

position of Cd is sometimes noted when reduced melts are rapidly solidified, and this is frequently observed on remelting these solids. The metal redissolves in the melt and is probably due to unavoidable decomposition of  $\text{Cd}_2(\text{AlCl}_4)_2$  that accumulates locally in the melt in excess of the equilibrium amount. With care, pure white solids and clear green chloride melts can be obtained.

Two procedures have been used for the melt reductions. For small, single samples the most convenient is the reaction of weighed amounts of  $\text{CdX}_2$  and Al (A. D. MacKay, 99.99%). For example, with the stoichiometry  $4 \text{ CdX}_2 + 2 \text{ Al} \rightarrow \text{Cd}(\text{AlX}_4)_2 + 3 \text{ Cd}$ , the additional weight loss of the Cd thus produced gives a direct measure of the per cent. reduction in the melt of 1:2 composition. The apparatus containing the weighed components is evacuated, flamed and sealed off and the relatively mild reaction initiated with a hand torch.

In order to conserve  $\text{CdCl}_2$ , which is more difficult to purify than  $\text{AlCl}_3$ , the study of the phase diagram (Fig. 1) was carried out starting with 10 g. samples of  $\text{Cd}(\text{AlCl}_4)_2$  that had been previously prepared in large quantities by melting the component salts in the proper proportion. As excessive supercooling obscured the liquidus points of partially reduced samples, the melting points (as well as peritectic decompositions of  $\text{Cd}_2(\text{AlCl}_4)_2$ ) were observed visually in a melting point block. Reduction limits were established by weight loss of the metal phase upon equilibration for 8 to 40 hr. (depending on sample and container size and the amount of agitation provided). The jacketed container was positioned in a vertical Marshall furnace that was shunted so as to reduce the gradient along the sample to  $1^\circ$  and which was controlled with a position-proportioning controller. Samples to be equilibrated below the melting point of Cd were first held at  $330^\circ$  for 2 hr. in order to speed up the approach to equilibrium with solid Cd. The equilibrium points at lower temperatures ( $230$ – $260^\circ$ ) could be approached from either direction. The fine metal sponge cleanly separated when a melt containing larger amounts of  $\text{Cd}_2^{+2}$  was equilibrated for 24 hr.; this metal was recovered and melted to a pellet with a minimum amount of salt. Solid buttons recovered needed only to be scraped free of salt and washed before weighing. The solubility of  $\text{Al}^{2+}$

and of the salts in Cd is quite negligible. There is some indication that in Pyrex containers the higher temperatures associated with the  $\text{CdCl}_2$ -Al reaction, or prolonged equilibration of the melts, have a slightly deleterious effect on the purity of the product.

A one-piece Soxhlet extractor was used without thimble for recrystallization of  $\text{Cd}_2(\text{AlCl}_4)_2$ . Benzene, dried with  $\text{CaH}_2$ , was added to the salt therein in the dry box and the apparatus evacuated and sealed off with the benzene cooled to  $-80^\circ$ . Magnetic susceptibilities were qualitatively observed as before.<sup>16</sup>

**Analyses.**—A modified form of the potentiometric EDTA titration described by Fritz, *et al.*,<sup>30</sup> was used for Cd and Al. Standard 0.05 *M* solutions of these were prepared from the pure metals, and the EDTA standardized against the  $\text{Cd}^{+2}$ . Unknown  $\text{Cd}^{+2}$  was titrated at pH 7–8 using acetylacetone to mask the  $\text{Al}^{+3}$  and pyridine as a buffer. The end point was detected potentiometrically with a pH meter equipped with a Hg electrode, the necessary  $\text{Hg}^{+2}$  ions being furnished by 1 drop of 0.01 *M* solution of the  $\text{Hg}^{+2}$ -EDTA complex. Aluminum was determined from a titration of  $\text{Cd}^{+2}$  plus  $\text{Al}^{+3}$ ; excess EDTA was added at pH 2 or lower and the solution allowed to stand for about 4 hr. before back titration with  $\text{Hg}^{+2}$  at pH 8. It was also necessary for unknown solutions to stand overnight at pH 2 or less prior to the addition of EDTA in order to avoid low results due to apparent hydrolytic polymerization of the  $\text{Al}^{+3}$ . Even so, the end-point was not sharp and the results were variable by  $\pm 0.5\%$ . Chloride was determined gravimetrically.

**X-Ray Data.**—Powder patterns were obtained as previously described.<sup>16</sup> The principal distances, with relative intensities in parentheses, are, for  $\text{Cd}(\text{AlCl}_4)_2$ : 6.24(2), 5.97(5), 5.74(10), 4.52(3b), 3.54(2), 3.12(2), 2.86(8), 2.28<sub>5</sub>(2), 2.21<sub>4</sub>(6), 2.15<sub>3</sub>(3), 1.883(7), 1.716(5), 1.692(2); for  $\text{Cd}_2(\text{AlCl}_4)_2$ : 10.5(4), 9.4(4), 8.8(8), 4.5<sub>6</sub>(6), 4.47(3), 3.24(10), 2.94(5), 2.81(3), 2.25<sub>5</sub>(3), 1.952(3b), 1.883(6).

(29) M. Hansen and B. Blumenthal, *Metallwirtschaft*, **10**, 925 (1931).

(30) J. S. Fritz, M. J. Richard and S. K. Karraker, *Anal. Chem.*, **30**, 1347 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY, ST. LOUIS, MISSOURI]

## Antimony (III)–Antimony (V) Exchange Reaction in HCl Solutions<sup>1</sup>

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The experimental study of the exchange reaction between Sb(III) and Sb(V) has been extended to HCl concentrations in the range from 6 *f* to 12 *f*. The exchange rate of 0.02 *f* Sb(III) with 0.02 *f* Sb(V) increases steadily with increasing HCl concentrations to a maximum value in approximately 9.3 *f* HCl, then decreases again between 9.3 *f* and 12 *f*. The experimentally determined rate law in concentrated HCl is  $R = (\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}})(1.39 \times 10^{12})e^{-17,200/RT}$  *f* min<sup>-1</sup>. Complex exchange curves have been observed in the 6.5 *f* to 8 *f* HCl region. The complexity is explained on the basis of slow interconversion among two or more forms of Sb(V) which exchange at different rates with Sb(III).

### Introduction

The purpose of this investigation was to extend Bonner's<sup>3</sup> data on the Sb(III)–Sb(V) exchange reaction in HCl solutions. We have measured the exchange rate as a function of the HCl concentration and also as a function of the antimony concentrations at several HCl concentrations.

In solutions about 6.5 *f* to 8 *f* in HCl the exchange curves are not straight lines. This indi-

cates that there is more than one reaction occurring. The effect appears to be due to the existence of at least two Sb(V) species with slow rates of interconversion.

### Experimental

**Tracer.**—The 60-day  $\text{Sb}^{124}$  tracer was obtained from the Atomic Energy Commission in the form of 200 mg. of metallic antimony which had been irradiated in the Oak Ridge pile. The metal was dissolved in aqua regia and the solution evaporated nearly to dryness. The residue was dissolved in 3 *f* HCl and the solution boiled. Hydrogen sulfide was passed into the hot solution to precipitate antimony sulfide. The precipitate was washed with dilute HCl and dissolved in concentrated HCl. The solution was boiled to remove  $\text{H}_2\text{S}$  and evaporated to a small volume. It was transferred to a 100 ml. volumetric flask and diluted to volume with concentrated HCl. Tracer solutions for exchange reactions were made by dilution of aliquots of this stock solution.

$\text{Sb}(\text{V})$  tracer solutions were prepared from this solution by the method described below for the production of inactive  $\text{Sb}(\text{V})$  stock solutions.

(1) Abstracted from the Ph.D. thesis of C. H. Cheek, Chemistry Department, Washington University, January 1953. Presented in part at the Symposium on Electron Exchange Reactions held at the American Chemical Society meeting in Memphis, Tenn., December, 1956.

(2) (a) Naval Research Laboratory, Radiation Division, Washington 25, D. C. (b) To whom reprint requests should be addressed. Chemistry Division, Univ. of Calif., Lawrence Radiation Laboratory, Livermore, Calif.

(3) N. A. Bonner, *This Journal*, **71**, 3909 (1949).

To test for radiochemical purity, a sample was sealed in a test tube and counted from time to time on the proportional counter used in the rest of the experiments. It decayed with the reported 60-day half-life over a period of seven half-lives. The 2.8-day  $\text{Sb}^{122}$  had decayed to a negligible amount before these experiments were started.

**Reagents and Analyses.**—Analytical grade reagents were used.

The Sb(III) stock solutions were made by dissolving  $\text{SbCl}_3$  crystals in HCl. These solutions were analyzed for Sb(III) by titrating aliquots with standard  $\text{KIO}_3$  solution to the ICl end-point in 3 *f* HCl.<sup>4</sup>

Stock solutions of Sb(V) were prepared by bubbling chlorine into hot solutions of Sb(III) in 6 *f* HCl or by treating the Sb(III) solutions with excess 30%  $\text{H}_2\text{O}_2$ . In either case the resulting Sb(V) solution was boiled to remove chlorine and to concentrate the solution to a thick syrup. The syrup was dissolved in concentrated HCl. The Sb(V) concentration was determined by thiosulfate titration of the iodine liberated from KI by aliquots of the solution.<sup>5</sup>

Chloride analyses were performed by a modified Volhard method. An excess of tartaric acid was added to solutions containing antimony to prevent hydrolytic precipitation before or during titration.

The isopropyl ether used in the separation procedure was kept free of peroxides by storing it over a solution of ferrous ammonium sulfate in dilute  $\text{H}_2\text{SO}_4$ . The bottle was shaken occasionally to reduce any peroxides that were present.

**Counting Procedures.**—Gamma radiation from the solutions was counted by placing a test tube containing the sample in a standard position against the side of a brass-walled proportional counter filled with flowing methane at atmospheric pressure. The test tubes were always filled to the same height and were calibrated so the corrections could be made for small differences in counting efficiency due to the differing dimensions of individual tubes. Counting efficiencies of samples in ether and in aqueous HCl were not measurably different. Except for very low-counting samples, all were counted long enough so that the standard deviation was less than 1%.

The counting rate of a  $\text{Co}^{60}$  standard was measured from time to time as a check on the reproducibility of the counter. No deviations were observed larger than those to be expected from statistical fluctuations.

**Separation Method.**—The two oxidation states were separated by extracting Sb(V) into diisopropyl ether from 8 *f* HCl.<sup>6</sup>

It was convenient to prepare separation mixtures in such a way that the two phases would have equal volumes after extraction. It was found that 15 ml. of 8 *f* HCl and 17.5 ml. of ether satisfied this condition.

The following experiments were carried out to test the separation method:

12 ml. of 7 *f* HCl and 17.5 ml. of ether were added to a glass-capped centrifuge tube. The tube was chilled in a beaker of crushed ice, and 3 ml. of 0.04 *f* Sb(V) tracer in 12 *f* HCl was added. The tube was shaken vigorously for 1 minute, then centrifuged for 5 minutes. A 10 ml. aliquot was taken from each phase and counted. The ether phase was then shaken with a fresh portion of 8 *f* HCl and the separated phases again counted. The distribution of the activity between the two phases after the second extraction was the same, within experimental error, as that after the first extraction. Several experiments of this kind gave an average of 99.7% of the activity in the ether phase.<sup>7</sup>

A similar set of experiments using Sb(III) tracer gave an average of 99.2% of the activity in the aqueous phase.

The above extraction efficiencies were used in making separation corrections for the exchange experiments.

Counting rates of separated fractions of completely exchanged solutions of known composition were consistent with the assumption that the extraction behavior of one oxidation state was not affected by the presence of the other oxidation states.

The extraction efficiency measurements also proved that

(4) E. H. Swift, "A System of Chemical Analysis," Prentice Hall, Inc., New York, N. Y., 1939, p. 271.

(5) E. H. Swift, *ibid.*, p. 384.

(6) F. Edwards and A. Voigt, *Anal. Chem.*, **21**, 1204 (1949).

(7) It is now known that this procedure gives the extraction coefficient for the less hydrolyzed form of Sb(V) (see ref. 10). This will make little difference to the experiments reported here.

the methods of preparing the antimony solutions produced the expected oxidation states.

An experiment was designed to test for separation-induced exchange. 17.5 ml. of ether and 9.0 ml. of 8 *f* HCl were added to a centrifuge tube in an ice bath. Three ml. of 0.02 *f* Sb(III) in 8 *f* HCl and 3.0 ml. of labeled 0.02 *f* Sb(V) in 8 *f* HCl were added. The extraction was then carried out as usual. Only 0.4% of the activity remained in the aqueous phase, indicating that no separation-induced exchange had occurred.

**Exchange Procedure.**—A detailed description of an exchange reaction between 0.0198 *f* Sb(III) and 0.0206 *f* Sb(V) in 10.5 *f* total chloride will serve as an example of the method.

To 10.0 ml. of labelled, 0.0515 *f* Sb(V) in 12.0 *f* total chloride were added the calculated amounts of 12.1 *f* HCl and water to give 20.0 ml. of a solution 10.5 *f* in total chloride. This solution was prepared in the reaction vessel, a 25 ml. volumetric flask. A separate solution of 0.0990 *f* Sb(III) in 10.5 *f* total chloride was prepared in a similar manner, but without tracer. The two solutions were suspended in a 25.0° water-bath and allowed to remain overnight.

To start the exchange, 5.0 ml. of the Sb(III) solution was pipetted into the reaction vessel. The time was noted at the instant the first of the Sb(III) solution entered the flask. The flask was swirled as the solution was added in order to mix the solutions as well as possible. When all the solution had been added, the flask was stoppered, removed from the water-bath, shaken vigorously for 10 seconds, then returned to the water-bath.

A 3.0 ml. aliquot was removed immediately and transferred to a centrifuge tube containing 12.0 ml. of 7.4 *f* HCl and 17.5 ml. of ether. The tube and contents had previously been cooled in an ice-bath.

Separation and counting were then carried out as described under "Separation Method." The time of separation was taken as the moment the first of the exchange mixture touched the separation mixture. During the course of the exchange run, four more 3.0 ml. aliquots were treated in the same way.

It should be noted that after addition of a three ml. aliquot of the exchange mixture to the separation mixture, the aqueous phase consisted of 15 ml. of 8 *f* HCl. For each exchange reaction the separation mixtures were prepared so that this was the case.

For each exchange experiment, both oxidation states of antimony were allowed to come to equilibrium at the same HCl concentration before mixing. This precaution eliminated heat effects due to changes in HCl concentration and ensured that the antimony species in solution were not changing during the experiment. The method of timing the exchange introduces a small error. This error is not more than about 15 seconds, the time required to empty a 3 ml. pipet. The error is nearly constant for all aliquots, so the time difference between points, and hence the slopes of the exchange curves are unaffected by the error.

## Experimental Results

The exponential exchange law<sup>8</sup> as applied to the Sb(III)-Sb(V) exchange is

$$Rt = \frac{-(\text{Sb}^{\text{III}})(\text{Sb}^{\text{V}})}{(\text{Sb})_{\text{T}}} \ln(1 - F)$$

where  $R$  is the constant rate at which Sb(III) becomes Sb(V) and Sb(V) becomes Sb(III),  $(\text{Sb})_{\text{T}}$  is the total antimony concentration, and  $F$  is the fraction exchange at time,  $t$ .  $F$  is determined in our experiments as the specific activity of the initially inactive species at time  $t$  divided by the specific activity of the same species after exchange is complete. The specific activities used in the determination of  $F$  are in purely arbitrary units, namely, the counting rate of a 10 ml. aliquot of the appropriate phase, corrected for the slight amount of incomplete separation.

(8) See, for example, A. C. Wahl and N. A. Bonner (editors) "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. I by O. E. Myers and R. J. Prestwood, p. 9.

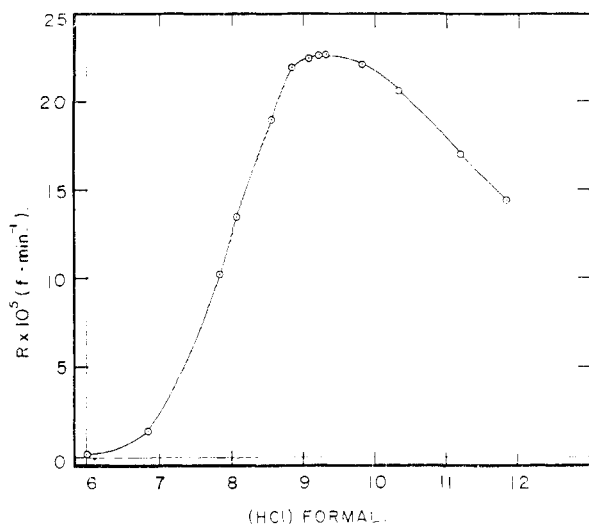


Fig. 1.—Dependence of rate of exchange on HCl concentration: 0.0198 *f* Sb(III), 0.0206 *f* Sb(V), 25°. The point at 6 *f* is from ref. 3.

#### Effect of HCl Concentration on Exchange Rate.—

To determine the effect of HCl concentration on the exchange rate a series of exchange experiments were performed at constant antimony concentrations and varying HCl concentrations.

TABLE I

EFFECT OF HCl CONCENTRATION ON THE EXCHANGE RATE AT 25° (0.0198 *f* Sb(III), 0.0206 *f* Sb(V))

HCl, <i>f</i>	<i>t</i> <sub>1/2</sub> , min.	<i>R</i> × 10 <sup>5</sup> , <i>f</i> × min. <sup>-1</sup>
6.84	472	1.48
7.84	68.0	10.3
8.09	52.0	13.5
8.59	36.7	19.1
8.84	31.8	22.0
9.09	31.1	22.5
9.29	31.0	22.6
9.59	31.0	22.6
9.84	31.7	22.1
10.34	34.0	20.6
11.24	42.5	16.5
11.84	48.7	14.4

Table I and Fig. 1 give the results of these experiments. For solutions 0.02 *f* in each oxidation state of antimony, the exchange rate increases rapidly with increasing HCl concentration up to about 9 *f*. A maximum rate is reached in approximately 9.3 *f* HCl, and above this value the rate steadily decreases.

Since the forms of the antimony complexes are unknown, the actual concentrations of HCl are not accurately known. The listed values are formal concentrations of HCl, obtained by subtracting from the total chloride formality the amount of chloride incorporated in the sum of the formalities of SbCl<sub>3</sub> and SbCl<sub>5</sub>. For the experiments described in this section the formal concentration of HCl is 0.16 formal unit less than the measured total chloride formality. In solutions of high HCl concentration the actual chloride concentration is somewhat less than the formal HCl concentration due to formation of complexes such

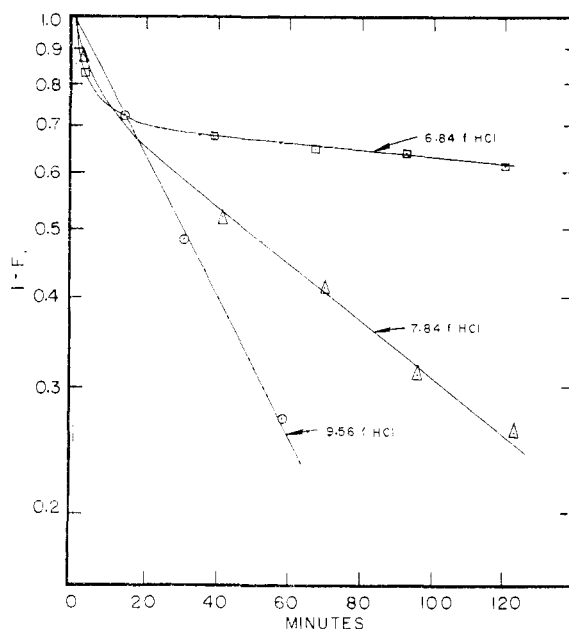


Fig. 2.—Some typical exchange curves: 0.0198 *f* Sb(III), 0.0206 *f* Sb(V), 25°.

as SbCl<sub>6</sub><sup>-</sup>, SbCl<sub>4</sub><sup>-</sup>, etc. In solutions of lower HCl concentration, the actual HCl concentration may be somewhat greater than the formal value because of hydrolysis of the antimony ions.

Some of the exchange curves for experiments described in this section are shown in Fig. 2. Definite curvature is observed for the experiments in 6.84 and 7.84 *f* HCl, indicating that the exchange reaction is complex. It appears that there is an initial rapid exchange upon mixing the antimony solutions in this concentration range, followed by a slower exchange. The half-times recorded in Table I were obtained from the slopes of the straight portions of the curves (*i.e.* at late times); no attempt was made to resolve the curves into their two components. Spectrophotometric evidence indicates that there are several species of Sb(V) ions present in the HCl concentration range concerned and that these species do not equilibrate rapidly. If some of these Sb(V) species exchange rapidly with Sb(III), while other species exchange only slowly, a complex exchange curve will be observed.

Exchange curves at 9.56 *f* and higher HCl concentrations showed no sign of curvature.

**Effect of Antimony Concentration on the Exchange Rate. Effects in Concentrated HCl.**—Table II shows the results obtained when the concentrations of Sb(III) and Sb(V) were varied independently in 11.8 *f* HCl solution. When the data are plotted as log *R* vs. log (Sb<sup>III</sup>) with the Sb(V) concentration held constant at 0.0228 *f* and log *R* vs. log (Sb<sup>V</sup>) with the Sb(III) concentration held constant at 0.0129 *f*, the slopes of the lines in the two curves are each 0.98 ± 0.04, indicating unit dependence of the exchange rate on the concentration of each oxidation state of antimony. The average value of the rate constant is 0.34 *f*<sup>-1</sup> min.<sup>-1</sup>.

TABLE II  
DEPENDENCE OF EXCHANGE RATE ON ANTIMONY CONCENTRATIONS IN CONCENTRATED HCl AT 25°

Sb(III), <i>f</i>	Sb(V), <i>f</i>	<i>t</i> / <i>s</i> , min.	$R \times 10^3$ , $f \times \text{min.}^{-1}$	$k, f^{-1} \times$ $\text{min.}^{-1}$
0.0129	0.00127	153	0.524	0.32
.0129	.00254	126	1.17	.36
.0129	.0052	110	2.33	.35
.0129	.0209	61.8	8.95	.33
.0129	.0228	56.5	10.1	.35
.0129	.0603	32.5	22.7	.29
.00258	.0228	78.0	2.06	.35
.0258	.0228	41.5	20.2	.34
.0402	.0400	25.0	55.6	.35

**Effects in 9.5 *f* HCl.**—In view of Bonner's<sup>3</sup> results in 6 *f* HCl and the results in concentrated HCl, it is apparent that the exchange mechanisms at the two HCl concentrations are different. In addition to the different effects of varying the HCl concentration in the two ranges, there are different dependences on the concentration of Sb(III), *i.e.*, 0.6 in 6 *f* HCl and 1.0 in concentrated HCl. Because of these differences, it was decided to measure the antimony dependences at an intermediate HCl concentration. The concentration of 9.5 *f* was chosen because of the interest in knowing the dependences at the maximum exchange rate and because the rates at this concentration would be least sensitive to the inevitable slight fluctuations of HCl concentration.

The factor actually held constant at 9.5 *f* was the total chloride. The formal concentration of HCl varied from 9.1 to 9.4. Variation of the HCl concentration in this range should not appreciably influence the rate of exchange.

Table III presents the results. For reactions in which the concentration of Sb(V) was kept constant at 0.0324 *f*, the plot of log (Sb<sup>III</sup>) *vs.* log

TABLE III  
DEPENDENCE OF EXCHANGE RATE ON ANTIMONY CONCENTRATIONS IN ~9.5 *f* HCl AT 25° (9.5 *f* Cl<sup>-</sup>)

Sb(III), <i>f</i>	Sb(V), <i>f</i>	<i>t</i> / <i>s</i> , min.	$R \times 10^3$ , $f \times \text{min.}^{-1}$	$k, f^{-1} \times$ $\text{min.}^{-1}$	$k', f^{-0.9}$ $\times \text{min.}^{-1}$
0.0305	0.0206	25.8	33.1	0.53	0.37
.0310	.0020	39.0	3.34	.54	.38
.0310	.0700	13.6	112	.52	.36
.000208	.0324	18.6	0.770	1.14	.49
.00052	.0324	28.0	1.27	0.754	.35
.00104	.0324	27.1	2.58	.77	.38
.00208	.0324	29.4	4.61	.68	.37
.00312	.0324	29.4	6.71	.66	.37
.00724	.0324	29.3	14.0	.60	.36
.0320	.0324	19.3	57.8	.56	.40
.0198	.0206	31.0	22.6	.55	.37
.0198	.0406	20.0	46.1	.57	.39
.0630	.0324	15.3	96.9	.47	.36
.00513	.0208	46.3	6.17	.58	.34
.01026	.0208	40.5	11.7	.55	.35
.0205	.0208	27.5	26.0	.61	.41
.0513	.0208	18.8	54.6	.51	.38
.1026	.0208	12.7	94.5	.44	.35

*R* has a slope of  $0.89 \pm 0.03$ . In this set of reactions, Sb(III) tracer was used. The determination of the dependence on Sb(III) was repeated, using an entirely different set of solutions, with

Sb(V) tracer. The logarithmic plot for these, the last five entries in the table, has a slope of  $0.91 \pm 0.04$ . The two determinations are in good agreement, and we believe that the deviation from unit dependence on Sb(III) is real. The last two columns in the table show the approximate constancy of

$$k' = \frac{R}{(\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}})^{0.90}}$$

compared to the variation of

$$k = \frac{R}{(\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}})}$$

Disregarding the discordant value of 0.49, the average value of *k'* for seventeen determinations is  $0.37 \pm 0.02$ , where the uncertainty is the root mean square deviation from the mean. Thus a satisfactory rate law in 9.5 *f* HCl at 25° is

$$R = 0.37(\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}})^{0.90} f \text{ min.}^{-1}$$

since the data indicate unit dependence on the concentration of Sb(V).

**Effect of Sb(III) Concentration in 4 *f* HCl.**—The determination of the dependence of the exchange rate on Sb(III) at various HCl concentrations down to 6 *f* indicated that the dependence might be decreasing continuously with decreasing HCl concentration. In order to test this possibility further, an attempt was made to determine the dependence on Sb(III) at an even lower HCl concentration.

Results of exchange experiments in 4 *f* total chloride are presented in Table IV. As indicated by the data, the reactions were exceedingly slow. The recorded rates and half-times were calculated

TABLE IV  
DEPENDENCE OF EXCHANGE RATE ON Sb(III) CONCENTRATION IN ~4 *f* HCl (4.00 *f* Cl<sup>-</sup>) AT 25°

Sb(III), <i>f</i>	Sb(V), <i>f</i>	<i>t</i> / <i>s</i> , days	$R \times 10^3$ , $f \times \text{day}^{-1}$
0.0276	0.0133	332	18.7
.0147	.0133	557	8.7
.00433	.0133	630	3.6
.00175	.0133	630	1.7

from the slopes of the exchange curves. The progress of the exchange was followed for only 115 days, a period short compared with the apparent half-times. Because of this and because of uncertainties as to the constancy of composition of such solutions over long periods of time, the results must be interpreted with caution.

It should be noted that the total chloride, and not the HCl concentration, was held constant at 4.00 *f*. The small changes in HCl concentration attending changes in Sb(III) concentration very probably have appreciable effects on the exchange rates. The logarithmic plot for the uncorrected rates has a slope of  $0.8 \pm 0.2$ . No quantitative corrections were attempted, since the effect of varying the HCl concentration has not been investigated in this range. It is reasonably certain, however, that the rate increases with increasing HCl concentration. The effect of correcting the rates for variations in HCl concentration would be an increase in the slope. It thus seems reasonable to believe that as the HCl

concentration decreases below 6 *f*, the Sb(III) dependence increases again rather than continuing to decrease.

**Effect on the Exchange Rate of Varying the Chloride Concentration.**—Several runs were made in which the hydrogen-ion concentration was held approximately constant at 5.8 *f* and the chloride concentration was varied by adding different amounts of 9.18 *f* LiCl solution. The data, presented in Table V, indicate a very marked increase in the exchange rate with increasing chloride concentration. It should be noted that the ionic strength was not held constant in this set of experiments.

TABLE V

EFFECT OF VARYING THE CHLORIDE CONCENTRATION ON THE EXCHANGE RATE AT 25°

(0.0205 <i>f</i> Sb(III), 0.0208 <i>f</i> Sb(V), 5.8 <i>f</i> H <sup>+</sup> )			
Total Cl <sup>-</sup> , <i>f</i>	Li <sup>+</sup> , <i>f</i>	<i>t</i> <sub>1/2</sub> , min.	<i>R</i> × 10 <sup>5</sup> , <i>f</i> × min. <sup>-1</sup>
6.0	0.0	4080	0.176
6.9	0.9	525	1.36
8.8	2.8	38.0	18.8
10.6	4.6	20.4	35.1

**Effect on the Exchange Rate of Varying Hydrogen Ion Concentration.**—With total chloride and antimony concentrations held constant, several experiments were performed to determine the effect of varying the hydrogen-ion concentration. This was done by adding calculated amounts of LiOH in preparing the solutions. Table VI presents the results. As noted for the last experiment listed, the chloride and antimony concentrations are slightly different from those of the other experiments. The very marked effect of the chloride concentration on the exchange rate at low acid concentrations makes an accurate correction difficult. Results of the other three exchange experiments, however, indicate a slight decrease in the exchange rate with increasing hydrogen-ion concentration.

It should be noted that the formal ionic strength was held constant at about 9.5 *f* for these experiments.

**Determination of Activation Energies.**—Experiments were performed in 9.3 *f* HCl and in concentrated HCl to determine the effect of temperature changes on the exchange rate. The results are presented in Table VII. The experimental activation energies calculated from the data are 18.4 and 17.2 kcal. per mole in 9.3 and 11.8 *f* HCl, respectively. The respective frequency factors from the Arrhenius equation are  $1.12 \times 10^{13} f^{-0.9} \text{ min.}^{-1}$  and  $1.39 \times 10^{12} f^{-1} \text{ min.}^{-1}$

Satisfactory rate laws in the temperature and concentration ranges investigated are, for 9.3 *f* HCl

$$R = (\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}}) 0.90 \times 1.12 \times 10^{13} e^{-18400/RT} f \text{ min.}^{-1}$$

and for 11.8 *f* HCl

$$R = (\text{Sb}^{\text{V}})(\text{Sb}^{\text{III}}) 1.39 \times 10^{12} e^{-17200/RT} f \text{ min.}^{-1}$$

#### Surface and Light Effects on the Exchange Rate.

—Three exchange experiments were carried out with identical solutions, one in the usual manner, one in a black flask and one in a 100 ml. flask packed

with glass beads. As indicated in Table VIII, the rates were all the same, within experimental error. There are, therefore, no appreciable effects due to surface area or illumination under the usual conditions.

TABLE VI

EFFECT OF VARYING THE HYDROGEN-ION CONCENTRATION ON THE EXCHANGE RATE AT 25°

(0.0162 *f* Sb(III), 0.0166 *f* Sb(V), 9.5 *f* total chloride)

H <sup>+</sup> , <i>f</i>	<i>t</i> <sub>1/2</sub> , min.	<i>R</i> × 10 <sup>5</sup> , <i>f</i> × min. <sup>-1</sup>
6.8	32.5	17.5 <sup>a</sup>
8.3	36.2	15.8 <sup>b</sup>
9.4	39.0	14.6
4.3	38.2	14.7 <sup>c</sup>

<sup>a</sup> The solution also contained 2.6 *f* lithium ion. <sup>b</sup> The solution also contained 1.1 *f* lithium ion. <sup>c</sup> The solution contained 5.1 *f* lithium ion, and the chloride and Sb(V) concentrations were slightly different, *i.e.*, 9.3 and 0.0160 *f*, respectively.

TABLE VII

EFFECT OF TEMPERATURE ON EXCHANGE RATES

Temp., °C.	HCl, <i>f</i>	Sb(III), <i>f</i>	Sb(V), <i>f</i>	<i>t</i> <sub>1/2</sub> , min.	<i>R</i> × 10 <sup>5</sup> , <i>f</i> × min. <sup>-1</sup>
0.1	11.8	0.0129	0.0209	899	0.615
16.2	11.8	.0129	.0209	156	3.56
25.0	11.8	.0129	.0209	61.8	8.95
35.7	11.8	.0129	.0209	23.4	23.6
0.6	9.3	.0205	.0208	492	1.45
25.0	9.3	.0205	.0208	27.5	26.0
35.1	9.3	.0205	.0208	11.5	62.3

TABLE VIII

SURFACE AND LIGHT EFFECTS ON THE EXCHANGE RATE AT 25°

(0.0205 *f* Sb(III), 0.0208 *f* Sb(V), 9.3 *f* HCl)

Conditions	<i>t</i> <sub>1/2</sub> , min.	<i>R</i> × 10 <sup>5</sup> , <i>f</i> × min. <sup>-1</sup>
Usual	27.5	26.0
Black flask	28.0	25.5
Flask packed with glass beads	28.4	25.2

#### Discussion

Because most of the data obtained in the work described here have been presented by Neumann and Brown,<sup>9</sup> this paper is being published principally to make the experimental details available. The accompanying paper by Bonner and Goishi<sup>10</sup> discusses the results and their interpretation in detail.

In the thesis from which this paper has been abstracted quite a bit of spectrophotometric data are described. These data are not included here because later more precise work by Neumann and Ramette<sup>11</sup> and Bonner and Goishi have superseded it.

The most important observations and conclusions drawn from this work are (a) complex exchange curves have been observed in the 6.5 *f* to 8 *f* HCl region and (b) the complex nature of the exchange can be explained by the existence of at least two Sb(V) species with slow rates of interconversion.

(9) H. M. Neumann and H. Brown, *THIS JOURNAL*, **78**, 1843 (1956).

(10) N. A. Bonner and W. Goishi, *ibid.*, **83**, 85 (1961).

(11) H. M. Neumann and R. W. Ramette, *ibid.*, **78**, 1848 (1956).