appear to be strong enough bases to rupture both bonds of Al_2Cl_6 and form strong colorless complexes of the type $R_2O{\cdot}AlCl_3$.

As might be expected, perfluorodibutyl ether forms no complex with aluminum chloride because of low basicity brought on by the presence of the fluorine atoms.

COLUMBUS, OHIO

[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rate of Radioactive Exchange between Antimony(III) and Antimony(V) in Hydrochloric Acid Solution[1]

BY H. M. NEUMANN AND HARMON BROWN

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By use of the known equilibrium and kinetic data on the Sb(V) system it is demonstrated that all of the exchange results can be interpreted on the assumption that $SbCl_6^-$ is the only species of Sb(V) that exchanges with Sb(III). The observed complexities of the exchange reaction result from the fact that under certain conditions the rate of formation of $SbCl_6^-$ is rate determining, while under other conditions the exchange process itself is rate determining. By performing the exchange reaction at conditions where chemical equilibrium does not exist, it is possible to show that the rate of exchange between $SbCl_6^-$ and Sb(III) decreases with increasing acidity. It is suggested that $SbCl_3$ is the exchangeable form of Sb(III), and some possible transition states are discussed.

The first work on the radioactive exchange between Sb(III) and Sb(V) in hydrochloric acid solution was that of Bonner.[2] The complexity of the system is apparent from the empirical rate law that he proposed: rate = $k[\text{Sb(III)}]^{0.6} \times [\text{Sb(V)}]^{1.1} \times [\text{Cl}^-]^9[\text{H}^+]^4$. Subsequently Cheek[3] has made a more extensive study of this system.

It will be demonstrated in this paper that most of the complexities of the system arise from the behavior of the Sb(V). Although a few new exchange experiments are reported, the primary purpose will be to correlate the known equilibrium[4] and kinetic[5] behavior of Sb(V) with the previous results of Bonner and Cheek.

It has been suggested[3] that possibly not all forms of Sb(V) are capable of exchanging with Sb(III), and that, as a result, the rate of formation of the exchangeable form might be the rate-determining step in the observed exchange. If this position were true it became most reasonable to assume that $SbCl_6^-$ was the exchangeable form. The data suggesting this assumption were: (1) the great increase in exchange rate with increasing acidity[2]; (2) the increasing equilibrium amounts of $SbCl_6^-$ at increasing acidity[4]; and (3) the slow rate of formation of $SbCl_6^-$, particularly at low acidities.[4] An additional argument is that $SbCl_6^-$ is the only form of Sb(V) reduced reversibly at the rotating platinum electrode,[5] and it is a general observation that reversible electrode reduction and radioactive exchange in these systems generally coincide.

Two preliminary exchange experiments were performed to test this hypothesis. In one experiment the Sb(V) added to the reaction mixture had been allowed to come to equilibrium in 6 *M* HCl, the acidity of the ultimate exchange mixture. In the second the Sb(V) came from a 12 *M* HCl solution, and hence was present entirely as $SbCl_6^-$. The experimental conditions for the exchange were then the same except for the form in which the Sb(V) was present. The first reaction had a half-time of 49 hours; the second a half-time of 12 min. This evidence clearly pointed to $SbCl_6^-$ as the exchangeable form of Sb(V).

Practically all exchange experiments of this type are performed in systems at chemical equilibrium, and this was the case in the work of Bonner and Cheek, and in the first of the two experiments just described. For acidities, like 6 *M* HCl, where the equilibrium amount of $SbCl_6^-$ is small, and the rate of formation of $SbCl_6^-$ slow, the rate of exchange is often determined by the rate of formation of $SbCl_6^-$, and hence such experiments do not give information about the exchange process itself.

To learn about the exchange process itself requires the experiment to be performed under non-equilibrium conditions, such as the second of the two experiments described above. It is true that there is a difficulty in that one must take into account the changing amount of $SbCl_6^-$; this difficulty will be considered when necessary.

Experimental

Reagents.—The radioactive tracer was the 60 day Sb^{124}, obtained from Carbide and Carbon Chemicals Co., Oak Ridge National Laboratory. It was obtained as the processed material, stated to be greater than 95% pure from a radiochemical point of view. It was further purified by reduction to Sb(III), extraction with isopropyl ether from hydrochloric acid solution to remove extractable impurities, oxidation to Sb(V), extraction of the Sb(V) into isopropyl ether, and back-extraction into water. Other reagents used in the exchange reaction were Baker and Adamson reagent grade $SbCl_3$ and $SbCl_5$, Baker Analyzed reagent hydrochloric acid, and Mallinckrodt analytical reagent LiCl.

Non-equilibrium Exchange Experiments.—A stock solution 0.0916 *M* in Sb(V), and containing the radioactive Sb^{124}, was prepared in concentrated HCl. A stock solution 0.104 *M* in Sb(III) was prepared in concentrated HCl. Two ml. of the Sb(III) stock solution was placed in a 10-ml. volumetric flask, and slightly less than six ml. of a hydrochloric acid solution added. The concentration of hydrochloric acid was such as to give approximately the final desired acidity. These solutions were thermostated at 25°. At what was considered zero time for the reaction 2 ml. of the Sb(V) stock solution was added, followed by hydrochloric acid until the volume was 10 ml. For expt. 4 the Sb(III) stock solution was 0.104 *M* in Sb(III), but it was in 2.4 *M* hydrochloric acid.

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[1] Presented in part at the Kansas City meeting of the American Chemical Society, March, 1954.

[2] N. A. Bonner, THIS JOURNAL, **71**, 3909 (1949).

[3] C. H. Cheek, Ph.D. thesis, Washington University, St. Louis, January, 1953.

[4] H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

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

At various time intervals 1-ml. aliquots were removed, the acidity adjusted to approximately 9 *M* by the addition of hydrochloric acid, and the Sb(V) extracted into isopropyl ether. During the time necessary for the extraction (about 1 min.) all of the Sb(V) is converted to extractable species. The two phases were placed in stoppered centrifuge cones, and the radioactivity determined by placing the cones in reproducible positions with respect to a Geiger-Müller counter. The half-time for each exchange was determined graphically by plotting log $(A - A_\infty)$ *vs.* time, where A is the activity. The infinite time samples were taken variously from 2–4 hours after beginning the reaction. The acidity was determined for each reaction mixture by titrating a 500-microliter aliquot with standard NaOH.

Equilibrium Exchange Experiments.—Two sets of experiments were performed under equilibrium conditions, one in 6 *M* HCl, and one in 11.7 *M* HCl. The methods of separation and counting were the same as those for the non-equilibrium experiments. Since the purpose of the experiment in 6 *M* HCl was to determine the effect of change in Sb(III) concentration, it was desirable to maintain all other concentrations constant. Because both the Sb(III) and Sb(V) are forming complexes of varying kind and amount it is difficult to know exactly the composition of the solution. The stock solutions of Sb(III) and Sb(V) were made up by dissolving $SbCl_3$ and $SbCl_5$, respectively, in 6 *M* HCl. It was assumed that the Sb(III) was present as $SbCl_4^-$, hence $[H^+] = 6$, and $[Cl^-] = 6 - [Sb(III)]$. Although the Sb(V) is present as a mixture of various hydrolytic products of $SbCl_6^-$, it was assumed that $Sb(OH)_2Cl_4^-$ represented the average extent of hydrolysis, and hence that $[H^+] = 6 + 2[Sb(V)]$ and $[Cl^-] = 6 + [Sb(V)]$. The amount of H^+ and Cl^- added from the aliquots of Sb(III) and Sb(V) stock solutions was then known, and the necessary remaining amounts for the reaction were added from HCl and LiCl stock solutions by means of a buret.

Results

Exchange under Non-equilibrium Conditions.—Table I gives the results of the experiments where the Sb(V) was added initially as $SbCl_6^-$. Because of the difficulty of temperature control due to heat of mixing no great claims of accuracy can be made, particularly for expt. 4. The value of k_x was calculated from the half-time (T_x) assuming a bimolecular reaction, *i.e.*, that the rate of exchange $= k_x[SbCl_6^-][Sb(III)] = k_x[Sb(V)][Sb(III)]$. This calculation ignores the fact that the concentration of $SbCl_6^-$ changes during each experiment, and the half-times (T_h) of hydrolysis of $SbCl_6^-$, known from data of the accompanying paper,[5] are included in the table to indicate how rapidly $[SbCl_6^-]$ is changing. In expts. 1 and 2 the fairly rapid attainment of equilibrium is balanced by the fact that the per cent. of Sb(V) present as $SbCl_6^-$ at equilibrium is large (97% in 10.8 *M* HCl, 67% in 8.8 *M* HCl). In expt. 3 the equilibrium per cent. of $SbCl_6^-$ is small (1%), but the half-time for the hydrolysis is long relative to that of the exchange, so that during the period of the exchange the concentration of $SbCl_6^-$ is not changing greatly. In expt. 4 the concentration of $SbCl_6^-$ is changing appreciably while the exchange is occurring so that k_x is only known approximately. Because of the approximations involved it is difficult to assess the likely accuracy of these values of k_x. It is felt that the values for expts. 1, 2 and 3 are probably correct within 20%, and the value for expt. 4 correct within a factor of two.

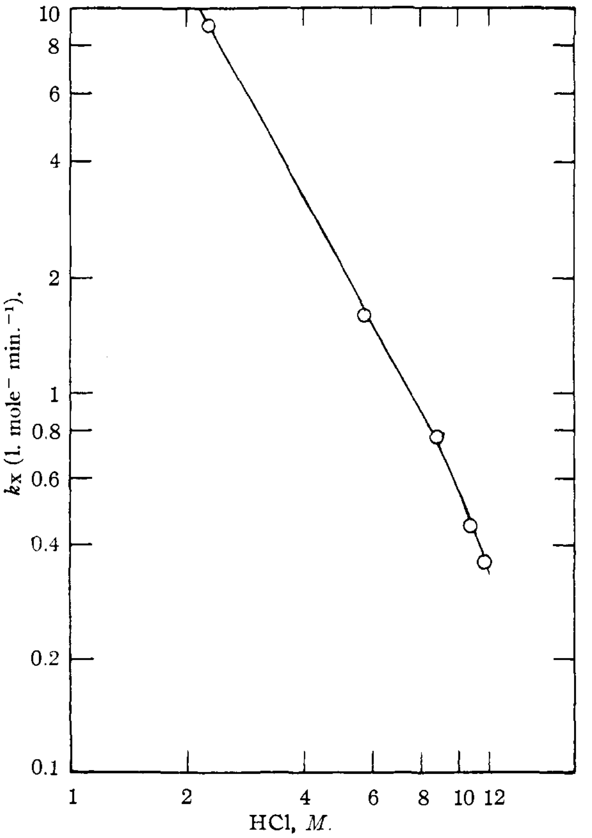


Fig. 1.—Rate constant for exchange between Sb(III) and $SbCl_6^-$ as a function of HCl concentration.

TABLE I

Expt.	HCl, *M*	T_x (min.)	k_x (l. mole^{-1} min.$^{-1}$)	T_h (min.)
1	10.8	39	0.45	25[a]
2	8.8	23	0.77	37
3	5.8	11	1.6	70
4	2.3	2	9	4.5

[a] Estimated by extrapolation.

The importance of expt. 4, in spite of the limitations indicated, arises in the following way. The effect of Sb(III) on the hydrolysis of $SbCl_6^-$ has been attributed to the ability of the Lewis acid $SbCl_3$ to abstract a chloride ion from $SbCl_6^-$. Hence a transition state of the form $Cl_5Sb\text{–}Cl\text{–}SbCl_3]^-$ is indicated. The question then arises as to whether this same transition state is responsible for exchange, particularly since both hydrolysis and exchange show increasing rate with decreasing acidity. A negative answer is indicated by the following argument. Using the data from the hydrolysis, the value of $(k_h - k_0)$, which is a measure of the concentration of the transition state $Cl_5Sb\text{–}Cl\text{–}SbCl_3^-$, is 91 times greater in 2.3 *M* HCl than in 5.8 *M* HCl. In the exchange experiment in 5.8 *M* HCl the half-time was 11 min. If the transition state responsible for hydrolysis were also responsible for exchange then the half-time for exchange in 2.3 *M* HCl should be about 0.1 min. This would mean that by the time the first sample was withdrawn (2 min. after mixing), complete exchange should have been observed. Such was not the case, and hence the transition state leading to exchange is different from that leading to hydrolysis.

Figure 1 shows these values of k_x as a function of the HCl concentration.

Equations Applicable to Equilibrium Experiments.—The observed rate of exchange at low acidities, in the system at chemical equilibrium, will appear complicated because at some extreme condition the rate of exchange will be determined by the rate of formation of $SbCl_6^-$; at the other extreme the rate will be determined by the actual exchange between $SbCl_6^-$ and the exchangeable form of Sb(III); and for some intermediate region both rates will be comparable. The mathematics of the two extreme cases are simple and will be indicated. In this C represents the exchangeable form of Sb(III), A represents $SbCl_6^-$, and B represents all species of Sb(V) other than $SbCl_6^-$. The following notation will be used: $S_A = [A^*]/[A]$, $S_B = [B^*]/[B]$, $S_C = [C^*]/[C]$, $F_A = [A]/([A] + [B])$, $F_B = [B]/([A] + [B])$. General equations that will be satisfied in any case are

$$[A^*] + [B^*] + [C^*] = [A^*]_\infty + [B^*]_\infty + [C^*]_\infty \quad (1)$$

$$\frac{d[A^*]}{dt} + \frac{d[B^*]}{dt} + \frac{d[C^*]}{dt} = 0 \quad (2)$$

Since the system is at chemical equilibrium, [A], [B] and [C] will be constant.

Case I: Rate of exchange governed by rate of formation of $SbCl_6^-$.

$$B \underset{}{\overset{R_F}{\rightleftarrows}} A \quad (3)$$

$$A^* + C \overset{\text{rapid}}{\rightleftarrows} C^* + A \quad (4)$$

$$\frac{d[B^*]}{dt} = R_F(S_A - S_B)$$

where R_F is the constant rate of formation of A, and, because the system is at equilibrium, also the constant rate of hydrolysis of A. Equation 4 means that $S_A = S_C$, and hence that

$$\frac{d[A^*]}{dt} = \frac{[A]}{[C]}\frac{d[C^*]}{dt}$$

Combination of this fact with equation 2 gives

$$\frac{d[B^*]}{dt} = \frac{-\{[A] + [C]\}}{[C]}\frac{d[C^*]}{dt}$$

and

$$\frac{d[C^*]}{dt} = \frac{-[C]R_F}{[A] + [C]}(S_C - S_B)$$

$$\frac{dS_C}{dt} = \frac{-R_F}{[A] + [C]}(S_C - S_B)$$

Equation 1 can be converted to show that

$$S_C - S_B = \frac{[A] + [B] + [C]}{[B]}(S_C - S_{C\infty})$$

The resulting differential equation is

$$\frac{d(S_C - S_{C\infty})}{dt} = \frac{dS_C}{dt} = \frac{-R_F\{[A] + [B] + [C]\}}{\{[A] + [C]\}[B]}(S_C - S_{C\infty})$$

which has the solution

$$\ln|S_C - S_{C\infty}| = \frac{-R_F\{[A] + [B] + [C]\}}{\{[A] + [C]\}[B]}t + \ln|S_{C_0} - S_{C\infty}|$$

The observed half-time, T_{XF}, obtained from plotting $\log|S_C - S_{C\infty}|$ *vs.* t will be related to the constants in the second term by the expression

$$T_{XF} = \frac{0.693[B]\{[A] + [C]\}}{\{[A] + [B] + [C]\}R_F}$$

Now R_F is not only the rate of formation of $SbCl_6^-$, but also its rate of hydrolysis, so that

$$R_F = k_h[A] = 0.693[A]/T_h$$

where T_h is the half-time for hydrolysis at the same temperature as the exchange. Finally

$$T_{XF} = \frac{[B]\{[A] + [C]\}}{\{[A] + [B] + [C]\}[A]}T_h = \frac{\{[A] + [C]\}F_B}{\{[A] + [B] + [C]\}F_A}T_h$$

Case II: Rate of exchange governed by actual rate of exchange between $SbCl_6^-$ and the exchangeable form of Sb(III).

$$B \overset{\text{rapid}}{\rightleftarrows} A \quad (5)$$

$$A^* + C \overset{R_X}{\rightleftarrows} C^* + A \quad (6)$$

The derivation here is essentially the same as the usual derivation of the exchange law, leading to the result that

$$\frac{d(S_C - S_{C\infty})}{dt} = \frac{R_X\{[A] + [B] + [C]\}}{\{[A] + [B]\}[C]}(S_C - S_{C\infty})$$

with solution

$$\ln|S_C - S_{C\infty}| = \frac{-R_X\{[A] + [B] + [C]\}}{\{[A] + [B]\}[C]}t + \ln|S_{C_0} - S_{C\infty}|$$

with $R_X = k_X[A][C]$. The observed half-time, T_{XX}, will be given by

$$T_{XX} = \frac{0.693}{k_X\{[A] + [B] + [C]\}F_A}$$

Comparison with Equilibrium Exchange Data.—Sufficient data are available to attempt to calculate the exchange rates predicted by the two models for any given experiment. Good values of T_h are known from the data of the accompanying paper,[5] k_X can be taken from Fig. 1, and F_A, F_B and [A] should be obtainable from the equilibrium data on the Sb(V) system.[4] Calculation of F_A from the equilibrium data required certain assumptions about the spectra of the various Sb(V) species, and the reliability of these assumptions has been discussed in connection with the kinetic data.[5] Since the kinetic data seemed to be more reliable for determining the relative concentrations of $SbCl_6^-$ and $Sb(OH)Cl_5^-$, the equilibrium constant

$$K = \frac{[Sb(OH)Cl_5^-](a_{HCl})^2}{[SbCl_6^-]a_{H_2O}} = 2.2 \times 10^4$$

obtained from the kinetic data, has been used to calculate F_A and F_B for acidities where $SbCl_6^-$ and $Sb(OH)Cl_5^-$ are the only forms of Sb(V) present. For acidities where other hydrolytic forms are also present it is still necessary to use the spectral data. Largest errors in F_A will then exist for HCl concentrations less than 9 *M*.

As a test of this proposed interpretation of the exchange results calculations of T_{XF} and T_{XX} have been made corresponding to those experiments of Bonner[2] which were done at 25° in solutions which did not contain added chloride salts. The results and some of the important quantities involved in the calculation are given in Table II. When T_{XX} and T_{XF} differ greatly, the larger value of the two is taken as the predicted half-time, T_{XP}. When

T_{XX} and T_{XF} are about the same neither of the mathematical models are applicable, and the actual half-life would be larger than T_{XX} or T_{XF}. In those cases where T_{XX} and T_{XF} are within a factor of two, T_{XP} is listed in the table as the larger value of the two with a + sign added to indicate that the expected value is greater than that calculated from the simple model. The agreement is as good as can be expected considering the limitations in the knowledge of F_A.

Table II

Half-times Predicted for Sb(III)–Sb(V) Exchange

Expt.[a]	F_A	T_h (hr.)	k_X (l. mole^{-1} min.$^{-1}$)	Half-times (hr.) T_{XF}	T_{XX}	T_{XP}	T_X[a]
1	0.0070	1.15	1.68	86	24	86	97.2
2	.0040	1.09	1.83	143	38	143	178.5
7	.0150	1.15	1.52	73	23	73	90.5
8	.0145	1.15	1.53	58	17	58	75.5
9	.0130	1.15	1.56	47	14	47	55.5
10	.0100	1.16	1.60	42	12	42	40.2
11	.0155	1.27	1.52	4.4	24	24	20.8
12	.0145	1.22	1.53	27	18	27+	41.0
13	.0120	1.14	1.58	51	14	51	53.0
14	.0080	1.00	1.62	65	11	65	47.5
15	.0130	1.16	1.54	46	14	46	49.0
16	.0105	1.16	1.59	55	16	55	60.5
17	.0120	1.15	1.57	49	15	49	49.5
18	.0160	1.21	1.51	41	28	41+	74.8
19	.0160	1.22	1.51	37	28	37+	62.0
20	.0105	1.16	1.59	55	16	55	61.5

[a] Experimental values from Bonner.[2] See that paper for additional details about composition of solutions.

Dependence on Concentration of Sb(III).—In addition to demonstrating the general validity of this interpretation, the results of Table II clearly point out how the fractional power dependence on [Sb(III)] arose. Experiments 11, 12 and 13 were alike except in the concentration of Sb(III), and their results lead to the $[\mathrm{Sb(III)}]^{0.6}$ term in the rate expression. It can be seen that these experiments cover a concentration range in which the transition from case I to case II occurs.

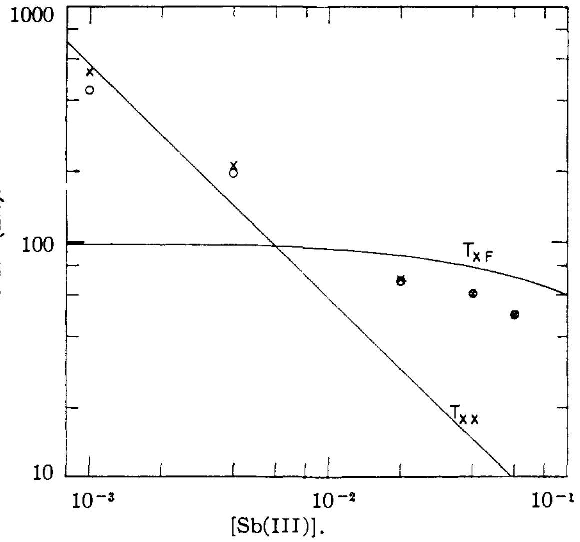


Fig. 2.—Dependence of the exchange rate on Sb(III) concentration in 6.0 M HCl. For case I: $T{\cdot}R$ is $T_X \dfrac{[A] + [B] + [C]}{[A] + [C]}$. the experimental points denoted by 0, and the curve T_{XF} gives the calculated values. For case II: $T{\cdot}R$ is $T_X \dfrac{[A] + [B] + [C]}{[C]}$, the experimental points denoted by X, and the curve T_{XX} gives the calculated values. The calculated values are based on F_A being equal to 0.013.

That the appearance of this transition does not occur as a result of the values chosen for F_A is apparent if one considers the conditions under which $T_{XF} = T_{XX}$. Using an average value of T_h of 1.2 hours, and using the approximations $\{[A] + [C]\} = [C]$ and $F_B \simeq 1$

$$T_{XF} \simeq \frac{1.2\,[C]}{\{[A] + [B] + [C]\}F_A}\ \text{hr.}$$

Using an average value of $k_X = 1.55$ l. min.$^{-1}$

$$T_{XX} \simeq \frac{0.0074}{\{[A] + [B] + [C]\}F_A}\ \text{hr.}$$

The same half-time is predicted by the two cases for

$$[C] \simeq \frac{0.0074}{1.2} = 0.006$$

In 6 M HCl the rate of exchange is then expected to be rate determining for $[C] << 0.006$, and the rate of formation of $SbCl_6^-$ is expected to be rate determining for $[C] >> 0.006$.

To make more clear this dependence of the observed exchange rate on the Sb(III) concentration, the equilibrium experiments in 6 M HCl already described were performed. The results are illustrated in Fig. 2. Case I predicts a plot of log $T_X([A] + [B] + [C])/([A] + [C])$ *vs.* log [C] should give a slope near zero. (It will not be zero because the hydrolysis of $SbCl_6^-$ is not independent of [Sb(III)].) Case II predicts that a plot of log T_X (([A] + [B] + [C])/[C]) *vs.* log [C] should give a slope of minus one. Although the second limiting condition is not realized in these experiments, the general behavior is that expected. It is easy to see that if one were not looking for these two regions of different behavior one would normally make the log (([A] + [B] + [C])/[C])T_X *vs.* log [C] plot and draw a straight line of slope 0.6 through the points.

The actual dependence of the exchange reaction on [Sb(III)] can be determined by performing the exchange in concentrated HCl. The results of these experiments are given in Table III. The constancy of k_x, calculated from

$$k_x = \frac{0.693}{T_x\{[A] + [B] + [C]\}}$$

(this is just case II with $F_A = 1.00$), demonstrates that the exchange is dependent on the first power of [Sb(III)] as would be expected. These experiments also provide the value of k_x in 11.7 M HCl shown in Fig. 1.

Table III

Exchange in 11.7 M HCl at 25°

[Sb(III)]	[Sb(V)]	T_x (min.)	k_X (l. mole^{-1} min.$^{-1}$)
0.003	0.010	140	0.38
.006	.010	126	.34
.010	.010	97	.36

Exchange at Equilibrium with Varying HCl Concentration.—Cheek[3] has reported the half-times for the exchange in HCl of varying concentration, when the Sb(III) concentration was 0.0198 *M* and the Sb(V) concentration was 0.0206 *M*. Calculations of T_{XF} and T_{xx}, corresponding to the conditions of these experiments, have been performed and the results shown in Fig. 3. As previously discussed, the actual half-life should correspond to the longer of the two predicted lives, or should be greater than either if both predictions are about the same. The results of Cheek can be seen to agree with the calculated values rather nicely. At acidities 9 *M* or higher the exchange process is rate determining, and at acidities lower than 7 *M* the formation process is rate determining. It should be kept in mind that the positions of the T_{XF} and T_{xx} curves are dependent on the Sb(III) and Sb(V) concentrations, and hence the point of crossing will not always be at 8.1 *M* HCl as it is in this case.

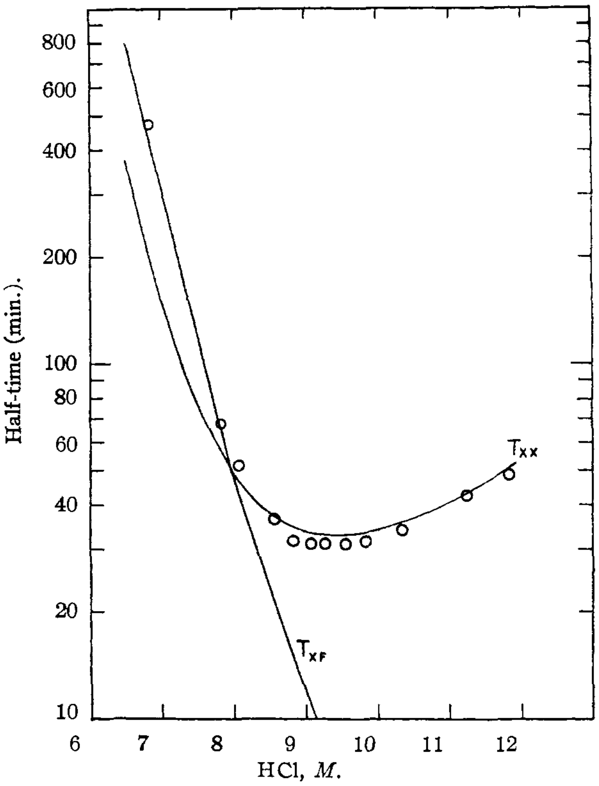
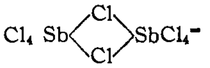


Fig. 3.—Observed half-time for exchange between Sb(III) and Sb(V) as a function of HCl concentration. The experimental points are those of Cheek, and the curves are the predicted values.

Discussion

Although the present interpretation clears up certain complexities of the observed exchange, there is still left unexplained why decreasing acidity leads to more rapid exchange between $SbCl_6^-$ and Sb(III). The exchange rate covers much too large a factor to attribute the decreasing rate at high acidities to the Sb(V) being present as non-exchangeable $HSbCl_6$, as such a position would require unreasonably large amounts of the latter to be present at high acidities, and would predict a leveling off of k_x at low acidities.

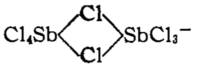
Most of the thinking in the past has considered exchange to occur between $SbCl_6^-$ and $SbCl_4^-$, not only because they are the best known and predominant species of the two oxidation states, but also because one can visualize a symmetric transition state



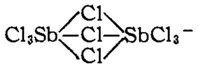
in which electron transfer is facilitated. The evidence clearly points to $SbCl_6^-$ as the exchangeable form of Sb(V), but there is no really good reason for supposing $SbCl_4^-$ is the exchangeable form of Sb(III). The assumption that $SbCl_3$ is the exchangeable form is probably more reasonable. The rather large dependence on HCl. concentration would then be the expected behavior. Furthermore, the formation of a transition state between $SbCl_3$, a neutral molecule, and $SbCl_6^-$, an anion, is more likely than between the two anions.

A transition state involving $SbCl_3$ and $SbCl_6^-$ already has been indicated to account for the effect on the hydrolysis of $SbCl_6^-$. This transition state is visualized to be $Cl_5Sb{-}Cl{-}SbCl_3^-$, *i.e.*, to have one bridging Cl atom. Electron transfer would not seem to be very probable for such a transition state, because transfer would leave the Sb(V) in an unlikely environment (coördination number four), and hence would require considerable energy.

If the number of bridging chlorine atoms is increased to two and three, one obtains the ions



and



which might well undergo exchange. The latter is particularly appealing because of its symmetry. Since all these transition states are formed from the same components, it would be expected that the hydrolysis would parallel the exchange. Experiment 4 of Table I indicates that this parallelism does not exist. Unfortunately the Sb(III) induced hydrolysis of $SbCl_6^-$ can only be studied conveniently at acidities less than 6 *M* and this is where the non-equilibrium exchange studies become least reliable. For the present then the nature of the transition state remains in doubt.

EVANSTON, ILLINOIS