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Synthetic Inorganic Ion-exchange Materials. X. Preparation and Properties of So-called Antimonic(V) Acid

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The preparation of so-called antimonic acid under various experimental conditions has been investigated in order to establish its usefulness as a chemically-stable cation-exchange material. In this experiment, the antimonic acid was mainly obtained by the hydrolysis of antimony pentachloride, and was rarely obtained from metallic antimony or potassium pyroantimonate. The hydrolyzed precipitate was amorphous at first, but it was gradually transformed into crystalline powder by keeping it in the mother liquor for a long time. The crystallization of the amorphous precipitate was facilitated by raising the temperature within a range of 0—80°C, and by increasing the concentration of strong mineral acid on aging, regardless of the kinds of starting antimony substances. The water-content of the air-dried samples is decreased by increasing the period of aging; the composition of the sample approximates $Sb_2O_5 \cdot 4H_2O$. The crystal of the antimonic acid is cubic and belong to the space group $O_h^7(Fd3m)$, with a lattice constant of 10.38_2 Å. The measurement of solubilities for the air-dried antimonic acid showed that both the amorphous and the glassy acids are soluble forms and that the crystalline is an insoluble form. The uptakes of potassium ions on these antimonic acids were little changed on the kinds of form; the uptake of lithium ions on the crystalline acid was very small as compared those on the amorphous and the glassy acids. This behavior may be attributed to the existence of different types of so-called antimonic acid, with different selectivities of their lithium ion adsorption, rather than to any difference in the size of the particle.

As was first shown in a previous paper,[1] the hydrous oxides of pentavalent metals, such as niobium, tantalum and antiomony, have useful cation adsorptive properties, including a high uptake of potassium ions. The so-called antimonic(V) acid has an especially large adsorption capacity, larger than that of any other metal hydrous oxides, which show a reasonable rate for adsorption and desorption when used in column operations. The adsorption and desorption of potassium ions on the antimonic acid have been found to be attributable to the exchange between the hydrogen ions in the acid and the potassium

1) M. Abe and T. Ito, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1259 (1965).

ions in the external solution in contact with the acid.[2] Furthermore, the mutual separation of alkali metal ions has been completely achieved with a relatively small antimonic acid column ($0.8\phi \times 6.0$ cm).[3]

However, the antimonic acid obtained by the hydrolysis of antimony pentachloride is gradually peptized or dissolved by contact with pure water or with an alkaline solution for a long time.

In this experiment, the preparation of antimonic acid under various conditions is studied in order to obtain a chemically-stable material.

Much pertinent information regarding the antimonic acid or hydrous antimony pentoxide is to be found in the literature pertaining to inorganic chemistry. This information is well summarized in the standard works of Mellor[4] (1929) and Gmelin[5] (1949). Even here, however, some confusion is apparent, and contradictory statements are not hard to find. No comprehensive investigations of the so-called antimonic acid have yet been made. Fremy[6] and Senderens[7] showed that the water-content in the antimonic acid varies according to the kind of starting antimony salt. However, Conrad,[8] Daubrawa[9] and others showed opposite results, according to which a definite hydrate is obtained under the same drying conditions in spite of the different kinds of starting salt. In previous works, much attention had been devoted to determining whether or not several hydrates, such as ortho-($Sb_2O_3 \cdot 3H_2O$), pyro-($Sb_2O_5 \cdot 2H_2O$) and meta-($Sb_2O_5 \cdot H_2O$), well known in the case of hydrated P_2O_5, exist in so-called antimonic acid. Analysis made by Conrad[8], Fremy[6] and others of the air-dried product have given results ranging from 15.77 to 20.02 per cent of water, a figure corresponding with that of the tetrahydrate. The results of the analysis made by Conrad,[8] Daubrawa[9] and Senderens[7] of the product dried over concentrated sulfuric acid show 12.87—14.53 per cent of water, figures in agreement with that of the trihydrate, $Sb_2O_5 \cdot 3\,H_2O$. According to Daubrawa and others, products dried at 100°C and at 175—200°C possess water contents corresponding with dihydrate as pyro-antimonic acid and with monohydrate as meta-antimonic acid. Senderens[7] regarded the trihydrate as ortho-antimonic acid. However, the dehydration curves of the hydrate obtained by the hydrolysis of the pentachloride were found by Simon and Thaler[10] to be of the continuous type, with the characteristics of hydrated metal oxides of the hydrogel type. Therefore, they question the existence of the above-mentioned stoichiometrical composition shown by Daubrawa[9] and others. Fremy[6] found that the tetrahydrate obtained by the hydrolysis of antimony pentachloride, and that obtained by the action of mineral acid on a solution of the alkali antimonate, have different properties. The former was said to be dissolved in a large amount of water, and to be precipitated by acid from an aqueous solution. Its precipitate was dissolved in concentrated ammonia, whereas that obtained from the latter acid was not so dissolved. Conrad, Beilstein, and Bläse showed, however, that there is no real difference between the two products.[4] Senderens and Delacroix agreed that a soluble and an insoluble form of antimonic acid existed, and they called them ortho-antimonic acid and pyro-antimonic acid; however they differed as to which was which.[4] Simon and Thaler proved that hydrated antimony pentoxide crystallized when heated with water under pressure.[10] The product gave a definite indication of the existence of $3Sb_2O_5 \cdot 5H_2O$, which had a point of inflection.

It appears that such confusion as is indicated in the above information regarding the hydrous antimony pentoxides is mainly due to uncertainty concernig the preparation and the resulting properties of the oxides.

In the present experiment, much attention was given to the temperature of the hydrolysis, the effect of aging, and the concentration of acids.

Preparation

Hydrolysis of Antimony Pentachloride. When liquid antimony pentachloride is added to a large amount of water, an irregular precipitate is easily obtainable by means of a violent hydrolysis and a simultaneous exothermic reaction. Hence, a concentrated antimony pentachloride solution was prepared, liquid antimony pentachloride being dropped into the same volume of cold distilled water; the mixture was then hydrolyzed in a large amount of water at the prescribed temperature. The precipitate was aged by being kept in the mother liquor for some time at the said temperature. When 30 m*l* of the concentrated solution was hydrolyzed in 1 *l* of distilled water, the acid concentration of the supernatant liquid became a 0.5 N hydrochloric acid solution as a result of a by-product formed by the hydrolysis. The adjustment of the hydrochloric acid concentration to 0.25 or to 1.0 N was carried out, respectively, by dilution with water or by the addition of concentrated hydrochloric acid to the hydrolyzed solution. The precipitated antimonic acid was filtered under suction. When the hydrochloric acid in the

2) M. Abe and T. Ito, *ibid.*, **87**, 1174 (1966).
3) M. Abe and T. Ito, This Bulletin, **40**, 1013 (1967).
4) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., Ltd., London (1929).
5) L. Gmelin, "Handbuch der anorganischen Chemie," 8th ed. Vol. 18 (1949).
6) E. Fremy, *Ann. chim. phys.*, **23**, 304 (1848).
7) J. B. Senderens, *Bull. Soc. Chim.*, **21**, 48 (1899).
8) C. P. Conrad, *Chem. news*, **40**, 189 (1879).
9) H. Daubrawa, *Ann. Chem. Liebigs*, **186**, 118 (1877).
10) A. Simon and E. Thaler, *Z. anorg. Chem.*, **161**, 116 (1927).

precipitate has almost all been washed away, the antimonic acid passed through fine filter-paper (such as Toyo filter paper 5C) by the peptization. Therefore, it was impossible to wash the antimonic acid until free from chloride ions by the filtration process. Very pure antimonic acid was obtained by washing the precipitate with cold water with the aid of a centrifuger operated at about 10000 rpm; as a result of this treatment, the metamorphosis of the precipitates was avoided. These products were dried at room temperature by the aid of a fan, then they were transformed into granular materials which were suitable for column operation.

Other Preparations. 1) S_{K-1}. A solution of 1.5 *l* of potassium pyroantimonate (32 g/*l*) was vigorously stirred, drop by drop, the same volume of 6 N nitric acid at 25—30°C. The precipitate was then kept in the mother liquor for 3 days at the same temperature. The potassium ions in the liquor were thus tenaciously adsorbed in the precipitate, they could not be removed only by washing with distilled water, though they could be remove by repeated washings with 2 N nitric acid. The precipitate was then washed with distilled water until it was free from nitric acid by means of a centrifuger, and dried in air using a fan.

2) S_{K-2}. A normal nitric acid was vigorously stirred into the above-mentioned potassium pyroantimonate solution at 25—30°C, and then the pH of the mother liquor was adjusted to 1 by dilution. The precipitate was kept in the mother liquor for 4 hr at 25—30°C, and then washed and dried in the same manner as S_{K-1}.

3) Sb-1 and Sb-2. The antimony metal (99.999%) (30 g) was dissolved in 150 m*l* of a mixed solution of $HCl+HNO_3$ (4 : 1). The solution was hydrolyzed and aged in 2 *l* of water at 20°C (Sb-1) or 60°C (Sb-2).

4) S_G. It has been known that freshly-prepared antimonic acid in a wet state can be dissolved in a large amount of water; the solution gradually becomes turbid when kept for a long time. To avoid such turbidity, the following treatment must be completed in a relatively short time; the amorphous precipitate in a wet state is rapidly dissolved in 300 m*l* of hot water. A glassly material was obtained by evaporating the moisture in the solution after cooling.

5) S_{200} *and* S_{300}. The above-mentioned fresh precipitate (10 g) was suspended in 100 m*l* of distilled water and then heated at 200 or 300°C for 4 hr under presure. The S_{200} sample was obtained as a fine crystalline powder, while the S_{300} sample was obtained as a thin hexagonal crystal.

Uptake of Lithium and Potassium Ions. Our previous report showed that when the antimonic acid was added to a neutral solution, hydrogen ions in the material were equivalently liberated as a result of exchange with the cation in the external solution. The measurement of the uptakes of lithium and potassium ions were made by both batch and column techniques, neutral solution of the corresponding salts being used. Each solution containing the liberated hydrogen ions was titrated with a standard 0.1 N sodium hydroxide solution.

Solubilities of Antimonic Acid. The solubilities of the antimonic acids were determined in various reagents. The procedure for determining the solubilities was as follows; the sample (0.4 g) of 100—200 mesh size was put into a 200-m*l* bottle equipped with a glass stopper, and then 100 m*l* of the reagent was added. The bottle was kept in a thermostated bath set at 25±0.05°C for a period of 1 to 10 days and shaken from time to time. The dissolved amount of the antimonic acid was measured by the polarographical method in 3 N hydrochloric acid, after the Sb^{5+} in the suppernatant liquor had been reduced to Sb^{3+} with a sodium sulfite solution.

X-Ray Examinations. The X-ray diffraction patterns of all the sample were measured with a Rigaku Denki Geiger Flex X-ray Diffractometer, filtered Cu$K\alpha$ being used.

Result and Discussion

Composition of So-called Antimonic Acid. The precipitates of the antimonic acid obtained by various preparations were dried in air with the aid of slow-moving electric fan. The time-composition curves of the antimonic acid samples are given in Fig. 1. The very rapid initial dehydration may be due to the evaporation of the adherent water in the precipitates, slow dehydration immediately follows, as in the case of the hydrous oxide gel of tin(IV), Zr and Ti. On the amorphous and glassy acid, the slow dehydration continued for a long time. These samples did not show a constant composition even if they were dried for a

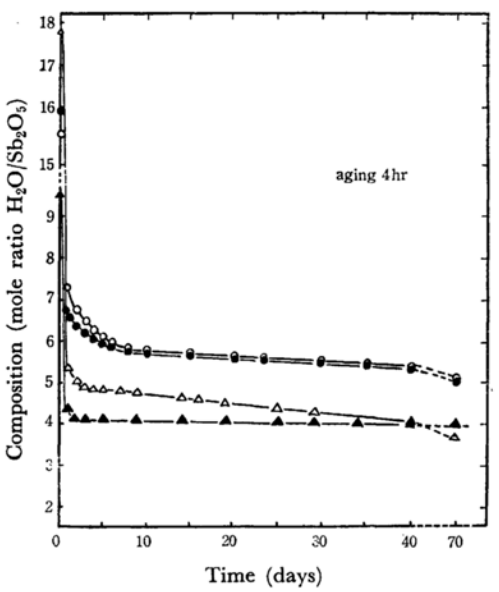

Fig. 1-1. Time-composition curves of precipitated antimonic acid (effect of hydrolyzed temperature).
Hydrolyzed temp. and initial composition of sample:
—○—, 0°C and 13.8 H_2O
—●—, 20°C and 15.4 H_2O
—▲—, 60°C and 7.1 H_2O
—△—, 90—98°C and 29.3 H_2O
All sample aged for 4 hr.

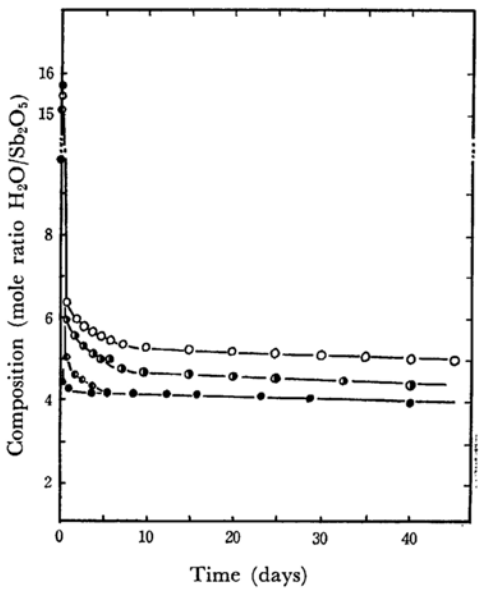

Fig. 1-2. Time-composition curves of precipitated antimonic acids (effect of aging).
Aging: —○—, 1 day —◑—, 3 days
—◐—, 5 days —●—, 7—30 days
Hydrolysis: 25°C

period of about 6 months. In contrast, the samples aged over 7 days at 25—30°C showed an almost constant weight for a relatively short time of about 3 weeks.

The water-composition of the antimonic acids was determined gravimetrically on the assumption that Sb_2O_4 was formed by ignition at 900°C for 2—3 hr. As Table 1 shows, the water-composition (mole ratio of H_2O/Sb_2O_5) obtained by the various preparations was decreased by raising the temperature of hydrolysis and by lengthening the period of aging. The decrease in the H_2O/Sb_2O_5 ratio in antimonic acid was slightly facilitated by increasing the concentration of hydrochloric acid, even under the same aging conditions. These values of the water-compositions agree with those reported by Simon and Thaler. When the sample was obtained by hydrolysis at 20°C and then aged at 70°C for 4 hr, the water-composition was almost the same as that of the sample which was hydrolyzed at 70°C and aged for 4 hr at the same temperature.

The samples aged for a long period of more than 7 days had a definite composition of $Sb_2O_5 \cdot 4H_2O$. The results of other preparations, such as S_{K-1}, S_{K-2}, Sb-1 and Sb-2, showed phenomena similar to that of hydrolysis of antimony pentachloride.

In the hydrothermic treatment of the freshly-prepared antimonic acid at 300°C, Simon and Thaler showed the formation of a definite hydrate, $3Sb_2O_5 \cdot 5H_2O$.[10] In the present experiment, however, it was shown that a thin hexagonal crystal had a relatively small water-composition, that is, $Sb_2O_5 \cdot 0.49H_2O$. The composition of S_{200}

Table 1. Compositions of antimonic acids by various preparations
(mole ratio H_2O/Sb_2O_5)

1) Effect of hydrolyzed temperature

Hydrolyzed temperature °C	0	20	40	60	90—98
Aging (same temp.)					
1 hr	5.14[A]	5.05[A]	—	4.46[A]	4.50[G]
4	5.05[A]	5.00[A]	5.05[A]	3.76[++++]	3.65[G]
24	4.91[A]	5.00[A]	4.91[+]	—	—

2) Effect of aging and concentration of acid (HCl) (hydrolysis and aging at 25—30°C)

Aging (day)	1	3	5	7	10	15—30
Concn. of acid						
0.25 N	5.02[A]	4.75[+]	4.10[++]	4.08[+++]	4.04[++++]	—
0.50	4.96[A]	4.45[+]	4.00[++]	4.09[++++]	4.07[++++]	4.07[++++]
1.0	5.00[A]	4.35[++]	4.08[+++]	4.09[++++]	—	—

3) Other preparations

Treatment	Hydrothermal		$K[Sb(OH)_6] + HNO_3$		Metallic Sb + Aqua regia		Dissolving and drying
Sample No.	S_{200}	S_{300}	S_{K-1}	S_{K-2}	Sb-1	Sb-2	S_G
H_2O/Sb_2O_5	2.57	0.49[H]	4.00[++++]	4.70[A]	5.15[A]	3.70[++++]	4.16[G]

A: Amorphous, G: Glassy material, H: Thin hexagonal crystal
Crystallization to cubic system increases in the following order: +, ++, +++ and ++++.
All the samples were dried for a period of 6 months at room temperature.

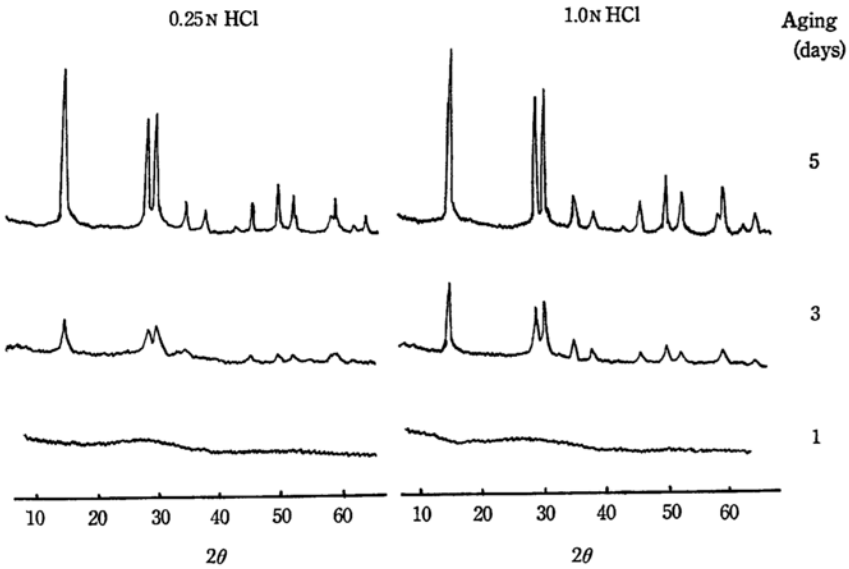

Fig. 2. Comparison between crystallization in 0.25 N and 1.0 N acid solution.

TABLE 2. COMPARISON OF THE CRYSTALLINE ANTIMONIC ACID WITH CORRESPONDING HYDRATED ANTIMONY PENTOXIDES IN THE CARDS OF THE A.S.T.M. FILE OF X-RAY DIFFRACTION DATA

	(1) $Sb_2O_5 \cdot 4H_2O$		(2) $Sb_2O_5 \cdot 3H_2O$		(3) $Sb_2O_5 \cdot H_2O$		(4) Sb_2O_5		(5) Sb_2O_5		(6) Sb_2O_5	
h k l	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
1 1 1	5.985	100			5.90	40	5.91	20	6.0	100	5.952	27
3 1 1	3.128	70	3.09	40	3.08	40			3.10	80	3.108	22
2 2 2	2.995	75	2.96	60	2.95	60	2.96	60	2.97	80	2.976	100
4 4 0	1.836	31	1.81	80	1.81	80	1.81	80	1.82	50	1.821	24
6 2 2	1.565	24	1.55	100	1.54	100	1.54	100	1.55	36	1.553	29
8 4 0	1.161	7	1.14	70	1.14	80	1.14	70	1.15	4	1.152	8
$\bar{a}$(Å)	10.38_2		10.2		10.2		10.2		10.3		10.305	
A.S.T.M. No.			2-1383		2-1386		2-1385		1-0154		11-690	

$\bar{a}$: lattice constant
(1): Present experiment, with Cu, 1.5405 Å at 25°C
(2) to (4): Natta and Baccaredda, with Mo, 0.7107 Å[12]
(5): Hanawalt and Rinn, with Mo, 0.709 Å[11]
(6): National Bureau of Standards, with Cu, 1.5405 Å at 26°C[13]

showed an intermediate value between those of S_{300} and the other dried samples.

X-Ray Examinations of Antimonic Acid. The X-ray diffraction paterns of the antimonic acids obtained by the hydrolysis of antimony pentachloride ranged from completely amorphous patterns to those containing a number of distinct reflections, as Figs. 2 and 3 show. The antimonic acids obtained by hydrolysis at 25°C began to crystallized after having been aged for a relatively long time at 25—30°C; the identical diffraction intensity was also shown after aging for a period of more than 10 days. The extent of the crystallization corresponded well with the change in the water-composition of the antimonic acid. Therefore, the results showed that the H_2O/Sb_2O_5 ratio of these acids decreased in proportion to the extent of crystallization.

The crystallization of the antimonic acids was facilitated by raising the temperature when the hydrolysis and the aging were carried out below 80°C. The extent of the crystallization of the sample obtained by hydrolysis at 60°C, followed by aging for 4 hr at the same temperature, was shown to be similar to that of another sample obtained by

11) J. D. Hanawalt and H. W. Rinn, *Ind. Eng. Chem., Anal. Ed.*, **18**, 310 (1946).
12) G. Natta and M. Baccaredda, *Gazz. chim. ital.*, **66**, 308 (1936).
13) H. E. Swanson, M. I. Cook, E. H. Evans and J. H. deGoot, *N. B. S (U.S.A) circ.*, **539**, Vol. 10, 8 (1960).

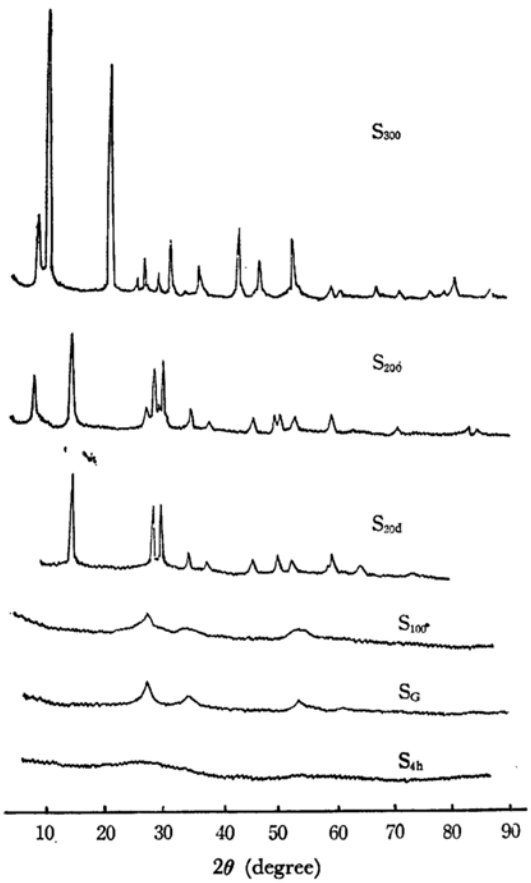

Fig. 3. X-Ray diffraction patterns of precipitated samples by various preparations.

hydrolysis at 25°C and by aging for 7 days at 30°C. Therefore, it seems that the crystallization of antimonic acid is facilitated by raising the temperature of the aging rather than that of the hydrolysis. The sample with a higher crystallization was shown to be a definite hydrate, $Sb_2O_5 \cdot 4\,H_2O$ (crystalline antimonic acid).

The comparison between 0.25 and 1.0 N portions of hydrochloric acid solutions on aging showed that the crystallization was facilitated by increasing the concentration of the acid. Similar results were observed in the samples obtained by other methods of preparation at temperature below 80°C.

The glassy sample produced by hydrolysis at 90—98°C was largely amorphous, except for the presence of five weak reflections (d: 3.28, 2.63, 1.72, 1.64 and 1.38 Å), indicating the presence of a new compound in a form different from the above-mentioned crystalline antimonic acid (Fig. 3).

The X-ray diffraction pattern of the S_G sample, which was made by treating prepared antimonic acid with hot water, was analogous to that of the glassy sample. The sample treated under a given pressure at 200°C showed a mixed pattern, composed of reflections indicating the crystalline antimonic acid and of reflections indicating an unknown material. The S_{300} sample showed a pattern different from that of any other prepared samples.

The X-ray diffraction data of the crystalline antimonic acid are compared in Table 2 with those of a number of antimony compounds indexed on the relevant cards published by the American Society for Testing Materials (A.S.T.M.). All of these substances belong to the same space group O_h^7 ($Fd3m$). The data relative to the crystalline antimonic acid are essentially similar to those of the Sb_2O_5 reported by Hanawalt and Rinn.[11] However, it seems that the conditions of

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR CRYSTALLINE ANTIMONIC ACID
(Cu$K\alpha$ 1.5405 Å, at 25°C intensity estimated by diffractometer)

$h\ k\ l$	d(Å)	I/I_0	a^*(Å)
1 1 1	5.985	100	10.366
3 1 1	3.128	70	10.374
2 2 2	2.995	75	10.375
4 0 0	2.594	15	10.376
3 3 1	2.381	11	10.379_5
4 2 2	2.119	2	10.380_9
5 1 1	1.998_4	17	10.382_9
4 4 0	1.835_8	31	10.384_8
5 3 1	1.754_8	22	10.381_5
5 3 3	1.583	11	10.380_4
6 2 2	1.565_2	24	10.382_4
4 4 4	1.498_3	6	10.380_5
7 1 1	1.453_8	12	10.382_2
7 3 1	1.351_6	12	10.381_8
8 0 0	1.298	3	10.384
7 3 3	1.268_4	1	10.382_3
8 2 2	1.223_3	1	10.380
7 5 1	1.198_7	4	10.381
6 6 2	1.190_7	8	10.380_3
8 4 0	1.160_8	7	10.382_5
9 1 1	1.139_5	5	10.381_3
9 3 1	1.088_3	4	10.381_7
8 4 4	1.059_7	4	10.382_8
9 3 3	1.043_4	3	10.381_7
9 5 1	1.003_5	4	10.380_3
10 2 2	0.9989	6	10.381
9 5 3	0.9677	2	10.377_4
11 1 1	0.9362	1	10.383_0
8 8 0	0.9174	1	10.379_2
11 3 1	0.9070	5	10.381_1
11 3 3	0.8807	4	10.383_3
10 6 2	0.8776	8	10.383_9
12 0 0	0.8652	5	10.382_4
11 5 1	0.8566_5	2	10.386_2
11 5 3	0.8337_8	3	10.380_5
12 4 0	0.8209	4	10.383_6

$\bar{a} = 10.38_2$ Å

a^*; lattice constant

preparing its antimony pentoxide were uncertain. According to Natta and Baccaredda,[12] hydrated antimony pentoxide prepared by the decomposition of potassium pyroantimonate with nitric acid was at first amorphous, but after 5 years it became a crystalline substance, $Sb_2O_5 \cdot 3H_2O$ and then after 10 years changed to another crystalline substance, $Sb_2O_5 \cdot H_2O$. The elementary cells of the hydrated Sb_2O_5 had lattice constants of 10.21—10.25 Å and belonged to the cubic system with the space group O_h^7, like cubic Sb_2O_3 (senarmontite).

The accurate lattice constant of the crystalline antimonic acid was determined by means of a Phillip X-ray diffractometer (Table 3). All the data were calibrated by standardized metallic silicon; they showed a lattice constant of 10.38_2 Å, which is larger than any other data listed in Table 2. The X-ray diffraction data of the crystalline antimonic acid were essentially identical in molecular crystal forms with the modification of Sb_2O_3 expressed by the mineral" senarmontite". The symmetry of the antimony trioxide is cubic, with a unit containing 16 molecules, and the structure consists of Sb_4O_6 molecules packed together in a unit cell in the same manner as the carbon atoms in a diamond.[14] The structure of the crystalline antimonic acid is probably similar to that of cubic antimony trioxide. The X-ray diffraction patterns of other crystalline powdered samples, such as S_{60}, $S_{K\text{-}1}$ and Sb-1, showed that in spite of different kinds of starting salt they were identical with that of the crystalline antimonic acid obtained by aging for a long time.

The freshly-prepared antimonic acid can be dissolved in pure water, but the solution becomes turbid and then a white precipitate appears. The X-ray investigation of the precipitate revealed the same compound as the crystalline antimonic acid.

Solubilities of Various Antimonic Acids in Water. As has been previously explained, there is contradictory information and confusion regarding the solubility of antimonic acid. The wet precipitate of pure antimonic acid is easily dissolved or peptized, but it becomes difficult to dissolve the acid dried for a long period. Such a phenomenon is similar to that observed in a number of hydrous oxide gels, such as stannic and zirconium hydrous oxide gel.

The physicochemical solubility must, in general, be determined in an equilibrium state. However, it is difficult to establish the conditions for determining the solubilities of the hydrous oxide because of the depolymerization or hydration which occurs in the oxides. In the present experiment, the solubilities of various antimonic acid sample were measured in order to examine the chemical stabilities with a view to their use as exchangers.

Three dried samples—a crystalline sample, S_{20d} aged for 20 days, an amorphous sample, S_{4h} aged for 4 hr at 25—30°C, and a dry sample, S_{4h}', dried S_{4h} in an air bath at 60°C for 24 hr—were studied in order to determine their time-solubility relationship. The S_{20d} and S_{4h} were dried more than 6 months in air at room temperature, just as in the case of the X-ray examinations. The sample S_{4h} was gradually dissolved in water; it took about 2 weeks to be completely dissolved. Such a slow dissolution of the amorphous samples in water may be due to depolymerization involving the hydration from a higher polymer of hydrous antimony pentoxide to a lower one (Fig. 4). The rate of the dissolution of S_{4h}' was slightly slower than that of S_{4h}, but S_{4h}' was completly dissolved after a long period. This is probably due to the fact that S_{4h} was changed to a higher polymer, S_{4h}', by drying at 60°C.

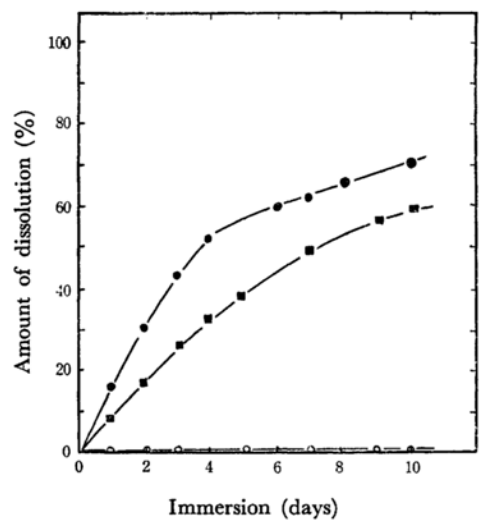

Fig. 4. Time-solubility curves for air-dried samples.
—●—; S_{4h} (amorphous)
—■—; S_{4h}' (amorphous) dried S_{4h} at 60°C for 24 hr
—○—; S_{20d} (crystalline)
Condition; 0.40 g of 100—200 mesh in 100 ml of pure water at 25°C.

The extent of the solubility of the crystalline antimonic acid, S_{20d}, was extremely small as compared with those of amorphous substances; the amount dissolved increased little even when S_{20d} was immersed for a long time. On the semi-crystalline sample aged for 3 days, for example, dissolution and peptization were simultaneously observed. The solubilities of the sample obtained by other methods of preparation (except for that obtained by the hydrothermal teratment) were measured under the same condition. From these results, it is fairly conclusive that the other crystalline

14) R. M. Bozorth, *J. Am. Chem. Soc.*, **45**, 1621 (1923).

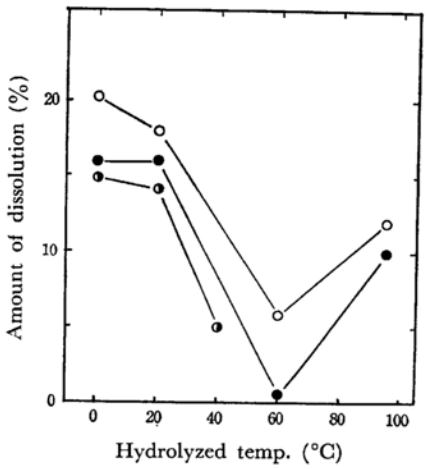

Fig. 5-1. Water-solubilities of the antimonic acids prepared by hydrolysis at various temperature.
Sample: 0.40 g 100—200 mesh of air-dried for 6 mounths.
Immersion: 25°C, 24 hr in 100 m*l* of water
—○—, aging for 1 hr at the same temp.
—●—, aging for 4 hr at the same temp.
—◑—, aging for 24 hr at the same temp.

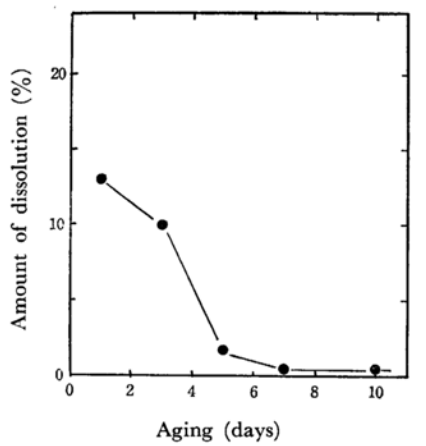

Fig. 5-2. Water-solubilities of the antimonic acids (effect of aging).
Sample: 0.40 g 100—200 mesh of air-dried for 6 mounths.
Immersion: 25°C, 24 hr in 100 m*l* of water.

sample, for example those aged for 4 hr at 60°C, have much smaller solubilities than an amorphous and glassy samples. The solubility of the glassy sample S_G was almost idential with that of the $S_{90°C}$ produced by hydrolysis at 90—98°C.

Consequently, it is evident that amorphous or glassy antimonic acid is a soluble form, while crystalline antimonic acid is an insoluble form. Such soluble and insoluble forms of antimonic acid can be formed by merely establishing suitable conditions for their preparation, regardless of the starting antimony substances.

It seems that the previous confusion regarding antimonic acid is due to the complex conditions of its preparation, such as temperature and the period of aging, the concentration of acid in the solution, and the temperature of the hydrolysis.

Chemical Stabilities. The chemical stabilities of the crystalline acid in common reagent are compared with those of amorphous substances in Table 4; the results are favorable. The soluble samples, both amorphous and glassy antimonic acid, are more stable in a dilute hydrochloric acid or in a neutral salt solution than in pure water or in an alkaline solution. Therefore, it is possible to use them as cation exchangers in these solutions. The crystalline antimonic acid is extremely stable against most reagents, and it is very difficult to dissolve it, even by heating it with concentrated hydrochloric acid; it is dissolved by the presence of potassium iodide. This high degree of stability of the crystalline antimonic acid is one of the important characteristics as an ion-exchange material.

Adsorptions of Lithium and Potassium Ions. Adsorptive properties of a number of hydrous oxides, as is well known, vary with the conditions of preparation, such as aging and hydrolysis.

Simon showed that the adsorptive amount of lithium ions on hydrated antimony pentoxide decreases with a rise in the temperature during the hydrolysis.[15] Our previous report showed that the uptake of potassium ions does not vary in spite of the changes in the temperature on hydrolysis.[2] To explain the difference between Simon's conclusion and ours, the uptake of lithium and potassium ions on various samples was determined by both column and batch techniques.

Table 4. Comparison of chemical stabilities between amorphous and crystalline antimonic acid
Concn. of antimony (mol/*l*) in immersed solution

Reagent	H_2O	1 N HCl	1 N KCl	1 N KOH
Amorphous antimonic acid*1	3.2×10^{-3}	1.8×10^{-3}	4×10^{-4}	4.0×10^{-3}
Crystalline antimonic acid*2	8.0×10^{-5}	4×10^{-5}	$<4\times10^{-5}$	2.5×10^{-4}

Sample taken: 0.4 g; total vol.: 100 m*l*; immersion: 24 hr at 25±0.05°C
*1: S_{4h}, *2: S_{20d} (Both samples were air-dried for 6 months and then sieved through 100—200 mesh.)

15) G. Jander and A. Simon, *Z. anorg. u. allgem. Chem.*, **127**, 68 (1923).

TABLE 5. UPTAKES OF LITHIUM IONS AND POTASSIUM IONS ON VARIOUS SAMPLES (BY BATCH EQUILIBRATION)

Sample No.	S_{1d}	S_{20d}	S_{K-1}	S_{K-2}	Sb-1	Sb-2	S_G	S_{200}	S_{300}
Form*	A	C	C	A	A	C	G	—	H
Li^+ uptake (meq./g)	0.93	0.33	0.34	0.72	0.95	0.30	0.69	<0.02	<0.02
K^+ uptake (meq./g)	1.25	1.29	1.28	1.25	1.23	1.30	1.18	0.80	0.52

Form*: A, amorpous; C, crystalline; G, glassy; H, hexagonal.
Sample taken: 1.00 g of 100—200 mesh size; immersion: 25°C, 48 hr; Alkali metals solution: 0.1 M, 100 m*l*.

The uptake of lithium ions on the antimonic acid obtained by the hydrolysis of antimony pentachloride was related to the extent of the crystallization of its acid as well as to the solubility. The uptake decreased with the growth of the crystal, as illustrated in Figs. 6-1 and 6-2. In contrast, the uptake of potassium ions was little changed by the difference in the extent of the crystallization. Of the samples obtained by other methods of preparation, the adsorptive properties were similar to those of the hydrolyzed sample. The results are summarized in Table 5. In batch equilibration made by the addition of a neutral salt solution, the uptakes of lithium ions are 0.72—0.92 meq./g on the amorphous antimonic acids and 0.30—0.34 meq./g on the crystalline antimonic acids, while those of potassium ions are 1.23—1.25 meq./g on the former and 1.28—1.30 meq./g on the latter.

The previous investigators regarded a number of freshly-precipitated oxide gels as hydrates of orthohydroxides and thought that the aging process consisted of either a polymerization or a condensation involving the isolation of water from one or more molecules of orthohydroxide, thus producing polyhydroxide of a gradually increasing complexity. They showed that no definite hydrates were actually formed out of the several products composed of the corresponding oxides of various particle sizes with various amounts of adsorbed water, and that the larger particles obtained by aging frequently showed a lower adsorption capacity for ions, a lower capacity responding to the decrease in specific surface. It is very difficult to explain the differences in adsorptive properties between amorphous and crystalline antimonic aicd as being due simply to the variety of particle sizes in these materials. These differences suggest the presence of two types of antimonic acid, with different selectivities of the adsorption for lithium ions.

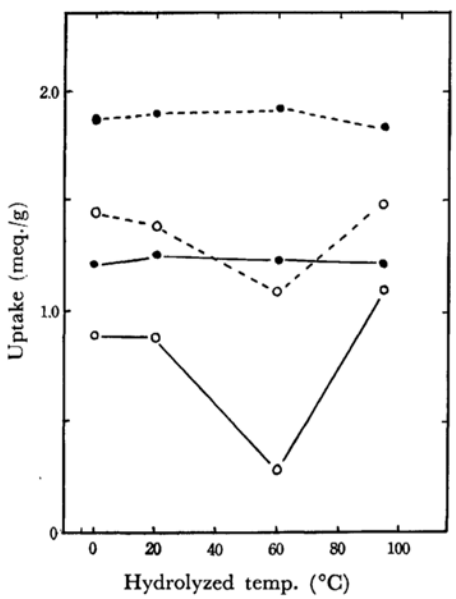

Fig. 6-1. Adsorption of lithium and potassium on the prepared sample by hydrolysis at various temperature.
—●—, K^+ uptake (Batch)
—○—, Li^+ uptake (Batch)
--●--, K^+ uptake (Column)
--○--, Li^+ uptake (Column)

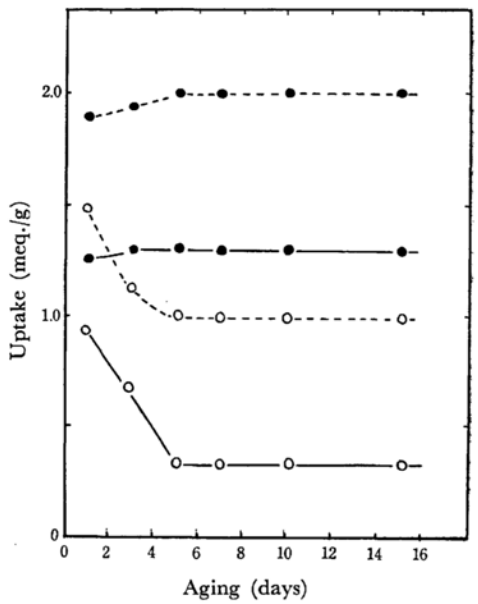

Fig. 6-2. Adsorption of lithium and potassium on the prepared samples by aging.
—●—, K^+ uptake (Batch)
—○—, Li^+ uptake (Batch)
--●--, K^+ uptake (Column)
--○--, Li^+ uptake (Column)

The samples, S_{200} and S_{300}, obtained by hydrothermal treatment, have limited use as cation exchangers, as they show a very small uptake of lithium and potassium ions.

Summary

1) The very pure products obtained by the hydrolysis of antimony pentachloride exist as three different types, amorphous, glassy, and crystalline antimonic acids, according to the different experimental conditions prevailing at temperatures below 100°C.

2) The freshly-prepared precipitate is an amorphous mass at first; it is transformed to a crystalline powder upon aging in contact with the mother liquid for a long period at 25—30°C. The crystallization of the antimonic acid can be facilitated by raising the temperature and by increasing the concentration of the acid in the solution used for aging. The glassy material is obtained by hydrolysis at 80—100°C and by washing and drying.

3) The preparation of this crystalline antimonic acid is accomplished under suitable conditions of temperature, aging, and concentration of acid, regardless of the starting antimony substances.

4) The experiment on the solubilities of the samples in various reagents revealed the presence of two soluble forms and one insoluble form of antimonic acid. The soluble forms are the amorphous and glassy forms, whereas the insoluble form is crystalline.

5) The crystal of the antimonic acid, $Sb_2O_5 \cdot 4H_2O$, has a cubic lattice (space group; $O_h^7 = Fd3m$) with a unit-cell dimension (lattice constant) of 10.38_2 Å, a value which can be deduced from the data for all the diffractions at 25°C.

6) The uptake of potassium ions on the crystalline antimonic acid is scarcely different from those of amorphous and glassy acid, whereas the uptake of lithium ions in the former is very small as compared with those of the latter two acids. Therefore, these results show the presence of more than two types of antimonic acids with different selectivities for lithium adsorption.

7) It has been shown that the sample produced by hydrothermal treatment at 300°C has a smaller water content than the definite hydrate, $3\,Sb_2O_5 \cdot 5H_2O$, reported by Simon and Thaler.[10] A sample with an intermediate water content is easily obtainable at 200°C.