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ACCELERATION OF THE ELECTRON EXCHANGE REACTION BETWEEN ANTIMONY TRICHLORIDE AND ANTIMONY PENTACHLORIDE IN CARBON TETRACHLORIDE BY ADDITION OF ANHYDROUS HYDROGEN CHLORIDE

Thesis for the Degree of M. S.
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Kenneth R. Price
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ABSTRACT

ACCELERATION OF THE ELECTRON EXCHANGE REACTION BETWEEN ANTIMONY TRICHLORIDE AND ANTIMONY PENTACHLORIDE IN CARBON TETRACHLORIDE BY ADDITION OF ANHYDROUS HYDROGEN CHLORIDE

by Kenneth R. Price

The electron exchange reaction between antimony trichloride and antimony pentachloride in anhydrous carbon tetrachloride has been studied in the presence of added anhydrous hydrogen chloride. In the absence of hydrogen chloride, Barker and Kahn (1) found the exchange to proceed by two paths; one path depended only on the concentration of antimony pentachloride and the other depended on the concentration of antimony trichloride and the concentration of antimony pentachloride squared.

The addition of hydrogen chloride was found to accelerate the exchange reaction beyond that predicted from the Barker and Kahn paths. A complex rate law was found that indicated a contribution by the Barker and Kahn paths plus a new path involving the hydrogen chloride. This third path involves antimony trichloride and hexachloroantimonic(V) acid. The rate law found was:

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[1] F. B. Barker and M. Kahn, J. Am. Chem. Soc., 78, 1317 (1956).

$$R = 1.6 \times 10^{-7}\,[SbCl_5] + 1.8 \times 10^{-4}\,[SbCl_3]\,[SbCl_5]^2 + 2.5 \times 10^{-5}\,[SbCl_3]\,[HSbCl_6]$$

The mechanism proposed involves the formation of a triply chloro-bridged diantimonate species consisting of two octahedra joined face to face. It is formed by the interaction of a hexachloroantimonic(V) acid molecule and an antimony trichloride molecule. The direct transfer of the electrons between the two bridged antimony species is likely.

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By

Kenneth R. Price

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FORWARD

Rather extensive studies of the antimony(III)-antimony (V) electron exchange reaction have been made in a variety of aqueous systems. In all cases, the system was found to be extremely complex due to competing hydrolytic reactions and the resulting complex equilibria produced.

To look more directly at the fundamental electron exchange reaction between antimony(III)-antimony(V), the exchange was studied in anhydrous carbon tetrachloride and two different paths for exchange were found to be operative.

The purpose of the present work was to study the effect of anhydrous hydrogen chloride on this exchange. There were some indications from earlier work that an accelerating effect could be expected and it was desired to learn something of the nature of this acceleration and its relation to oxidation-reduction reaction mechanisms in general.

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DEDICATION

To My Mother

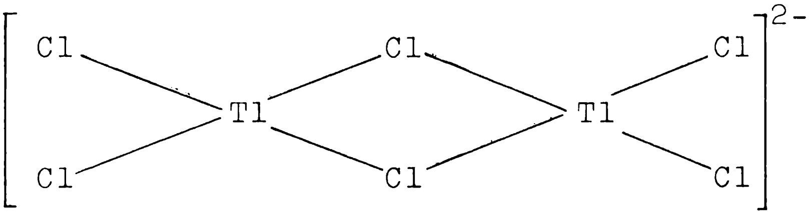
INTRODUCTION

One of the most active areas of research in inorganic chemistry is concerned with the study of the mechanisms of inorganic reactions. Oxidation-reduction reactions, though well known to all chemists, have not received much attention until comparatively recently.

Probably one of the most important factors that has led to intensive study of oxidation-reduction reactions has been the availability of a wide variety of radioactive tracers which has made it possible to study the electron transfer equilibria between two different oxidation states of the same element. A large number of reactions have been studied kinetically and mechanisms have been proposed. However, the actual mechanism by which the electrons themselves are transferred from one species to another is still to be understood.

Several different views concerning the actual transfer of the electrons have been advanced in recent years. Taube (1, 2, 3, 4, 5, 6) and his students have extensively studied the oxidation of chromium(II) by a large variety of monosubstituted pentamminecobalt(III) species of the type $[Co(NH_3)_5X]^{2+}$ where X has been chloride, bromide, nitrate, thiocyanate, acetate, pyrophosphate, sulfate, and various mono-and dicarboxylic acid anions. In these reactions, X, or part of it, is transferred to the reducing agent, i.e., X is found in the coordination sphere of chromium(III) at the conclusion of the electron transfer process. The work tends to support what has been formulated as the bridge mechanism of electron transfer. Here, the essential feature is that the bridge provides an appropriate route for flow of the electron between oxidant and reductant. The net transfer of atoms is not necessarily an essential feature. Whether or not this happens is related to the substitution lability of the ions left sharing the bridge after completion of the electron transfer process. In such reactions as that between chromium(II) and hexachloroiridate(IV), the bridging chloride remains with the iridium nucleus following the electron transfer. (11)

In a variety of oxidation-reduction systems (7, 8, 9, 10, 21), a catalysis effect by certain anions has been observed. This effect has usually been explainable in terms of the anion forming a bridge between the oxidant and reductant in the activated complex. Frequently a double bridge is postulated as in the thallium(I)-thallium(III) exchange in aqueous hydrochloric acid (7, 8).



Similar types of bridges have been proposed for activated complexes in the tin(II)-tin(IV) (12) exchange reaction and Brubaker and Mickel (10) have postulated sulfate bridging in the thallium(I)-thallium(III) exchange in aqueous sulfuric acid.

Libby (13) has interpreted the bridging role in electron transfer processes with emphasis on the controlling role of the Franck-Condon principle. In solution there is present a factor which tends to inhibit the transfer of electrons between species. This factor is the relative long time required for the re-orientation of the solvent molecules to the new environment compared to the fast movement of the electrons themselves. Hence the electron must make a transition against an energy barrier comparable in magnitude to the amount of energy required for the re-orientation of the solvent molecules to the new environment produced. The role of the bridge, according to Libby, then is to reduce this energy barrier by drawing closer together the two positive ions, causing their hydration spheres to intermingle and thereby reduce their dissimilarities. This contrasts to the Taube view of the bridge as an electron conductor. The electron conducting bridge concept has excellent support in the work of Taube on systems (4, 6) in which the bridge is designed with an extensive pi-electron network over which electrons can travel freely. Further support is found in the work of Wang and Brinigar (22) in their study of aerobic oxidation of cytochrome c. In their model for cytochrome c, they find rapid electron movement across a bridge of 1, 2-di-(4-pyridyl) ethylene and very little electron movement when the ethane derivative is employed as the bridging group.

It is rather difficult to define exactly the role of the bridge. More than likely, no one single interpretation will be adequate for all oxidation-reduction systems. The role of the bridge is probably a function of the particular system and conditions prevailing within the system under consideration.(14)

In substitution inert systems such as hexacyanoferrate (II)-(III)(15) and permanganate-manganate (16) that have rapid exchange reactions, it is difficult to envision any role played by a bridge. The high symmetry of these species would, however, tend to minimize the energy required for re-orientation of the coordination sphere following the exchange process. Electron transfer in these and similar systems are certain to involve some sort of an outer sphere activated complex.

R. A. Marcus (17, 18, 19) has from theoretical considerations proposed an electron tunneling mechanism to account for transfer in these substitution inert systems in which the electron leaks through a potential energy barrier. Tunneling can occur through several layers of solvent leaving the individual hydration atmospheres undisturbed.

From the theory comes an equation that predicts electron exchange rates purely on theoretical grounds.

There are a few reactions in which the net oxidation-reduction process can be explained by atom, radical, or molecule transfer. Notable among these is the electron exchange reaction between phosphorus trichloride and phosphorus pentachloride in anhydrous carbon tetrachloride. (20) A chlorine molecule is made available for reaction with phosphorus trichloride as a result of the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine. Considerable evidence has been accumulated for an atom transfer mechanism in the iron(II)-iron(III) exchange. (23, 24) The indications are that oxidation-reduction is achieved by hydrogen atom transfer. Hydrogen atom transfer may play a significant role in biological oxidation-reduction phenomenon.

HISTORICAL BACKGROUND

The electron exchange reaction between antimony(III) and antimony(V) has been extensively studied in a variety of aqueous systems. The first work on the system was that by Bonner (25) who studied the exchange in 6M hydrochloric acid at 25°C. The following empirical rate law for the system was proposed:

$$R = k[Sb(III)]^{0.6}[Sb(V)]^{1.1}[Cl^-]^{9}\ [H^+]^{4}$$

Cheek (26) later extended the work of Bonner into higher acid regions and concluded that not all forms of antimony(V) present in the system are exchangeable. Hence, the rate of formation of the exchangeable form might well be the rate determining step in the exchange. Due to the complexity of the rate law, no decisive evidence was obtained to support a mechanism. It was assumed that the exchangeable species were tetrachloroantimonate(III) and hexachloroantimonate(V).

Newmann and Ramette (27) re-examined the system in light of some new non-equilibrium exchange experiments. In experiments in which antimony(V) was added to the system in the form of hexachloroantimonate(V) ion they found a half life time for the exchange equal to about 12 minutes; when the antimony(V) was added as an equilibria mixture of antimony(V) in 6M hydrochloric acid, the half life time for the exchange was equal to 49 hours, which was decisive evidence that the hexachloroantimonate(V) ion was the exchangeable form of antimony(V) in the system. It is also supported by the observed rate increase of the exchange with increasing acidity, which would be expected since there are larger equilibria concentrations of hexachloroantimonate(V) at higher acidities (41) and the rate of formation of hexachloroantimonate(V) is faster at higher acidities.

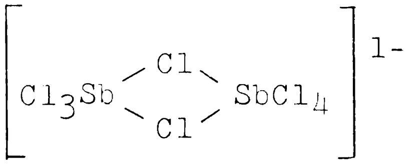
Neumann and Ramette (27) also performed a series of non-equilibrium experiments in which the antimony(V) was added as the hexachloroantimonate(V) ion and only the final acidities were varied. In these experiments, the rate was found to increase as acidity decreased. The same behavior was observed in the rate of hydrolysis of hexachloroantimonate (V) by Neumann and Brown.(28) This behavior was interpreted as being due to increased amounts of antimony trichloride molecules which serve as Lewis acids to extract a chloride ion from hexachloroantimonate(V) by formation of a bridged intermediate.

$$SbCl_3 + SbCl_6^- \longrightarrow [Cl_5Sb - Cl - SbCl_3]^-$$

$$[Cl_5Sb\text{-}Cl\text{-}SbCl_3]^- \longrightarrow SbCl_5 + SbCl_4^-$$

$$SbCl_5 + H_2O \longrightarrow [Sb(OH)Cl_5]^- + H^+$$

Antimony(V) chloride being a stronger Lewis acid than is antimony(III) chloride, the bridged intermediate probably splits into hexachloroantimonate(V) and antimony(III) chloride many more times than it does into antimony(V) chloride and tetrachloroantimonate(III). From comparison of exchange rates with hydrolysis rates in the presence and absence of antimony trichloride in solutions of equal acidities, it is readily apparent that exchange is too slow to be explained by way of the monobridged species. However, the observations do support antimony(III) chloride molecules as the exchangeable form of antimony(III) and suggests an activated complex containing either two or three chloride bridges.



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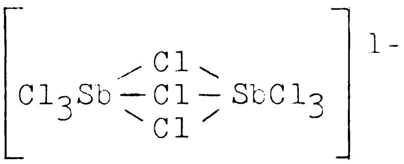


Even though there is no specific evidence to favor one over the other, the three bridged species appears more attractive because of the high symmetry it possesses.

Barker and Kahn (29) studied the exchange between antimony(III) chloride and antimony(V) chloride in anhydrous carbon tetrachloride. They observed a measurable exchange and postulated the two term rate law,

$$R = k_1 \,[SbCl_3] + k_2 \,[SbCl_3] \,[SbCl_5]^2$$

to account for their observations. The first term corresponds to the dissociation of antimony(V) chloride and the second term calls for a trinuclear activated complex, supposely formed from an antimony(V) chloride dimer and an antimony(III) chloride molecule. There is evidence for the existence of antimony(V) chloride dimers in non-polar solvents.

Kolditz and Rochnsch (30) looked at the exchange of chloroantimonates in acetonitrile. They found no exchange between antimony(III) chloride and tetramethylammonium hexachloroantimonate(V). The lack of exchange in this system may well be due to competition for coordination sites by the solvent.

Brubaker and Sincius (31) studied the antimony(III)-antimony(V) system in aqueous sulfuric acid in the absence and presence of added chloride. Essentially no exchange was observed in sulfuric acid alone, but exchange could be initiated by the addition of chloride. In the sulfate-chloride media, results indicated that sulfate was involved in the activated complex, but no clear cut evidence of such was obtained due to the complexity of the system.

Turco and Faroane (32) studied the antimony exchange in aqueous hydrochloric acid with added bromide. The postulated rate law was complex and added no useful information concerning antimony exchange. Turco (33) also studied the antimonate(III)-antimonate(V) system in 1.8M potassium hydroxide and found no exchange.

There has been some work done on antimony exchange between organoantimony derivatives. Nefedov and Wang (34) found rapid exchange in ethanol between tri-m-tolyl stibine and tri-m-tolyl stibine dichloride. The rapid exchange can be accounted for by a molecule transfer mechanism in which a chlorine molecule is made available by dissociation of the dichloride species which then reacts with the antimony(III) derivative. Nefedov *et al.* also studied the exchange between the trimethylstibine derivatives and found not only antimony exchange but also methyl exchange. Reutov *et al.* (36) studied the heterogeneous system composed of triphenylstibine and powdered elemental antimony in tetralin. Exchange was found in this system between the antimony metal and the stibine derivative.

Due to the interest of antimony halides as Friedel-Crafts catalysts, a few chloride exchange studies between antimony halides and various organic halogen compounds has been made.(38, 39, 40) Chloride exchange has also been observed between nitrosyl chloride and antimony(III) chloride. (37)

THEORETICAL

Electron exchange reactions can be represented in general terms as

$$M^*X + MY = MX + M^*Y$$

where M represents a metal in two different oxidation states and the star (*) indicates a radioactive tracer. For the specific case of the antimony(III)-antimony(V) exchange, the equation becomes

$$Sb^*Cl_3 + SbCl_5 = SbCl_3 + Sb^*Cl_5$$

This is an oxidation-reduction reaction in which the products and reactants are identical. In such a reaction, the enthalpy change is essentially zero and the free energy decrease is equivalent to that calculated from the entropy of mixing. The entropy increase in the system is due to the progressive distribution of the radioactive material among both oxidation states as exchange occurs. The point of equilibrium is reached when the isotope is randomly distributed between the two oxidation states.

The rate of appearance of radioactive atoms in the initially unlabeled species is governed by an exponential rate law first derived by McKay.(42) The rate law in its logarithmic form is:

$$\ln(1-F) = \frac{-R(A + B)}{AB} t \text{ , where}$$

R = observed rate of exchange

t = time elapsed since mixing

A,B = total concentrations of the reactants

F = fraction exchanged, x/x_∞, with

x = specific activity at time t in initially untagged species.

x_∞ = specific activity at time t_∞ in initially untagged species, i. e., the maximum value that x is capable of obtaining, corresponding to total random distribution of the isotope between the two oxidation states.

A plot of ln(1-F) versus t will be linear for the entire run with a slope proportional to R. It is advantageous that R is evaluated from the entire run and not an extrapolated point as is usually the case with kinetics of ordinary chemical reactions.

R can also be calculated from the derived relation

$$R = \frac{0.693\ AB}{(A + B)t_{\frac{1}{2}}}$$

by obtaining the half life, $t_{\frac{1}{2}}$, graphically from the semilog plot.

Usual techniques of chemical kinetics are used to relate R to the concentrations of the reactants in order to determine the empirical rate law and the order of the various reactants. Typically, the rate may be given by an expression such as:

$$R = k(A)^a\ (B)^b$$

Independent variation of A and B can be made and a and b determined from the slopes of plots of log R versus log A at constant B and log R versus log B at constant A, respectively.

The value x_∞ is usually obtained by determining the specific activity of the initially unlabeled species after at least ten half lives have elapsed. When the half life is long, this procedure becomes impractical and x_∞ is determined by either reduction or oxidation of the two species to identical oxidation states by chemical means and determining the specific activity of the resulting sample. This value is equivalent to x_∞.

The study of an exchange usually requires that a chemical separation procedure be used to separate the two oxidation states. Frequently in such a process, transitory intermediates are produced which may be capable of rapid exchange. Prestwood and Wahl (43) have shown that this induced exchange will have no affect on the slope of the plot of ln(1-F) versus t, even though the intercept will not be that required by the McKay equation as stated. It is advantageous to keep the zero time exchange at a minimum in order to obtain a good R value. Usually this can be done by careful selection of the separation process to be employed.

EXPERIMENTAL PROCEDURES

Materials

Carbon tetrachloride (C. P. grade) was further purified by refluxing 6 parts of carbon tetrachloride with one part of 5% aqueous sodium hydroxide for 3-4 hours to remove any carbon disulfide present. After three washings with distilled water, ten parts of sulfur-free carbon tetrachloride was stirred vigorously with one part of concentrated sulfuric acid until there was no further coloration of the acid layer (about 1-2 hours). The acid treated material was then washed with water and given a rough preliminary drying by storage over calcium chloride for a minimum of 24 hours with occasional shakings. The calcium chloride dried carbon tetrachloride was refluxed for nine hours under a stream of chlorine gas, followed by several hours of reflux under dry nitrogen to remove all the free chlorine. The chlorine treated carbon tetrachloride was then refluxed for several hours with solid anhydrous sodium carbonate (30 gms. per liter of carbon tetrachloride) and fractionated. A middle fraction was collected and stored in amber bottles away from sunlight. When needed, this fraction was refluxed with phosphorus pentoxide under a stream of dry nitrogen and distilled into dry amber bottles.

All carbon tetrachloride used for exchange runs was purified by this procedure. The carbon tetrachloride used for the preparation of labeled antimony trichloride was the sulfur-free carbon tetrachloride that had been dried by standing over calcium chloride.

The chlorine gas employed was used direct from the Matheson cylinder as received. Nitrogen was dried by passage through gas towers of concentrated sulfuric acid, calcium sulfate, and magnesium perchlorate assembled in that order. All other reagents were reagent grade.

Unlabeled anhydrous antimony trichloride was the analyzed reagent obtained from the Fisher Scientific Company. It was used as received without further purification and once opened was kept stored in a dessicator under a nitrogen atmosphere. Anhydrous antimony trichloride labeled with antimony-125 tracer was prepared by the method of Michael and Murphy (44) as modified by Epperson, Knox and Tyree.(45) Two millicuries of high purity, carrier-free antimony-125 was obtained in a 6M hydrochloric acid solution from the Oak Ridge Nuclear Division of Union Carbide. The sample was diluted to 50 ml. with 6M hydrochloric acid and aliquots taken for the synthesis when needed. One ml. of the tracer solution (0.04 millicurie) was added to 5 ml. of the antimony carrier solution prepared by saturating 6M hydrochloric acid with antimony(III) oxide that had been purified by repeated hydrolysis. The active solution was then hydrolyzed by carefully pouring it into 6 ml. of hot 3M potassium carbonate. The resulting precipitate of hydrated antimony(III) oxide was separated by centrifugation, washed several times in hot water, once in acetone, and dried for several hours at 120-130°C. in a drying oven. The dry solid (about 0.65 gm.) was introduced into a thick walled, carefully annealed ampule having an internal volume of 30 ml. After addition of 5 ml. of dry carbon tetrachloride, the ampule was sealed with an oxygen torch, placed in a stainless steel pressure bomb, and heated for 18-24 hours at 300-350°C. The heating was done with a sleeve-type electrical resistance heater constructed to fit the bomb. Water was introduced into the steel bomb before sealing in order to counteract the build-up of pressure in the ampule and keep it from breaking. After cooling to room temperature, the ampule was removed and stored unopened until needed. The method produces large, well-formed crystals of high purity and proceeds quantitatively. About 1 gram of material was obtained, the only losses being purely manipulative ones. The synthesis is not affected by small amounts of water in the reactants since the water is converted to phosgene and hydrogen chloride.

The antimony pentachloride used was the Baker and Adamson reagent grade material. Before use, it was distilled under vacuum at a temperature never exceeding 50°C. A middle fraction was collected for use.

Sulfur dioxide and hydrogen sulfide were used directly as received from the Matheson cylinders. Matheson hydrogen chloride was passed through concentrated sulfuric acid and magnesium perchlorate towers before use. Nitrogen used for inert atmospheres in the preparation of anhydrous solutions was dried in the same manner as described previously in the purification of carbon tetrachloride.

Primary standard arsenic(III) oxide from the Fisher Scientific Company was used in the standardization of potassium bromate. The potassium bromate was A. R. grade obtained from Matheson, Coleman, and Bell Company. The Aerosol OT used as a dispersant in the antimony separation procedure was obtained as a gift from the Vikon Chemical Company.

All other materials were reagent grade unless specified otherwise.

Preparation of Stock Solutions

The techniques used in the preparation of stock solutions of antimony(III) chloride and of antimony(V) chloride in carbon tetrachloride were designed to prevent hydrolysis without having to resort to dry box operations. As long as non-turbid solutions were obtained, the solutions were considered to be essentially anhydrous.

Figure I shows the assembled glassware required. The glassware was assembled while hot and allowed to cool

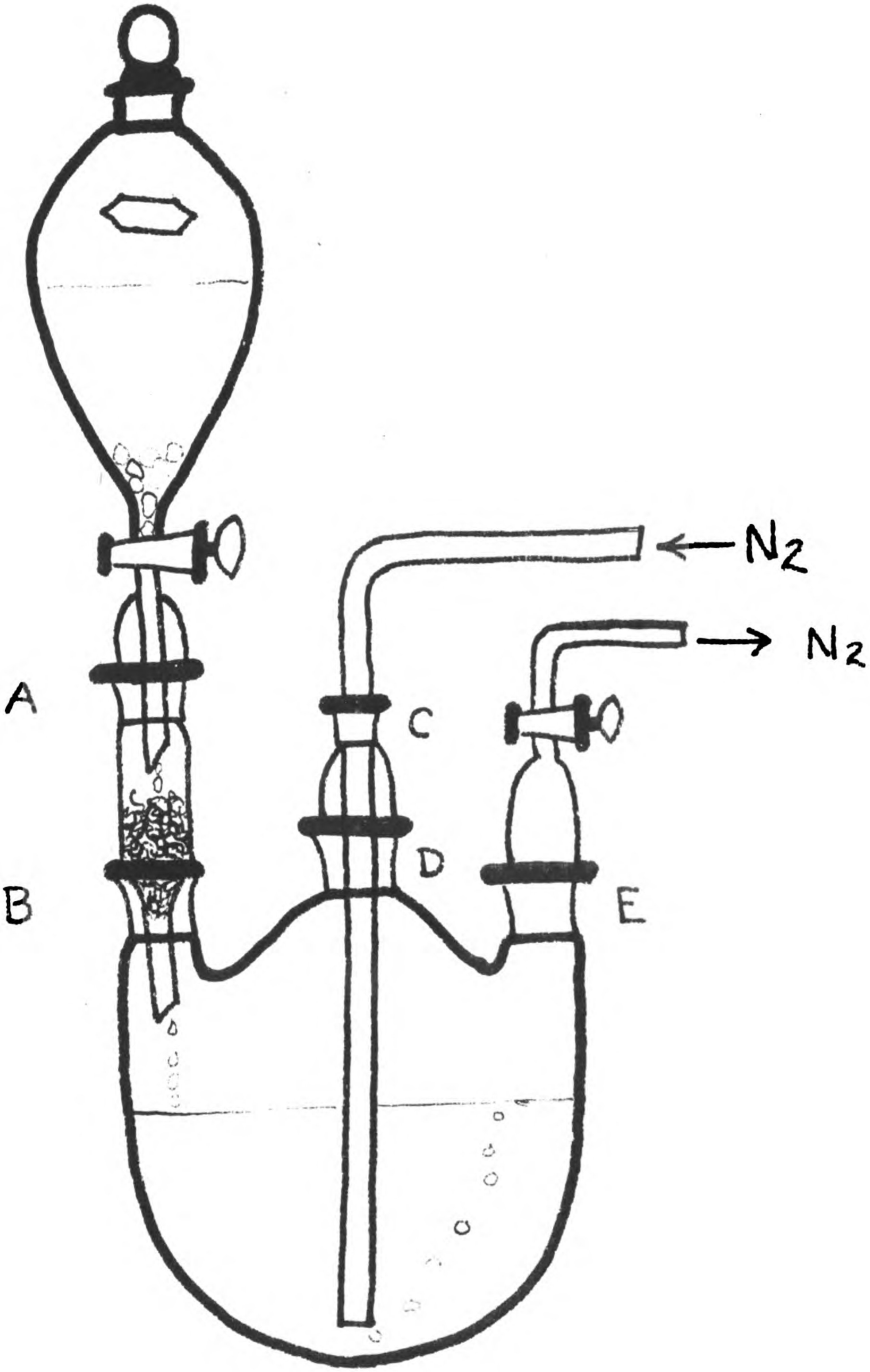


FIGURE I

to room temperature as dry nitrogen flowed through. Upon cooling to room temperature, the separatory funnel was removed at joint A and attached to a test tube containing a standard tapered joint in order to keep the delivery exit of the funnel dry. The opening left at joint A to the flask was stoppered. Solid anhydrous antimony trichloride was introduced into the separatory funnel followed by about 300 ml. of purified carbon tetrachloride. The funnel was stoppered and shaken to prepare a saturated solution of antimony trichloride in carbon tetrachloride. Any moisture that might have been present in the carbon tetrachloride was removed by reaction with the excess antimony trichloride producing antimony(III) oxide which was later filtered out. The funnel was reattached to the flask at joint A, the glass stopper in the funnel entrance hole replaced with a drying tube containing magnesium perchlorate, and the solution allowed to filter into the flask. The stopcock on the gas outlet tube always remained open and dry nitrogen flowed through continuously.

During the time of filtration, the ampule containing the prepared active antimony trichloride was opened by heating the seal until the inside pressure (about 2 atm.) was released. The top of the ampule was then removed by application of a hot blob of molten glass to a scratch made around the top of the ampule. The carbon tetrachloride containing the reaction by-products was decanted off, the crystals washed twice with fresh anhydrous carbon tetrachloride and introduced into a small separatory funnel that had been allowed to cool in a dessicator. About 50 ml. of anhydrous carbon tetrachloride was added, the funnel stoppered and shakened to dissolve the labeled antimony trichloride. The larger separatory funnel was then replaced with the smaller one and the radioactive material allowed to filter into the flask. The funnel and filtration assembly was then removed at joint B and replaced with a ground glass stopper. The nitrogen flow rate was increased to insure good mixing of the active material with the non-labeled antimony trichloride. A hot glass bottle was allowed to cool to room temperature in a vacuum dessicator and then filled with nitrogen gas. The prepared solution was transferred to the dry bottle by forcing it out of the flask by way of the gas outlet tube. This was accomplished by insertion of the end of the gas outlet tube into the bottle and tilting the flask using the build-up of nitrogen pressure to empty the flask. The bottle was fitted with a Teflon lined cap and stored in a dessicator containing a nitrogen atmosphere. If no turbidity developed within 12 hours, the solution was used for exchange runs within the next 24 hour period. The concentration of the resulting solution was usually around 0.25-0.30 molar with respect to antimony trichloride. Rigorous adherence to the above procedures was necessary to obtain a clear solution.

The same set-up and precautions were used in the preparation of antimony pentachloride solutions. The necessary quantity of pure carbon tetrachloride was added to the liquid antimony pentachloride in the container in which the antimony pentachloride fraction was collected during its purification. The resulting solution was then introduced into the flask by way of the separatory funnel-filtration assembly. Storage precautions were the same as those taken for the antimony trichloride solution. Final concentrations were about 0.7-0.9 molar with respect to antimony pentachloride.

Exchange Runs and Separation of Antimony Oxidation States

Reaction mixtures for exchange runs were prepared by dilution of freshly made stock solutions. 100 ml. amber bottles were oven dried and allowed to cool in a vacuum dessicator under vacuum. After cooling, dry nitrogen was admitted to the dessicator so that the bottles were filled with a nitrogen atmosphere. To one such bottle was added the quantity of antimony trichloride stock solution and pure carbon tetrachloride to give the final concentration desired; the same thing was done to give 100 ml. of antimony pentachloride solution of the desired concentration in another bottle. Each of these were then treated with anhydrous hydrogen chloride by use of the apparatus pictured in Figure II. The amount of hydrogen chloride added was

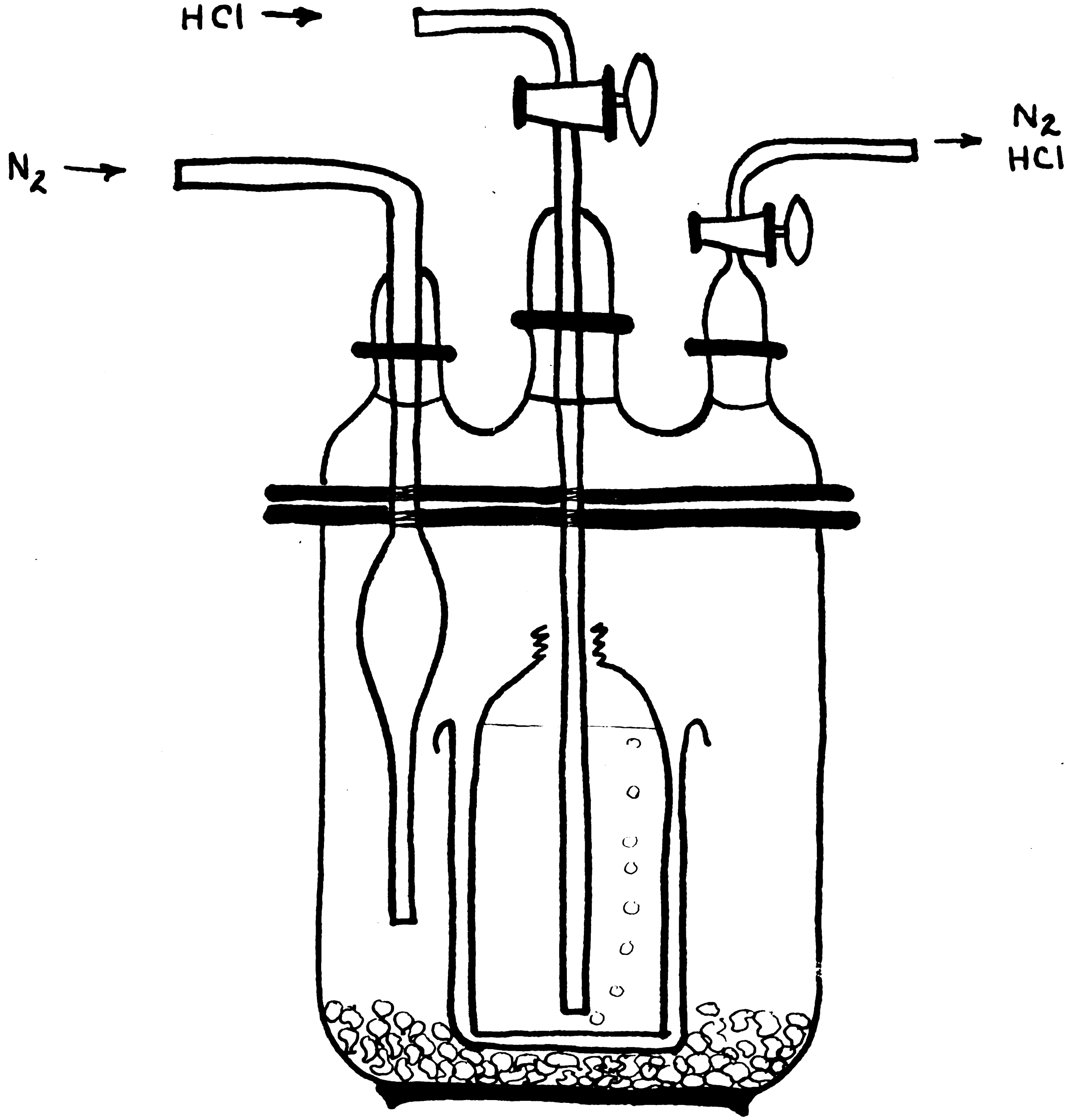


FIGURE II

controlled by the length of treatment. For a solution in which saturation was desired, it was necessary to also bubble nitrogen through the solution for several minutes following the hydrogen chloride treatment so that the solution could be handled without excessive fuming. Following hydrogen chloride treatment of a given sample, the hydrogen chloride entry tube was removed and its opening to the chamber sealed. Before opening the chamber to remove the treated solution, it was flushed vigorously with dry nitrogen. The solution so treated was stored under a dry inert atmosphere until needed. The storage period never exceeded 6 hours.

Exchange was initiated by mixing 100 ml. of the antimony trichloride and 100 ml. of the antimony pentachloride solutions. The resulting solution was shaken to mix well and then distributed by pipetting into ampules. 10.0 ml. of the reaction mixture was pipetted into each of twenty ampules. The ampules had previously been matched for size, dried, and filled with dry nitrogen. After sealing the ampules with an oxygen torch, they were wrapped in metal foil and numbered consecutively in the order in which they were filled. Zero time for the exchange was taken to be the time at which the sealed ampules were placed in the constant temperature bath. The entire operation from the mixing of the two solutions until the placing of the ampules in the bath required 30 minutes. It was carried out in the absence of artificial light except for a faint indirect incandescent light required to level the meniscus to the mark. The bath temperature was maintained at 50.0 ± 0.1°C.

At intervals of approximately 24 hours, ampules were removed from the bath and the reaction quenched by cooling under the tap. The ampules were then opened and the contents poured into 25 ml. of a solution consisting of 22.5 parts absolute ethanol, 1 part of 37% hydrofluoric acid, 1.5 parts concentrated hydrochloric acid, and 0.0005 part Aerosol OT . The solutions were treated with hydrogen sulfide for 2 minutes to precipitate the antimony trichloride as the sulfide. After centrifugation, the antimony trichloride fractions were discarded. The supernatants containing the antimony(V) fractions were poured into 25 ml. of 2N hydrochloric acid that had been saturated with boric acid. Following gentle boiling to remove the separated carbon tetrachloride, the solutions were treated with hydrogen sulfide to precipitate the antimony(V) as the sulfide. The precipitated sulfides were collected by centrifugation and dissolved in 5-6 ml. of 6M hydrochloric acid. Following filtration to remove undissolved sulfide and free sulfur, 4.0 ml. of each solution was pipetted into a 1 dram vial for gamma-scintillation counting.

To determine x_∞, the contents of an ampule was emptied into about 30 ml. of 2N hydrochloric acid and boiled gently to remove the carbon tetrachloride. 4.0 ml. of the resulting solution was pipetted into a 1 dram vial for counting and the remainder preserved for determination of total antimony content per ml.

Counting Procedure and Equipment

All activities of radioactive material was determined by gamma-scintillation counting using a NaI(Tl) well-type scintillation crystal in conjunction with a photomultiplier tube. Since the radiochemical purity of the antimony-125 tracer used was high, integral scintillation counting techniques were employed. The instrumentation used was the R. C. L. Mark 13, Model 1 Scalar in conjunction with the Mark 15, Model 30 Pulse Amplifier. Voltage input was controlled by an A. C. voltage requlator.

In all cases a minimum of 12,800 counts were recorded. Due to the essentially 4π geometry, no corrections beyond background were applied. Activities were kept low enough so that coincidence corrections were not needed. Reproducibility of count rates was within 1%. All samples for a given run, including the x∞ samples, were counted within a 2-3 hour period so there was no need to correct for antimony-125 decay or for any long range intrumentation changes.

Analytical Procedures

Due to the difficulty in handling anhydrous carbon tetrachloride solutions of antimony halides, it was not possible to prepare reaction mixtures of known concentrations by dilution of stock solutions. Hence, the antimony and chloride content had to be determined individually for each run.

Antimony(III) was determined by titration with standard potassium bromate in 2N hydrochloric acid at 90°C. with methyl orange as an irreversible indicator.(46) The same titration was employed for determination of antimony(V) after reduction to antimony(III) with water saturated with sulfur dioxide. A five minute boiling period was required to remove the excess sulfur dioxide before the bromate titration could be carried out. Earlier attempts to use solid sodium sulfite or sodium acid sulfite resulted in high values even after replacement of the HCl destroyed by the sulfite addition. No trouble was encountered in using the sulfur dioxide saturated water as a reductant.

To determine the antimony content of the reaction mixture for a given run, an ampule was selected and an aliquot from it was added to 100 ml. of 2N hydrochloric acid. After gentle boiling to remove the carbon tetrachloride, the antimony(III) was determined by titration with potassium bromate. The antimony(V) produced by the titration and the antimony(V) originally present was reduced to antimony(III) with sulfur dioxide and the titration repeated. The antimony(V) content was taken as the difference between the two determinations. Generally three separate ampules were taken for these analysis and each ampule was analyzed in duplicate.

Due to the nature of antimony sulfide precipitates and the separation procedure employed for the two oxidation states, the quantity of antimony recovered was never constant throughout a given run. Hence, specific activity of the antimony had to be determined in order to calculate fraction exchanged. The samples prepared for counting were transferred quantitatively to titration flasks after they had been counted, treated with sulfur dioxide, boiled, and titrated with potassium bromate. As a check, the reduction was repeated and the sample titrated again. Agreement was usually better than 0.03 ml titrant.

Standard solutions of potassium bromate were re-standardized daily before use by titration against an arsenic oxide solution of known titer prepared from primary standard arsenic(III) oxide. This same solution was used throughout the entire study for standardization of potassium bromate. If there was much change in the titer of the potassium bromate solution from the last time it was standardized, it was discarded and a fresh solution made. The titer of the potassium bromate solution was usually of the order of 1 ml. = 0.05 mmoles.

The total chloride content of an aliquot of the reaction mixture was determined gravimetrically by weighing as silver chloride. An aliquot from a selected ampule was added to 50 ml. of 0.5M tartaric acid, excess silver nitrate was then added and the carbon tetrachloride driven off in the subsequent heating stage required for the coagulation of silver chloride before filtration. Precautions were taken to insure that significant amounts of hydrogen chloride were not lost during the pipetting of aliquots. Duplicate analysis on a given ampule usually gave essentially identical results, but there was variation from ampule to ampule. The chloride concentration was taken as the arithmetic average of the results obtained from three separate ampules. The tartrate required to keep the antimony in solution interfered with the indicators used for volumetric determinations of chloride, making the more lengthy gravimetric analysis necessary.

Analyses of reactions mixtures were made at room temperature, hence the analytically determined concentrations had to be corrected for the increase in volume of carbon tetrachloride at the higher temperature used for the runs. This correction was made by utilization of the cubic coefficient of expansion for carbon tetrachloride. (47)

RESULTS AND DISCUSSIONS

The rate law found by Barker and Kahn (30) for the antimony trichloride-antimony pentachloride electron exchange reaction in anhydrous carbon tetrachloride at 50°C. is given by,

$$R = 1.6 \times 10^{-7} [SbCl_5] + 1.8 \times 10^{-4} [SbCl_3] [SbCl_5]^2$$

Table I summarizes the results of exchange experiments carried out in the present work on the same system with anhydrous hydrogen chloride added. In all cases, an acceleration of the exchange rate beyond that which would be predicted by the Barker and Kahn rate law in the absence of hydrogen chloride is observed. Typical McKay plots for the system are shown in Figure III. The rate of exchange was calculated from a least squares determined slope of the corresponding McKay plot.

It seemed likely that as long as $SbCl_3$ and $SbCl_5$ species were present, that the Barker and Kahn paths were operative and that the presence of HCl added still another path for exchange. Emphasis was placed on addition of a third term to the Barker and Kahn rate law. The following terms were tried:

$$k_3[SbCl_3][SbCl_5][HCl]$$

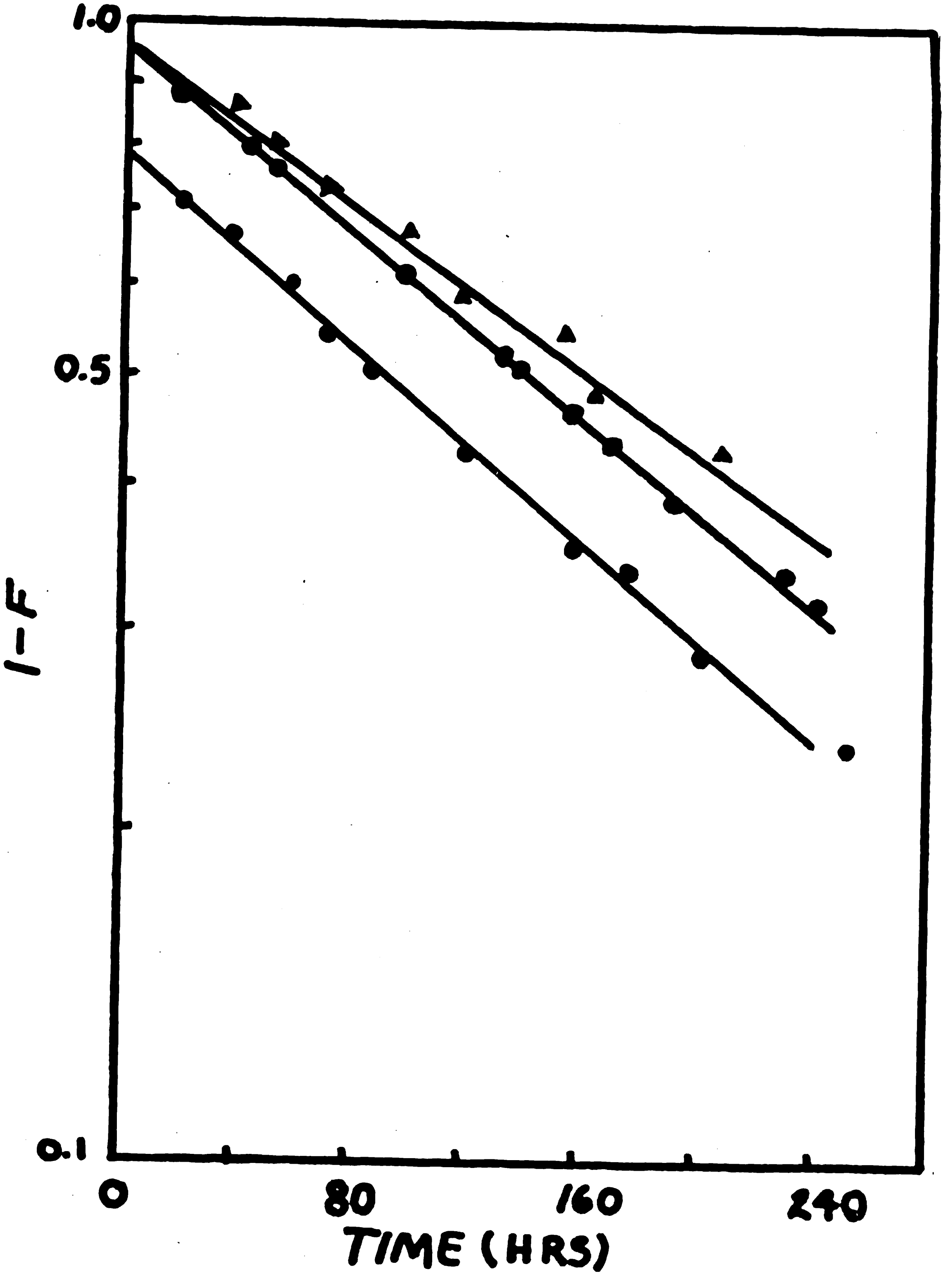
$$k_3[SbCl_3][SbCl_5][HCl]^2$$

TABLE I

Experiment Number	$[SbCl_3]$	$[SbCl_5]$	$[HCl]$	$R \times 10^6$ (1)	$R_c \times 10^6$ (2)	$k_3 \times 10^5$ (3)
1	0.04320	0.006811	0.02862	0.005498	0.005498	1.87
2	0.04356	0.04856	0.009163	0.02685	0.00791	1.98
3	0.04482	0.04727	0.008247	0.02429	0.00577	1.56
4	0.04279	0.04690	0.005733	0.02485	0.00521	2.12
5	0.04632	0.02272	0.01118	0.01162	0.00866	1.67
6	0.03151	0.02110	0.04650	0.01354	0.01354	2.04
7	0.04301	0.03476	0.01129	0.01913	0.01111	2.29
8	0.04416	0.03989	0.03496	0.03157	0.02835	1.87
9	0.01589	0.04349	0.04406	0.01810	0.01810	2.62
10	0.02101	0.04380	0.05326	0.002194	0.002194	2.38
11	0.02771	0.04550	0.03581	0.03581	0.02316	2.33

(1) Experimentally observed rate
(2) Rate corrected for Barker and Kahn path
(3) Least Squares value:
$2.50 \pm 0.23 \times 10^{-5}$ liter mole^{-1} sec^{-1}

FIGURE III



$k_3[SbCl_3][SbCl_5]^2[HCl]^2$
$k_3[SbCl_3][SbCl_5]^2[HCl]^3$
$k_3[SbCl_3]^2[SbCl_5][HCl]$

None of the above were found to fit the experimental data.

In treating solutions of antimony pentachloride with hydrogen chloride, a visible reaction was observed take place. The most logical product of this reaction is the hexachloroantimonic(V) acid. Assuming that this was the case, and that all hydrogen chloride present in the system was present in hexachloroantimonic(V) acid, the data could be fitted to the following rate law:

$$R = k_1 [SbCl_5] + k_2[SbCl_3][SbCl_5]^2 + k_3[SbCl_3][HSbCL_6]$$

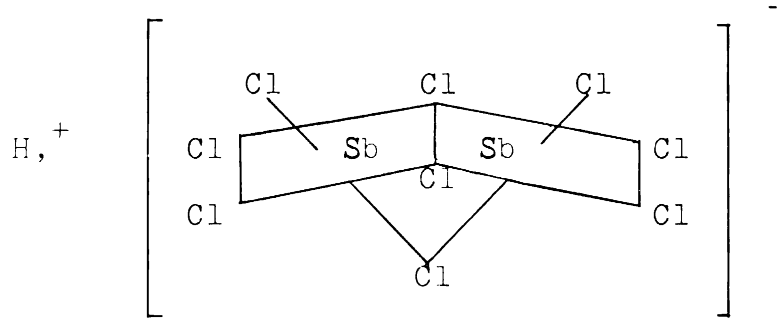
The concentration of antimony pentachloride used was corrected for that converted to the hexachloroantimonic(V) acid. When the hydrogen chloride is in excess of the antimony pentachloride, the Barker and Kahn paths are no longer operative and the path involving the antimonic acid becomes the sole avenue for exchange. It was also necessary to assume that the dissociation constant for the hexachloroantimonic(V) acid into hydrogen chloride and antimony pentachloride was small.

The values for k_1 and k_2 were taken from the data of Barker and Kahn and the k_3 value was calculated from the least squares slope of a plot of

$$\frac{R - k_1[SbCl_5] - k_2[SbCl_3][SbCl_5]^2}{[SbCl_3]} \qquad \text{versus } [HSbCl_6]$$

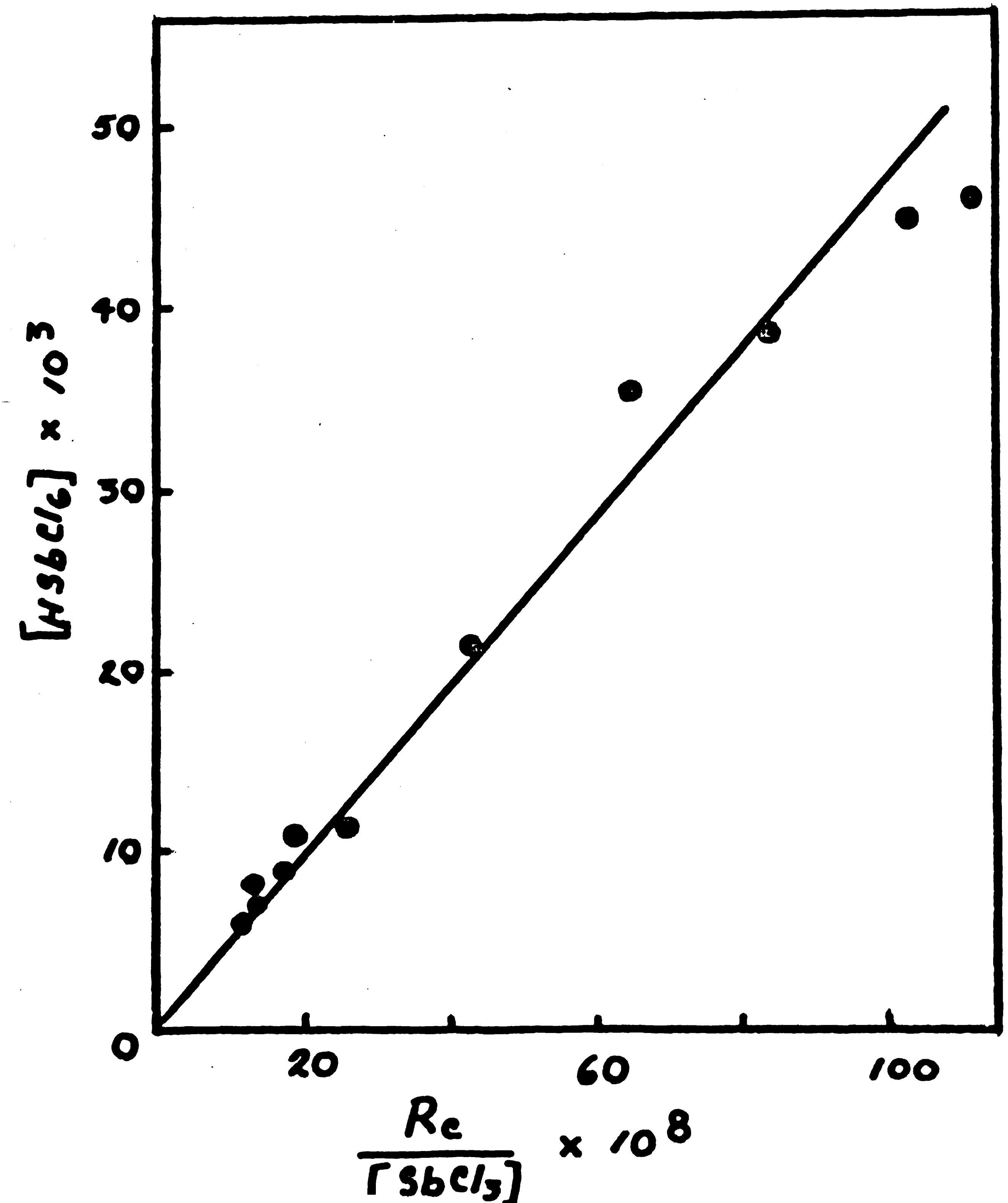
The data are shown plotted in Figure IV. The value for k_3 was found to be $2.50 \pm 0.23 \times 10^{-5}$ liter mole^{-1} second^{-1}.

The activated complex for the path involving hydrogen chloride can reasonably be formulated as two octahedra sharing a common face, i.e.,



Such a structure would be expected to result in a lesser antimony to antimony interaction distance relative to the corresponding distance in a di-bridged species. The conditions are such that in relation to actual mechanism of electron transfer, the bridging chlorides would appear to function more as an aid to electron tunneling than as an electron conductor in the Taube sense.

FIGURE IV


50
40
30
20
10
0
20
60
100
$[HSbCl_6] \times 10^3$
$\frac{R_c}{[SbCl_3]} \times 10^8$

DISCUSSION OF ERROR

The potential sources of error in the determination of the rate of exchange in these experiments can be classified as follows:

1. Analysis of the reaction mixture for antimony and chloride content.
2. Maintenance of constant chloride concentration in all the ampules of a given run.
3. Separation of oxidation states and determination of specific activity and x_∞ values.
4. Radiochemical assay.
5. Sampling time, temperature control, and other factors related to the actual carrying out of the exchange runs.

A reaction mixture of approximate concentration desired was prepared and distributed into twenty ampules and sealed. Analytical data were obtained from sampling of the twenty ampules rather than from the prepared reaction mixture. Ampules were distributed as follows:

3 ampules - Antimony analysis

3 ampules - Chloride analysis

3 ampules - x_∞ determination

Remainder - McKay plot points

The order of filling the ampules was preserved and for each set of data, ampules were selected so that one came from the early stages of the filling operation, one from the middle stage, and one from the late stage. The final value was taken as the arithmetic mean of these analysis.

In general, the agreement between ampules for the antimony analysis was quite good. However, there was a steady decrease in the chloride concentration as one proceeded from an early filled ampule to a late filled one and the decrease became more pronounced as the hydrogen chloride concentration increased. This variation ranged from less than 1 part per thousand at low hydrogen chloride concentration up to 10 parts per thousand at the higher concentrations of hydrogen chloride. This decrease was due to the loss of hydrogen chloride from the reaction mixture during the pipetting into the ampules. The solution in the ampules prepared last had been exposed to the open atmosphere longer and consequently had lost a proportionately greater amount of hydrogen chloride by vaporization than had the ampules sealed earlier. The ease at which hydrogen chloride was lost to the atmosphere was a consequence of the limited solubility of hydrogen chloride in carbon tetrachloride.

Scatter in the McKay plots was very sensitive to the volume of free space within the ampules. This was obviously related to the actual concentration of hydrogen chloride in the liquid phase. Due to the lower solubility of hydrogen chloride in carbon tetrachloride at the temperature of the run relative to the solubility at room temperature, hydrogen chloride was lost from the liquid phase and the quantity lost was a function of the free volume available within the ampule. This made it necessary to keep the free space within all the ampules as near the same volume as possible. The relatively good fit of the points in the McKay plots indicates that this factor was fairly well controlled for a given run.

It is likely that the hydrogen chloride concentration determined at room temperature for a given run is proportional to the actual hydrogen chloride concentration in the liquid phase at the temperature of the run. In order to make a significant comparisons between different runs, it was necessary to keep the free volume as constant as possible throughout the complete study. It is felt that the major source of deviation in the derived data for this study was a consequence of this factor.

Besides this recognized error in analyzing for chloride, there are present the normal errors encountered in quantitative analytical procedures such as accuracy of buret and pipette calibrations, concentrations of standard solutions, and weighing errors. However, the known accuracy of the analytical methods employed was far greater than that expected for the final results of this study, so these factors were felt to be quite insignificant and only routine care in analytical techniques was taken.

The rate of exchange is very dependant on the value of x_∞. This value was determined in triplicate and the arithmetic mean taken for the calculation of the fraction exchanged. Agreement between determinations was quite good.

Due to taking a minimum of 12,800 counts in the radioassay procedures, errors were theoretically below 1% in activity measured. Excellent reproducibility of count rates was obtained and hence, it is felt that no significant error can be credited to the radioassay procedure.

It is also felt that temperature control and sampling time introduced no significant error in the results relative to the error produced by the chloride concentration variation. It was shown that no significant exchange occurred at room temperature during the thirty minutes required to prepare the ampules, hence, zero time was taken as the time the wrapped ampules were placed in the constant temperature bath. Preliminary experiments also indicated that the separation procedure was sound and that the antimony(V) fraction was not contaminated with the antimony(III) material. Since absolute specific activity was determined, many potential sources of error were eliminated from consideration.

APPENDIX A

TIME (HOURS)	1-F	Concentration of Reactants
Experiment 1 (Run Q)		Slope = -0.001461
9.08	0.942	$[SbCl_3]$ = 0.04320
34.22	0.868	
44.20	0.835	
80.88	0.738	$[SbCl_5]$ = 0.006811
112.9	0.674	
129.8	0.644	
226.9	0.501	
249.1	0.393	$[HCl]$ = 0.02862
Experiment 2 (Run 3)		Slope = -0.001828
10.83	0.918	$[SbCl_3]$ = 0.04356
26.08	0.859	
46.00	0.781	
58.41	0.745	$[SbCl_5]$ = 0.04856
107.4	0.592	
133.3	0.529	
139.1	0.506	$[HCl]$ = 0.009163
154.1	0.476	
164.4	0.467	
181.0	0.420	
208.4	0.399	
228.6	0.370	
Experiment 3 (Run 5)		Slope = -0.001650
78.33	0.675	$[SbCl_3]$ = 0.04482
103.8	0.623	
109.6	0.638	
134.9	0.563	$[SbCl_5]$ = 0.04727
151.5	0.536	
159.9	0.529	
174.9	0.484	$[HCl]$ = 0.008247
201.8	0.430	
226.7	0.386	
255.2	0.358	

TIME (HOURS)	1-F	Concentration of Reactants
Experiment 4 (Run 6)		Slope = -0.001736
12.50	0.918	$[SbCl_3]$ = 0.04279
39.75	0.774	
76.83	0.615	
102.1	0.590	$[SbCl_5]$ = 0.04690
107.9	0.568	
123.2	0.545	
133.3	0.549	$[HCl]$ = 0.005733
149.8	0.434	
177.2	0.464	
200.2	0.380	
225.5	0.378	
253.5	0.322	
269.8	0.325	
Experiment 5 (Run 7)		Slope = -0.001192
20.92	0.877	$[SbCl_3]$ = 0.04632
43.75	0.825	
67.00	0.773	
87.42	0.676	$[SbCl_5]$ = 0.02272
140.0	0.607	
166.8	0.520	
188.1	0.482	$[HCl]$ = 0.01118
234.7	0.551	
Experiment 6 (Run 8)		Slope = -0.001675
20.25	0.879	$[SbCl_3]$ = 0.03151
42.67	0.821	
65.92	0.746	$[SbCl_5]$ = 0.02110
86.42	0.702	
138.9	0.557	$[HCl]$ = 0.04650

TIME (HOURS)	1-F	Concentration of Reactants
Experiment 7	(Run P)	Slope = -0.001555
7.05	0.910	$[SbCl_3]$ = 0.04301
42.20	0.808	
63.42	0.717	
90.92	0.667	$[SbCl_5]$ = 0.03476
110.9	0.611	
139.9	0.574	$[HCl]$ = 0.01129
153.8	0.507	
201.2	0.462	
Experiment 8	(Run 2)	Slope = -0.002355
6.50	0.920	$[SbCl_3]$ = 0.04416
42.33	0.765	
63.75	0.666	$[SbCl_5]$ = 0.03989
87.75	0.587	
125.8	0.474	$[HCl]$ = 0.03496
157.8	0.436	
222.5	0.309	
257.5	0.280	
Experiment 9	(Run B)	Slope = -0.002431
25.08	0.789	$[SbCl_3]$ = 0.01589
46.18	0.708	
70.00	0.617	$[SbCl_5]$ = 0.04399
80.67	0.546	
96.62	0.496	$[HCl]$ = 0.04406
117.3	0.450	
140.1	0.407	
158.2	0.321	
181.6	0.326	
210.7	0.291	

TIME (HOURS)	1-F	Concentration of Reactants
Experiment 10	(Run C)	Slope = -0.002415
21.60	0.757	$[SbCl_3]$ = 0.02101
66.50	0.572	$[SbCl_5]$ = 0.04380
78.65	0.559	$[HCl]$ = 0.05326
93.10	0.478	
113.6	0.455	
136.6	0.425	
153.8	0.343	
177.1	0.342	
207.3	0.388	
Experiment 11	(Run D)	Slope = -0.002285
19.75	0.771	$[SbCl_3]$ = 0.02771
40.80	0.721	$[SbCl_5]$ = 0.04550
64.55	0.628	$[HCl]$ = 0.03581
77.13	0.576	
92.03	0.536	
111.8	0.477	
134.8	0.425	
152.8	0.384	
176.0	0.379	
205.3	0.320	

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