexes is favoured in nitrate solutions, evidently due to the stronger tendency of nitrate to enter the coordination sphere of the acceptor, thereby making the formation of hydroxo or oxo bridges more difficult. The complex \(^4\text{Sb(OH)}\text{Cl}_4\)\(^−\) provides another example of the same tendency which should be even more marked in chloride systems on account of the much stronger affinity of this ligand to antimony(III). The existence of the monomer Sb(OH)\(_2\)\(^{2+}\) in nitric acid is therefore compatible throughout with the existence of the dimer Sb\(_2\)(OH)\(_2\)\(^{4+}\) in perchloric acid. The equilibrium most likely to account for \(m/n = 3/2\) would thus be

\[
\text{Sb}_2\text{O}_4(\text{OH})_4(\text{NO}_3)_4(s) + 6\text{H}^+ \rightleftharpoons 4\text{Sb(OH)}_4^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O}
\]

with the equilibrium constant given in Table 6.

**DISCUSSION**

This investigation has shown that in aqueous perchloric and nitric acid solutions of \(C_\text{H} \leq 2.00\) M the predominating complex is Sb(OH)\(_2\)\(^{2+}\). This complex exists in equilibrium with all the solid phases employed. It has also been postulated by several previous investigators.\(^1\)\(^+\)\(^2\) As

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**Table 6.** Equilibrium constants \(K'\) (\textit{cf. eqn. (4)}) for the reactions Sb\(_2\)O\(_{4−j}\)(OH)\(_j\)(Z\(_j\))(s) + \(m\)H\(^+\)⇌\(n\)Sb\(_2\)(OH)\(_p\)\(_{3−p}\) + \(q\)H\(_2\)O + \(k\)Z\(^−\) at \(I = 5\) M and 25.0 °C. The errors stated correspond to 3σ.

<table>
<thead>
<tr>
<th>Solid phase</th>
<th>Complex formed; constant (K')</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Sb(OH)}_4^{2+})</td>
</tr>
<tr>
<td>(m) (n) (K' \times 10^{14})</td>
<td>(m) (n) (K' \times 10^{17})</td>
</tr>
<tr>
<td>Sb(_2)O(_4)(or)</td>
<td>4 4 60 ± 2</td>
</tr>
<tr>
<td>Sb(_2)O(_4)(s)</td>
<td>4 4 19.0 ± 0.6</td>
</tr>
<tr>
<td>Sb(_2)O(_4)(OH)Cl(_2)+4H(_2)O</td>
<td>3 4 8.6 ± 0.2 (M)</td>
</tr>
<tr>
<td>Sb(_2)O(_4)(OH)(_2)(NO(_3))(_2)</td>
<td>2 4 3.5 ± 0.3 (M(^2))</td>
</tr>
</tbody>
</table>
Table 7. Determinations of the equilibrium constant of the reaction
\[ \text{Sb}_2\text{O}_4^{(c)} + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Sb(OH)}_2^{(c)} + \frac{1}{2}\text{H}_2\text{O}. \]
All determinations have been performed by solubility measurements.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Solid phase</th>
<th>Medium</th>
<th>Equilibrium constant ( \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sb\textsubscript{2}O\textsubscript{4}(or)</td>
<td>HClO\textsubscript{4}</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Sb\textsubscript{2}O\textsubscript{4}(or)</td>
<td>HCl</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Sb\textsubscript{2}O\textsubscript{4}(or)</td>
<td>HClO\textsubscript{4}</td>
<td>8.5</td>
</tr>
<tr>
<td>This work</td>
<td>Sb\textsubscript{2}O\textsubscript{4}(or)</td>
<td>HClO\textsubscript{4}</td>
<td>8.8 ± 0.1</td>
</tr>
<tr>
<td>This work</td>
<td>Sb\textsubscript{2}O\textsubscript{4}(c)</td>
<td>HClO\textsubscript{4}</td>
<td>6.6 ± 0.1</td>
</tr>
</tbody>
</table>

already mentioned, some of these have also calculated the equilibrium constants for its formation from Sb\textsubscript{2}O\textsubscript{4}(or), the reaction generally being written in the form \( 1/2 \text{Sb}_2\text{O}_4^{(or)} + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Sb(OH)}_2^{(c)} + 1/2 \text{H}_2\text{O} \). Our value is in very good accord with these previous measurements, especially if the fairly large differences in medium are taken into account (cf. Table 7).

Generally, the complex has been written in the form SbO\textsuperscript{2+}. From measurements of the present type it is of course impossible to differentiate between the two formulæ. It seems nevertheless extremely improbable that both protons dissociate from one molecule of water and we therefore prefer the formulation Sb(OH)\textsuperscript{2+}.

Besides the well-established Sb(OH)\textsubscript{2}\textsuperscript{4+}, at least two further complexes have been found in this investigation. Thus in perchloric acid solutions in equilibrium with Sb\textsubscript{2}O\textsubscript{4} (orthorhombic or cubic) a complex of charge \( \text{4+} \) exists. Its concentration becomes perceptible \((\approx 10 \% \text{ of the total solubility } S)\) at a value of \( C_H = 2.4 \text{ M} \) (corresponding to \( S = 2.5 \text{ mM} \)) for Sb\textsubscript{2}O\textsubscript{4}(or) and at a value of \( C_H = 3.0 \text{ M} \) (corresponding to \( S = 2.3 \text{ mM} \)) for Sb\textsubscript{2}O\textsubscript{4}(c). At the highest values of \( S \) reached, \( \text{viz.} \ 5.59 \text{ mM} \) for Sb\textsubscript{2}O\textsubscript{4}(or) at \( C_H = 4.0 \text{ M} \), and \( 4.14 \text{ mM} \) for Sb\textsubscript{2}O\textsubscript{4}(c) at \( C_H = 4.5 \text{ M} \), considerable amount of the antimony is present as the dimer, to the extent of \( 34 \% \) and \( 27 \% \), respectively. The equilibrium constant \( K_d' = (K_d'/K_d')^1 \) for the reaction

\[ 2\text{Sb(OH)}_2^{(c)} + 2\text{H}^+ \rightleftharpoons 2\text{Sb}_2\text{O}_4^{(c)} + 2\text{H}_2\text{O} \]
is found to be \( 4.8 \pm 0.3 \text{ M}^{-3} \) if the values of \( K_d' \) and \( K_d' \) found from the Sb\textsubscript{2}O\textsubscript{4}(or) curve are used, and \( 3.2 \pm 0.1 \text{ M}^{-2} \) if the values from the Sb\textsubscript{2}O\textsubscript{4}(c) curve are used. Presumably, this difference is mainly due to the fairly rapid change of the activity conditions which has been postulated as the most likely cause of the slightly low values of \( S \) found when SbOp(70) in the solid phase and \( C_H \geq 3 \). It is quite probable that a corresponding deviation takes place also for the oxide curves. If so, it should be relatively more marked for Sb\textsubscript{2}O\textsubscript{4}(c) than for Sb\textsubscript{2}O\textsubscript{4}(or), especially as the solutions where the dimer is the predominant species are more acid in the former case. Such a deviation should result in values of \( K_d' \) for both oxides which are rather too low, especially in the case of Sb\textsubscript{2}O\textsubscript{4}(c).

Though great caution must always be taken when deducing the structures of hydrolytic complexes in solution from those found for solid oxide salts, valuable information may nevertheless be obtained in this way, as has been shown in several instances. Thus, the entities Th(OH)\textsubscript{4}Th\textsuperscript{4+} and UO\textsubscript{4}(OH)\textsubscript{2}UO\textsuperscript{4+} which have been established in solution both by emf and X-ray investigations \textsuperscript{15-20} are also found in solids.\textsuperscript{31,32} Also, the complexes Pb\textsubscript{4}(OH)\textsubscript{4}\textsuperscript{4+} and Pb\textsubscript{4}(OH)\textsubscript{6}\textsuperscript{4+} indicated in solution by emf measurements \textsuperscript{33} have later been found as discrete entities in crystalline oxide salts.\textsuperscript{34-36}

The dimer Sb\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{4+}, compatible with the present measurements, could have at least three different structures. The antimony atoms may be joined by a double hydroxo bridge: Sb\textsubscript{2}(OH)\textsubscript{4}Sb\textsuperscript{4+}, which would be similar to the arrangement in the thorium(IV) and uranyl(VI) complexes mentioned above, or the complex may contain a single hydroxo bridge: Sb(OH)Sb(OH)\textsuperscript{4+}. The final possibility would involve a single oxo bridge: SbO\textsuperscript{2+}.

In oxide salts, antimony(III) is three or four coordinated. The most common polyhedron is the trigonal bipyramid, where one of the equatorial corners is occupied by the lone pair of electrons. The other common coordination geometry is that of the tetrahedron, with the lone pair of electrons at one corner. If the complex with the double hydroxo bridge is a fragment of the solid oxide salt, then polyhedra with shared edges must be a feature of their structure. It also seems reasonable that the distance between the antimony atoms within the units is significantly shorter than any other Sb — Sb-distances in the oxide salt. The complexes with single hydroxo or oxo bridges are consistent with crystal structures containing
polyhedra with shared equatorial corners. In such cases the antimony atoms should be joined only by single oxygen bridges in the solid state.

In this series of investigations, the structures \( \text{Sb}_2\text{O}_4(\text{OH})_2\text{ClO}_4 \cdot \text{H}_2\text{O} \) \( (= \text{Sbop}(70)) \) and \( \text{Sb}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_2 \) \( (= \text{Sbom}) \) have been determined. In both compounds coordination polyhedra share edges, the shortest antimony-to-antimony distance being that between antimony atoms joined via two oxygens. This is also the case in the structure of \( \text{Sb}_2\text{O}_4\text{Cl}_2 \). The only known structure which contains polyhedra sharing equatorial corners is \( \text{SbF}_6 \). The model for \( \text{Sb}_2(\text{OH})_4^{2+} \) most consistent with the crystal structures seems to be a complex in which two antimony atoms are joined by a double hydroxo bridge. A complex of similar structure, \( \text{Bi}(\text{OH})_4\text{Bi}^{3+} \), has also been found by Aurivillius' in the crystal structures of \( \text{Bi(OH)}_2\text{CrO}_4 \) and \( \text{Bi(OH)}_3\text{SeO}_4\cdot\text{H}_2\text{O} \).

The monomer \( \text{Sb}(\text{OH})^{2+} \), which has been postulated to exist in the nitrate medium, has a counterpart in the complex \( \text{Bi(OH)}^{2+} \). The latter is present in hydrolysed perchloric acid solutions of bismuth(III), although admittedly not as a predominating species. The concentration of \( \text{SbOH}^{2+} \) becomes perceptible \( (\approx 10 \%) \) at \( C_\text{Sb} \approx 1 \text{ M} \). At the highest concentration of nitric acid used \( (5 \text{ M}) \) it reaches \( \approx 40 \% \). The equilibrium constant \( K = (K_\text{s}/K_\text{c})^4 \) for the reaction

\[
\text{Sb(OH)}_3^{2+} + \text{H}^+ \rightleftharpoons \text{SbOH}^{3+} + \text{H}_2\text{O}
\]

is found to be \( 0.139 \pm 0.008 \text{ M}^{-1} \), corresponding to an acid dissociation constant \( K_\text{s} = 1/K = 7.2 \pm 0.4 \text{ M} \) for \( \text{SbOH}^{2+} \). This very high value of \( K_\text{s} \) found for a partly hydrolysed species illustrates the strongly acidic properties of antimony(III).

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