BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2366—2371 (1968)

Synthetic Inorganic Ion-exchange Materials. XII. Some Observation on Surface Structure and Cation-exchange Behaviour of Three Different Antimonic Acids

Mitsuo ABE and Takuji ITO

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received September 20, 1967)

The cation-exchange behaviour and surface functionality of three different antimonic acids, amorphous, glassy and crystalline, were studied by thermogravimetric measurement, infrared absorption spectrometry and change in uptake of potassium ions upon heating. The ion-exchange capacities of the amorphous and glassy antimonic acids decrease with the loss of chemically bonded water. In contrast, the capacities of the crystalline acid heated within 200°C rarely change because of the loss of the interstitial (free) water and no drastic change occurs in the surface structure of the crystal. The crystalline acid with free water removed adsorbs moisture upon exposure to the atomsphere at room temperature. Upon heating above 300°C, the tenaciously bonded water was removed and the cation-exchange capacity decreased simultaneously. The infrared absorption spectra indicated that the surface functionality of the crystalline acid, similar to that of crystalline sodium antimonate $Na[Sb(OH)_6]$, is different from those of the amorphous and glassy acids. It seems that chemically bonded water in the crystalline acid is tenaciously combined as Sb-OH.

In recent years, increased interest in inorganic ion-exchangers has appeared.1-3) Disadvantages in present types of organic ion-exchangers, such as instability at high temperature and at high levels of ionizing radiation and the limitation in selectivity, sparked the development of inorganic ion-exchangers.

In previous papers we showed that antimonic acid4) and polyvalent antimonates5,6) have useful cation exchange properties for akali metal ions,

---

1) K. A. Kraus, H. O. Philips, T. A. Carlson and J. S. Jonson, Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, paper No. 15/p/1832 (1958).

2) C. B. Amphlett, L. A. McDonald and M. J. Redman, *J. Inorg. Nucl. Chem.*, **6**, 220 (1958).

3) For example, K. A. Kraus and H. O. Philips, *J. Am. Chem. Soc.*, **78**, 644 (1956); L. Baseste and J. Pelsmackers, *J. Inorg. Nucl. Chem.*, **21**, 124 (1961).

4) M. Abe and T. Ito, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1174 (1966).

5) M. Abe and T. Kenjo and T. Ito, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 291 (1967).

6) M. Abe and T. Ito, *ibid.*, **70**, 440 (1967).

including a suitable rate for adsorption and desorption in column operation. The antimonic acid showed that differences in selectivity for alkali metal ions are very large and that mutual separation can be achieved with a small column ($0.8\phi \times 6.0$ cm).⁷⁾ The antimonic acid obtained through the hydrolysis of antimony pentachloride was gradually peptized by immersing it in pure water for a long period of time. Preparation of the antimonic acid under various conditions has been studied to obtain a chemically stable material⁸⁾; at first, the hydrolyzed precipitate was in an amorphous state, but was gradually transformed into a crystalline powder when it was kept for long time in the mother liquid. Freshly prepared amorphous precipitate in a wet state was dissolved in hot water, and glassy material obtained by cooling the solution rapidly and then evaporating the moisture.

In the investigation of the Sb-O-H_2O system, the thermal decomposition of the three different antimonic acids has already been studied by thermogravimetry and differential thermal analysis, and X-ray powder diffraction analysis and chemical analysis of the oxygen content were made of the thermally decomposed products⁹⁾;

$$\begin{tikzcd}
S_A:\ Sb_2O_5\cdot nH_2O \arrow[r] & Sb_2O_5(\text{amorphous}) \arrow[d] & & \\
S_G:\ Sb_2O_5\cdot nH_2O(G) \arrow[r] & Sb_2O_5(G) \arrow[r] & Sb_6O_{13}(C) \arrow[r] & Sb_2O_4 \\
S_C:\ Sb_2O_5\cdot 4H_2O(A) \arrow[r] & Sb_2O_5\cdot 2H_2O(A) \arrow[r] & Sb_2O_5(B) \arrow[u] &
\end{tikzcd}$$

(A), (B) and (C), which are cubic space groups $Fd3m(O_h{}^7)$, have lattice constants of 10.38_2, 10.28 and 10.305 Å, respectively. In order to clarify problems involving the mechanism of the ion exchange ability, the present paper describes the ion-exchange properties and infrared spectra of the three different antimonic acids dried at increasing temperature.

Experimental

Preparations of the Three Different Antimonic Acids. All samples were prepared as described previously⁸⁾: concentrated antimony pentachloride solution (1 : 1), prepared by dropping liquid antimony pentachloride into the same volume of cold water, was hydrolized in a large amount of water at 25°C; $\mathbf{S_A}$, the hydrolyzed precipitate was kept in mother liquor at 25°C for 4 hr, and washed until free of Cl^- with a centrifuger (about 10000 rpm); $\mathbf{S_C}$ the crystalline antimonic acid was obtained by aging the precipitate in mother liquor at 30°C for 20 days; $\mathbf{S_G}$ the antimony pentachloride solution (30 m*l*) was hydrolyzed in 1 *l* of water at 20°C, and let stand for 4 hr. The precipitate, washed with water, was then dissolved in 300 m*l* of hot water. The glassy gel, (G) having five weak inflexions (d; 3.28, 2.63, 1.72, 1.64 and 1.38 Å), was obtained by cooling the solution rapidly and then evaporating the moisture.

When these products were dried with a fan at room temperature over a period of 6 months, they were transformed into granular material suitable for column operation. The dried samples were ground and separated into 100—200 mesh size, and in the sieves the granules of the antimonic acids were washed with water in roder to remove small quantities of adherent antimonic acid dust.

Uptake of Potassium Ions. When the antimonic acid is added to a solution of potassium chloride, hydrogen ions in the material are equivalently liberated by cation exchange in the external solution. The uptake of potassium ions was determined as follows; 50 m*l* of 0.1 N KCl solution was added to 0.4 g of the antimonic acid sample in a 100 m*l* bottle with a glass stooper, and after 48 hr, each solution, containing liberated hydrogen ions, was titrated with standard 0.1 N NaOH solution.

Measurement of Infrared Absorption Spectra. Infrared spectra was measured with a standard KBr disk and hexachloro-1,3-butadiene (H. C. B.) mulls technique, using an Hitachi EPI-S recording spectrometer. Measurements were carried out in comparison with the KBr blank disk, and the H. C. B. was previously dehydrated with anhydrous calcium sulfate.

Results and Discussion

Uptakes of Potassium Ions on Three Different Antimonic Acid at Various Drying Temperatures. The uptake of potassium ions by the antimonic acids, heated for 4 hr at 60°C to 1000°C and then kept in the atmosphere at room temperature, is shown in Fig. 1. The uptakes of

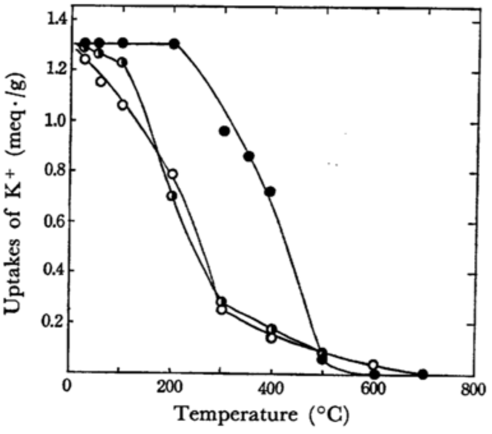


Fig. 1. K^+-uptakes on three different antimonic acids after heating to 900°C.
○: Amorphous antimonic acid
●: Crystalline antimonic acid
◑: Glassy antimonic acid

---

7) M. Abe and T. Ito, This Bulletin, **40**, 1013 (1967).
8) M. Abe and T. Ito, *ibid.*, **41**, 333 (1968).
9) M. Abe, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 2226 (1967).

the heated amorphous and glassy samples decreased continuously with increasing temperature, and showed no exchange properties above 600°C. In contrast, the uptake of the crystalline samples heated at 60 to 200°C scarcely decreased with increasing temperature, but decreased rapidly above 300°C, and then the samples heated to 700°C showed no ion-exchange properties, similar to the amorphous and glassy samples.

Thermal Decomposition and Re-hydration Processes. The particular investigation of the thermal decomposition of three different antimonic acids has been reported previously.[9] The changes in weight loss of the samples heated under the same condition are illustrated in Fig. 2. The amorphous acid was continuously dehydrated without loss of oxygen by heating below 600°C, and then transformed into Sb_2O_5 (G) showing weak X-ray diffraction intensities. The loss of oxygen began from 650°C and Sb_2O_5(G) transformed into Sb_6O_{13}(C). As the decrease in potassium ion uptake is comparable to the amount of dehydration, it is evident that the ion-exchange capacity decreases with the loss of hydrated water. These results suggest that the concentration of exchangeable hydrogen ions in the material phase is decreased by this treatment.

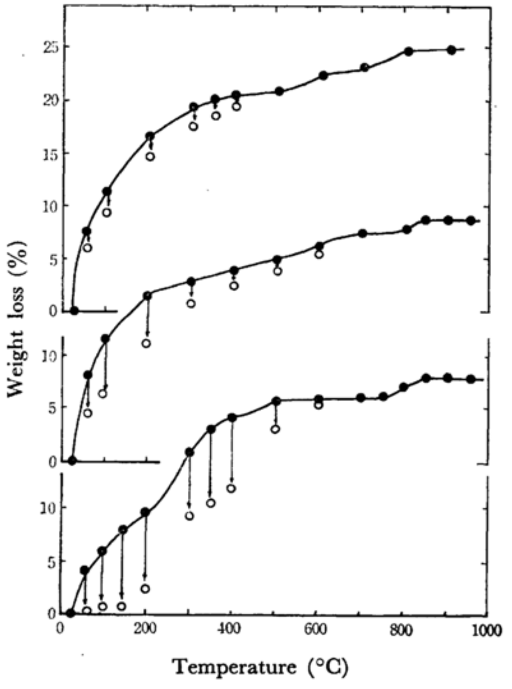


Fig. 2. Water adsorption on the heated antimonic acid samples.
(Top) amorphous antimonic acid
(Middle) glassy antimonic acid
(Bottom) crystalline antimonic acid
●: Heated for 4 hr and then weighted after 15 min
○: Weighted after admission for 1 month at room temperature

On the crystalline antimonic acid, the decrease in the uptake is different from that obtained for the amorphous or glassy acids. The weights of all the samples, heated at below 200°C and then kept in air at room temperature for a relatively short time, return to the initial values by adsorbing moisture from the atomosphere. X-ray diffraction analysis indicated that no drastic change in the structure of the crystal occurs when the free water molecule are lost.

The loss of water, found to be reversible, is attributed to the removal of the free water which can be desorbed by heating and adsorbed by cooling without change in the crystal structure. With increasing the temperature above 300°C, the crystalline antimonic acid begins to lose bonded water which constitutes part of the crystal structure. The reversibility of the free water decreased simultaneously with increasing temperature, and samples heated above 700°C showed no adsorptive properties toward moisture. It is evident that the decrease in uptake of the crystalline acid does not occur with the removal of free water, but with a decrease in the bonded water by heating above 300°C.

Infrared Absorption Spectra of the Three Different Antimonic Acids. Any difference between the amorphous or glassy acids and the

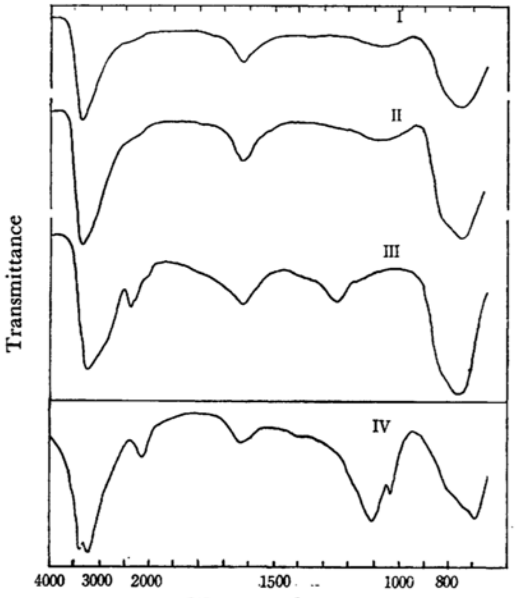


Fig. 3. Infrared absorption spectra of three different antimonic acids and sodium antimonate.
I: Amorphous acid
II: Glassy acid
III: Crystalline acid
IV: Sodium antimonate

crystalline acid in adsorptive properties toward lithium ions is expected to depend on surface functionality. Hence, surface functionality refers collectively to the chemical functional groups which terminate the bulk structure of the solid and their immediate environment, as reported by McDonald.10)

The absorption band between 2800 and 3800 cm^{-1} with a maximum at 3350 cm^{-1} is characteristic of interstitial water and OH groups, and the band between 1500 and 1760 cm^{-1}, with a maximum at 1630 cm^{-1}, is due to the deformation vibration of the interstitial water. The absorption bands for the amorphous and glassy acids are similar to those obtained for a number of metallic hydrous oxides (such as Zr, Sn and Th11)), with the exception of the stretching vibration of Sb-O with a maximum at 750 cm^{-1}.

The crystalline antimonic acid showed band having maxima at 2430 and 1280 cm^{-1} in addition to the bands found for the amorphous and glassy acids. Its spectrum is almost the same as that of sodium antimonate $Na(Sb(OH)_6]$ (tetragonal crystal system *P*4/*n*), as illustrated in Fig. 3. It has been known that the OH groups in the antimonate coordinate with one atom of antimony. Siebert12) deduced that the intense absorption band between 1000 and 1200 cm^{-1} on the antimonate must be assigned to the Sb-OH deformation vibration of the antimonyl group in octahedra, and the maximum intensity at 2145 cm^{-1} is probably due to an overtone of the Sb-OH deformation vibration. The band between 1100 and 1350 cm^{-1} of the crystalline acid can be assigned to the Sb-OH deformation vibration, though it is shifted to higher frequency in comparison with that of the antimonate. It is concluded that the crystalline antimonic acid is different from the amorphous and glassy acids, not only in fundamental crystal structure, but also in surface functionality. The broad adsorption band between about 2700 and 3800 cm^{-1} implies that hydrogen bonding exists between OH groups and the water molecules surrounding them.

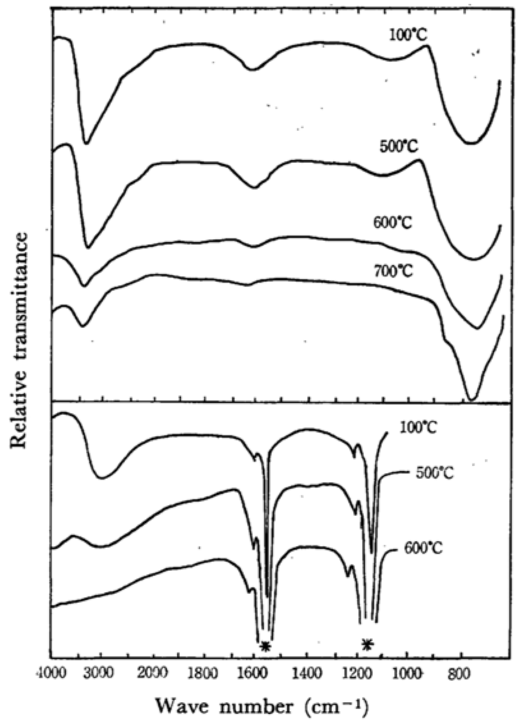


Fig. 4. Infra-red absorption spectra of amorphous antimonic acid after heating to 700°C for 4 hr.
(Top) KBr disk method
(Bottom) H.C.B. suspended method
* absorption band of H.C.B.

Infrared Spectra of Three Different Antimonic Acids at Various Drying temperatures. Infrared absorption spectra of the amorphous acid heated for 4 hr at 100 to 700°C are shown in Fig. 4. Absorption bands due to OH groups continuously decreased with increasing temperature, and a drastic change in the band at 750 cm^{-1} was caused by heating to 700°C, indicating the formation of Sb_6O_{13}.9) Measurements with an H. C. B. mull showed that absorption bands involving OH groups and water disappear at 600°C. The disappearance of both the OH and H_2O bands supports our conclusion9) that the product heated at 700°C is not Sb_3O_6OH as reported by Dihlström *et al.*13) and Schrevelius,14) but Sb_6O_{13}. Similar changes were observed upon heat treatment of the glassy antimonic acid. The decrease in intensity of the OH-band below 600°C is ascribed to the condensation of acid groups in the amorphous or glassy antimonic acids to Sb-O-Sb. Sb_2O_5 was formed on heating at 600°C for 4 hr. By the condensation of acid groups, as assumed in metallic hydrous oxide,11,15) it is possible to explain the irreversible loss of water in these acids. The condensation decreases the concentration of exchangeable hydrogen ions in the materials, and therefore causes a lower uptake of potassium ions. However, information obtained from this measurement is not enough to arrive at a proper conclusion on the surface functionality of amorphous antimonic acid. Further confirmation of the surface functionality

---

10) R. S. McDonald, *J. Phys. Chem.*, **62**, 1168 (1958).

11) C. H. Wirguin and A. A. Yaron, *J. Inorg. Nucl. Chem.*, **28**, 2378 (1966).

12) H. Siebert, *Z. Anorg. Allgem. Chem.*, **301**, 161 (1959).

13) K. Dihlström and A. Westgem, *ibid.*, **235**, 153 (1937).

14) N. Shrewelius, Studier över antimonat, hydroantimonate och fluoantimonat; Dissertation, University of Stockholm (1943). *Cf.* C. J. Vitaliano and B. Mason, *Am. Min.*, **37**, 982 (1952).

15) V. Vesely and V. Pekarek, *J. Inorg. Nucl. Chem.*, **25**, 697 (1963).

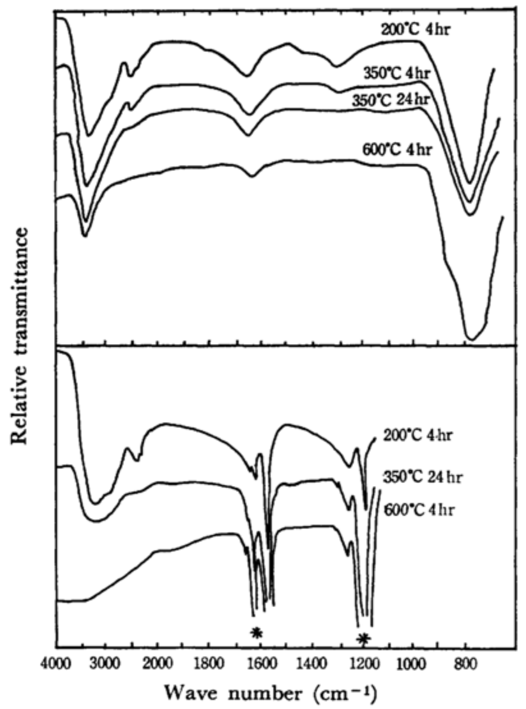


Fig. 5. Infrared absorption spectra of crystalline antimonic acid after heating to 600°C.
(Top) KBr disk method
(Bottom) H.C.B. suspended method
* absorption band of H.C.B.

must be obtained by checking other physical and chemical properties.

In the crystalline antimonic acid, little change was observed when samples were heated at 60—200°C, but at 300°C, the absorption bands of Sb-OH decreased with increasing temperature, corresponding to the removal of strongly bonded water, which comprises part of the crystal structure, as deduced from the results of X-ray examinations.⁹⁾ These results indicate the existence of strongly bonded water combined with Sb-OH. It is possible to interpret that the uptake of the alkali metal ions on the crystalline acid scarcely changes due to the removal of interstitial water, but decreases rapidly upon decomposition of the Sb-OH groups. The infrared spectra of the crystalline acid heated at 700°C showed a change in the intensity of the Sb-O stretching vibration, indicating a drastic change to Sb_6O_{13}, as in the amorphous acid.

Infrared Spectra of Three Different Antimonic Acid adsorbed Alkali Metal Ions. The ion-exchange properties of the surface sites of the hydrous oxides of metals is very important problem, but little is known concerning their immediate environment except in the case of amorphous silica.¹⁰⁾

When the hydrogen forms of the amorphous samples were converted to sodium or potassium forms by treatment with a solution of 0.1 N NaCl or 0.1 N KCl, using a column technique, the infrared spectra scarcely changed from those of the hydrogen forms, as illustrated in Fig. 6.

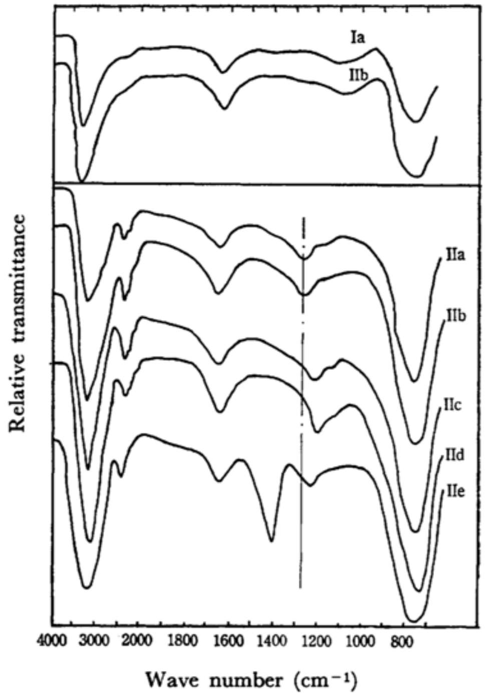
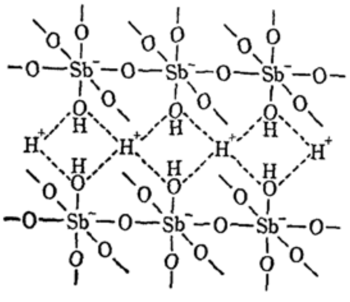


Fig. 6. The infrared absorption patterns of antimonic acids before and after exchange with alkali metals (KBr disk).
(Top) amorphous antimonic acid, Ia: H-form, Ib: K-form, (Bottom) crystalline antimonic acid, IIa: H-form, IIb: 1.1 mep.K^+/g, IIb: 2.2 meq.K^+/g, IId: 2.8 meq.Na^+/g, IIe 2.0 meq.NH_4^+/g

The spectra of the crystalline acid was similar to that of the hydrogen form, except that the deformation band of Sb-OH was shifted to a lower vibration frequency with the adsorption of alkali metal ions. It has been known that an atom or molecule adsorbed near a surface perturbs the motions of atoms of the group, causing a shift in some group vibration frequency.¹⁰⁾ Such a shift is evidence that the deformation frequency at 1280 cm⁻¹ on the hydrogen form is affected by the chemically adsorbed ions. It is possible to explain a shift to lower frequency, assuming that an increase in reduced mass occurs near the surface groups by conversion to alkali metal forms. If hydrogen ions in Sb-OH exchange to the alkali metal ions in the external solution, the absorption intensity of Sb-OH should apparently decrease. However, little change in the intensities were observed in conversions by any alkali metal ions.

From these results, it is possible to propose the following structure for the crystalline antimonic acid $H_2Sb_2O_5(OH)_2$:

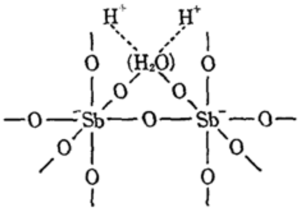


$H_2Sb_2O_5(OH)_2$

The hydrogen ions in the structure may be combined as H_3O^+. If 5 molecules of water are removed from two $H[Sb(OH)_6]$ molecules, modified from $Na[Sb(OH)_6]$, such a structure is easily deduced. It seems that, however, the hydrogen bonding surface groups are constrained by rigid three-dimensional bonding, in the same manner as the Sb_4O_6 molecule in senarmontite (cubic Sb_2O_3),⁹⁾ and that the ion-exchangeable hydrogen ions are surrounded by six oxygen atoms, as Na^+ in $Na[Sb(OH)_6]$.

In the amorphous and glassy acids, though information obtained from infrared spectra measurements is too little to allow an evaluation of the surface functionality, the results on the irreversible loss of the water by the heated samples indicates that a large part of water included in these materials are chemically bonded, and decreases continuously with increasing temperature, involving condensation of the acid groups. From a previous experiment, it was thought that the difference between the amorphous and glassy acids is only the difference in particle size.⁹⁾ The matrix of the glassy acid is Sb_2O_5 (structure G), and scarcely changes with increasing temperature (below 600°C). The ion-exchange capacity correspondingly decreased with the loss of water molecules in the material. Therefore, it seems that the water included in the amorphous or glassy acids is not simply interstitial water but bonded water. The existence of isolated OH groups was not observed through hydrogen bonding in the materials.

The following surface structure is probable for the amorphous and glassy acids, although the structure of the hydrogen bonded water molecules is uncertain.



$Sb_2O_5 \cdot nH_2O$

We have already pointed out that disparity of lithium adsorptions on the antimonic acid obtained by various preparations is not due to a difference in particle size of the materials, but the existence of different typs having a difference in selectivity toward lithium ion adsorption.⁸⁾ In present experiment, it may be concluded that the difference in selectivity is closely connected to the difference in surface functionality in the antimonic acids.