A KINETIC STUDY OF THE ELECTRON EXCHANGE REACTION BETWEEN ANTIMONY(III) AND ANTIMONY(V)

By

Joseph A. Sincius

A THESIS

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and Applied Science
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ABSTRACT

The kinetics of the exchange reaction between Sb(III) and Sb(V) was studied in aqueous sulfuric acid, and in aqueous sulfuric acid systems containing added chloride ion. No exchange was observed in aqueous sulfuric acid, but the addition of chloride initiated exchange, and the concentration of chloride had a significant effect on the observed rate. In addition to a study of the influence of chloride concentration, experiments were performed in which the effect of independent variation in the concentrations of antimony(III), antimony(V), sulfate, and hydrogen ion was determined at two levels of chloride concentration, 6.00 M and 0.20 M. Supplementary spectrophotometric examinations of antimony(III) and antimony(V) solutions were also performed.

In 6.00 M chloride, it was found that the reaction was first order with respect to antimony(III) and antimony(V), that sulfate ion has no effect, and that the dependence of exchange rate exhibits a maximum at approximately 9 M hydrogen ion. The exchange mechanism is apparently identical with that observed previously in hydrochloric acid solutions.

In 0.20 M chloride, while the rate maintains a unit dependence with respect to antimony(III), the reaction exhibits a fractional order of 0.76 with respect to antimony(V). At this level of chloride concentration the rate of exchange is approximately second order with respect to chloride, but undergoes a sharp maximum at approximately 9 M hydrogen ion, and a similar, although much less pronounced maximum at 0.60 M sulfate. The two antimony oxidation states are apparently involved in complex equilibria with chloride, sulfate, and hydrogen ions. Both chloride and sulfate are involved in the activated complex, although the relative importance of chloro or sulfato bridging is difficult to assess. While some qualitative observations as to mechanism can be made, a quantitative evaluation must await a more accurate knowledge of the nature of the solution species and their equilibrium relationships.

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I. INTRODUCTION

The study of the mechanisms of inorganic reactions is one of the newest general fields of research in inorganic chemistry. With the availability of radioactive tracers, reactions of oxidation - reduction are receiving considerable attention because it has become possible to study the electron transfer equilibria between different oxidation states of the same element. Of particular interest are the exchange reactions where the net effect is the transfer of two electrons, since these may proceed either by the simultaneous transfer of two electrons, or alternatively by the stepwise exchange of one electron at a time through the intermediate oxidation state. The exchange reaction:

$$Sb(III) + Sb^*(V) = Sb^*(III) + Sb(V)$$

is such a two electron transfer system. While hydrochloric acid solutions and the chloro-complexes of antimony have been extensively studied, antimony species in sulfate media, particularly those of the (V) oxidation state, have received little or no attention. Oxidation - reduction rates are of particular interest here because of the possibility of sulfate bridges in the electron transfer, such as have been postulated in the analagous reactions of Tl(I)-Tl(III) and Sn(II)-Sn(IV). The kinetics of the Sb(III)-Sb(V) reaction has been observed in aqueous hydrochloric acid, but the results were difficult to interpret because of competing hydrolysis reactions. It was decided to investigate this reaction in aqueous sulfuric acid, and also to observe the catalysis by chloride ion in this medium, where competing hydrolysis reactions should not be a problem.

II. HISTORICAL

A. Electron Exchange

Although most of the reactions in inorganic chemistry involve oxidation - reduction, the actual mechanism by which electrons are transferred is unknown. Such processes are difficult to study because they proceed virtually instantaneously so that it is impossible to measure a rate, and the systems are generally very labile with respect to changes in the coordination sphere, so that intermediate stages which would supply evidence about the nature of the activated complex, change to final products too rapidly for convenient observation. With the availability of radioactive isotopes it has become possible to observe electron transfer equilibria between the ions of a metal in two oxidation states. These are oxidation - reduction reactions in which the reactants and products are identical. The enthalpy change is about zero, but the free energy decreases by the amount calculated from the entropy of mixing. The entropy at equilibrium when all the isotopes are uniformly distributed is greater than that of the original system.

Exchange rates for simple ionic species vary tremendously, and are particularly dependent on the presence of anionic catalysts, such as chloride. Apparently a definite energy barrier exists between products and reactants, the height of which depends on the particular exchange system under consideration.

Libby (1) has discussed these phenomena on the basis of the Franck - Condon principle. Electron transfer in aqueous solution should be inhibited by the relatively longer time required for the movement of the hydration atmospheres as compared to the transit time for the electron. The electron must be able to make the transition against a barrier comparable in magnitude to the amount of energy involved in the subsequent slow reorientation of the water molecules to the new charge situation. The catalysis of small negative ions is presumed to be the result of bridge formation which causes the two positive ions to approach more closely, and share their hydration atmospheres to a considerable extent, so that dissimilarities are reduced. While a bridging group clearly can function to lower the potential energy barrier, its exact role is difficult to define. It may serve as a path for the transfer, the electron moving through the molecular orbitals of a bridging group held by chemical bonds to the two exchanging species, or the process may be atom or group, rather than electron, transfer.

Marcus, Zwolinski, and Eyring (2) have advanced an "electron tunneling" hypothesis, in which the electron leaks through the potential energy barrier in the well known quantum-mechanical phenomenon. Several layers of solvent may separate the reactants, and the individual hydration atmospheres are not disturbed. Systems such as $Fe(CN)_6^{-4}$- $Fe(CN)_6^{-3}$, MnO_4^{-2}- MnO_4^{-}, and $IrCl_6^{-3}$- $IrCl_6^{-2}$ are substitution inert and a bridged intermediate is difficult to envision, but nevertheless rapid exchange takes place. These are highly symmetrical reactants, however, and the rearrangement of the coordination spheres during and after electron transfer is probably a minimum.

The bridge mechanism of electron transfer has been supported by the work of Taube (3, 4, 5, 6, 7), who demonstrated that the oxidation of chromium(II) by a variety of monosubstituted pentamminecobalt(III) species of the type $[Co(NH_3)_5X]^{+2}$ takes place with the transfer of X to the reducing agent, where X has been chloride, bromide, nitrate, thiocyanate, acetate, pyrophosphate, and sulfate. Aquo and hydroxo bridges are also possible. The net atom transfer in each of these reactions is not necessarily an essential part of the electron transfer. In a reaction studied between Cr(II) and $IrCl_6^{-2}$, the bridging chloride remained with Ir(III) rather than Cr(III). The essential feature is that an appropriate bridge provides a more accessible route for the flow of electrons, and whether group transfer takes place depends on the relative substitution lability of the ions left sharing the bridge after electron transfer.

Systems in which the net result is a transfer of two electrons have also been studied. Because of the charge difference of two between the reactants, dissimilarity in coordination atmospheres will be considerable, and the energy barrier from the necessary subsequent rearrangement will be higher. The "tunneling" hypothesis is even less attractive because quantum mechanical calculations indicate a very low probability for a simultaneous transfer of two electrons. Most such two electron exchanges have been studied in halide or pseudohalide media such as chloride and cyanide. In Tl(I)-Tl(III) (8), Sn(II)-Sn(IV) (9), and Sb(III)-Sb(V) (10, 11, 12) exchange equilibria, transition states which contain two univalent anion bridges are proposed, and the exchange does not necessarily proceed stepwise through the intermediate oxidation state. These results have promoted an interest in the possibility of a single bridge by a divalent negative ion such as sulfate.

Sulfate bridges have been postulated by Brubaker and Mickel in the Tl(I)-Tl(III) exchange (13). It is of interest to note that on the addition of chloride to the Tl(I)-Tl(III) system in aqueous sulfate (14), the rate of exchange is first diminished as the sulfate complexing is replaced by chloride, and only increases when sufficient chloride is present to approach the double chloride bridged intermediate proposed by Dodson. In the Sn(II)-Sn(IV) reaction in aqueous sulfuric acid studied by Gordon (15), sulfato species are apparently the exchanging groups, and presumably sulfate bridging is involved in the activated complex.

B. Antimony Chemistry

The first publication on antimony appeared in 1604, and was attributed to a fifteenth century monk, Basilius Valentinus. A pertinent quotation from this work, entitled "The Triumphal Chariot of Antimony is as follows: " But antimony, like mercury, can best be compared to a round circle, without end, and the more one investigates it, by suitable means, the more one discovers in it, and learns from it; it cannot be mastered, in short, by one person alone because of the shortness of human life" (16). The enthusiasm of many experimenters has been blunted on the frustrating chemistry of antimony.

The chief use of antimony is in alloys, particularly those with lead, which are employed in batteries, bullets, and type metal. There has been considerable recent interest in the application of metal antimonides as transistor and thermoelectric materials.

Antimony compounds display the anticipated +3 and +5 oxidation states. In the +3 state, antimony is amphoteric, the trioxide (actually Sb_4O_6) dissolving in acids or alkalis, with the isoelectric point at pH 8.6 (17). Little evidence exists for a definite antimonous acid, precipitates of hydrous trioxide being obtained (18). The +3 cation forms a sulfate and nitrate, but only with concentrated acids, and these are readily hydrolyzed to form the basic antimonyl salts containing the SbO^+ group. The antimonites, commonly formulated as $MSbO_2$, are also subject to extensive hydrolysis in water. In 2.5 N KOH an ionic weight in accord with the formula $Sb(OH)_4^-$ was established by Brintzinger by dialysis measurements.

According to the position of antimony in the fifth group of the periodic table, one might anticipate an ortho, a meta, and a pyroantimonic acid. However, no definite hydrates of antimony pentoxide have been found (20). Antimony pentoxide apparently can occur with any arbitrary water content, and the varying properties that have confused investigators are the result of differences in the method of preparation.

The salts of antimonic acid were initially regarded as "meta" salts of the type $MSbO_3 \cdot xH_2O$, but from the calculations of Pauling (21), and the x-ray investigations of Beintema (22), they have been shown to be derived from an acid of the formula $HSb(OH)_6$. The sodium salt, long known as sodium pyroantimonate, and assigned the formula $Na_2H_2Sb_2O_7 \cdot 5H_2O$, is sometimes used as a test for sodium ion because of its insolubility. That the antimony(V) species present in basic solution is actually $Sb(OH)_6^-$ has been shown by the dialysis measurements of Brintzinger (19), and the spectral studies of Souchay and Peschanski (22).

If either the trioxide or pentoxide is heated above 300°, the so-called antimony tetroxide is obtained, but the existence of tetravalent antimony has never been established.

The crystal structure of the tetroxide (Sb_4O_8) is similar to that of $SbTaO_4$, and contains both Sb(III) and Sb(V) atoms. The solubility and oxidation state of the tetroxide in water and in dilute and concentrated acids and alkalis has been investigated by Konopik and Zwiauer (25), who concluded that the tetroxide is present as $Sb(III)Sb(V)O_4$, although the exact nature of the species was not established.

Both oxidation states form a variety of complexes; those with oxygen, sulfur, and halide donor groups are of particular importance. Chelate complexes with organic ligands such as oxalate, citrate, tartrate, and acetylacetonate are well known. Antimony trihalides form a number of complex halides of the type $MSbX_4$, M_2SbX_5, and M_3SbX_6, while antimony(V) yields halide complexes such as $MSbF_6$, $MSbCl_6$, and $MSbBr_6$.

The identification of antimony species in aqueous solution has been rather limited, and the solution chemistry of antimony is almost entirely that of complexes. As mentioned above, in basic solution, the dominant species are $Sb(OH)_4^-$ and $Sb(OH)_6^-$. The effect on Sb(V) species upon acidification of basic solutions has been studied spectroscopically by Souchay and Peschanski (23), who treated potassium antimonate solution with acetic, formic, or chloroacetic acid until the final solution was 1-2 <u>N</u> in acid and 12×10^{-3} <u>M</u> in antimony. Spectral changes observed with decreasing pH were interpreted in terms of anionic polymerization. Antimonate ion was claimed to be $Sb(OH)_6^-$ at high pH, and $HSb_6O_{17}^{-3}$ at pH values below 2.5; no appreciable amounts of other ions were shown to exist above pH = 0.9.

The antimony species that have received the most attention are those observed in hydrochloric acid media, since most investigators prefer to work in areas where solubility problems are not so critical. In high hydrogen ion, high chloride systems, the dominant species appear to be $SbCl_4^-$ and $SbCl_6^-$.

$SbCl_6^-$ has been reported as the polarographically reducible species in 4-6 N HCl, or in 6 N $HClO_4$ containing 0.2 N HCl (26). In the absence of chloride, no reduction wave other than the hydrogen ion discharge occurs. Similarly, polarographic data for the reduction of Sb(III) in hydrochloric acid indicated that the antimony is essentially all present as $SbCl_4^-$ (27). The formal potential of the antimonous - antimonic half-cell for chloride solutions has been investigated by Brown and Swift (28) who postulated the following equilibria:

$$SbCl_4^- + 2Cl^- = SbCl_6^- + 2e$$

$$SbCl_6^- + xHOH = Sb(OH)_xCl_y^- + xH^+ + (6-y)Cl^-$$

$$SbCl_6^- + SbCl_4^- = Sb_2Cl_{10}^{-2}$$

The spectra of Sb(III) and Sb(V) in hydrochloric acid solutions have received considerable attention because of "interaction absorption". Abnormally deep and intense coloration is often exhibited by systems containing an element in two different oxidation states. Such optical interaction has been observed for Sn(II)-Sn(IV), Fe(II)-Fe(III), and Cu(I)-Cu(II). For Sb(III)-Sb(V), this phenomenon has been shown to be the result of a dimer between $SbCl_6^-$ and $SbCl_4^-$ (29, 30, 31), and not a complex of Sb(IV). Additional spectral studies on Sb(V) species in hydrochloric acid solutions have been performed by Neumann (32, 33), who interpreted spectral changes with decreasing hydrochloric acid concentration as the stepwise hydrolysis of $SbCl_6^-$, yielding equilibria involving $Sb(OH)Cl_5^-$, $Sb(OH)_2Cl_4^-$, and $Sb(OH)_3Cl_3^-$. $Sb(OH)Cl_5^-$ is the predominant form in 8 *M* acid, and $Sb(OH)_2Cl_4^-$ in 6 *M* acid. $Sb(OH)_3Cl_3^-$ and more hydrolyzed species are the most important in acid concentrations below 5 *M*.

C. Antimony(III)-(V) Electron Exchange

Antimony(III)-(V) electron exchange has been investigated in aqueous hydrochloric acid by Bonner (10), who examined the system principally in 6 *M* hydrochloric acid at 25°C., and derived the empirical rate law:

$$R = (8.8 \pm 0.9) \times 10^{-11} [Sb(III)]^{0.6} [Sb(V)]^{1.1} [Cl^-]^{9} [H^+]^{4}$$

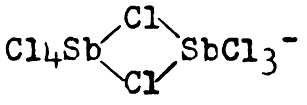
While Bonner proposed no mechanism for the exchange, his results indicated that the interaction dimer observed in spectroscopic studies was apparently not the primary activated complex in 6 *M* HCl, although formation of the dimer could be a rate-determining step in one of several exchange processes.

Cheek (11) observed the exchange in the hydrochloric acid concentration range of 6-12 M, and found unit Sb(V) dependence, but an Sb(III) dependence which decreased from unity in 12 M acid to 0.9 in 9.5 M HCl, a difference which was felt to be real. In ~4 M HCl, a dependence of 0.8 was indicated, although experimental error was estimated to be at least 20% in this set of determinations. Although insufficient data were collected to make an estimate of order, a marked increase in the exchange rate with increasing chloride (6-10.6 M) at hydrogen ion concentrations of approximately 6 M was observed, while increasing hydrogen ion from 4.3 to 6.8 M at 9.5 M total chloride resulted in a slight decrease in rate.

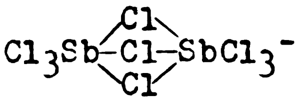
Cheek attempted to relate Sb(III)-Sb(V) interaction spectra with exchange rates, but concluded that the exchange proceeds by several paths, some of which do not involve the interaction complex. The decreasing dependence of the exchange rate on the Sb(III) concentration with decreasing hydrochloric acid was explained as the consequence of slow interconversion of several forms of Sb(V) at equilibrium.

Neumann has studied the equilibrium (32) and kinetic (33) behavior of Sb(V) in hydrochloric acid solution, and has correlated this work with the results of Bonner and Cheek, as well as performing some new exchange experiments (12).

The observed complexities of the exchange reaction were interpreted on the assumption that $SbCl_6^-$ is the only species that exchanges with Sb(III), and that in more dilute hydrochloric acid solutions the rate determining step is the formation of $SbCl_6^-$ and not the exchange process. Experiments performed under non-equilibrium conditions where all the Sb(V) was initially present as $SbCl_6^-$ indicated that the rate of exchange decreases with increasing acidity. In studying the kinetics of the hydrolysis of $SbCl_6^-$, the Sb(III) catalysis that had been observed was attributed to the ability of the Lewis acid $SbCl_3$ to abstract a chloride ion from $SbCl_6^-$. $SbCl_3$ was also postulated as the exchanging species of Sb(III) instead of $SbCl_4^-$, because decreasing acidity leads to a more rapid exchange between $SbCl_6^-$ and Sb(III), and the formation of a transition state between a neutral molecule and an anion is more probable. Neumann suggests transition states for the exchange such as :



and



Two additional Sb(III)-Sb(V) systems have been studied by Turco, who observed the effect of bromide in 3.2 molal HCl (34). The rate constant at 26° was found to be given by the expression:

$$k = (4.4 \pm 0.2)\text{x}10^{-4}\,[Sb(III)]^{\sim 0.15}\,[Sb(V)]^{1.1}\,[Br^-]^{3.5}\,[H^+]^{4.2}$$

The fractional orders observed were not explained, a not unexpected consequence since the system is sufficiently complex in HCl without introducing bromide as another variable.

In 1.8 $\underline{N}$ KOH, no exchange was observed between antimonite and antimonate (35).

III. THEORETICAL

The exponential rate law which governs the appearance of radioactive atoms in the initially untagged species has been derived by McKay (36), and in its logarithmic form appears as follows:

$$\ln(1-F) = -R\,\frac{(a+b)}{ab}\,t \quad \text{, where:}$$

R = observed rate of exchange
a, b = total concentrations of the reactants
F = fraction of exchange, x/x_∞, with:
  x = specific activity at time t in initially untagged species
  x_∞ = specific activity at time t_∞ in initially untagged species

This exponential law is followed regardless of the mechanism by which exchange occurs, the number of exchangeable atoms in each species, or the concentration of the radioactive atoms. The only restriction in its application is that the exchange reaction must occur in a stable, homogeneous phase, and that the atoms of each oxidation state are either chemically equivalent or are involved in an equilibrium among themselves which is rapid compared to the rate of exchange. A plot of $\ln(1-F)$ *vs.* t will be linear for the entire run, and R may be calculated from the slope. The great advantage in the study of exchange kinetics as opposed to the kinetics of ordinary chemical reactions is that R is evaluated from the entire run, and not from an extrapolated point.

More conveniently, $t^{\frac{1}{2}}$ can be obtained graphically, and R evaluated from a derived relation:

$$R = \frac{0.693\ ab}{(a + b)\ t^{\frac{1}{2}}}$$

To determine the reaction order with respect to the reactants or any other species, general kinetic procedures are applied. The rate may be typically given by a relation such as:

$$R = k(a)^{\alpha}(b)^{\beta}(c)^{\gamma}$$

The concentrations of a, b, and c may be independently varied, and α, β, γ, the orders of the reaction with respect to the individual reactants evaluated, e.g., from the slope of the plot of log R vs. log (a) :

$$\left(\frac{\partial \log R}{\partial \log (a)}\right)_{(b)(c)} = \alpha$$

Since it is necessary to apply a chemical separation method, transitory intermediates may form which exchange more rapidly than the homogeneous system. Prestwood and Wahl (37) have shown that in the semi-log plot of (1-F) vs. t, while the intercept will not be unity, the slope will not be affected, so that $t^{\frac{1}{2}}$ and R may be correctly evaluated.

IV. EXPERIMENTAL PROCEDURES

A. Materials

The antimony metal and antimony trioxide employed were the Baker and Adamson reagent grade product, while the sulfuric and hydrochloric acids were reagent grade materials purchased from E. I. du Pont de Nemours and Company. Perchloric acid was obtained from the Mallinckrodt Chemical Works. Lithium perchlorate was prepared from Mallinckrodt reagent grade lithium carbonate, a slight excess of which was added to reagent perchloric acid, recrystallized as the trihydrate, and dried over anhydrous lithium perchlorate. Where lithium perchlorate was necessary in preparing solutions for exchange, it was weighed directly, but in general, where possible, the use of lithium perchlorate was conveniently avoided by the judicious combination of perchloric acid and lithium chloride solution, prepared from Mallinckrodt analytical reagents, and standardized by titration with silver nitrate. Lithium sulfate monohydrate was the Fisher "Certified" analytical grade material. The "thionalide", α-mercapto-N-2-naphthylacetamide, was Eastman Kodak #5828, while the 8-hydroxyquinoline (8-quinolinol) was Eastman #794. The cupferron, ammonium nitrosophenylhydroxylamine, was "Baker's Analyzed" reagent grade. All of the other analytical reagents and chemicals employed in this work were reagent grade materials from reputable suppliers, and were used without additional purification, except perhaps for a routine drying operation for the primary analytical standards.

The antimony tracer used in the exchange experiments was Sb^{125}. This nuclide decays to an excited state of its daughter Te^{125} with a half-life of 2.7 years. Maximum β energies observed and their distribution are 0.128 Mev 33%, 0.299 Mev 49%, and 0.616 Mev 18%. Associated γ energies are 0.035, 0.110, 0.175, 0.425, 0.601, and 0.637 Mev. The metastable daughter nucleus attains its ground state by isomeric transition with a half-life of 58 days through emission of 0.0354 and 0.109 Mev γ radiation.(38).

Three Sb^{125} activity units were obtained from the Oak Ridge National Laboratory, each containing 0.4 millicuries of Sb^{125} in 6.2 grams of metallic tin that had been subjected to neutron irradiation for 28 days.

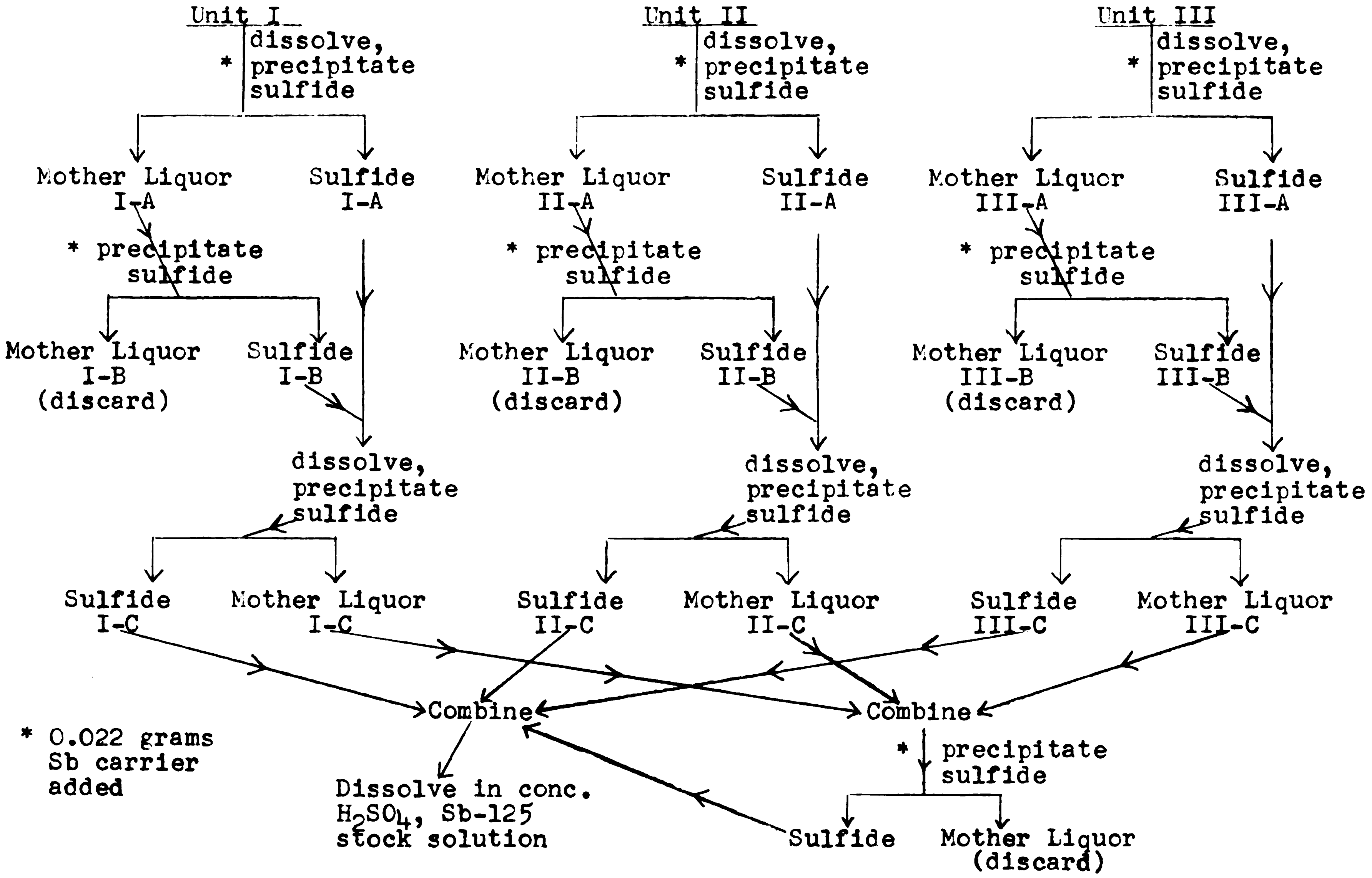
$$Sn^{124}(n,\gamma)Sn^{125} \xrightarrow[\substack{\text{10 minutes} \\ \text{10 days}}]{\beta^-} Sb^{125}$$

Separation of the Sb^{125} from the gross amount of tin was accomplished by fractional sulfide precipitation from a medium in which the tin was present as the oxalato Sn(IV) complex (39, 40, 41). Since each unit contained only approximately 3.8×10^{-7} grams of Sb^{125} in 6.2 grams of tin, it was necessary to employ isotopic carrying. The procedure followed is outlined on page 20.

Each unit was dissolved in 25 ml. of concentrated hydrochloric acid, 5 ml. of 12 M sulfuric acid solution containing 0.022 grams of antimony were added, and the tin oxidized with elemental bromine. A hot solution of 120 grams of oxalic acid dihydrate and 20 grams of potassium hydroxide in 100 ml. of water was added, and the antimony was precipitated by hydrogen sulfide by a pressure technique (42). The antimony sulfide was separated and washed by centrifugation. Another addition of antimony carrier was made to the mother liquor, and a second sulfide precipitate collected. The combined sulfides were dissolved in 5 ml. of concentrated sulfuric acid, and reprecipitated from a medium containing 10 grams of oxalic acid dihydrate in 100 ml. of solution.

The combined sulfides from all three units were dissolved in 30 ml. of hot, concentrated sulfuric acid, yielding an Sb^{125} stock solution which contained approximately 0.15 grams of antimony in 25 ml. of concentrated sulfuric acid.

An aluminum absorption curve was determined for the product, and yielded a range of 220 mg./cm.^{2}, corresponding to a maximum β energy of 0.61 Mev (43). A half-life for the isotope was established employing a National Bureau of Standards RaD-RaE standard. This determination was rather inadequate, decay being observed for a period of only 8 months, but the data yielded a value of 2.6 years, which



* 0.022 grams Sb carrier added

SEPARATION OF SB^{125} BY FRACTIONAL SULFIDE PRECIPITATION agrees as well as can be expected with the accepted value.

B. Antimony Stock Solutions

Antimony metal was dissolved in hot, concentrated, sulfuric acid. The white, crystalline antimony(III) sulfate which precipitated on cooling was separated by filtration through fritted glass, and was recrystallized twice from concentrated sulfuric acid. Antimony(III) stock solutions were prepared by adding an excess of antimony(III) sulfate to hot 12 M sulfuric acid, cooling the solution to room temperature, filtering through fritted glass, and adding a small amount of 12 M sulfuric acid to the filtrate to avoid saturation effects. Two such stock solutions were prepared, and contained 0.0368 and 0.0595 M antimony(III) in 12.76 and 12.74 M sulfuric acid, respectively.

In order to obtain solutions in this concentration range, any hydrolysis of antimony(III) must be avoided. If the antimony(III) sulfate is hydrolyzed with water, or if the starting material is antimony trioxide instead of the metal, maximum antimony concentrations that are realized are of the order of 0.01 M, and a solid phase separates slowly, even if the hydrolyzed sulfate or reagent grade antimony trioxide is digested with hot, concentrated, sulfuric acid for extended periods. Solutions prepared as described above, however, have been stable for more than a year.

The classical preparation of the +5 oxidation state involves the chlorine oxidation of antimony(III) in hydrochloric acid solution (44, 45). This route was initially avoided because of the difficulty of removing traces of chloride from the hydrolyzed product and the need to avoid any possibility of chloride contamination in the exchange experiments in aqueous sulfuric acid which were the primary objective. However, neither the reaction of metallic antimony with concentrated nitric acid nor the oxidation of of a hydrobromic acid solution of antimony trioxide with elemental bromine resulted in quantitative conversion. Antimony(V)/antimony(III) ratios of about two forced acceptance of the chlorination procedure until a superior technique was evolved.

Antimony trioxide was dissolved in concentrated hydrochloric acid, filtered through hardened Whatman #50 paper, and treated with purified chlorine for several hours. The color of the solution proceeded from a light yellow to a dark orange, to a pale greenish-yellow. These transitions are apparently the result of Sb(III)-Sb(V) interaction absorption in hydrochloric acid (29, 46), which disappears as the oxidation goes to completion. The solution was concentrated, cooled in an ice-salt bath, and saturated for three hours with hydrogen chloride generated from concentrated hydrochloric and sulfuric acid. A dense deposit of white crystals of hexachloroantimonic(V) acid separated. These were collected on fritted glass, washed with ice-cold hydrochloric acid, and recrystallized twice from hydrochloric acid by cooling and resaturating with hydrogen chloride. The product remained crystalline only when cold, degenerating into a soupy slurry at room temperature. The hexachloroantimonic acid was hydrolyzed with water, and washed by digestion and decantation with fifteen 1500 ml. portions of water over a period of three weeks. Peptization difficulties were avoided by acidifying the wash water slightly with sulfuric acid. Even after this extensive washing, the supernate yielded a qualitative test for chloride. The hydrolyzed material was collected on a filter, washed into a two liter, round-bottomed, two neck flask, 250 ml. of concentrated sulfuric acid were added, and the mixture was heated to 140-150 °C. while being agitated with a slow stream of nitrogen. Water was periodically added to the pot, while the distillate was analyzed for chloride by addition of silver nitrate and comparison with 0.1 and 1.0 p.p.m. standards in Nessler tubes. After 2300 ml. of distillate were collected in this manner, chloride tests were finally negative. The filtered product was a white, viscid semi-solid (20), which was converted to a white powder after drying at 110 °C. Oxidation state analysis indicated a complete conversion to antimony(V).

Because of its solubility, or slow solution kinetics, preparation of solutions of this material was difficult.

It did not dissolve appreciably in concentrated hydrochloric acid, nor did it dissolve completely in boiling, concentrated sulfuric acid in finite time, except for one fortuitous and never duplicated combination of conditions, when complete solution occurred, yielding an antimony(V) concentration of 0.108 M. Other antimony(V) solutions in sulfuric acid were prepared by heating the product with acid, removing undissolved material by filtration, and concentrating the filtrate. Completely stable solutions up to 0.079 M antimony(V) prepared in this manner were used in some early spectral work, but not in any exchange studies.

The method just described for obtaining sulfuric acid solutions of antimony(V) is circuitous, tedious, and vulnerable to criticism as to trace chloride impurities. An optimum technique was found where the antimony(III) was oxidized to antimony(V) _in situ_, utilizing the mixture of peroxydisulfuric acid and its decomposition products, peroxymonosulfuric acid and hydrogen peroxide, that results from the electrolysis of sulfuric acid solutions.

Peroxydisulfuric acid was produced by a high current density anodic oxidation of sulfuric acid (47, 48, 49, 50). The anode was a one centimeter length of heavy platinum wire; the cathode was a 15 centimeter spiral of finer platinum. The source of potential was a six volt automobile storage battery used at full capacity. The 9 M sulfuric acid electrolyte, cooled in an ice bath, was electrolyzed at 1.5

amperes for eight hours. Current efficiencies of approximately 33% were obtained, based on total oxidizing power of the product solutions.

Immediately after preparation, the "peroxy acid" was added in 2-300% excess to antimony(III) solutions in 12 M sulfuric acid, and the mixture allowed to stand for twelve hours. Gentle heat was applied until oxygen evolution ceased, then increased in intensity to concentrate the antimony(V). Unless the antimony solution was extremely dilute, the increase in heat resulted in the appearance of a fine, white, solid phase, which slowly dissolved. Stock solutions of antimony(V) prepared in this manner yielded antimony concentrations of 0.05-0.08 M, although higher concentrations could be attained with no precipitation difficulties.

The normal procedure in electron exchange studies is to prepare a solution of the two oxidation states, allow them to equilibrate, and take zero time as the moment of addition of a small amount of tracer. This technique presumes that the exchanging species in the gross mixture and the tracer stock solution are identical, or reach equilibrium instantaneously. Because of the complexities inherent in the antimony(III)-(V) system, such an assumption appeared unwarranted, so that antimony(V) stock solutions for exchange work were prepared with Sb^{125} initially present. An appropriate quantity of Sb^{125} solution was added to antimony(V) in sulfuric acid solution, and the "peroxy acid" oxidation process repeated. The product was diluted with 6 M sulfuric acid to yield an antimony(V) in approximately 12 M sulfuric acid stock, containing the necessary Sb^{125} tracer, suitable to be used in the preparation of the final exchanging solutions.

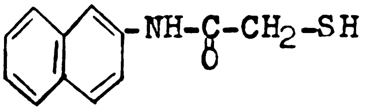
C. Solutions for Exchange

For each kinetic run two individual antimony(III) and antimony(V) solutions were prepared in 50 ml. volumetric flasks. Each pair was identical in all respects except antimony content. The order of addition of components, when used, was always the same, as follows: solid lithium perchlorate trihydrate, solid lithium sulfate monohydrate, water, hydrochloric acid, lithium chloride solution, perchloric acid, sulfuric acid, antimony(III) or antimony(V) stock solution, and finally, after temperature equilibration, water to volume. The solids were weighed to the tenth of a milligram on the analytical balance, while the calculated amounts of each stock solution were added from clean, dry burets, whose stopcocks were lubricated only with the solution to be added. The exchange solutions were equilibrated at constant temperature for at least twelve hours after preparation, and mixed at zero time.

D. Separation of Antimony Oxidation States

In the observation of the kinetics of the exchange, the tracer was always present initially in the (V) state. Antimony(III) was separated at definite time intervals, and the growth of activity observed, since this technique offers the least probability for separation-induced exchange due to transitory complexes and separation intermediates (51). While antimony(III)-(V) separations have been utilized in previous exchange investigations, this study presented the unique problem that the antimony solutions were 10-100 times more dilute. It was necessary to be able conveniently to separate, mount, and count approximately 5×10^{-3} millimoles of antimony(III). Three distinct separations were used, two of which involved β counting of a gravimetric precipitate, while the third was based on liquid phase γ scintillation counting of an antimony(III) extract.

The first method evolved employed "thionalide", the β-aminonaphthalide of thioglycollic acid, to precipitate the antimony(III) thionalate, $Sb(C_{12}H_{10}ONS)_3$ (52, 53, 54).



"Thionalide"

The reagent behaves in a manner analagous to hydrogen sulfide, cations forming insoluble sulfides, in general, form insoluble "thionalates". The precipitation of antimony(V) was prevented by the formation of the hexafluoroantimonate(V) complex with potassium fluoride. The advantage of this reagent is the bulky nature and high molecular weight of the precipitate. The chief disadvantage is its sensitivity to oxidation, an insoluble disulfide being formed, the presence of which prevents direct gravimetric determination of antimony recovery.

The precipitate was separated by filtration through 22 mm. Whatman #42 paper on a stainless steel filter with a removeable chimney to facilitate mounting of the sample. Since antimony(III) thionalate is readily soluble in acetone, it was easily possible to dissolve the precipitate, destroy the complex by nitric-sulfuric digestion, and determine the antimony colorimetrically by the tetraiodoantimonate method (vide infra). Separation and recovery of the antimony(III) was in excess of 99%.

The thionalide method was successfully applied to exchange studies in aqueous sulfuric acid media in which no electron transfer occurred. When systems with chloride present were studied, it was necessary to abandon the method because induced exchange became a problem (>50%), and also extensive oxidation of the reagent resulted in increased and unreproducible contamination of the antimony(III) thionalate with disulfide, leading to inconsistent self-absorption errors in the counting procedure.

The second gravimetric separation that was applied was the use of 8-hydroxyquinoline to precipitate the antimony(III) oxinate (54, 55), a method that has been successful in other antimony exchange systems (3, 34). Oxine precipitation, however, was not sufficiently sensitive in this concentration range, and it was necessary to supply additional antimony(III) as a carrier. Induced exchange again became a problem in the presence of appreciable chloride, although the technique was quite satisfactory in low chloride systems. Filtration and mounting were accomplished as described for the thionalide separation.

The successful separation that was employed in all exchange runs for which rates were determined involved the precipitation of antimony(III) with cupferron (ammonium nitrosophenylhydroxylamine)(56, 57). Antimony(V) is not precipitated by this reagent. Since a gravimetric separation would be inaccurate because of the small particle size of the precipitate, uncertainty in its composition, and its instability, the antimony(III) cupferrate was extracted with chloroform (58), and an appropriate aliquot taken for γ counting. Induced exchange was a minimum.

The cupferron was freshly prepared as a 1% aqueous solution at least every eight hours, and maintained at 0 °C. to avoid decomposition. A 5 ml. aliquot of the exchanging solution was pipetted into a 125 ml. separatory funnel containing 70 ml. of ice-cold water and 5 ml. of reagent solution, and the mixture agitated; antimony(III) cupferrate precipitated. The mixture was then shaken for 30 seconds with 5 ml. of reagent grade chloroform, and the phases allowed to separate for two minutes. The chloroform extract was filtered through a glass wool plug into a 10 ml. volumetric flask. An additional 5 ml. of cupferron reagent were added to the separatory funnel, and the mixture again extracted with 4 ml. of chloroform. After a third extraction with 1½ ml. of chloroform, the glass wool plug was washed with ½ ml. of fresh chloroform and the extract made up to volume. A 4 ml. aliquot of the solution was pipetted into a one dram screw cap vial. To prevent loss of chloroform by evaporation and consequent variation in counting geometry, it was necessary to seal the vials by stoppering them with a cork cut off flush with the top of the vial, coated with Goodyear "Pliobond" adhesive, and covered with a circle of aluminum foil before the cap was screwed on tightly.

It was essential to use an ice-cold aqueous phase because the extracted antimony(III) cupferrate complex is not stable, and there is a possibility of decomposition and "bleed back" into the aqueous phase (59). Similarly, the antimony(III) cupferrate solution in chloroform decomposes, a solid phase separating in a manner of minutes if the solution is kept at room temperature. It is impossible to secure a representative aliquot for counting if there is even a slight turbidity present. Extracting a cold aqueous phase, however, yields a chloroform solution stable for at least fifteen minutes.

E. Counting Procedures

The filter papers with the thionalide or 8-hydroxyquinoline precipitates were mounted under cellulose film on cards cut to fit the plastic holder of an R. C. L. steel castle, and counted in the center of, and two cm. below, a 2.7 mg./cm.^{2} G-M tube monitored by a Nucleur Corporation scaling unit (Model 163). When the equipment became available shortly after the inception of this work, β counting of the solid samples was accomplished with a Baird Associates - Atomic Instrument Proportional Counter and a mylar window, gas flow tube. In all such samples, activities observed were very low so that no correction other than that for background was necessary.

All of the kinetic runs where significant exchange was observed were counted in new, one dram, screw cap vials, sealed as previously described, in a well-type NaI(Tl) scintillation counter. Because of the essentially 4π geometry and efficiency of scintillation detection, only background corrections were applied. A minimum of 10,000 counts were registered for each sample. Since all the samples from individual runs could be easily counted within two hours, no correction was necessary for the decay of Sb^{125}.

It is customary to obtain equilibrium activities when $t = \infty$ for McKay plots by taking samples after 10 half-lives. A calculated equilibrium activity was used in this project because of the long half-lives encountered, and also because of the non-linearity of the McKay plots observed under some circumstances. In general, kinetic runs were sampled for approximately two half-lives, and 8 - 14 samples were obtained. Beyond two half-lives, or (1-F) values of 0.200, errors in radioassay increase appreciably (15, 68), and small errors in the rather involved separation technique introduce considerable scatter in the points of the McKay plot.

Equilibrium activities were calculated from the following relation:

$$A_\infty = A_o \left(\frac{M_3}{M_3 + M_5} \right) \qquad \text{where:}$$

A_∞ = equilibrium activity at $t = \infty$
A_o = observed activity of an equivalent aliquot of the exchanging solution
M_3, M_5 = molar concentrations of Sb(III) and Sb(V) respectively

Three samples were taken from each run for equilibrium activity calculations, and were mounted in a manner identical to that of the kinetic specimens. The three equilibrium activity samples were counted at the beginning, at the half-way point, and at the end of a kinetic run sample counting sequence. The average of all these results yielded A_o.

Although the volumetric equipment used in taking these standard samples was deliberately varied, the observed activities agreed within counter statistics. This technique also served to monitor the counting equipment for drift.

F. Light Absorption Measurements

Absorption spectra for qualitative or semi-quantitative purposes were recorded on a Beckman DK-2 recording spectrophotometer. All quantitative measurements were obtained with a Beckman model DU spectrophotometer equipped with a photomultiplier tube and a line-operated, constant voltage, D.C. power supply. Since all spectral studies were made below 400 $m\mu$, a hydrogen discharge lamp served as the light source. Glass-stoppered, matched quartz cells with 10 mm. light paths were used, with distilled water as the reference solvent. All sample absorptions were corrected by simultaneous blanks on the appropriate media in which antimony absorption was being observed.

G. Analytical Methods

Acid solutions were standardized by titration with half-normal, carbonate-free sodium hydroxide solution, which had been standardized with potassium acid phthalate and stored in a paraffin-coated bottle protected from the atmosphere by an ascarite guard tube. To avoid errors from too many volumetric operations, 500 or 1000 λ portions of the fairly concentrated acid stock solutions were measured by Research Specialties Co. "Lambda-Pettes" which are calibrated to contain, not deliver, thereby avoiding viscosity effects and drainage errors.

Antimony solutions were analyzed by titration with decinormal potassium bromate, prepared from oven-dried, primary standard reagent. Titrations were performed in 2-3 N hydrochloric acid solution, with naphthol blue-black as an irreversible indicator (60). Antimony(V) was determined by reduction with sodium sulfite, evolution of excess SO_2 by boiling, and bromate titration. For samples requiring more than 5 ml. of titrant, a 10 ml. buret calibrated every 0.05 ml. was employed, while a micro-buret calibrated every 0.01 ml. served in semi-micro work. The colorimetric tetraiodoantimonate method which is based on the light absorption of the SbI_4^- complex ion, was applied to small quantities of antimony (61, 62). The colorimetric reagent is a concentrated potassium iodide - ascorbic acid solution, the ascorbic acid serving to reduce any iodine liberated by oxidizing agents in the sample. Absorption measurements were taken at 425 $m\mu$ vs. a reagent blank, and the system followed Beer's law in the concentration range considered ($0.1 - 3 \times 10^{-3}$ millimoles Sb/50 ml.).

Chloride determinations were made by the Caldwell - Moyer modification of the Volhard method (63). Where antimony was present in chloride titrations, it was complexed with tartaric acid. The silver nitrate solution was standardized gravimetrically as silver chloride, and volumetrically by titration of aliquots of standard sodium chloride solution.

Sulfate was determined gravimetrically as barium sulfate which was ignited in platinum crucibles. When necessary, antimony was removed as the metal on fine iron wire.

V. RESULTS

A. Electron Exchange in Aqueous Sulfuric Acid

The initial purpose of this study was to examine Sb(III)-Sb(V) exchange in aqueous sulfuric acid. Considerable difficulty was experienced with precipitation from mixed Sb(III)-Sb(V) solutions. This phenomenon was a function of Sb(III), Sb(V), and sulfuric acid. In 12 M sulfuric acid, Sb(III)-Sb(V) mixtures in all proportions up to individual concentration maxima of 0.02 M have been stable for one year. As the acid is diluted below 9 M, precipitation occurs from mixtures of Sb(III) and Sb(V) solutions which are individually stable.

A survey was made in which [Sb(III)], [Sb(V)], and [H_2SO_4] were varied. The precipitates were collected on fritted glass, and the filtrates and precipitates analyzed. The maximum compatible concentrations of Sb(III) and Sb(V) that are stable, or at least metastable, in 3-9 M sulfuric acid are approximately 3-4 x 10^{-3} M. The conditions for precipitate formation were difficult to establish because the process is a function of time. Clear filtrates slowly separate additional solid phase. All the precipitates contained equimolar quantities of Sb(III) and Sb(V). Sulfate ion was present, but not in any discernible stoichiometric proportion, and may have been the result of adsorption and occlusion of sulfuric acid on the bulky and amorphous precipitates. These had been sucked dry in the vacuum filtration process, but were not washed because of the danger of peptization and fear of hydrolysis.

With the 1-1 Sb(III)-Sb(V) ratio, no great imagination is necessary to postulate $[SbO][Sb(OH_6)]$ to be the composition of the precipitates. The elimination of three molecules of water from this "antimonyl antimonate" yields the formula for the tetroxide, Sb_2O_4. The absence of sulfate in the precipitates, however, has not been established. Spectroscopic evidence (vide infra) indicates that Sb(V) species in aqueous sulfuric acid are involved in complex equilibria. These may involve $Sb(SO_4)_3^-$, $Sb(OH)_6^-$, and the obvious intermediates. The rapidity of precipitation is an inverse function of the sulfuric acid concentration. Continuing precipitation with time may be the result of the slow formation of additional $Sb(OH)_6^-$.

After these preliminary observations, the exchange reaction between Sb(III) and Sb(V) was studied in the acid range 3-12 M. In no case was exchange observed. The systems examined are given in Table I.

B. Electron Exchange in Aqueous Sulfuric Acid with Added Chloride Ion

The lack of exchange observed in aqueous sulfuric acid was dissappointing, but it did present the opportunity to initiate exchange by appropriate modifications. Addition of

TABLE I

EXCHANGE RUNS IN AQUEOUS SULFURIC ACID

$[H_2SO_4]$ $\underline{M}$	$[Sb(III)]$ $\underline{M}$	$[Sb(V)]$ $\underline{M}$	Hours Observed	Comments
2.97	2.40×10^{-3}	2.39×10^{-3}	133	No exchange. Precipitate observed after 800 hours.
3.99	2.40×10^{-3}	2.39×10^{-3}	813	No exchange. Slight precipitate observed after 1600 hours.
6.00	2.40×10^{-3}	2.39×10^{-3}	1588	No exchange.
6.00	5.00×10^{-3}	4.77×10^{-3}	82	No exchange. Slight precipitate observed after 150 hours.
8.96	2.50×10^{-3}	2.39×10^{-3}	73	No exchange. Slight precipitate observed after 150 hours.
12.0	2.50×10^{-3}	2.39×10^{-3}	1549	No exchange.
11.9	10.2×10^{-3}	10.7×10^{-3}	787	No exchange.

chloride ion was the obvious choice, since Sb(III) and Sb(V) do exchange in hydrochloric acid, and chloride has a pronounced catalytic effect in many exchange systems. Preliminary experiments in which hydrochloric acid was added indicated that chloride did indeed promote exchange, suggesting a study of the process in such chloride containing media.

Since the exchanging Sb(III) and Sb(V) species were certain to be involved in complex equilibria, constant ionic strength was maintained in an attempt to eliminate activity coefficients as variables. Whether the principal of ionic strength as originally defined by Lewis and Randall (64) applies is open to considerable question, since the system is hardly a dilute electrolyte. However, maintenance of constant ionic strength should be subject to less criticism than its neglect, and some concession to thermodynamics should be made in a kinetic study.

Choice of an ionic strength also was required because of the necessity to consider the dissociation of bisulfate ion in the calculation of the concentration of the species present. The second ionization constant of sulfuric acid is defined as:

$$K_2 = \frac{(a_{H^+})(a_{SO_4^=})}{(a_{HSO_4^-})}$$

For concentration calculations, it is necessary to apply the concentration "equilibrium constant", K_{2c}:

$$K_{2c} = \frac{(H^+)(SO_4^=)}{(HSO_4^-)}$$

which is related to the thermodynamic dissociation constant by:

$$K_2 = K_{2c}\frac{(\gamma_{H^+})(\gamma_{SO_4^=})}{(\gamma_{HSO_4^-})} = K_{2c}\cdot\gamma_R$$

Values of γ_R and K_{2c} at various ionic strengths were available from the Raman data of Smith (65) and Maranville (66), based upon K_2 at 25° = 0.0104, and concentration calculations were made according to the method of Young and Blatz (67). Necessary assumptions were that HCl and $HClO_4$ were equivalent, that these components as well as the salts lithium sulfate, lithium chloride, and lithium perchlorate which were occassionally necessary to maintain ionic strength were completely ionized, and that the correspondence of the dissociation constant of bisulfate ion to the ionic strength is not altered by their presence.

In general, ionic strength (molar scale) was maintained at 10.5, with K_{2c} = 3.19. In the study of the effect of hydrogen ion and of sulfate on the rate of exchange, it was sometimes necessary to vary the ionic strength to provide a significant concentration range of the species being investigated. In such cases, the appropriate value of K_{2c} from the data of Smith was applied, and any such deviation is noted in the tables of data. The concentrations of

Sb(III) and Sb(V) were always negligible in comparison to the other species present, so their contribution to the ionic strength was neglected. Temperature was maintained at 24.80 ± 0.02 °C. for all runs, except for one series at an elevated temperature.

1. Variation of Exchange Rate with Chloride Ion

The effect of chloride ion on the exchange rate was investigated in the concentration range 0 - 6 M chloride. The sum of hydrochloric and perchloric acid concentrations was maintained at 6.00 M, so that for any exchange run: M $HClO_4$ = 6.00 - M HCl. The exchange rate, R, was calculated from the half-times obtained from plots of log(1-F) vs. t. The data are presented in Table II. In Figure 1, the log-log plot of R vs. chloride concentration, the rates of duplicate runs are averaged when they are in close agreement.

The log-log plot of R vs. chloride, although reasonably linear for low chloride concentrations, indicates a continuously decreasing chloride dependence. The slope was statistically evaluated for arbitrary portions of the curve, with the following results:

(Cl^-) Range	Slope
0.025-0.20 M	2.05
0.15 -0.60 M	1.41
0.50 -1.50 M	0.82
1.50 -6.00 M	0.28

TABLE II

VARIATION OF EXCHANGE RATE WITH CHLORIDE CONCENTRATION

$\mu = 10.5$, $K_{2c} = 3.19$, $[H^+] = 9.75$ M, $[SO_4^=] = 0.74$ M, $[HSO_4^-] = 2.27$ M, $[H_2SO_4] = 3.01$ M, $[ClO_4^-] = (6.00 - [Cl^-]$ M$)$ M, $[Sb(III)] = 1.31 \times 10^{-3}$ M, $[Sb(V)] = 1.30 \times 10^{-3}$ M

$[Cl^-]$ M		$t_{\frac{1}{2}}$ (hours)	R (moles/liter-hour)
None	(a)	No exchange observed in 1700 hours.	
0.025	(a)	7,522	5.99×10^{-8}
0.05	(a)	2,048	2.20×10^{-7}
0.10	(a)	463	9.72×10^{-7}
0.15	(a)	173	2.60×10^{-6}
0.20	(b)	118	3.82×10^{-6}
0.30	(a)	66.3	6.79×10^{-6}
0.40	(a)	39.9	1.13×10^{-5}
0.40		40.1	1.13×10^{-5}
0.50	(a)	31.7	1.42×10^{-5}
0.60	(a)	23.3	1.93×10^{-5}
0.60		25.9	1.74×10^{-5}
0.70		26.7	1.69×10^{-5}
0.80		21.2	2.13×10^{-5}
1.00		20.6	2.20×10^{-5}
1.50		12.0	3.77×10^{-5}
2.00		11.2	4.02×10^{-5}
2.00		10.8	4.19×10^{-5}
2.00		10.6	4.27×10^{-5}
2.00		10.2	4.43×10^{-5}
3.00	(a)	10.2	4.42×10^{-5}
4.00	(a)	9.33	4.83×10^{-5}
5.00	(a)	8.75	5.15×10^{-5}
6.00		6.10	7.41×10^{-5}
6.00		7.62	5.93×10^{-5}

(a) $[Sb(V)] = 1.29 \times 10^{-3}$ M
(b) Average of 11 runs (see Table X)

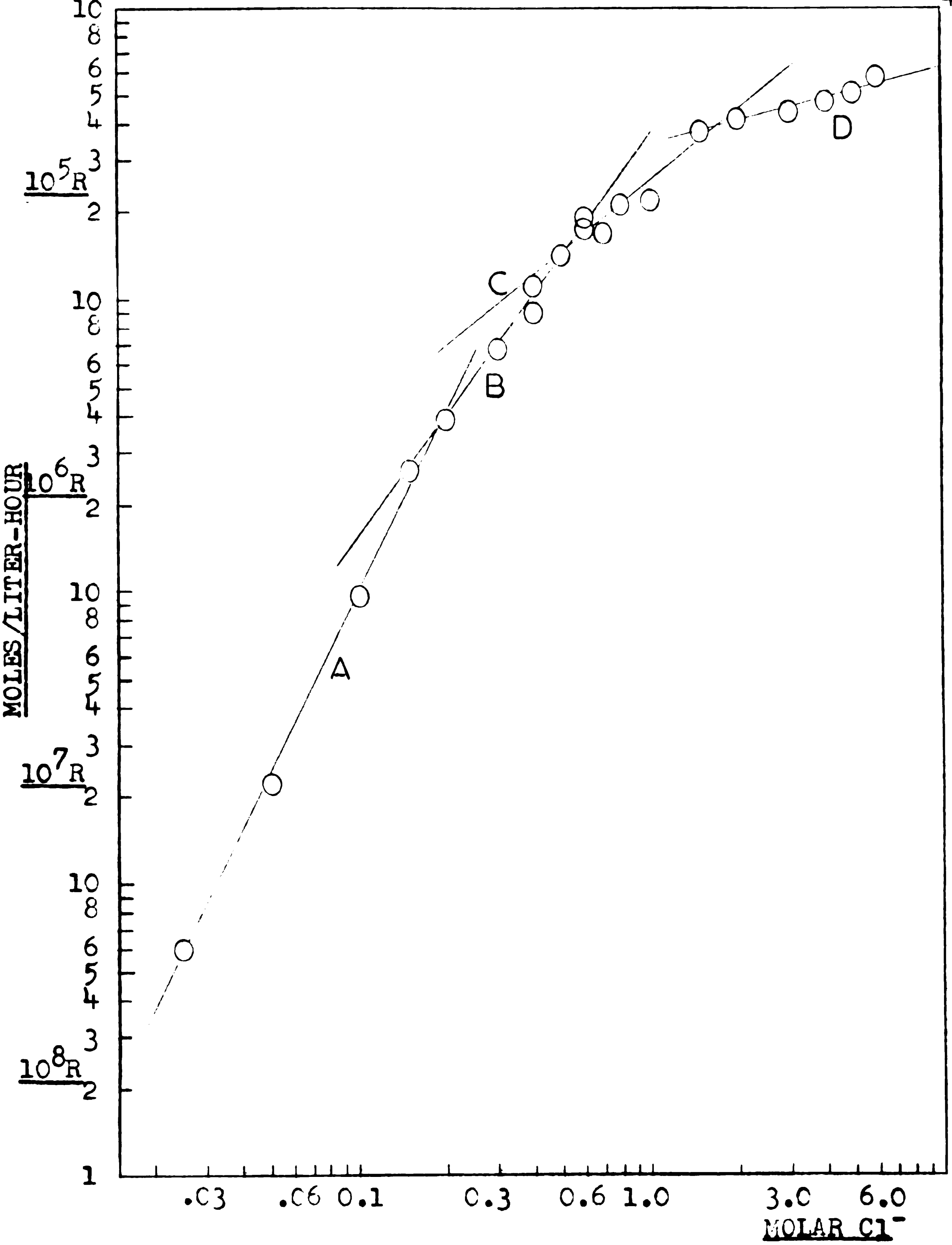


FIGURE 1. EXCHANGE RATE AS A FUNCTION OF CHLORIDE

A- Slope = 2.05 B- Slope = 1.41 C- Slope = 0.82
D- Slope = 0.28

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The decreasing slope at high chloride is most probably the result of the system approaching a pseudo-zero order chloride dependence because of the gross excess present, and should not be interpreted as lack of participation of chloride in the exchange reaction.

The McKay plots did not all yield the anticipated linear relationship between log(1-F) and t. At 6 <u>M</u> chloride, the plots are linear. With decreasing chloride concentration, deviation from linearity at low (1-F) values occurs, reaching a maximum in the region 1-2 <u>M</u>. From 1-0.4 <u>M</u> chloride, this deviation decreases, until the McKay plots are again linear. Typical examples are illustrated in Figures 2, 3, and 4. Half-times for exchange and rates for runs exhibiting this phenomenon were obtained from the linear portions.

The observed curvature could be the result of several effects. Two different species could be involved in the electron exchange, and the equilibrium between these species could be kinetically slow. Alternatively, the curvature could be the result of the formation of a non-exchanging species, either a hydrolyzed form or perhaps an interaction dimer. Absorption spectra of the individual Sb(III) and Sb(V) solutions, and the Sb(III)-Sb(V) exchange solution in 2 <u>M</u> chloride were obtained one hour and 24 hours after zero time. If hydrolysis were occurring, one would anticipate the absorption to shift toward shorter wavelengths; if an interaction dimer were forming, a shift to

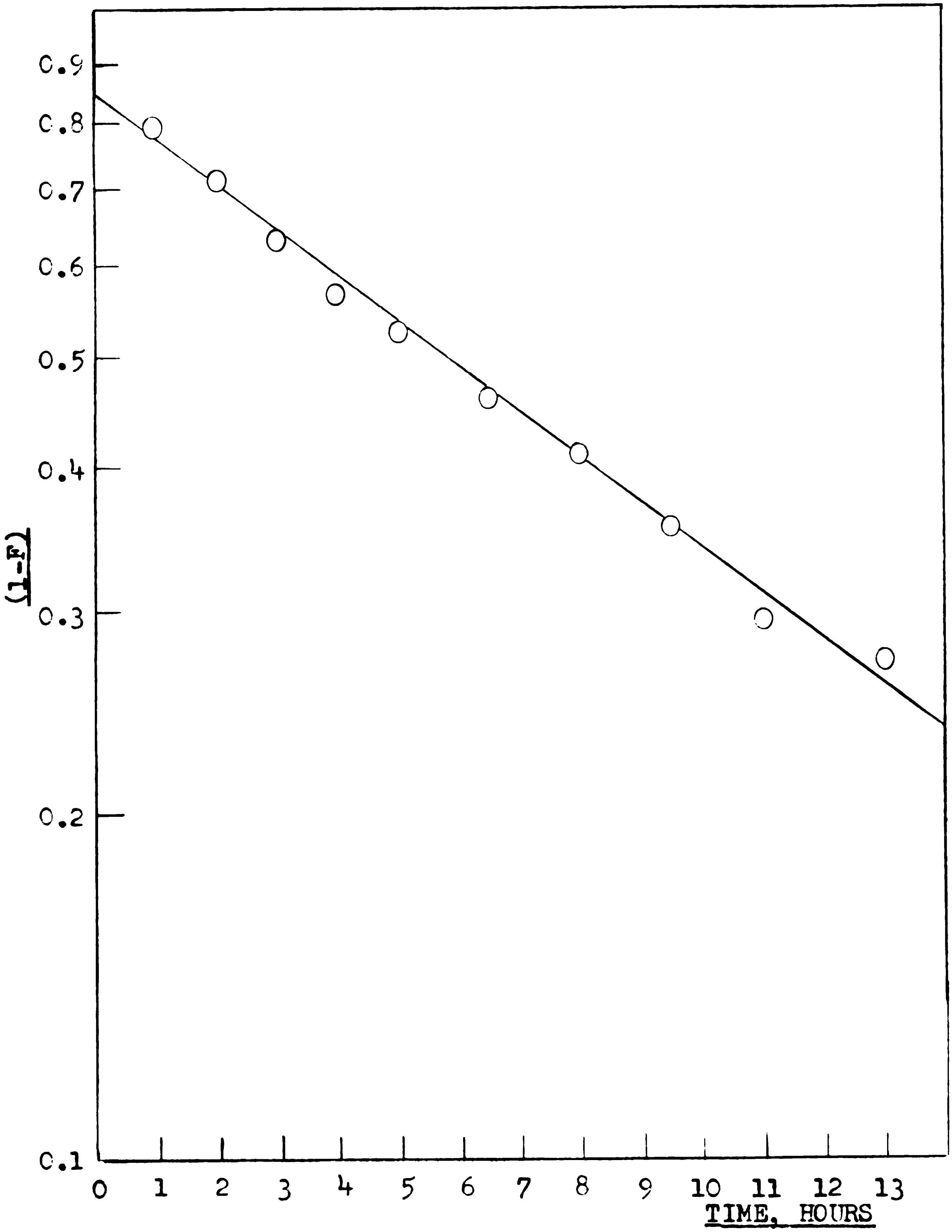


FIGURE 2. TYPICAL EXCHANGE IN 6.00 M CHLORIDE

$t_{\frac{1}{2}}$ = 7.62 hours

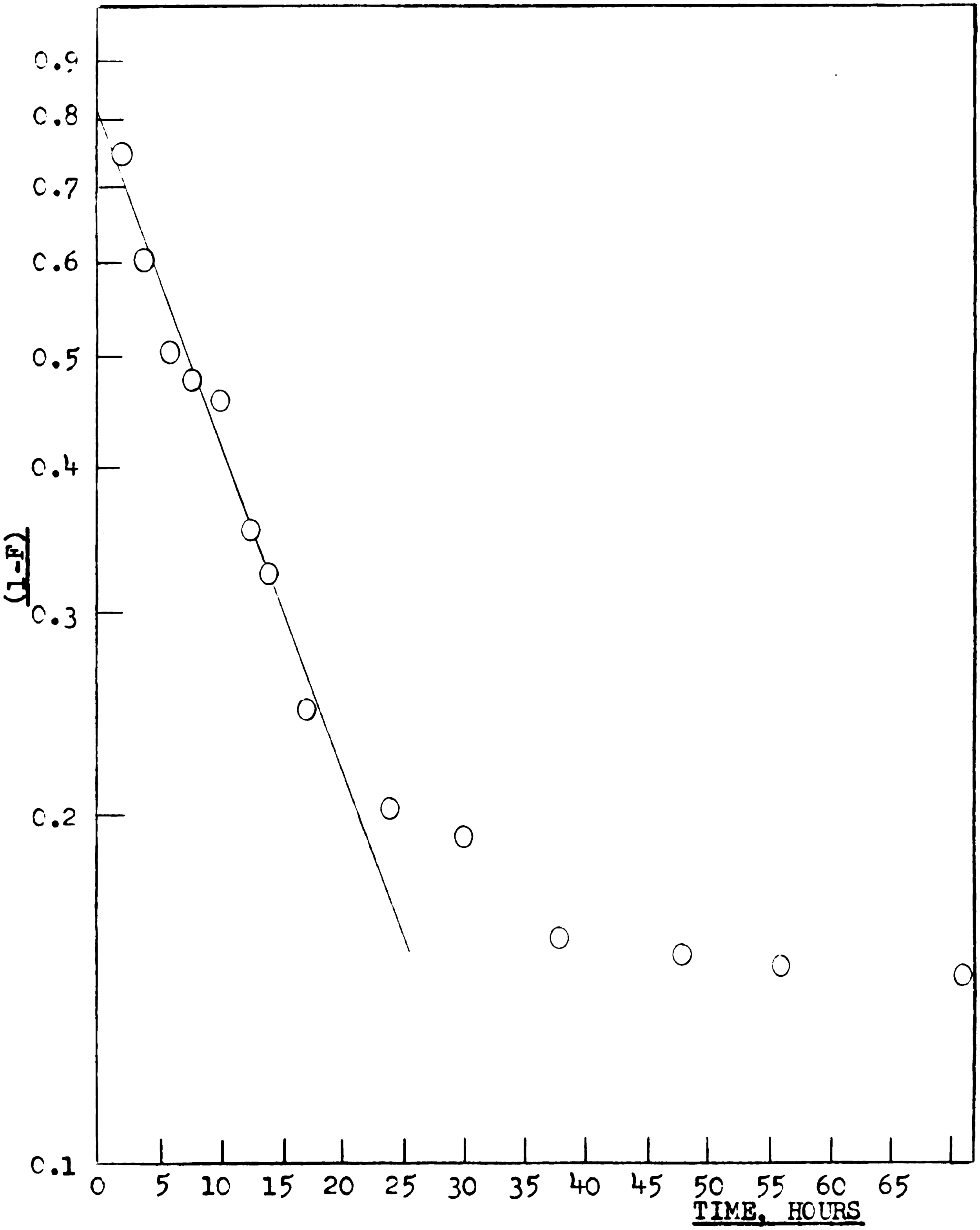


FIGURE 3. TYPICAL EXCHANGE IN 2.00 M CHLORIDE

$t_{\frac{1}{2}}$ = 10.6 hours

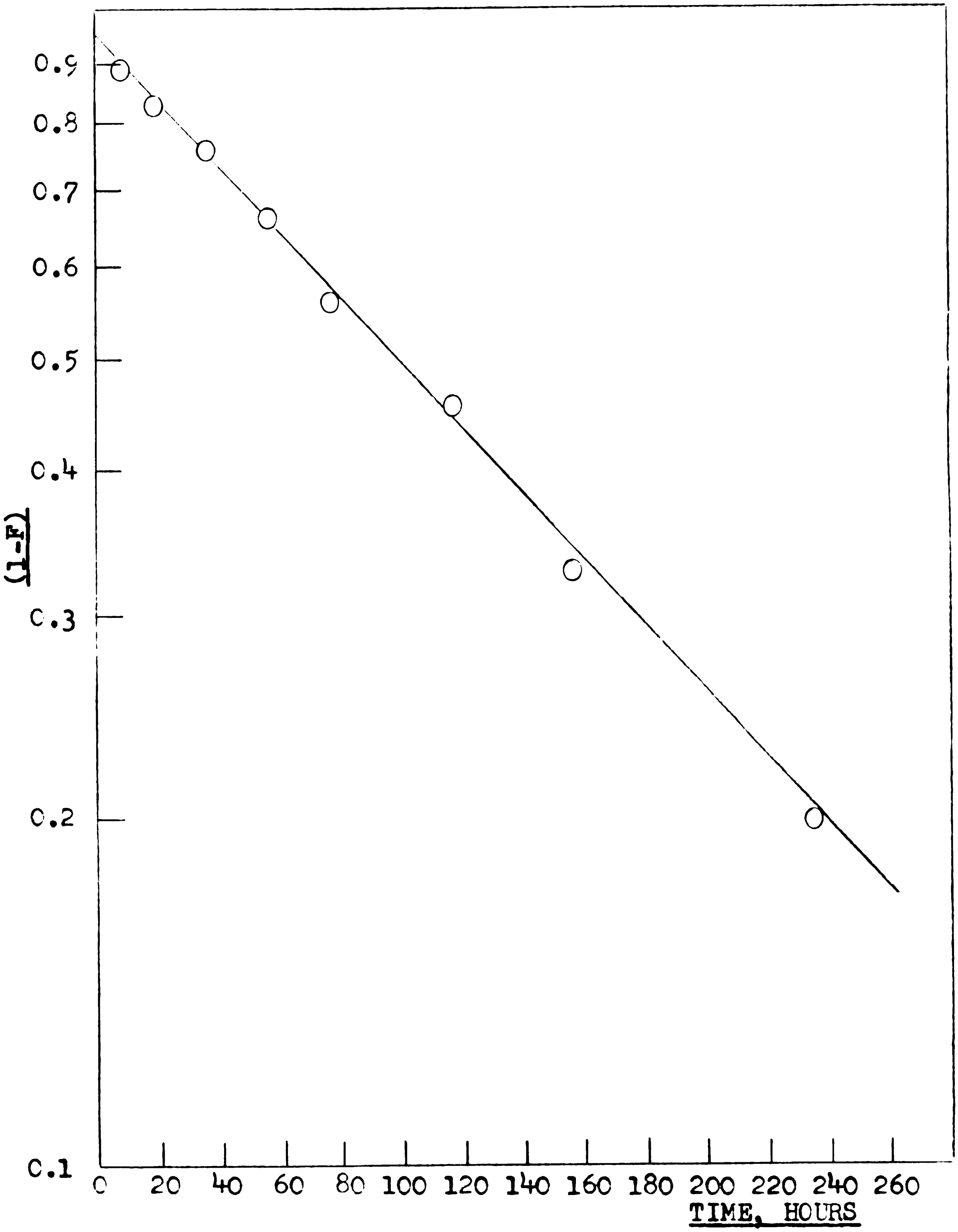


FIGURE 4. TYPICAL EXCHANGE IN 0.20 M CHLORIDE

$t_{\frac{1}{2}}$ = 123 hours

longer wavelengths would be expected. The spectra, however, exhibited absolutely no change. Runs in 0.20 and 2.00 M chloride were made at 42.0 °C. to observe the effect of temperature. It was necessary to assume that this temperature change had a negligible effect in calculating the concentrations of the species in the exchange solutions. The data obtained are given in Table III, and McKay plots are illustrated in Figures 5 and 6.

By examination of the data at the two temperatures for the runs in 0.20 and 2.00 M chloride, it is immediately obvious that a pseudo-Arrhenius plot of log R vs. 1/T will yield two quite different slopes, with the slope of the 2.00 M exchange being considerably greater. This observation is in agreement with the more pronounced curvature of the non-linear McKay plots at 24.8 °C. as compared to 42.0 °C. Apparently there are at least two mechanisms for the exchange, and the exchanging species are functions of the chloride concentration. In the intermediate region of chloride concentration, the processes are competing, with a kinetically slow equilibrium between the exchanging species.

TABLE III

EXCHANGE AT 42.0° C.

$\mu = 10.5$, $K_{2c} = 3.19$, $[H^+] = 9.75\ \underline{M}$, $[SO_4^=] = 0.74\ \underline{M}$, $[HSO_4^-] = 2.27\ \underline{M}$, $[H_2SO_4] = 3.01\ \underline{M}$, $[ClO_4^-] = (6.00 - [Cl^-]\ \underline{M})\ \underline{M}$, $[Sb(III)] = 1.31 \times 10^{-3}\ \underline{M}$, $[Sb(V)] = 1.31 \times 10^{-3}\ \underline{M}$

$[Cl^-]$ $\underline{M}$	$t_{\frac{1}{2}}$ (hours)	R (moles/liter-hour)
2.00	2.00	2.28×10^{-4}
2.00	2.22	2.04×10^{-4}
0.20	53.4	8.50×10^{-6}
0.20	58.2	7.80×10^{-6}

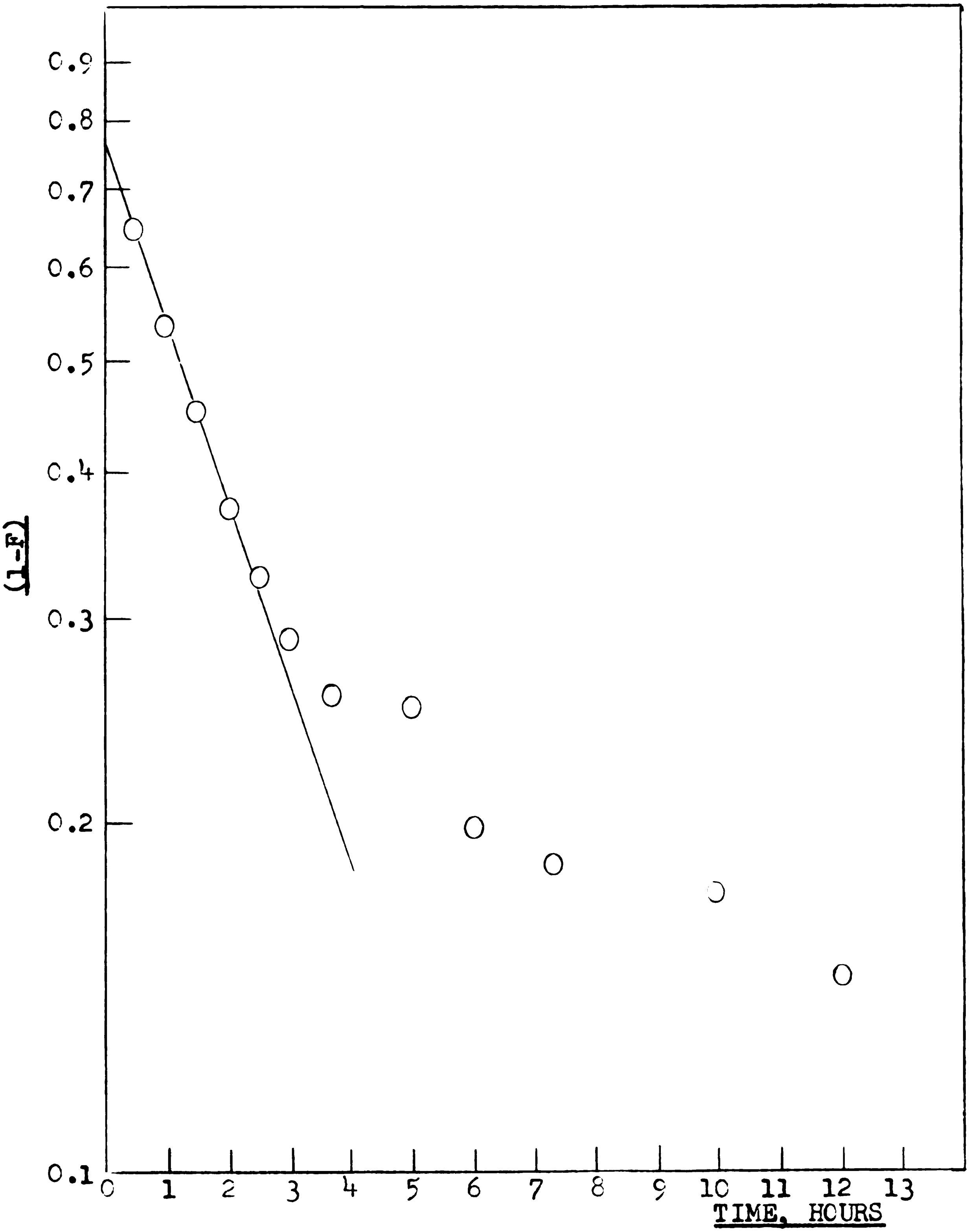


FIGURE 5. EXCHANGE IN 2.00 M CHLORIDE AT 42.0° C.

$t_{\frac{1}{2}}$ = 2.00 hours

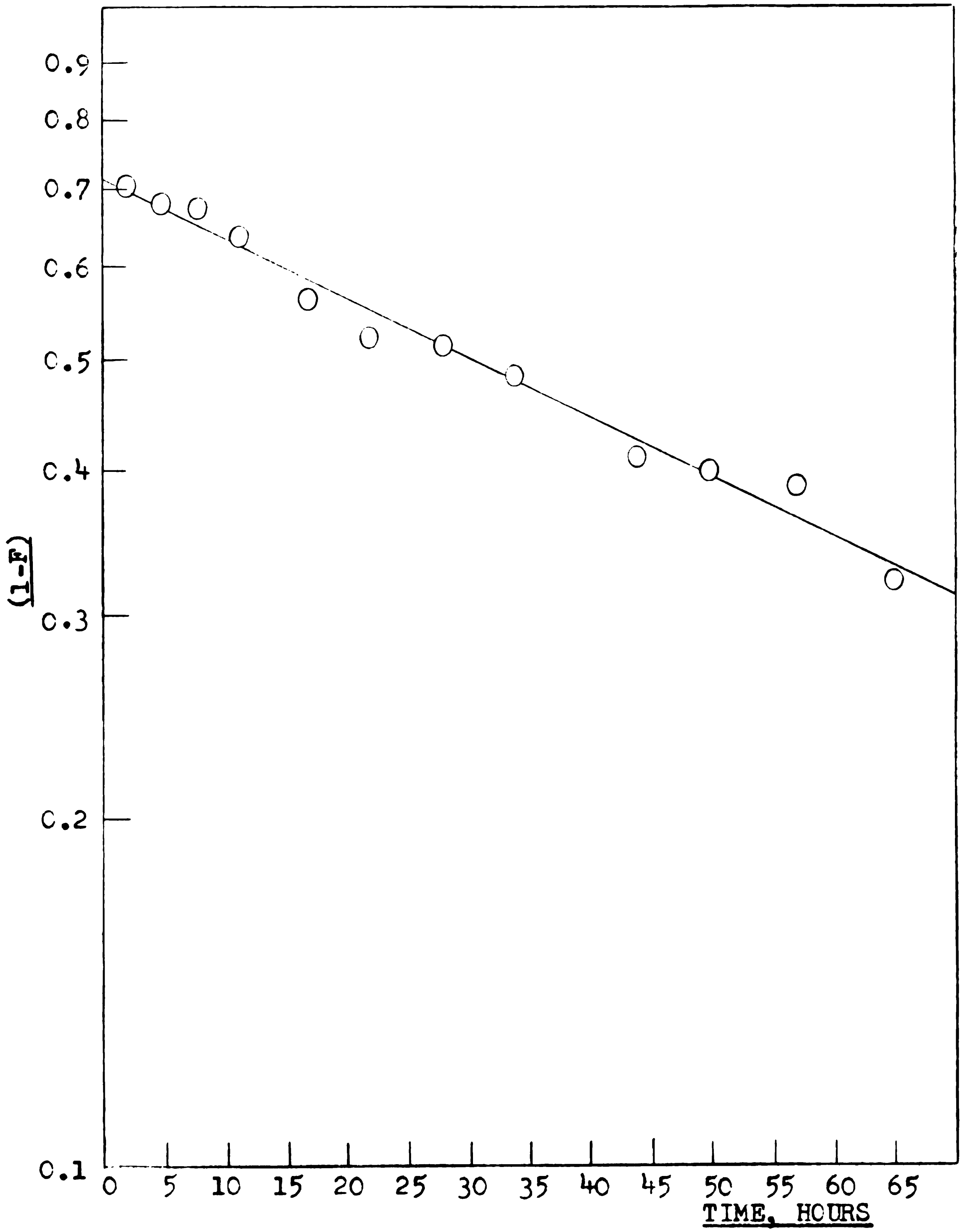


FIGURE 6. EXCHANGE IN 0.20 M CHLORIDE AT 42.0° C.

$t_{\frac{1}{2}}$ = 58.2 hours

2. The Dependence of Exchange Rate on the Concentration of Sb(III) and Sb(V)

The dependence of the exchange rate on the concentrations of Sb(III) and Sb(V) was determined at 6.00 and 0.20 M chloride. The study of the exchange in 6.00 M chloride was chronologically the initial investigation performed, and the concentrations of the solution species and the ionic strength are somewhat different than those employed in the bulk of this work. However, at 6.00 M chloride, sulfate does not influence the exchange, and the effect of ionic strength is negligible (note runs at constant concentration and varying ionic strength in Tables VIII and X). The only important variation is that due to hydrogen ion, but at 10 M (H^+), a difference of 0.25 in molarity should not produce an important change in mechanism.

In 6.00 M chloride, the orders with respect to Sb(III) and Sb(V) were found to be 1.04 ±.10 and 0.97 ±.10. In 0.20 M chloride, the Sb(III) dependence was still unity, a value of 1.01 ±.09 being derived from the kinetic data, but Sb(V), with an observed order of 0.76 ±.08 , displayed a significant deviation. Kinetic results are presented in Tables IV and V, while the log-log plots are illustrated in Figures 7 and 8.

TABLE IV

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF Sb(III) AND Sb(V) IN 6.00 M CHLORIDE

$\mu = 12.0$, $K_{2c} = 2.31$, $[H_2SO_4] = 3.00$ M, $[Cl^-] = 6.00$ M, $[H^+] = 10.0$ M, $[SO_4^=] = 0.56$ M, $[HSO_4^-] = 2.44$ M, $[Li^+] = 1.44$ M, $[ClO_4^-] = 1.88$ M

[Sb(III)] M	[Sb(V)] M	$t_{\frac{1}{2}}$ (hours)	R (moles / liter-hour)	R/ab (liters / mole-hours)
$1.31\text{x}10^{-3}$	$0.645\text{x}10^{-3}$	11.5	$2.60\text{x}10^{-5}$	30.8
$1.31\text{x}10^{-3}$	$1.29\text{x}10^{-3}$	10.0	$4.50\text{x}10^{-5}$	26.7
$1.31\text{x}10^{-3}$	$1.29\text{x}10^{-3}$	10.2	$4.42\text{x}10^{-5}$	26.1
$1.31\text{x}10^{-3}$	$1.94\text{x}10^{-3}$	8.85	$8.14\text{x}10^{-5}$	32.1
$1.31\text{x}10^{-3}$	$2.58\text{x}10^{-3}$	6.48	$9.29\text{x}10^{-5}$	27.5
$0.655\text{x}10^{-3}$	$1.29\text{x}10^{-3}$	12.7	$2.37\text{x}10^{-5}$	28.1
$1.97\text{x}10^{-3}$	$1.29\text{x}10^{-3}$	6.94	$7.78\text{x}10^{-5}$	30.7
$2.62\text{x}10^{-3}$	$1.29\text{x}10^{-3}$	6.27	$9.55\text{x}10^{-5}$	28.3

TABLE V

DEPENDENCE OF EXCHANGE RATE ON THE CONCENTRATION OF Sb(III) AND Sb(V) IN 0.20 M CHLORIDE

$\mu = 10.5$, $K_{2c} = 3.19$, $[H^+] = 9.75$ M, $[SO_4^=] = 0.74$ M,
$[HSO_4^-] = 2.27$ M, $[H_2SO_4] = 3.01$ M, $[ClO_4^-] = 5.80$ M

[Sb(III)] M	[Sb(V)] M	$t_{\frac{1}{2}}$ (hours)	R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
0.655×10^{-3}	1.29×10^{-3}	148	2.03×10^{-6}
1.31×10^{-3}(a)	1.30×10^{-3}	118	3.82×10^{-6}
1.97×10^{-3}	1.29×10^{-3}	84.1	6.42×10^{-6}
2.62×10^{-3}	1.29×10^{-3}	73.7	8.13×10^{-6}
3.93×10^{-3}	1.29×10^{-3}	56.9	1.18×10^{-5}
6.55×10^{-3}	1.29×10^{-3}	35.7	2.09×10^{-5}
1.34×10^{-3}	0.645×10^{-3}	120	2.51×10^{-6}
1.31×10^{-3}	1.94×10^{-3}	95.5	5.67×10^{-6}
1.31×10^{-3}	2.58×10^{-3}	94.3	6.39×10^{-6}
1.31×10^{-3}	0.419×10^{-3}	135	1.64×10^{-6}
1.31×10^{-3}	3.78×10^{-3}	78.2	8.62×10^{-6}
1.31×10^{-3}	4.97×10^{-3}	63.1	1.14×10^{-5}

(a) Average of 11 runs (see Table X)

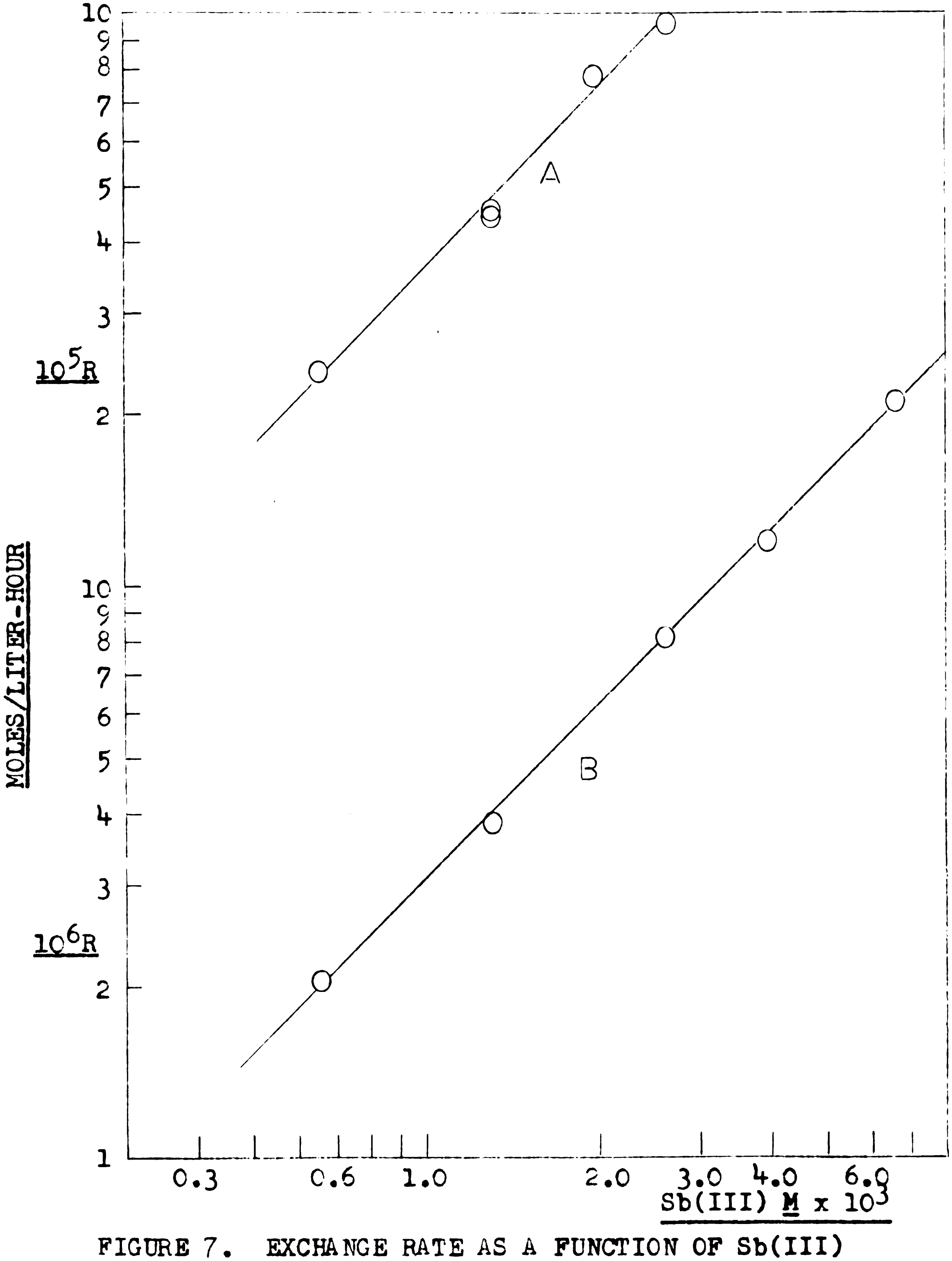


FIGURE 7. EXCHANGE RATE AS A FUNCTION OF Sb(III)

A - Slope = 1.04
$[Cl^-] = 6.00$

B- Slope = 1.01
$[Cl^-] = 0.20$

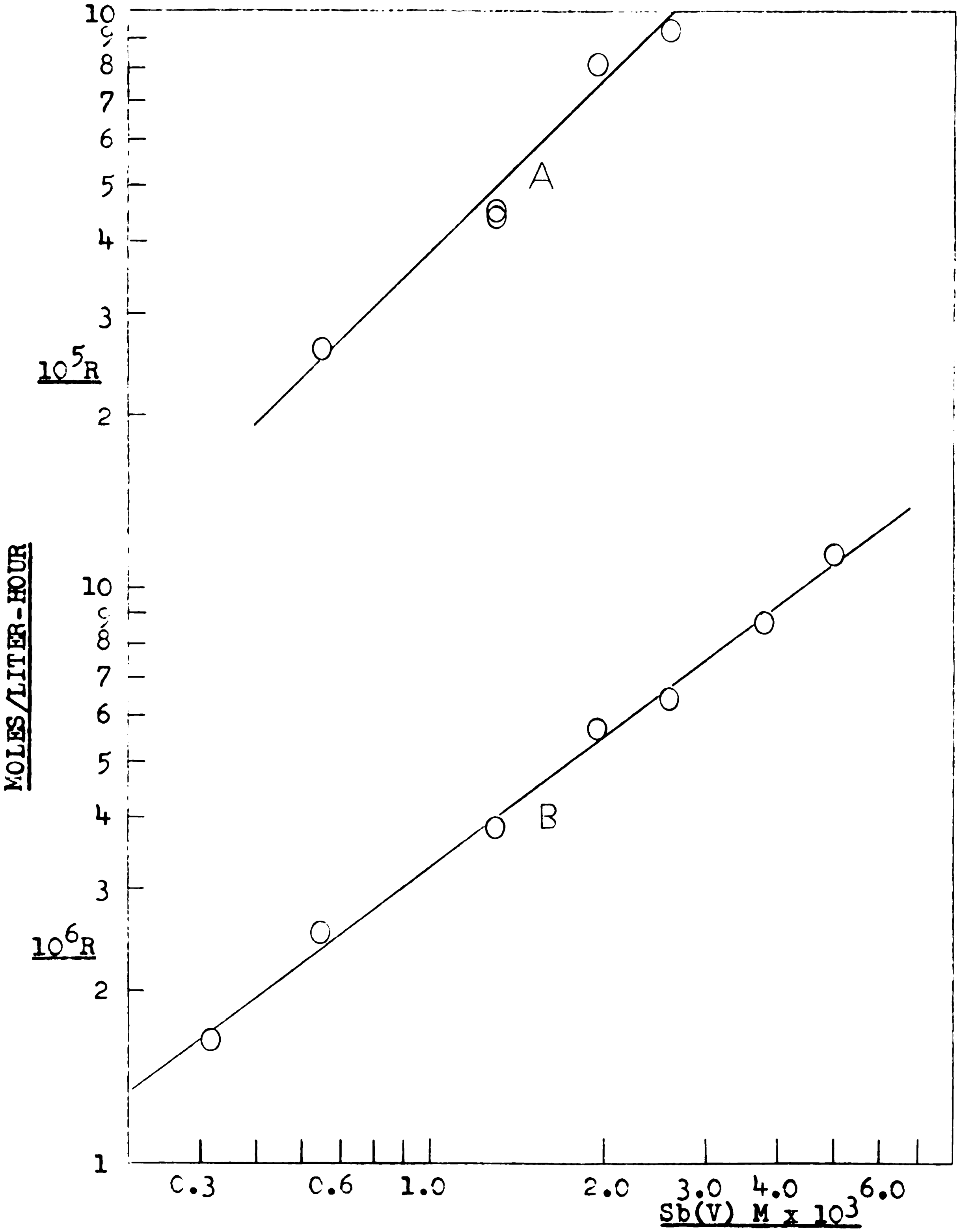


FIGURE 8. EXCHANGE RATE AS A FUNCTION OF Sb(V)

A - Slope = 0.97 $[Cl^-] = 6.00$

B - Slope = 0.76 $[Cl^-] = 0.20$

3. Variation of Exchange Rate with Sulfate Ion Concentration

The effect of sulfate ion was observed in the range 0.20 - 1.25 M in solutions containing 0.20 M chloride. While Sb(III), Sb(V) and hydrogen ion concentrations were held constant, it was necessary to permit ionic strength and bisulfate ion concentration to vary. Kinetic data obtained in 0.20 M chloride are shown in Table VI, while the log-log plot of rate vs. sulfate concentration is given in Figure 9.

In 0.20 M chloride, the exchange rate exhibits a parabolic dependence on sulfate concentration, with the maximum occurring in the region 0.6 - 0.7 M sulfate. The curve is approximately symmetrical, and an estimation of of slope yields 0.7 - 0.9 before the maximum, and minus 0.7 - 0.9 beyond the maximum. Apparently the region 0.6 - 0.7 M sulfate is the most favorable for the formation of the exchanging species. The considerable experimental scatter in the region of the maximum is probably the result of significant rate changes due to small errors in the preparation of the exchanging solutions.

In 6.00 M chloride the rate of exchange is independent of sulfate concentration as would be expected in the presence of such a large excess of chloride. Kinetic results in 6.00 M chloride are given in Table VII.

TABLE VI

DEPENDENCE OF EXCHANGE RATE ON SULFATE ION CONCENTRATION IN 0.20 M CHLORIDE

$[H^+]$ = 9.75 M, $[Cl^-]$ = 0.20 M, $[Sb(III)]$ = 1.31 x 10^{-3} M,
$[Sb(V)]$ = 1.30 x 10^{-3} M

μ	K_{2c}	$[SO_4^=]$ M	$[HSO_4^-]$ M	$[Li^+]$ M	$[ClO_4^-]$ M	$t_{\frac{1}{2}}$ (hours)	R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
10.1	3.24	0.20	0.60	0.15	8.70	220	2.06x10^{-6}
10.1	3.24	0.25	0.75	0.10	8.40	221	2.05x10^{-6}
10.1	3.24	0.31	0.94	0.04	8.03	181	2.50x10^{-6}
10.5	3.19	0.37(a)	1.13	0.38	8.06	152	2.96x10^{-6}
10.5	3.19	0.37	1.13	0.38	8.06	150	3.01x10^{-6}
10.5	3.19	0.44	1.36	0.31	7.62	146	3.10x10^{-6}
10.5	3.19	0.52(a)	1.58	0.23	7.16	123	3.66x10^{-6}
10.5	3.19	0.52	1.58	0.23	7.16	135	3.35x10^{-6}
10.5	3.19	0.57	1.73	0.18	6.86	107	4.23x10^{-6}
10.5	3.19	0.62	1.88	0.13	6.56	97.4	4.64x10^{-6}
10.5	3.19	0.68	2.07	0.07	6.19	118	3.80x10^{-6}
10.5	3.19	0.74(b)	2.27	--	5.80	118	3.82x10^{-6}
10.7	3.14	0.83	2.57	0.12	5.44	111	4.06x10^{-6}
10.7	3.14	0.93	2.87	--	4.82	124	3.65x10^{-6}
11.0	3.02	1.06	3.44	0.20	4.19	136	3.33x10^{-6}
11.0	3.02	1.14	3.66	0.11	3.72	127	3.56x10^{-6}
11.0	3.02	1.20	3.88	0.05	3.32	156	2.90x10^{-6}
11.0	3.02	1.25	4.05	--	3.00	181	2.50x10^{-6}

(a) $[Sb(V)]$ = 1.29 x 10^{-3} M
(b) Average of 11 runs (see Table X)

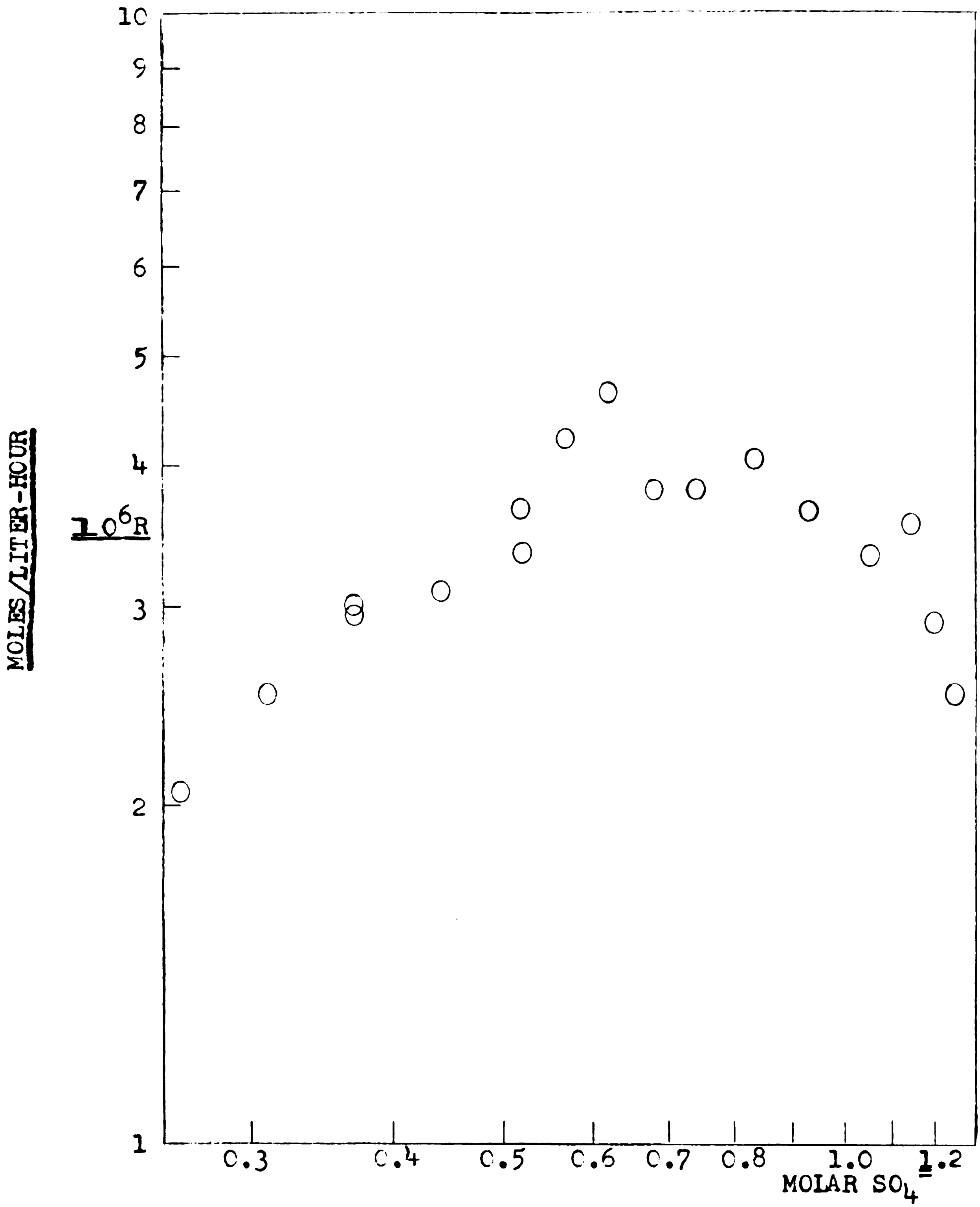


FIGURE 9. EXCHANGE RATE AS A FUNCTION OF SULFATE

TABLE VII

DEPENDENCE OF EXCHANGE RATE ON SULFATE ION CONCENTRATION IN 6.00 M CHLORIDE

$[H^+] = 9.75$ M, $[Cl^-] = 6.00$ M, $[Sb(III)] = 1.31 \times 10^{-3}$ M,
$[Sb(V)] = 1.30 \times 10^{-3}$ M

μ	K_{2c}	$[SO_4^=]$ M	$[HSO_4^-]$ M	$[Li^+]$ M	$[ClO_4^-]$ M	$t_{\frac{1}{2}}$ (hours)	R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
10.1	3.24	0.20	0.60	0.15	2.70	7.02	6.44×10^{-5}
10.5	3.19	0.52	1.58	0.23	1.36	7.65	5.91×10^{-5}
10.5	3.19	0.74	2.27	--	--	7.62	5.93×10^{-5}

TABLE VIII

DEPENDENCE OF EXCHANGE RATE ON HYDROGEN ION CONCENTRATION IN 6.00 M CHLORIDE

$[SO_4^=] = 0.74$ M, $[Cl^-] = 6.00$ M, $[Sb(III)] = 1.31 \times 10^{-3}$ M,
$[Sb(V)] = 1.30 \times 10^{-3}$ M

μ	K_{2c}	$[H^+]$ M	$[HSO_4^-]$ M	$[Li^+]$ M	$[ClO_4^-]$ M	$t_{\frac{1}{2}}$ (hours)	R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
10.5	3.19	8.00	1.86	1.76	0.42	8.06	5.61×10^{-5}
10.5	3.19	8.50	1.98	1.26	0.30	7.66	5.90×10^{-5}
10.5	3.19	9.75	2.27	--	--	7.62	5.93×10^{-5}
11.0	3.02	10.25	2.09	--	--	8.96	5.05×10^{-5}
11.7	2.60	11.00	3.13	--	0.39	10.1	4.48×10^{-5}

4. Variation of Exchange Rate with Hydrogen Ion Concentration

The magnitude of the rate of exchange between Sb(III) and Sb(V) was determined for hydrogen ion concentrations of 8 - 11 M in both 0.20 and 6.00 M chloride. In order to effect the desired changes in hydrogen ion, it was necessary to permit the ionic strength and bisulfate ion concentrations to vary. These data are summarized in Tables VIII and IX. The log-log plot of R vs.(H^+) for solutions containing 0.20 M chloride (Figure 10) displays a sharp maximum at about 9 M hydrogen ion. Statistical evaluation of the data yielded a slope of 9.0 in the region 8 - 9 M hydrogen ion, and a negative 5.5 slope in the hydrogen ion range of 9 - 11 M. In solutions containing 6 M chloride, the rate of exchange is not as sensitive to hydrogen ion variation, but an apparent maximum exists at approximately the same concentration as in 0.20 M chloride (Figure 10).

C. Spectroscopic Studies

A comprehensive spectroscopic investigation of Sb(III) and Sb(V) solutions was not conducted, but some spectral data were recorded. In aqueous sulfuric acid, Sb(III) and Sb(V) exhibit the same type of absorption spectra as have been reported for hydrochloric acid solutions. No peaks are observed in the accessible spectral region; absorption increases steadily with decreasing wave length. The position of the absorption band is a function of both

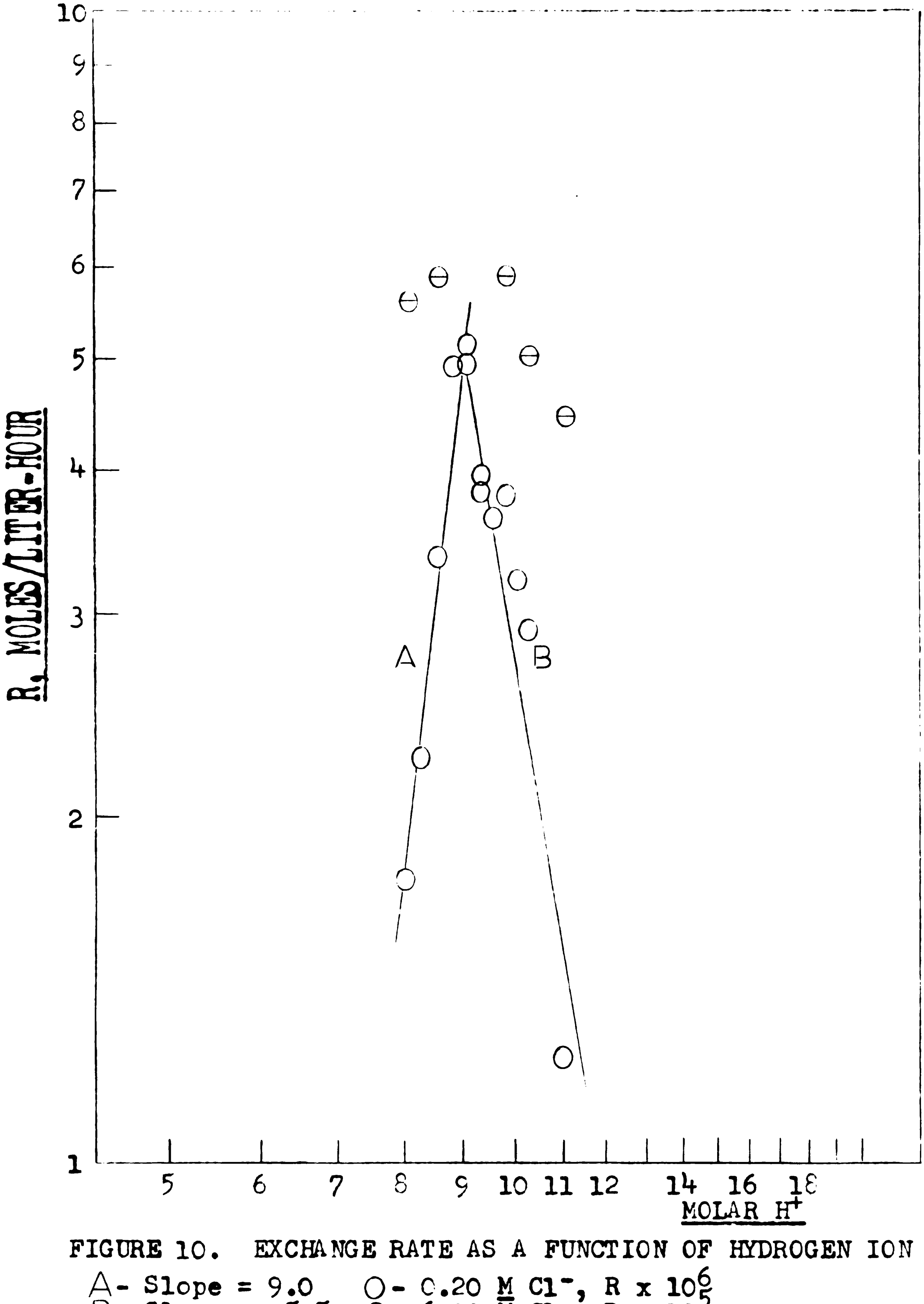


FIGURE 10. EXCHANGE RATE AS A FUNCTION OF HYDROGEN ION

A- Slope = 9.0 ○- 0.20 M Cl^-, R x 10^6

B- Slope = -5.5 ⊖- 6.00 M Cl^-, R x 10^5

TABLE IX

DEPENDENCE OF EXCHANGE RATE ON HYDROGEN ION CONCENTRATION IN 0.20 M CHLORIDE

$[SO_4^{=}]$ = 0.74 M, $[Cl^-]$ = 0.20 M, $[Sb(III)]$ = 1.31×10^{-3} M, $[Sb(V)]$ = 1.30×10^{-3} M

μ	K_{2c}	$[H^+]$ M	$[HSO_4^-]$ M	$[Li^+]$ M	$[ClO_4^-]$ M	$t_{\frac{1}{2}}$ (hours)	R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
9.0	3.18	8.00	1.86	0.26	4.72	255	1.77×10^{-6}
9.0	3.18	8.25	1.92	--	4.65	201	2.25×10^{-6}
9.5	3.24	8.50	1.94	0.26	5.14	134	3.37×10^{-6}
10.1	3.24	8.75	2.00	0.61	5.68	91.7	4.93×10^{-6}
10.1	3.24	9.00	2.06	0.36	5.62	87.7	5.16×10^{-6}
10.1	3.24	9.00	2.06	0.36	5.62	91.3	4.97×10^{-6}
10.1	3.24	9.25	2.11	0.11	5.66	114	3.97×10^{-6}
10.5	3.19	9.25	2.15	0.51	5.93	118	3.83×10^{-6}
10.5	3.19	9.50	2.20	0.26	5.88	124	3.65×10^{-6}
10.5	3.19	9.75*	2.27	--	5.80	118	3.82×10^{-6}
10.7	3.14	10.00	2.36	--	5.96	141	3.21×10^{-6}
11.0	3.02	10.25	2.51	--	6.06	155	2.92×10^{-6}
11.7	2.60	11.00	3.13	--	6.19	367	1.23×10^{-6}

* Average of 11 runs (see Table X)

antimony and sulfuric acid concentrations; with decreasing acid or antimony, the absorption is shifted toward shorter wave lengths. Typical spectra in aqueous sulfuric acid are depicted in Figures 11 and 12. The effect of variation in sulfuric acid concentration at constant wavelength is indicated in Figure 13. Antimony(III) solutions obeyed Beer's law for all acid concentrations and wavelengths observed (Figure 14), but antimony(V) displays pronounced deviations (Figure 15). Continuous variation experiments with Sb(III) and Sb(V) were performed in 12.7 and 4.00 M sulfuric acid, but no interaction absorption was discovered.

Figure 16 illustrates the spectra that were obtained with solutions containing 0.20 M chloride, simulating those utilized in the kinetic work. The presence of chloride shifts both the Sb(III) and Sb(V) absorption to longer wave lengths, but a much more drastic effect is observed with Sb(V).

To show any interaction between sulfate ion and Sb(III) and Sb(V), experiments were performed in which sulfate concentration was varied while hydrogen ion was maintained constant at 9.75 M. The result for Sb(III) absorbance at fixed wavelengths vs. sulfate ion is depicted in Figure 17. A similar experiment for Sb(V) could not be successfully completed. Spectra were recorded approximately 18 hours after the preparation of the solutions, and in this time interval precipitation occurred from 0.20, 0.44, and 0.74 M sulfate. The amount of precipitate observed varied from a heavy deposit in 0.20 M sulfate, to a faint opalescence in 0.74 M sulfate. The complete Sb(V) spectra for sulfate concentrations of 1.06 and 1.25 M are illustrated in Figure 18.

Similar experiments were performed in solutions containing 0.20 M chloride, where no difficulty with Sb(V) precipitation was experienced. The resulting spectra are portrayed in Figures 19, 20, and 21.

While the spectroscopic data do not establish the nature of the species present, qualitative observations are possible. It may be presumed that in aqueous sulfuric acid, Sb(V) is present as an equilibrium mixture of sulfate complexes. Sb(V) spectra are markedly dependent on sulfuric acid concentration, and the behavior of Sb(V) at constant hydrogen ion with the variation of sulfate indicates sulfate complexing and not only anionic polymerization. In 0.20 M chloride, decreasing absorption with increasing sulfate concentration reveals a competition between chloride and sulfate, and the Sb(V) solution species are presumably an equilibrium mixture of complexes of sulfate and chloride.

Sb(III) apparently forms a sulfato complex, but the equilibria involved are probably not as complicated as those for Sb(V). Beer's law is followed in aqueous sulfuric acid, which indicates that the number of species present is limited. It is interesting to note the apparent maximum in absorption at approximately 0.6 M sulfate in the variation of absorbance with sulfate at constant hydrogen ion (Figure 17). This is the region of the maximum exchange rate in the kinetic study of the effect of sulfate, and indicates that the exchanging species for Sb(III) may be a sulfato complex.

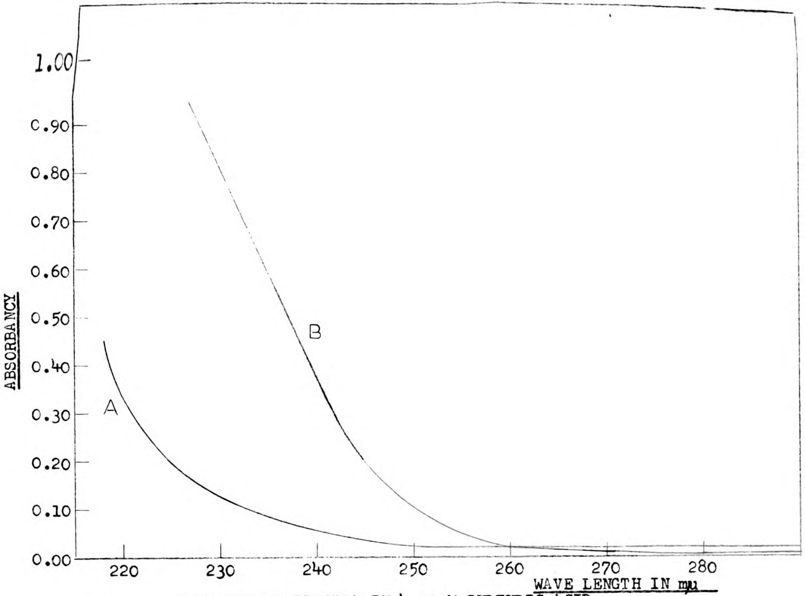


FIGURE 11. ULTRAVIOLET SPECTRA IN 4.00 M SULFURIC ACID

A - 3.00 x 10^{-3} M Sb(V) B- 3.00 x 10^{-3} M Sb(III)

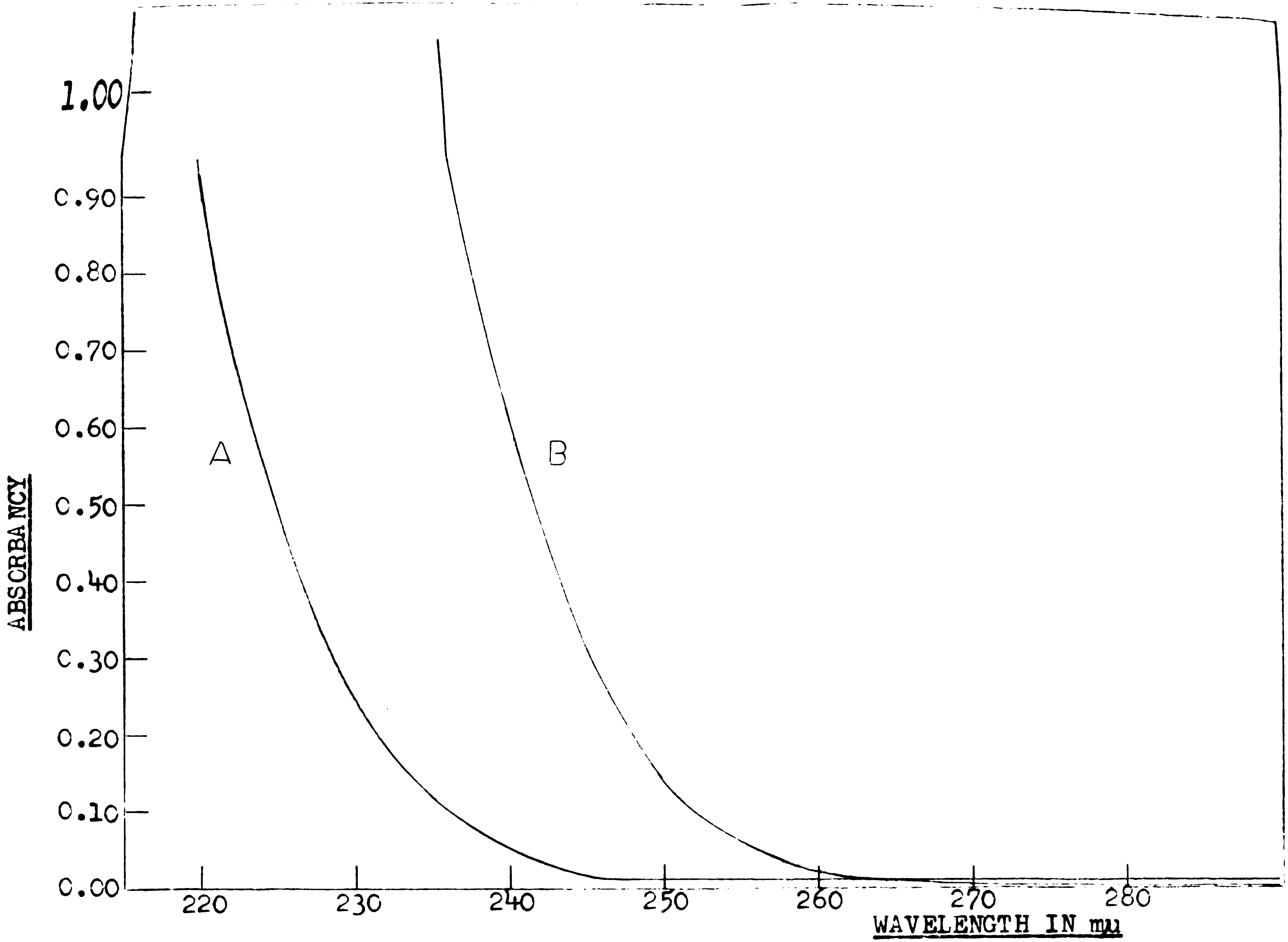


FIGURE 12. ULTRAVIOLET SPECTRA IN 12.7 M SULFURIC ACID

A - 3.42 x 10^{-3} M Sb(V) B- 3.48 x 10^{-3} M Sb(III)

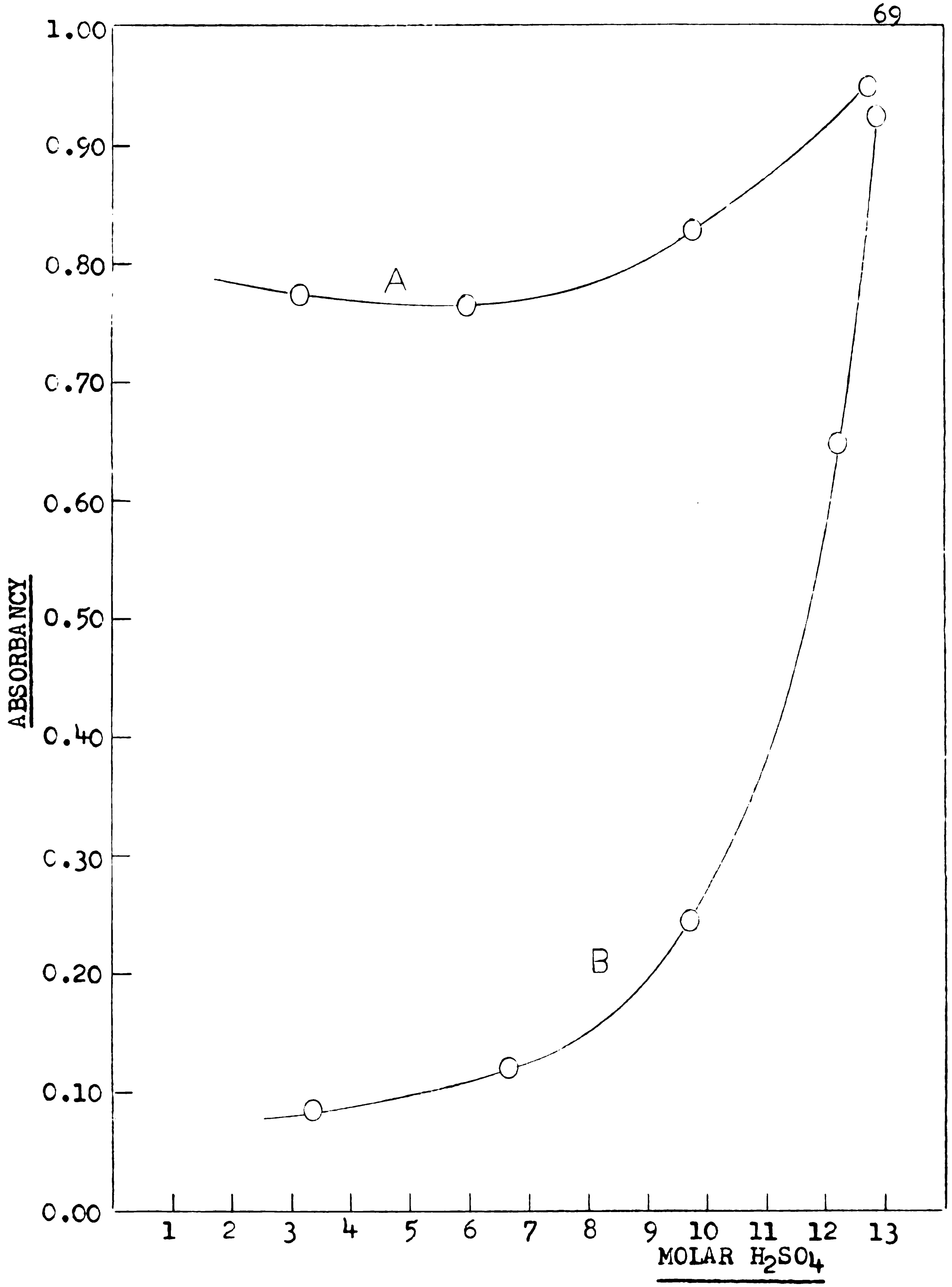


FIGURE 13. ANTIMONY ABSORBANCE AS A FUNCTION OF SULFURIC ACID

A- 6.95×10^{-3} $\underline{M}$ Sb(III) at 242 mu B- 6.44×10^{-3} $\underline{M}$ Sb(V) at 228 mu

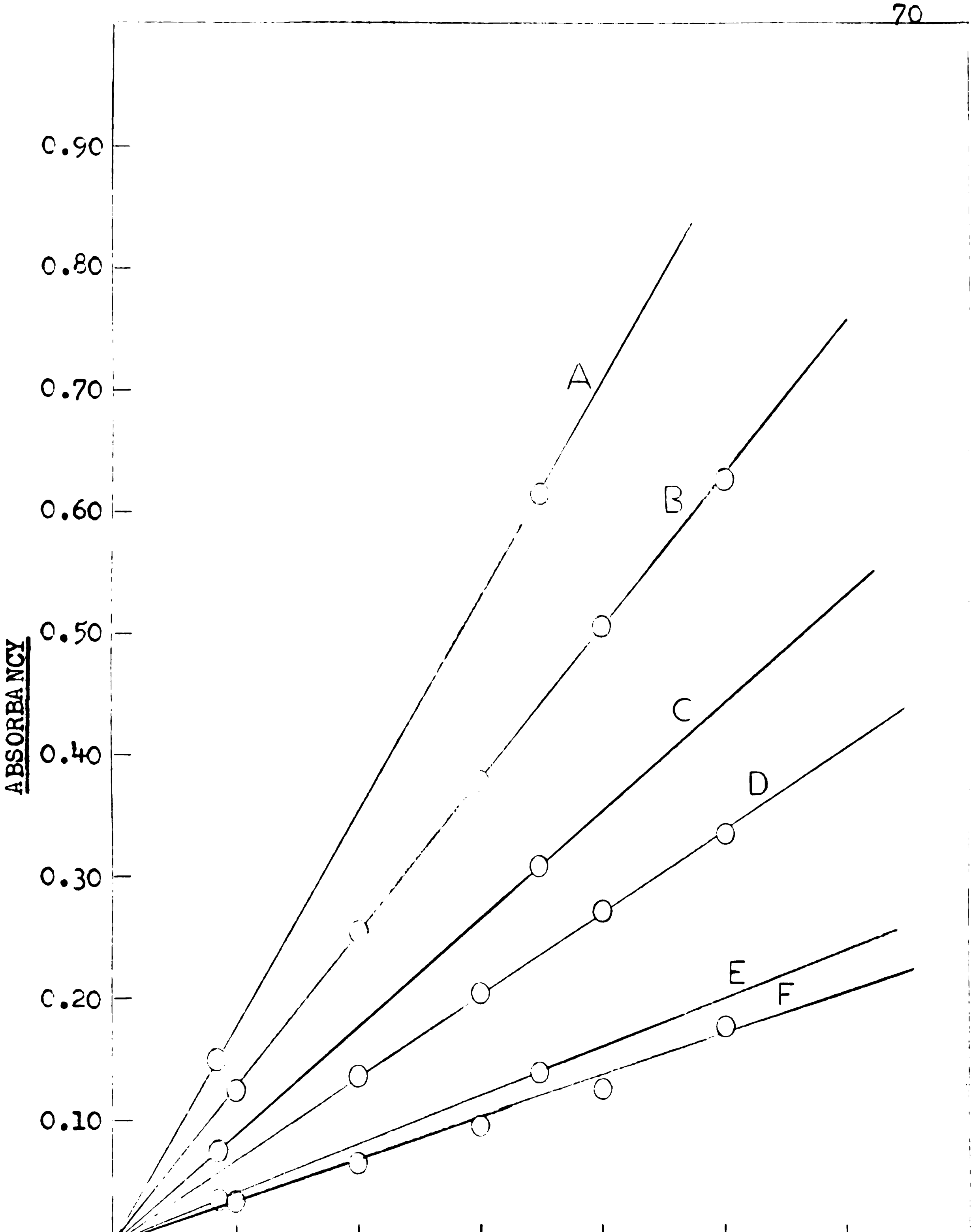


FIGURE 14. ABSORBANCY AS A FUNCTION OF Sb(III)
A - 240 mμ, 12.7 M H_2SO_4 B - 240 mμ, 4.00 M H_2SO_4 C - 245 mμ, 12.7 M H_2SO_4 D - 245 mμ, 4.00 M H_2SO_4 E - 250 mμ, 12.7 M H_2SO_4 F - 250 mμ, 4.00 M H_2SO_4

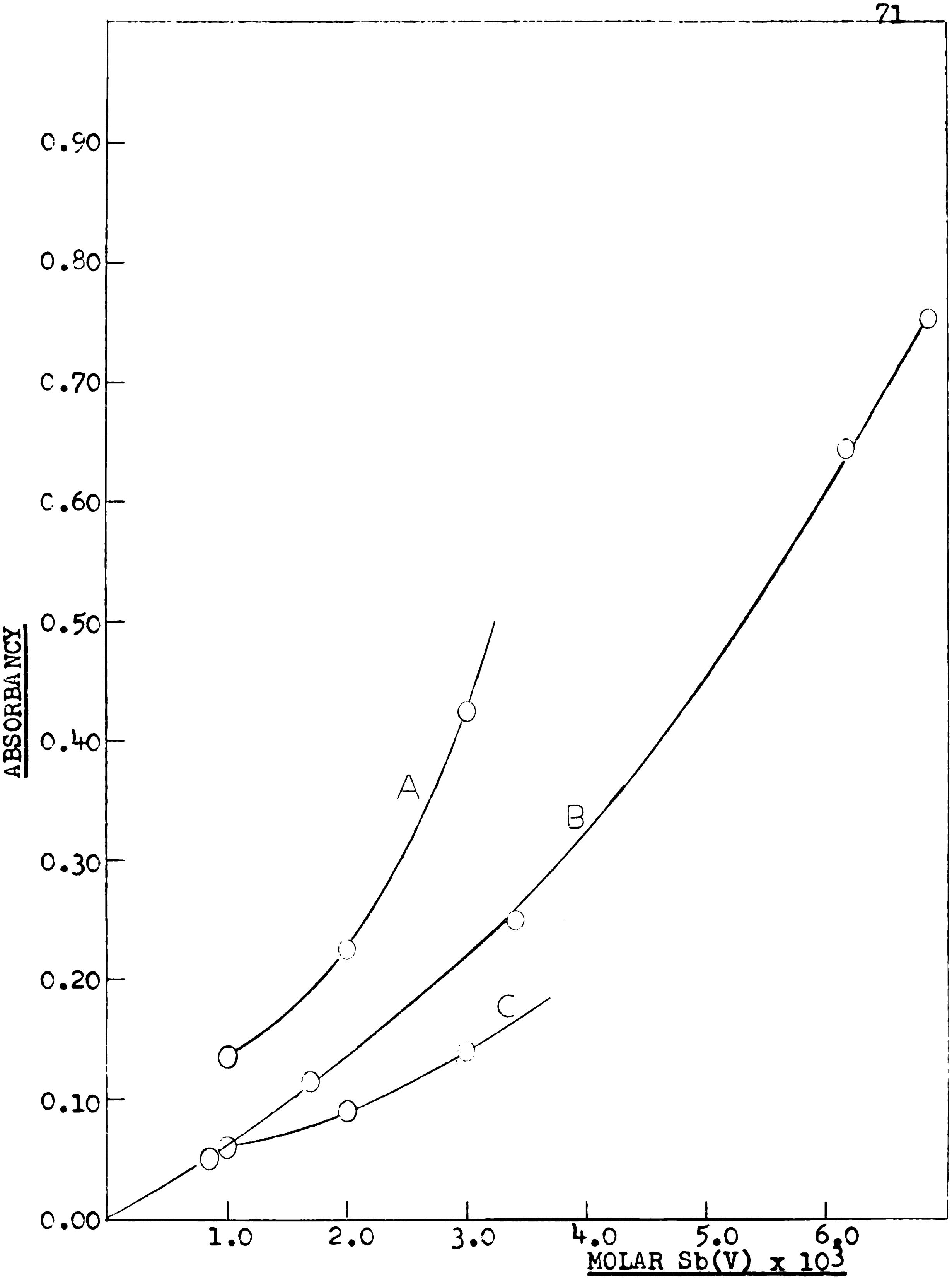


FIGURE 15. ABSORBANCY AS A FUNCTION OF Sb(V)

A- 218 mμ, 4.00 M H_2SO_4 B- 230 mμ, 12.7 M H_2SO_4
C- 230 mμ, 4.00 M H_2SO_4

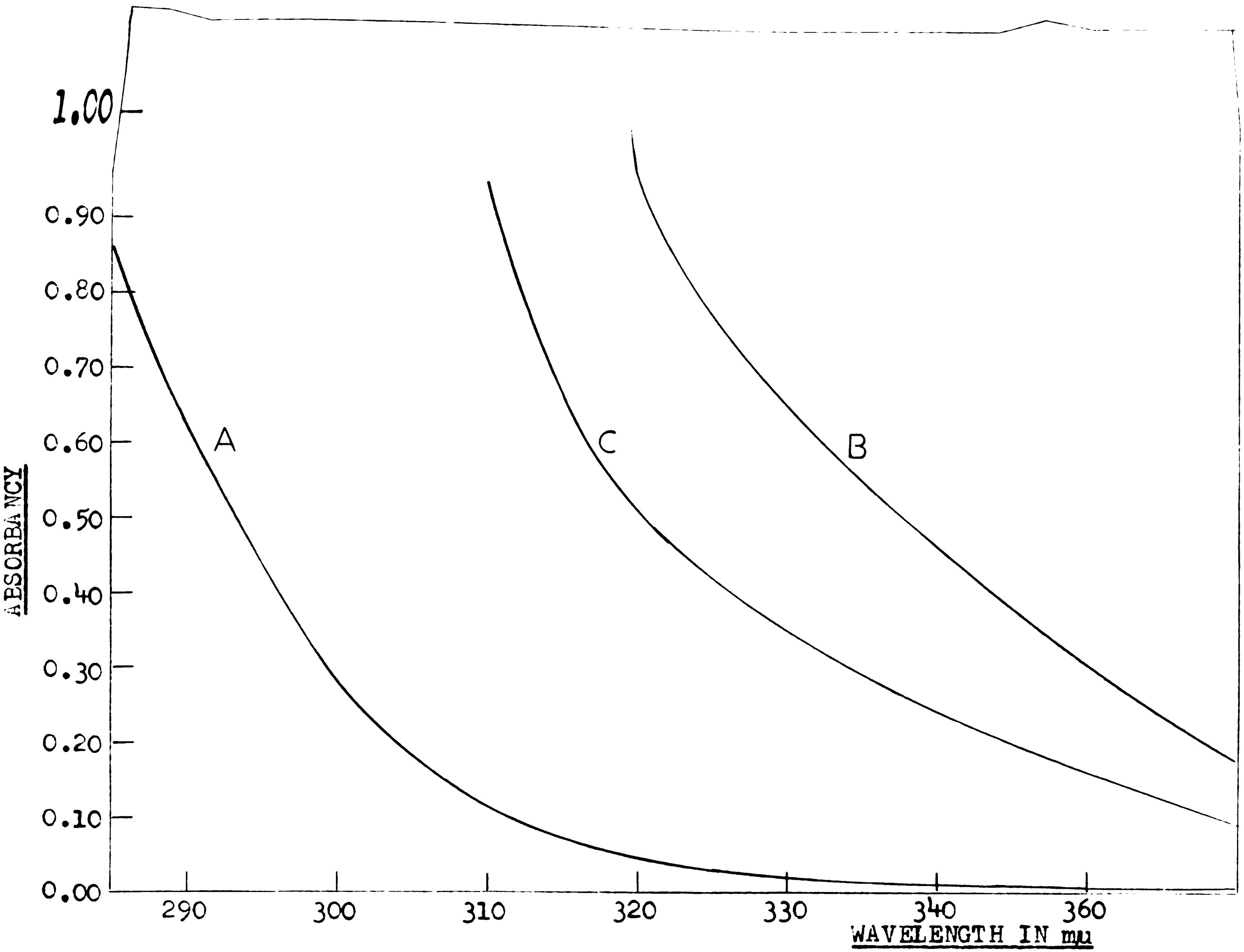


FIGURE 16. ANTIMONY SPECTRA IN EXCHANGE SOLUTION MEDIA
$(H^+)=9.75, (SO_4^=) = 0.74, (HSO_4^-) = 2.27, (ClO_4^-) = 5.80, (Cl^-) = 0.20$
A- 2.32×10^{-3} M Sb(III) B- 2.32×10^{-3} M Sb(V) C- 1.31×10^{-3} M Sb(III)
1.31×10^{-3} M Sb(V)

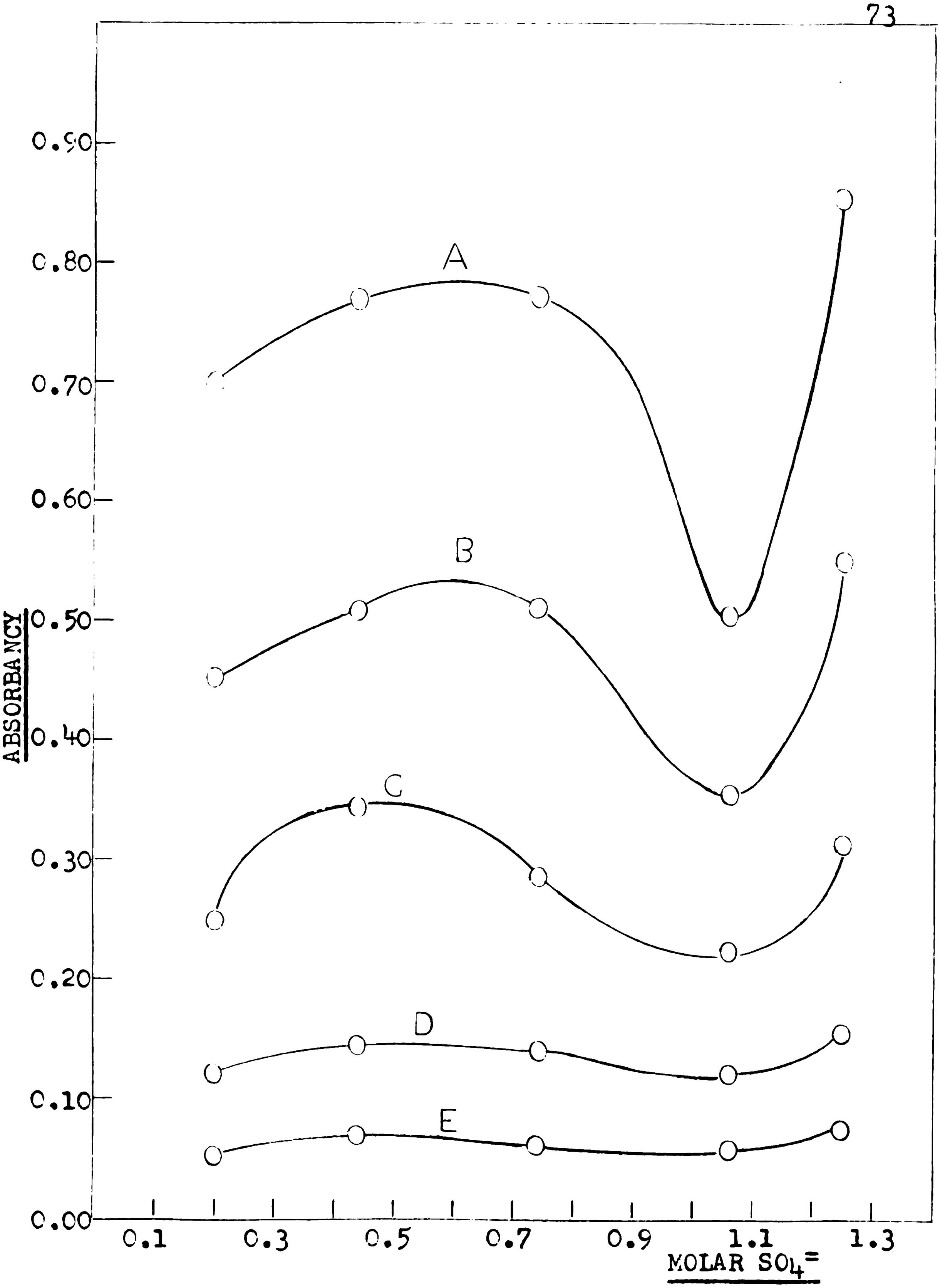


FIGURE 17. Sb(III) ABSORBANCE AS A FUNCTION OF SULFATE
$(H^+) = 9.75$ M $Sb(III) = 2.62 \times 10^{-3}$ M
A - 230 mμ B - 235 mμ C - 240 mμ D - 245 mμ E - 250 mμ

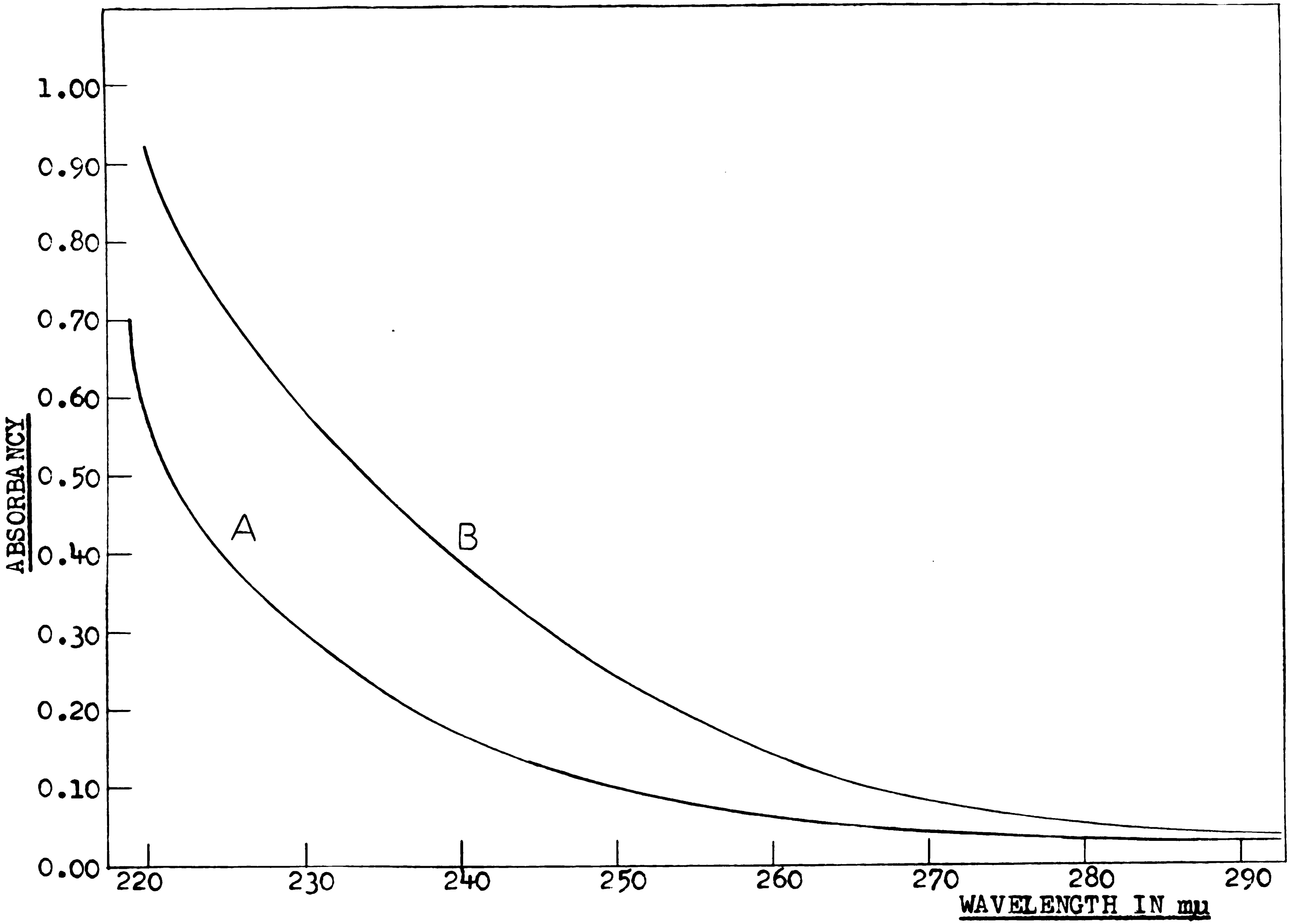


FIGURE 18. THE EFFECT OF SULFATE ON Sb(V) SPECTRA
$H^+ = 9.75\ \underline{M}$ $Sb(V) = 2.62 \times 10^{-3}\ \underline{M}$
A- $1.25\ \underline{M}\ SO_4^=$ B- $1.06\ \underline{M}\ SO_4^=$

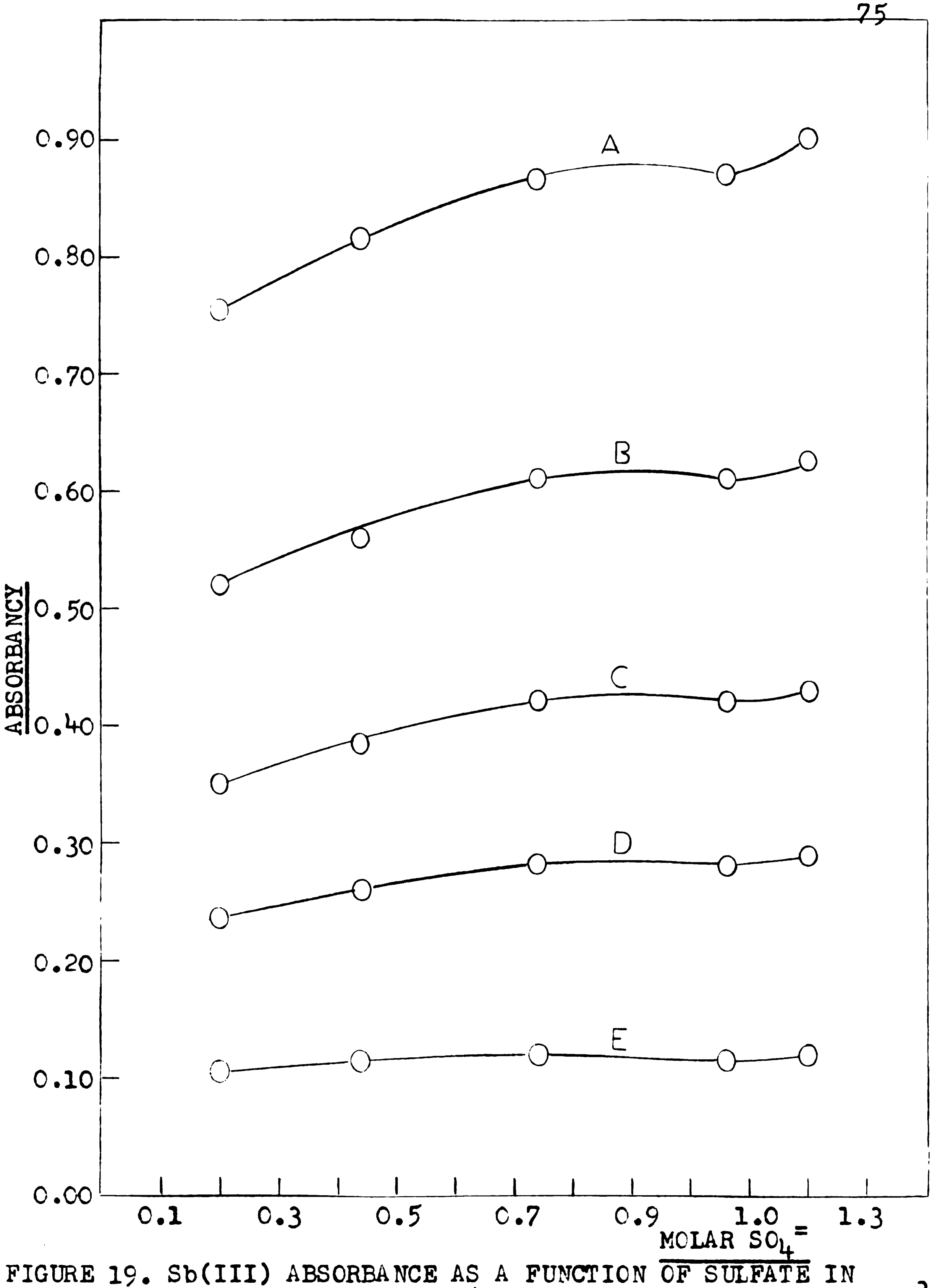


FIGURE 19. Sb(III) ABSORBANCE AS A FUNCTION OF SULFATE IN 0.20 M CHLORIDE $H^+ = 9.75$ M, Sb(III) = 2.62×10^{-3} M

A- 285 mμ B- 290 mμ C- 295 mμ D- 300 mμ E- 310 mμ

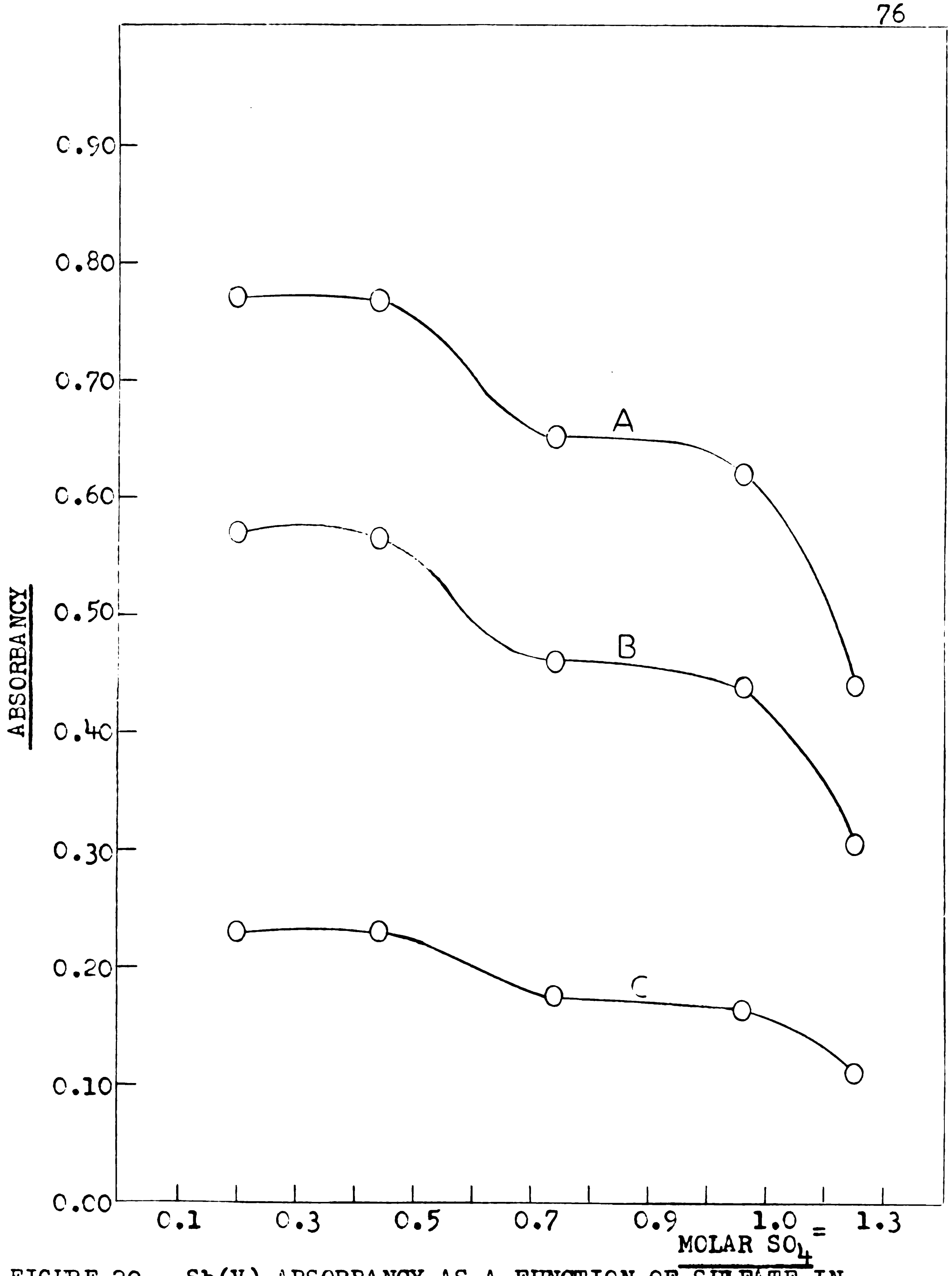


FIGURE 20. Sb(V) ABSORBANCY AS A FUNCTION OF SULFATE IN 0.20 M CHLORIDE $H^+ = 9.75$ M, Sb(V) = 2.62×10^{-3} M
A - 330 mμ B - 340 mμ C - 360 mμ

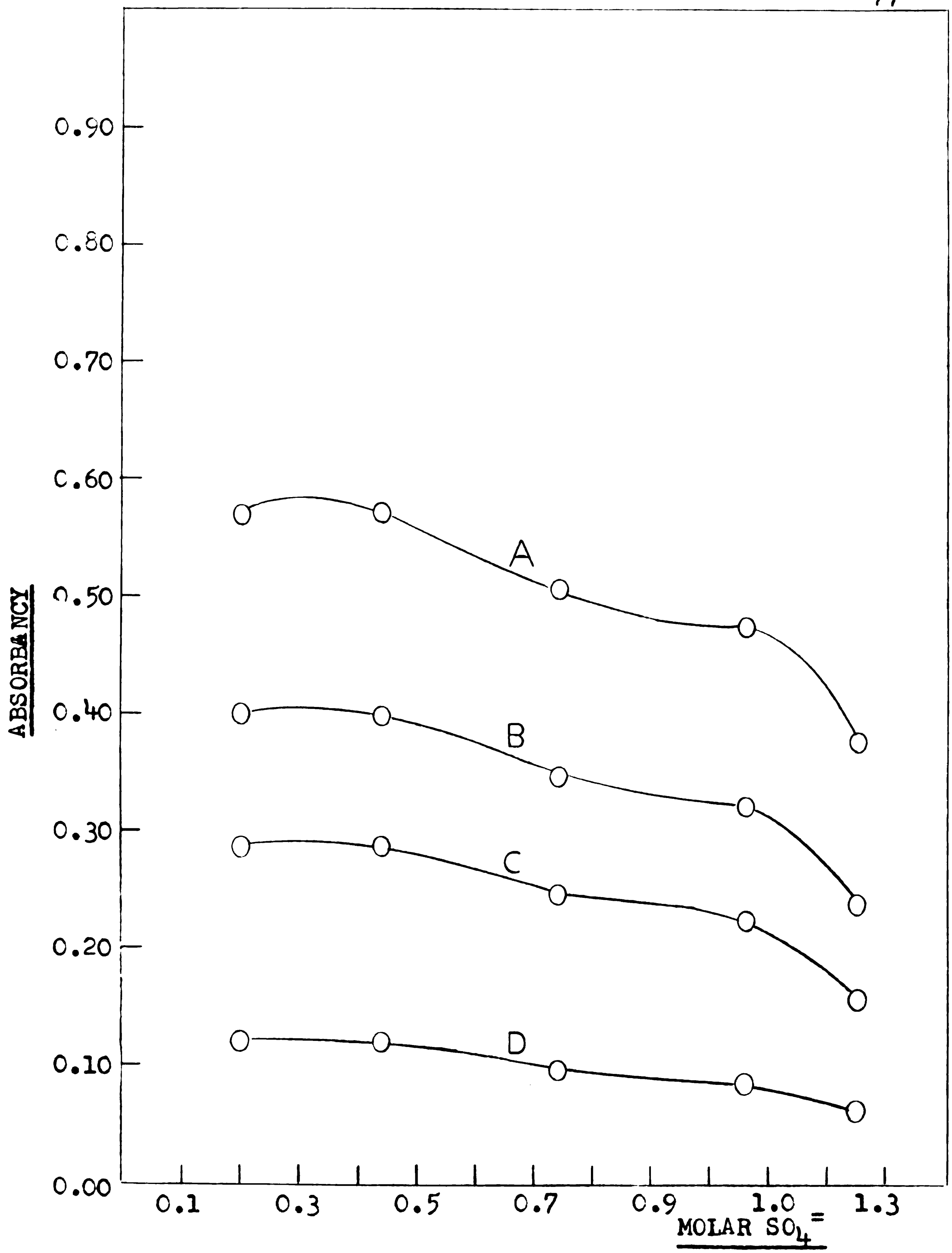


FIGURE 21. Sb(III)-(V) ABSORBANCY AS A FUNCTION OF SULFATE IN 0.20 M CHLORIDE $H^+ = 9.75$ M, Sb(III) = 1.31×10^{-3} M

A- 320 mu B- 330 mu C- 340 mu Sb(V) = 1.31×10^{-3} M

D- 360 mu

D. Discussion of Errors

The sources of error in the rate of exchange as determined by these experiments may be classified as follows:

1. Preparation and standardization of stock solutions.
2. Preparation of solutions for exchange runs.
3. Conduct of kinetic experiments, separation of antimony oxidation states, and mounting of samples.
4. Radiochemical assay.

It was necessary to prepare and standardize stock solutions of sulfuric, perchloric, and hydrochloric acid, lithium chloride, antimony(III), and antimony(V). For each run five to seven components were measured or weighed into each of two flasks. All these operations were subject to the normal errors of quantitative procedures. Errors introduced by temperature variation and sampling time inaccuracy were insignificant because the temperature of the exchanging solutions was easily maintained within ± 0.02 °C., and a generous estimate of ± 15 seconds in sampling time may be compared to exchange half-times of 50 - 100 hours. The shortest half-time observed was two hours.

In the separation method employed, both positive and negative errors are possible, either from incomplete extraction of Sb(III), or possible contamination of the chloroform phase with Sb(V). This error is minimized by the fact that all the points established for a run were used to evaluate a statistical slope from which the rate of exchange was calculated. The accurate determination of equilibrium activity at infinite time is most critical. As described previously, three samples were taken from each run to establish this quantity. These values, in general, agreed within the limits of the radioassay. Securing of a minimum of 10,000 counts in this process should limit these errors to 1%, and indeed reproducibility was found to be within these limits.

With all these potential sources of error, it is difficult to assess the contribution of each and sum them to yield a meaningful approximation of the error in the determined rate of exchange. An estimation of the precision of this work is possible, however, because of the repeated determination of the rate of exchange under standard conditions, for sample solutions with the following concentrations: $[H^+] = 9.75\ \underline{M}$, $[SO_4^=] = 0.74\ \underline{M}$, $[HSO_4^-] = 2.27\ \underline{M}$, $[Cl^-] = 0.20\ \underline{M}$, $[ClO_4^-] = 5.80\ \underline{M}$, $[Sb(III)] = 1.31 \times 10^{-3}\ \underline{M}$, and $[Sb(V)] = 1.30 \times 10^{-3}\ \underline{M}$.

This rate of exchange was determined eleven times during the course of this study. Usually each set of kinetic runs that were prepared included a "standard sample", which served to monitor the quality of the stock solutions and the correctness of the experimental procedures. Results obtained are summarized in Table X.

Calculation of the standard deviation σ, where:

$$\sigma^2 = \frac{1}{n}\sum_{i}^{n}(R_i - \bar{R})^2$$

yields a value for the rate of:

$$R = (3.82 \pm 0.14) \times 10^{-6} \text{ moles/liter-hour}$$

A precision of the same order would be anticipated for all the exchange runs performed.

TABLE X

RATE OF EXCHANGE OF "STANDARD" RUN

$[H^+] = 9.75\ \underline{M}$, $\mu = 10.5$, $K_{2c} = 3.19$, $[SO_4^=] = 0.74\ \underline{M}$, $[HSO_4^-] = 2.27\ \underline{M}$, $[Cl^-] = 0.20\ \underline{M}$, $[ClO_4^-] = 5.80\ \underline{M}$, $[Sb(III)] = 1.31 \times 10^{-3}\ \underline{M}$, $[Sb(V)] = 1.30 \times 10^{-3}\ \underline{M}$

	$t_{\frac{1}{2}}$ (hours)		R $\left(\frac{\text{moles}}{\text{liter-hour}}\right)$
	123		3.66×10^{-6}
	115		3.95×10^{-6}
	118		3.82×10^{-6}
	121		3.74×10^{-6}
	115	(a)	3.93×10^{-6}
	112	(b)	4.04×10^{-6}
	111		4.06×10^{-6}
	121		3.74×10^{-6}
	122		3.69×10^{-6}
	123		3.68×10^{-6}
	122		3.71×10^{-6}
Average:	118		3.82×10^{-6}

(a) $\mu = 10.7$, $K_{2c} = 3.14$
(b) $\mu = 11.0$, $K_{2c} = 3.02$

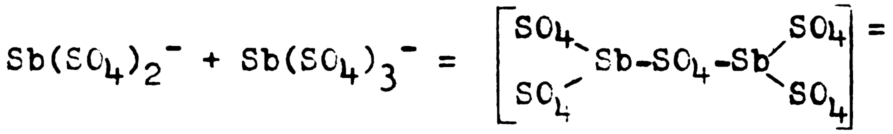
VI. DISCUSSION

While some study has been made of the chloro-species of antimony, no previous work has been reported in aqueous sulfuric or in hydrochloric - sulfuric mixtures. Because of the complex equilibria which exist in these media, any discussion of exchange mechanisms must remain qualitative until a more complete evaluation of antimony species is available.

No exchange was observed in aqueous sulfuric acid. Some deductions as to the nature of the antimony species and for the absence of exchange can be made by interpretation of the spectra recorded in this medium. Observations of the spectra of antimony(III) seem to indicate that some sulfate complexing does take place. In the plot of Sb(III) absorbance at fixed wavelength vs. sulfuric acid concentration, a shallow minimum is observed at 6 - 7 M H_2SO_4. This is the region of maximum sulfate ion concentration from the data of Smith (65). The plot of Sb(III) absorbance at 9.75 M $[H^+]$ vs. $[SO_4^=]$ also indicates interaction between sulfate ion and antimony(III). Antimony(III) species may be postulated as SbO^+, $SbSO_4^+$, and $Sb(SO_4)_2^-$. Solid phases obtained from antimony solutions in sulfuric acid have been shown to be $(SbO)_2SO_4$ and $Sb_2(SO_4)_3$.

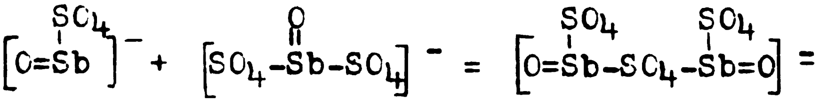
Antimony(V) absorption is even more sensitive to sulfuric acid concentration. With $SbCl_6^-$, Neumann (32) observed that as chloride ligands are replaced by hydroxo groups, the wavelength of the sharp increase in absorption is displaced toward the ultraviolet. A similar displacement is obtained for Sb(V) as sulfuric acid concentration is diminished. It is logical, therefore, to postulate species ranging from $Sb(SO_4)_3^-$ at high acid concentrations, to $Sb(OH)_6^-$ at low concentrations.

If these conclusions as to the nature of the antimony species in sulfuric acid are correct, it is difficult to explain the lack of exchange. Exchange mechanisms such as:



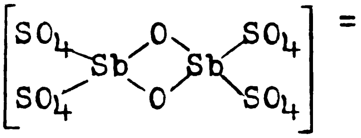
$$Sb(SO_4)_2^- + Sb(SO_4)_3^- = \left[\begin{matrix}SO_4 & & SO_4\\ & Sb-SO_4-Sb & \\ SO_4 & & SO_4\end{matrix}\right]^=$$

or:



$$\left[O=\overset{SO_4}{Sb}\right]^- + \left[SO_4-\overset{O}{\overset{\|}{Sb}}-SO_4\right]^- = \left[O=\overset{SO_4}{Sb}-SO_4-\overset{SO_4}{Sb}=O\right]^=$$

are particularly attractive because of symmetry and a minimum subsequent rearrangement in coordination spheres. The conclusion is forced that the system is not as simple as wishful thinking fancies it to be. For such high oxidation states, anionic polymerization is a well known phenomenon. Souchay and Peschanski (23) reported the principal Sb(V) species in weak, weakly complexing acid media of pH 2.5 - 0.9 to be $HSb_6O_{17}^{-3}$. Undoubtedly, Sb(V) in sulfuric acid also exists as a polymeric species. In the preparation of Sb(V) by the oxidation of Sb(III) with "peroxy acid", a solid phase separates as the oxidizing medium is heated, and dissolves slowly on prolonged digestion. This is presumably an insoluble antimonic acid which dissolves as sulfato complexes form. If Sb(V) exists only as a dimer such as:



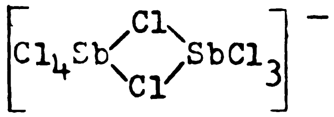
no exchange would be expected, and the true species are probably much larger than this.

In aqueous sulfuric acid solutions containing 6.00 M chloride, an electron exchange reaction did occur between Sb(III) and Sb(V). With $[H^+]$ constant at 10.00 M, an empirical rate law:

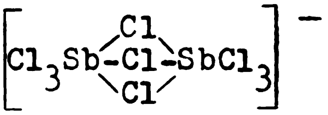
$$R = k[Sb(III)]^{1.04}[Sb(V)]^{0.97}$$

can be written. Sulfate ion concentration was found to have no effect on the rate, and a chloride term is omitted from the rate expression because at this extremely high ratio of chloride to antimony, the system is approaching a pseudo-zero order dependence on chloride, and the observed slope of 0.28 obtained from the log-log plot of R vs. $[Cl^-]$ in the region 1.50 - 6.00 M chloride is meaningless. This result is in agreement with that of Cheek (11), who found a first order Sb(III) and Sb(V) dependence in 9 - 12 M hydrochloric acid. In this medium, the exchange apparently takes place exclusively between chloro complexes of antimony.

The exchange rate approaches a maximum in the region 9 - 10 M hydrogen ion. At $[H^+] = 10.00$, according to Neumann (12, 32, 33), Sb(V) should be present almost entirely as $SbCl_6^-$, and his postulation of $SbCl_3$ as the exchanging species of Sb(III) explains the effect of hydrogen ion. Increasing hydrogen ion beyond the observed maximum at $[H^+] = 9$, favors the formation of $SbCl_4^-$, a non-exchanging species, as the activity of HCl increases. The exchange intermediates that Neumann proposed:



and



seem reasonable for this system also.

In aqueous sulfuric acid containing 0.20 M chloride, rate data indicate that both chloride and sulfate participate in the electron exchange reaction. A standard system of $[H+] = 9.75$ M, $[SO_4^=] = 0.74$ M, $[HSO_4^-] = 2.27$ M, $[ClO_4^-] = 5.80$ M, $[Sb(III)] = 1.31 \times 10^{-3}$ M, and $[Sb(V)] = 1.30 \times 10^{-3}$ M was adopted, and $[H^+]$, $[SO_4^=]$, $[Cl^-]$, $[Sb(III)]$, and $[Sb(V)]$ independently varied.

At constant hydrogen ion and sulfate concentration, the following empirical rate law can be written:

$$R = k\,[Sb(III)]^{1.01}\,[Sb(V)]^{0.76}\,[Cl^-]^{2.04}$$

for the concentration range 0.025 - 0.20 M chloride. The proper exponent of the chloride term is debatable because the points at 0.20 M chloride are in a region of changing slope in the log-log plot, and also fit the slope of 1.41 determined for the region 0.15 - 0.60 M chloride. The true order is undoubtedly some intermediate value.

Sulfate and hydrogen ion dependence are difficult to place in an empirical rate expression since both exhibit a maximum. The sulfate maximum occurs at 0.6 - 0.7 M ($SO_4^{=}$), and the observed slopes are approximately ± (0.7 - 0.9). The hydrogen ion maximum occurs at about 9 M (H^+), with a slope in the log-log plot of 9.0 in the range 8 - 9 M, and a negative 5.5 slope in the range 9 - 11 M. In this system, antimony species exist in equilibria involving chloride, sulfate, and hydrogen ion. Spectral data indicate that both Sb(III) and Sb(V) are present as chloro-sulfato complexes, and the order with respect to any particular species is probably a parameter determined by the concentrations of each of the other species.

If the assumption is made that the neutral molecule $SbClSO_4$ is the exchanging form of Sb(III), the effect of hydrogen ion may be interpreted as in the hydrochloric acid system. Increasing hydrogen ion will increase the concentration of this species compared to such forms as SbO^+, $SbSO_4^+$, and $SbCl^{++}$. However, as hydrogen ion continues to increase, anionic species such as $SbCl_4^-$, $Sb(SO_4)_2^-$ and $SbCl_2SO_4^-$ should result. Furthermore, beyond the maximum, anionic polymerization of Sb(V) may be favored, as well as protonation of potential bridging chloro and sulfato ligands.

The initial increase in rate with increasing sulfate may be the result of the formation of $SbClSO_4$, the presumed antimony(III) exchanging species. Increasing sulfate beyond the maximum may favor polymerization of Sb(V), the formation of anionic Sb(III) species, or may result in the prevention of necessary chloro-bridges in the activated complex.

While both sulfate and chloride are involved in the transition state, it is difficult to assess their relative contribution as bridging groups in the exchange. The initiation of exchange by small amounts of chloride is probably the result of its effect on the nature of the Sb(V) species, where the initial action of chloride may be to decompose the Sb(V) sulfato polymers. The fractional order observed for Sb(V) indicates the presence of at least two Sb(V) species, one of which does not participate in the exchange. Because of the lack of accurate knowledge concerning the nature of the ions in solution, it seems rather futile to postulate the mechanism of the exchange reaction in 0.20 M chloride. The existence of two independent mechanisms, one operative at high chloride concentrations and the other at low chloride, is confirmed by the phenomenon of non-linear McKay plots observed in the intermediate region of chloride concentration. If this non-linearity were the result of the slow formation kinetics of the same exchanging chloro species at all levels of chloride concentration, it would be expected that the curvature in the McKay plots would be an inverse function of chloride, and not proceed through a maximum in the vicinity of 2.00 M chloride.

More work is needed before this system can be properly evaluated. Ion migration studies to determine the anionic or cationic nature of the species are certainly indicated, as well as dialysis measurements to determine the relative ionic weights if a resistant membrane could be found. A detailed spectroscopic examination of these systems including a study of the effect of the independent variation of hydrogen ion would be useful. Probably the most effective tool would be a comprehensive phase study, with careful analysis of the solid phases, for the systems Sb(III) - HCl - H_2SO_4 and Sb(V) - HCl - H_2SO_4 .

VII. SUMMARY

The kinetics of the exchange reaction between Sb(III) and Sb(V) was studied in aqueous sulfuric acid, and in aqueous sulfuric acid systems containing added chloride ion. No exchange was observed in aqueous sulfuric acid, but the addition of chloride initiated exchange, and the concentration of chloride had a significant effect on the observed rate. In addition to a study of the influence of chloride concentration, experiments were performed in which the effect of independent variation in the concentrations of antimony(III), antimony(V), sulfate, and hydrogen ion was determined at two levels of chloride concentration, 6.00 M and 0.20 M. Supplementary spectrophotometric examinations of antimony(III) and antimony(V) were also performed.

In 6.00 M chloride, it was found that the reaction was first order with respect to antimony(III) and antimony(V), that sulfate ion has no effect, and that the dependence of exchange rate exhibits a maximum at approximately 9 M hydrogen ion. The exchange mechanism is apparently identical with that observed previously in hydrochloric acid solutions.

In 0.20 M chloride, while the rate maintains a unit dependence with respect to antimony(III), the reaction exhibits a fractional order of 0.76 with respect to antimony(V). At this level of chloride concentration, the rate of exchange is approximately second order with respect to chloride, but undergoes a sharp maximum at approximately 9 M hydrogen ion and a similar, although much less pronounced maximum at 0.60 M sulfate. The two antimony oxidation states are apparently involved in complex equilibria with chloride, sulfate, and hydrogen ions. Both chloride and sulfate are involved in the activated complex, although the relative importance of chloro or sulfato bridging is difficult to assess. While some qualitative observations as to mechanism can be made, a quantitative evaluation must await a more accurate knowledge of the nature of the solution species and their equilibrium relationships.

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APPENDIX

ORIGINAL KINETIC DATA

ORIGINAL DATA FROM TABLE II
(page 42)

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} M Sb(III)	2.95	0.916	387
1.29×10^{-3} M Sb(V)	3.79	0.892	800
$\mu = 10.5$	4.96	0.858	1208
9.75 M H^+	6.23	0.819	1611
0.74 M $SO_4^=$	34.35	---	∞
2.27 M HSO_4^-			
5.975 M ClO_4^-			
0.025 M Cl^-			
$t_{\frac{1}{2}}$ = 7,522 hrs.			
1.31×10^{-3} M Sb(III)	4.78	0.864	200
1.29×10^{-3} M Sb(V)	6.81	0.807	388
$\mu = 10.5$	8.42	0.761	600
9.75 M H^+	10.45	0.703	800
0.74 M $SO_4^=$	11.32	0.679	995
2.27 M HSO_4^-	13.66	0.612	1208
5.95 M ClO_4^-	16.34	0.536	1428
0.05 M Cl^-	16.27	0.538	1611
$t_{\frac{1}{2}}$ = 2048 hrs.	35.21	---	∞
1.31×10^{-3} M Sb(III)	8.02	0.790	100
1.31×10^{-3} M Sb(V)	13.49	0.647	200
$\mu = 10.5$	15.67	0.590	300
9.75 M H^+	18.43	0.518	389
0.74 M $SO_4^=$	21.18	0.446	484
2.27 M HSO_4^-	21.94	0.426	555
5.90 M ClO_4^-	26.66	0.302	701
0.10 M Cl^-	38.20	---	∞
$t_{\frac{1}{2}}$ = 463 hrs.			

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} M Sb(III)	9.37	0.764	49
1.29×10^{-3} M Sb(V)	12.98	0.673	101
$\mu = 10.5$	17.63	0.556	151
9.75 M H^+	22.08	0.444	200
0.74 M $SO_4^=$	26.26	0.339	251
2.27 M HSO_4^-	31.51	0.206	390
5.85 M ClO_4^-	39.70	---	∞
0.15 M Cl^-			
$t_{\frac{1}{2}}$ = 173 hrs.			
1.31×10^{-3} M Sb(III)	8.47	0.755	15
1.29×10^{-3} M Sb(V)	11.42	0.670	29
$\mu = 10.5$	17.05	0.507	50
9.75 M H^+	22.09	0.362	74
0.74 M $SO_4^=$	26.62	0.231	96
2.27 M HSO_4^-	24.57	0.290	120
5.70 M ClO_4^-	26.71	0.228	145
0.30 M Cl^-	30.14	0.129	170
$t_{\frac{1}{2}}$ = 66.3 hrs.	34.60	---	∞
1.31×10^{-3} M Sb(III)	6.52	0.803	8
1.29×10^{-3} M Sb(V)	10.01	0.697	19
$\mu = 10.5$	14.63	0.557	31
9.75 M H^+	17.25	0.478	42
0.74 M $SO_4^=$	18.90	0.428	51
2.27 M HSO_4^-	21.30	0.356	68
5.60 M ClO_4^-	27.26	0.175	94
0.40 M Cl^-	32.98	---	∞
$t_{\frac{1}{2}}$ = 39.9 hrs.			

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} M Sb(III)	16.55	0.818	5
1.30 x 10^{-3} M Sb(V)	23.32	0.744	9
μ = 10.5	27.98	0.693	15
9.75 M H^+	37.30	0.590	23
0.74 M $SO_4^=$	43.81	0.519	30
2.27 M HSO_4^-	48.15	0.471	35
5.60 M ClO_4^-	48.61	0.466	39
0.40 M Cl^-	52.53	0.423	47
$t_{1/2}$ = 40.1 hrs.	54.99	0.396	52
	64.81	0.288	58
	91.06	---	∞
1.31 x 10^{-3} M Sb(III)	9.76	0.722	10
1.29 x 10^{-3} M Sb(V)	17.19	0.510	21
μ = 10.5	25.21	0.282	44
9.75 M H^+	28.45	0.189	55
0.74 M $SO_4^=$	29.55	0.158	69
2.27 M HSO_4^-	31.09	0.114	101
5.50 M ClO_4^-	35.10	---	∞
0.50 M Cl^-			
$t_{1/2}$ = 31.7 hrs.			
1.31 x 10^{-3} M Sb(III)	7.10	0.795	5
1.29 x 10^{-3} M Sb(V)	10.54	0.695	10
μ = 10.5	14.59	0.578	14
9.75 M H^+	20.14	0.418	23
0.74 M $SO_4^=$	21.79	0.370	29
2.27 M HSO_4^-	28.91	0.164	50
5.40 M ClO_4^-	30.32	0.123	60
0.60 M Cl^-	34.58	---	∞
$t_{1/2}$ = 23.3 hrs.			
1.31 x 10^{-3} M Sb(III)	8.79	0.731	7
1.29 x 10^{-3} M Sb(V)	15.22	0.534	18
μ = 10.5	17.57	0.462	24
9.75 M H^+	19.07	0.416	31
0.74 M $SO_4^=$	22.50	0.310	40
2.27 M HSO_4^-	25.07	0.232	50
5.30 M ClO_4^-	32.63	---	∞
0.70 M Cl^-			
$t_{1/2}$ = 26.7 hrs.			

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	16.60	0.815	3
1.30×10^{-3} $\underline{M}$ Sb(V)	23.23	0.742	6
$\mu = 10.5$	27.68	0.692	9
9.75 $\underline{M}$ H^+	34.63	0.615	12
0.74 $\underline{M}$ $SO_4^=$	36.79	0.591	15
2.27 $\underline{M}$ HSO_4^-	40.84	0.546	18
5.40 $\underline{M}$ ClO_4^-	47.26	0.475	24
0.60 $\underline{M}$ Cl^-	50.02	0.444	27
$t_{\frac{1}{2}}$ = 25.9 hrs.	55.75	0.380	30
	61.52	0.316	33
	58.52	0.349	36
	60.98	0.322	39
	89.95	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	19.19	0.794	3
1.30×10^{-3} $\underline{M}$ Sb(V)	27.27	0.708	6
$\mu = 10.5$	34.30	0.632	9
9.75 $\underline{M}$ H^+	42.70	0.542	12
0.74 $\underline{M}$ $SO_4^=$	45.95	0.508	15
2.27 $\underline{M}$ HSO_4^-	50.19	0.462	18
5.20 $\underline{M}$ ClO_4^-	56.23	0.397	24
0.80 $\underline{M}$ Cl^-	57.84	0.380	27
$t_{\frac{1}{2}}$ = 21.2 hrs.	65.48	0.298	30
	66.27	0.290	33
	68.63	0.265	36
	93.32	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	25.00	0.723	4
1.30×10^{-3} $\underline{M}$ Sb(V)	39.16	0.566	9
$\mu = 10.5$	46.00	0.490	12
9.75 $\underline{M}$ H^+	47.03	0.478	16
0.74 $\underline{M}$ $SO_4^=$	61.28	0.320	22
2.27 $\underline{M}$ HSO_4^-	64.22	0.288	26
5.00 $\underline{M}$ ClO_4^-	65.19	0.277	33
1.00 $\underline{M}$ Cl^-	68.46	0.241	37
$t_{\frac{1}{2}}$ = 20.6 hrs.	71.78	0.204	41
	90.16	---	∞

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	21.23	0.766	2
1.30×10^{-3} $\underline{M}$ Sb(V)	30.49	0.664	4
$\mu = 10.5$	40.07	0.559	6
9.75 $\underline{M}$ H^+	45.16	0.503	8
0.74 $\underline{M}$ $SO_4^=$	51.36	0.434	10
2.27 $\underline{M}$ HSO_4^-	51.81	0.429	12
4.50 $\underline{M}$ ClO_4^-	56.23	0.381	14
1.50 $\underline{M}$ Cl^-	62.98	0.306	17
$t_{\frac{1}{2}}$ = 12.0 hrs.	90.79	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	11.88	0.652	4
1.29×10^{-3} $\underline{M}$ Sb(V)	16.03	0.531	8
$\mu = 10.5$	21.37	0.375	13
9.75 $\underline{M}$ H^+	34.17	---	∞
0.74 $\underline{M}$ $SO_4^=$			
2.27 $\underline{M}$ HSO_4^-			
4.00 $\underline{M}$ ClO_4^-			
2.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 11.2 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	23.13	0.745	2
1.30×10^{-3} $\underline{M}$ Sb(V)	32.37	0.643	4
$\mu = 10.5$	41.35	0.544	6
9.75 $\underline{M}$ H^+	47.03	0.482	8
0.74 $\underline{M}$ $SO_4^=$	51.64	0.431	10
2.27 $\underline{M}$ HSO_4^-	58.43	0.356	12
4.00 $\underline{M}$ ClO_4^-	56.55	0.377	14
2.00 $\underline{M}$ Cl^-	67.45	0.257	18
$t_{\frac{1}{2}}$ = 10.8 hrs.	75.39	0.169	24
	90.76	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	22.71	0.744	2
1.30×10^{-3} $\underline{M}$ Sb(V)	35.05	0.606	4
$\mu = 10.5$	43.69	0.508	6
9.75 $\underline{M}$ H^+	46.25	0.480	8
0.74 $\underline{M}$ $SO_4^=$	48.46	0.455	10
2.27 $\underline{M}$ HSO_4^-	57.26	0.356	11.5
4.00 $\underline{M}$ ClO_4^-	59.58	0.330	14
2.00 $\underline{M}$ Cl^-	88.86	---	∞
$t_{\frac{1}{2}}$ = 10.6 hrs.			

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	23.78	0.739	2
1.30×10^{-3} $\underline{M}$ Sb(V)	34.72	0.619	4
$\mu = 10.5$	41.65	0.542	6
9.75 $\underline{M}$ H^+	55.20	0.394	10
0.74 $\underline{M}$ $SO_4^{=}$	59.05	0.351	12
2.27 $\underline{M}$ HSO_4^-	60.26	0.338	14
4.00 $\underline{M}$ ClO_4^-	91.03	---	∞
2.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 10.2 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	11.93	0.643	4
1.29×10^{-3} $\underline{M}$ Sb(V)	17.19	0.486	8
$\mu = 10.5$	20.98	0.373	12
9.75 $\underline{M}$ H^+	33.44	---	∞
0.74 $\underline{M}$ $SO_4^{=}$			
2.27 $\underline{M}$ HSO_4^-			
3.00 $\underline{M}$ ClO_4^-			
3.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 10.2 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	11.01	0.678	3
1.29×10^{-3} $\underline{M}$ Sb(V)	16.15	0.527	6
$\mu = 10.5$	20.45	0.402	10
9.75 $\underline{M}$ H^+	24.05	0.296	14
0.74 $\underline{M}$ $SO_4^{=}$	34.17	---	∞
2.27 $\underline{M}$ HSO_4^-			
2.00 $\underline{M}$ ClO_4^-			
4.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 9.33 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	7.98	0.767	2
1.29×10^{-3} $\underline{M}$ Sb(V)	13.89	0.595	5
$\mu = 10.5$	18.92	0.461	8
9.75 $\underline{M}$ H^+	22.36	0.348	12
0.74 $\underline{M}$ $SO_4^{=}$	34.31	---	∞
2.27 $\underline{M}$ HSO_4^-			
1.00 $\underline{M}$ ClO_4^-			
5.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 8.75 hrs.			

Original Data from Table II - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III)	18.77	0.787	1
1.30 x 10^{-3} $\underline{M}$ Sb(V)	26.12	0.704	2
μ = 10.5	34.76	0.606	3
9.75 $\underline{M}$ H^+	41.81	0.526	4
0.74 $\underline{M}$ $SO_4^=$	45.74	0.482	5
2.27 $\underline{M}$ HSO_4^-	49.89	0.435	6.5
6.00 $\underline{M}$ Cl^-	57.80	0.345	8
$t_{\frac{1}{2}}$ = 6.10 hrs.	64.21	0.272	9.5
	67.27	0.238	11
	68.37	0.225	12.5
	88.26	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	18.53	0.793	1
1.30 x 10^{-3} $\underline{M}$ Sb(V)	25.48	0.715	2
μ = 10.5	33.25	0.628	3
9.75 $\underline{M}$ H^+	38.21	0.572	4
0.74 $\underline{M}$ $SO_4^=$	42.05	0.529	5
2.27 $\underline{M}$ HSO_4^-	47.78	0.465	6.5
6.00 $\underline{M}$ Cl^-	52.52	0.412	8
$t_{\frac{1}{2}}$ = 7.62 hrs.	57.54	0.356	9.5
	63.00	0.295	11
	65.20	0.270	13
	89.35	---	∞

ORIGINAL DATA FROM TABLE III
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	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III)	36.02	0.643	0.5
1.31 x 10^{-3} $\underline{M}$ Sb(V)	47.11	0.533	1.0
μ = 10.5	55.33	0.452	1.5
9.75 $\underline{M}$ H^+	63.70	0.369	2.0
0.74 $\underline{M}$ $SO_4^=$	68.10	0.325	2.5
2.27 $\underline{M}$ HSO_4^-	100.94	---	∞
4.00 $\underline{M}$ ClO_4^-			
2.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 2.00 hrs.			

Original Data from Table III - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	37.69	0.619	0.5
1.31×10^{-3} $\underline{M}$ Sb(V)	45.21	0.543	1.0
$\mu = 10.5$	54.60	0.448	1.5
9.75 $\underline{M}$ H^+	60.14	0.392	2.0
0.74 $\underline{M}$ $SO_4^=$	98.84	---	∞
2.27 $\underline{M}$ HSO_4^-			
4.00 $\underline{M}$ ClO_4^-			
2.00 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 2.22 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	26.73	0.736	2
1.31×10^{-3} $\underline{M}$ Sb(V)	29.84	0.705	5
$\mu = 10.5$	31.22	0.691	8
9.75 $\underline{M}$ H^+	33.42	0.669	11
0.74 $\underline{M}$ $SO_4^=$	38.23	0.622	17
2.27 $\underline{M}$ HSO_4^-	46.56	0.539	22
5.80 $\underline{M}$ ClO_4^-	49.02	0.515	28
0.20 $\underline{M}$ Cl^-	50.46	0.501	34
$t_{\frac{1}{2}}$ = 53.4 hrs.	58.17	0.425	44
	60.65	0.400	50
	62.70	0.380	57
	69.79	0.309	66
	100.06	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	29.99	0.706	2
1.31×10^{-3} $\underline{M}$ Sb(V)	31.57	0.680	5
$\mu = 10.5$	33.23	0.674	8
9.75 $\underline{M}$ H^+	37.11	0.636	11
0.74 $\underline{M}$ $SO_4^=$	44.17	0.566	17
2.27 $\underline{M}$ HSO_4^-	48.94	0.520	22
5.80 $\underline{M}$ ClO_4^-	49.00	0.519	28
0.20 $\underline{M}$ Cl^-	52.88	0.481	34
$t_{\frac{1}{2}}$ = 58.2 hrs.	59.64	0.415	44
	61.38	0.398	50
	62.83	0.383	57
	69.28	0.320	66
	101.88	---	∞

ORIGINAL DATA FROM TABLE IV
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	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III) 0.645 x 10^{-3} $\underline{M}$ Sb(V) μ = 12.0 10.0 $\underline{M}$ H^+ 6.00 $\underline{M}$ Cl^- 1.44 $\underline{M}$ Li^+ 1.88 $\underline{M}$ ClO_4^- 0.56 $\underline{M}$ $SO_4^=$ 2.44 $\underline{M}$ HSO_4^- $t_{1/2}$ = 11.5 hrs.	4.87	0.783	3
	7.22	0.679	5
	9.16	0.593	8
	11.93	0.469	12
	13.94	0.380	16
	17.67	0.214	24
	33.55	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III) 1.29 x 10^{-3} $\underline{M}$ Sb(V) μ = 12.0 10.0 $\underline{M}$ H^+ 6.00 $\underline{M}$ Cl^- 1.44 $\underline{M}$ Li^+ 1.88 $\underline{M}$ ClO_4^- 0.56 $\underline{M}$ $SO_4^=$ 2.44 $\underline{M}$ HSO_4^- $t_{1/2}$ = 10.0 hrs.	5.12	0.846	1
	9.41	0.717	3
	12.16	0.635	5
	15.01	0.549	7
	19.81	0.405	10
	20.82	0.374	13
	23.32	0.299	16
	33.28	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III) 1.29 x 10^{-3} $\underline{M}$ Sb(V) μ = 12.0 10.0 $\underline{M}$ H^+ 6.00 $\underline{M}$ Cl^- 1.44 $\underline{M}$ Li^+ 1.88 $\underline{M}$ ClO_4^- 0.56 $\underline{M}$ $SO_4^=$ 2.44 $\underline{M}$ HSO_4^- $t_{1/2}$ = 10.2 hrs.	7.42	0.783	2
	11.20	0.673	4
	17.25	0.496	7
	18.00	0.474	9
	22.20	0.351	12
	23.67	0.308	17
	34.21	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III) 1.935 x 10^{-3} $\underline{M}$ Sb(V) μ = 12.0 10.0 $\underline{M}$ H^+ 6.00 $\underline{M}$ Cl^- 1.44 $\underline{M}$ Li^+ 1.88 $\underline{M}$ ClO_4^- 0.56 $\underline{M}$ $SO_4^=$ 2.44 $\underline{M}$ HSO_4^- $t_{1/2}$ = 6.65 hrs.	7.08	0.829	1
	12.42	0.699	3
	16.25	0.606	5
	22.47	0.456	7
	26.39	0.361	9
	41.29	---	∞

Original Data from Table IV - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	9.55	0.793	1
2.58×10^{-3} $\underline{M}$ Sb(V)	14.82	0.678	2
$\mu = 12.0$	15.82	0.656	3
10.0 $\underline{M}$ H^+	22.87	0.503	5
6.00 $\underline{M}$ Cl^-	24.92	0.458	7
1.44 $\underline{M}$ Li^+	31.51	0.315	9
1.88 $\underline{M}$ ClO_4^-	45.98	---	∞
0.56 $\underline{M}$ $SO_4^=$			
2.44 $\underline{M}$ HSO_4^-			
$t_{\frac{1}{2}} = 6.48$ hrs.			
0.655×10^{-3} $\underline{M}$ Sb(III)	5.79	0.746	2
1.29×10^{-3} $\underline{M}$ Sb(V)	9.35	0.589	5
$\mu = 12.0$	9.65	0.576	7
10.0 $\underline{M}$ H^+	12.09	0.469	9
6.00 $\underline{M}$ Cl^-	13.77	0.395	12
1.44 $\underline{M}$ Li^+	14.46	0.365	14
0.56 $\underline{M}$ $SO_4^=$	15.06	0.338	17
1.88 $\underline{M}$ ClO_4^-	22.76	---	∞
2.44 $\underline{M}$ HSO_4^-			
$t_{\frac{1}{2}} = 12.7$ hrs.			
1.965×10^{-3} $\underline{M}$ Sb(III)	6.68	0.839	1
1.29×10^{-3} $\underline{M}$ Sb(V)	14.62	0.647	3
$\mu = 12.0$	19.74	0.523	5
10.0 $\underline{M}$ H^+	23.50	0.432	7
6.00 $\underline{M}$ Cl^-	24.22	0.415	9
1.44 $\underline{M}$ Li^+	30.56	0.262	12
0.56 $\underline{M}$ $SO_4^=$	32.38	0.218	14
1.88 $\underline{M}$ ClO_4^-	41.40	---	∞
2.44 $\underline{M}$ HSO_4^-			
$t_{\frac{1}{2}} = 6.94$ hrs.			
2.62×10^{-3} $\underline{M}$ Sb(III)	9.09	0.807	1
1.29×10^{-3} $\underline{M}$ Sb(V)	17.09	0.637	3
$\mu = 12.0$	23.35	0.504	5
10.0 $\underline{M}$ H^+	29.35	0.376	7
6.00 $\underline{M}$ Cl^-	32.44	0.311	9
1.44 $\underline{M}$ Li^+	35.84	0.238	12
0.56 $\underline{M}$ $SO_4^=$	38.05	0.191	14
1.88 $\underline{M}$ ClO_4^-	47.06	---	∞
2.44 $\underline{M}$ HSO_4^-			
$t_{\frac{1}{2}} = 6.27$ hrs.			

ORIGINAL DATA FROM TABLE V
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	c/s	(1-F)	t(hrs.)
0.655×10^{-3} $\underline{M}$ Sb(III)	8.85	0.659	60
1.29×10^{-3} $\underline{M}$ Sb(V)	12.45	0.520	84
$\mu = 10.5$	13.79	0.468	129
9.75 $\underline{M}$ H^+	16.48	0.368	180
0.74 $\underline{M}$ $SO_4^{=}$	18.87	0.272	227
2.27 $\underline{M}$ HSO_4^-	19.91	0.232	290
5.80 $\underline{M}$ ClO_4^-	22.07	0.149	361
0.20 $\underline{M}$ Cl^-	25.93	---	∞
$t_{\frac{1}{2}} = 148$ hrs.			
1.965×10^{-3} $\underline{M}$ Sb(III)	10.24	0.749	25
1.29×10^{-3} $\underline{M}$ Sb(V)	15.36	0.623	50
$\mu = 10.5$	20.02	0.508	75
9.75 $\underline{M}$ H^+	23.77	0.416	110
0.74 $\underline{M}$ $SO_4^{=}$	30.52	0.250	145
2.27 $\underline{M}$ HSO_4^-	32.34	0.206	180
5.80 $\underline{M}$ ClO_4^-	34.19	0.160	220
0.20 $\underline{M}$ Cl^-	40.72	---	∞
$t_{\frac{1}{2}} = 84.1$ hrs.			
2.62×10^{-3} $\underline{M}$ Sb(III)	10.57	0.777	20
1.29×10^{-3} $\underline{M}$ Sb(V)	19.14	0.596	45
$\mu = 10.5$	25.06	0.472	70
9.75 $\underline{M}$ H^+	27.88	0.412	96
0.74 $\underline{M}$ $SO_4^{=}$	31.40	0.338	120
2.27 $\underline{M}$ HSO_4^-	37.22	0.215	145
5.80 $\underline{M}$ ClO_4^-	41.12	0.133	175
0.20 $\underline{M}$ Cl^-	47.43	---	∞
$t_{\frac{1}{2}} = 73.7$ hrs.			
3.93×10^{-3} $\underline{M}$ Sb(III)	10.17	0.805	13
1.29×10^{-3} $\underline{M}$ Sb(V)	18.04	0.654	30
$\mu = 10.5$	26.46	0.493	50
9.75 $\underline{M}$ H^+	33.40	0.360	75
0.74 $\underline{M}$ $SO_4^{=}$	37.44	0.283	96
2.27 $\underline{M}$ HSO_4^-	41.08	0.213	120
5.80 $\underline{M}$ ClO_4^-	44.43	0.149	145
0.20 $\underline{M}$ Cl^-	45.74	0.124	170
$t_{\frac{1}{2}} = 56.9$ hrs.	52.21	---	∞

Original Data from Table V - cont.

	c/s	(1-F)	t(hrs.)
6.55×10^{-3} $\underline{M}$ Sb(III)	11.47	0.801	10
1.29×10^{-3} $\underline{M}$ Sb(V)	19.36	0.665	20
$\mu = 10.5$	33.68	0.417	45
9.75 $\underline{M}$ H^+	38.36	0.336	56
0.74 $\underline{M}$ $SO_4^=$	43.42	0.248	78
2.27 $\underline{M}$ HSO_4^-	50.64	0.123	101
5.80 $\underline{M}$ ClO_4^-	53.23	0.079	120
0.20 $\underline{M}$ Cl^-	52.60	0.089	140
$t_{\frac{1}{2}}$ = 35.7 hrs.	57.77	---	∞
1.34×10^{-3} $\underline{M}$ Sb(III)	4.22	0.823	30
0.645×10^{-3} $\underline{M}$ Sb(V)	8.39	0.649	73
$\mu = 10.5$	10.37	0.566	109
9.75 $\underline{M}$ H^+	12.40	0.481	150
0.74 $\underline{M}$ $SO_4^=$	16.63	0.304	200
2.27 $\underline{M}$ HSO_4^-	18.75	0.215	249
5.80 $\underline{M}$ ClO_4^-	20.27	0.151	340
0.20 $\underline{M}$ Cl^-	23.90	---	∞
$t_{\frac{1}{2}}$ = 120 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	10.79	0.738	26
1.935×10^{-3} $\underline{M}$ Sb(V)	16.65	0.595	49
$\mu = 10.5$	20.29	0.507	75
9.75 $\underline{M}$ H^+	26.84	0.347	145
0.74 $\underline{M}$ $SO_4^=$	30.24	0.265	180
2.27 $\underline{M}$ HSO_4^-	35.04	0.148	220
5.80 $\underline{M}$ ClO_4^-	35.71	0.132	270
0.20 $\underline{M}$ Cl^-	41.13	---	∞
$t_{\frac{1}{2}}$ = 95.5 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	12.23	0.736	22
2.58×10^{-3} $\underline{M}$ Sb(V)	19.17	0.586	45
$\mu = 10.5$	24.45	0.472	69
9.75 $\underline{M}$ H^+	27.54	0.405	95
0.74 $\underline{M}$ $SO_4^=$	30.17	0.348	120
2.27 $\underline{M}$ HSO_4^-	34.98	0.244	145
5.80 $\underline{M}$ ClO_4^-	34.85	0.247	175
0.20 $\underline{M}$ Cl^-	38.36	0.171	215
$t_{\frac{1}{2}}$ = 94.3 hrs.	46.28	---	∞

Original Data from Table V - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} M Sb(III) 0.419 x 10^{-3} M Sb(V) μ = 10.5 9.75 M H^+ 0.74 M $SO_4^{=}$ 2.27 M HSO_4^- 0.20 M Cl^- 5.80 M ClO_4^- $t_{\frac{1}{2}}$ = 135 hrs.	5.12	0.882	12
	8.40	0.806	27
	9.21	0.788	38
	13.19	0.696	54
	14.61	0.663	72
	17.09	0.606	86
	20.61	0.525	102
	20.17	0.535	120
	22.77	0.475	134
	25.62	0.409	156
	43.36	---	∞
1.31 x 10^{-3} M Sb(III) 3.78 x 10^{-3} M Sb(V) μ = 10.5 9.75 M H^+ 0.74 M $SO_4^{=}$ 2.27 M HSO_4^- 0.20 M Cl^- 5.80 M ClO_4^- $t_{\frac{1}{2}}$ = 78.2 hrs.	34.53	0.736	10
	43.26	0.670	20
	49.13	0.625	30
	58.41	0.554	43
	67.40	0.485	50
	61.92	0.527	60
	73.39	0.440	70
	80.41	0.386	80
	87.67	0.331	91
	86.04	0.343	100
	84.85	0.352	107
	93.87	0.283	120
	96.39	0.264	130
	99.06	0.244	140
	106.00	0.191	150
	130.97	---	∞
1.31 x 10^{-3} M Sb(III) 4.97 x 10^{-3} M Sb(V) μ = 10.5 9.75 M H^+ 0.74 M $SO_4^{=}$ 2.27 M HSO_4^- 0.20 M Cl^- 5.80 M ClO_4^- $t_{\frac{1}{2}}$ = 63.1 hrs.	42.91	0.688	10
	55.37	0.598	20
	64.66	0.530	31
	71.91	0.477	43
	75.01	0.455	50
	77.77	0.435	60
	87.46	0.364	70
	97.68	0.290	80
	99.50	0.277	91
	107.25	0.221	100
	96.88	0.296	107
	108.05	0.215	120
	112.60	0.182	130
	109.60	0.203	140
	121.91	0.114	150
	137.60	---	∞

ORIGINAL DATA FROM TABLE VI
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	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	17.12	0.819	16
1.30×10^{-3} $\underline{M}$ Sb(V)	21.61	0.771	36
$\mu = 10.1$	26.05	0.724	57
9.75 $\underline{M}$ H^+	31.49	0.667	76
0.20 $\underline{M}$ Cl^-	33.61	0.644	97
0.20 $\underline{M}$ $SO_4^=$	39.76	0.579	111
0.60 $\underline{M}$ HSO_4^-	41.80	0.557	131
8.70 $\underline{M}$ ClO_4^-	44.78	0.526	150
0.15 $\underline{M}$ Li^+	45.22	0.521	171
$t_{\frac{1}{2}}$ = 220 hrs.	47.79	0.494	196
	94.45	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	16.33	0.825	12
1.30×10^{-3} $\underline{M}$ Sb(V)	19.64	0.789	25
$\mu = 10.1$	21.67	0.767	39
9.75 $\underline{M}$ H^+	27.41	0.705	52
0.20 $\underline{M}$ Cl^-	30.15	0.676	64
0.25 $\underline{M}$ $SO_4^=$	34.32	0.631	76
8.40 $\underline{M}$ ClO_4^-	34.56	0.629	87
0.10 $\underline{M}$ Li^+	39.47	0.576	109
0.75 $\underline{M}$ HSO_4^-	42.18	0.547	123
$t_{\frac{1}{2}}$ = 221 hrs.	44.06	0.527	144
	45.38	0.512	171
	50.11	0.462	197
	93.06	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	17.11	0.815	12
1.30×10^{-3} $\underline{M}$ Sb(V)	19.28	0.792	24
$\mu = 10.1$	22.79	0.754	39
9.75 $\underline{M}$ H^+	27.53	0.703	52
0.20 $\underline{M}$ Cl^-	30.18	0.674	64
0.31 $\underline{M}$ $SO_4^=$	33.40	0.639	76
0.94 $\underline{M}$ HSO_4^-	35.31	0.619	87
8.03 $\underline{M}$ ClO_4^-	39.39	0.574	109
0.04 $\underline{M}$ Li^+	42.72	0.539	122
$t_{\frac{1}{2}}$ = 181 hrs.	46.08	0.502	144
	52.28	0.435	171
	54.28	0.414	197
	92.57	---	∞

Original Data from Table VI - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III)	5.44	0.849	20
1.29 x 10^{-3} $\underline{M}$ Sb(V)	10.24	0.715	50
μ = 10.5	16.01	0.554	100
9.75 $\underline{M}$ H^+	18.85	0.475	142
8.06 $\underline{M}$ ClO_4^-	21.82	0.394	190
0.20 $\underline{M}$ Cl^-	24.26	0.325	240
0.37 $\underline{M}$ $SO_4^=$	27.36	0.238	295
1.13 $\underline{M}$ HSO_4^-	29.24	0.186	339
$t_{\frac{1}{2}}$ = 152 hrs.	35.92	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	16.03	0.808	20
1.30 x 10^{-3} $\underline{M}$ Sb(V)	22.14	0.734	45
μ = 10.5	29.29	0.649	75
9.75 $\underline{M}$ H^+	34.80	0.582	95
1.13 $\underline{M}$ HSO_4^-	38.45	0.539	115
0.37 $\underline{M}$ $SO_4^=$	48.55	0.418	195
0.20 $\underline{M}$ Cl^-	55.13	0.339	215
8.06 $\underline{M}$ ClO_4^-	58.76	0.295	240
0.38 $\underline{M}$ Li^+	62.59	0.249	265
$t_{\frac{1}{2}}$ = 150 hrs.	83.35	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	18.27	0.811	12
1.30 x 10^{-3} $\underline{M}$ Sb(V)	22.42	0.768	24
μ = 10.5	26.26	0.728	36
9.75 $\underline{M}$ H^+	30.05	0.689	48
0.20 $\underline{M}$ Cl^-	36.87	0.618	61
0.44 $\underline{M}$ $SO_4^=$	41.46	0.571	74
1.36 $\underline{M}$ HSO_4^-	44.80	0.536	85
7.26 $\underline{M}$ ClO_4^-	45.21	0.532	96
0.31 $\underline{M}$ Li^+	47.38	0.510	108
$t_{\frac{1}{2}}$ = 146 hrs.	49.62	0.487	120
	51.27	0.469	132
	56.35	0.417	150
	96.64	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	6.03	0.822	20
1.29 x 10^{-3} $\underline{M}$ Sb(V)	13.23	0.610	79
μ = 10.5	17.75	0.476	120
9.75 $\underline{M}$ H^+	20.80	0.386	165
7.16 $\underline{M}$ ClO_4^-	23.82	0.297	216
0.20 $\underline{M}$ Cl^-	27.89	0.177	315
0.52 $\underline{M}$ $SO_4^=$	29.73	0.123	339
1.58 $\underline{M}$ HSO_4^-	34.68	---	∞
$t_{\frac{1}{2}}$ = 123 hrs.			

Original Data from Table VI - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III)	18.23	0.779	20
1.30 x 10^{-3} $\underline{M}$ Sb(V)	27.90	0.661	45
μ = 10.5	33.81	0.590	75
9.75 $\underline{M}$ H^+	40.25	0.512	95
1.58 $\underline{M}$ HSO_4^-	42.13	0.489	115
0.52 $\underline{M}$ $SO_4^=$	49.93	0.394	140
0.20 $\underline{M}$ Cl^-	54.95	0.333	195
7.16 $\underline{M}$ ClO_4^-	56.80	0.311	215
0.23 $\underline{M}$ Li^+	63.44	0.230	240
$t_{1/2}$ = 135 hrs.	64.57	0.216	265
	82.40	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	14.31	0.831	12
1.30 x 10^{-3} $\underline{M}$ Sb(V)	19.94	0.764	27
μ = 10.5	23.88	0.718	39
9.75 $\underline{M}$ H^+	31.94	0.623	54
0.57 $\underline{M}$ $SO_4^=$	34.98	0.587	73
1.73 $\underline{M}$ HSO_4^-	42.81	0.494	87
0.20 $\underline{M}$ Cl^-	43.50	0.486	102
6.86 $\underline{M}$ ClO_4^-	49.77	0.412	123
0.18 $\underline{M}$ Li^+	49.14	0.420	135
$t_{1/2}$ = 107 hrs.	59.69	0.295	155
	60.65	0.284	177
	62.49	0.262	199
	84.67	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	22.28	0.728	20
1.30 x 10^{-3} $\underline{M}$ Sb(V)	32.43	0.605	45
μ = 10.5	42.43	0.483	75
9.75 $\underline{M}$ H^+	47.27	0.424	95
1.88 $\underline{M}$ HSO_4^-	52.44	0.360	115
0.62 $\underline{M}$ $SO_4^=$	55.55	0.323	140
0.20 $\underline{M}$ Cl^-	60.43	0.263	170
6.56 $\underline{M}$ ClO_4^-	63.88	0.221	195
0.13 $\underline{M}$ Li^+	66.24	0.192	215
$t_{1/2}$ = 97.4 hrs.	71.44	0.129	240
	72.40	0.117	265
	82.00	---	∞

Original Data from Table VI - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	16.71	0.833	8
1.30×10^{-3} $\underline{M}$ Sb(V)	20.98	0.791	15
$\mu = 10.5$	23.55	0.765	23
9.75 $\underline{M}$ H^+	28.19	0.719	31
0.20 $\underline{M}$ Cl^-	29.72	0.703	39
0.68 $\underline{M}$ $SO_4^=$	36.11	0.640	49
2.07 $\underline{M}$ HSO_4^-	38.06	0.620	60
6.19 $\underline{M}$ ClO_4^-	41.34	0.587	71
0.07 $\underline{M}$ Li^+	46.94	0.531	80
$t_{\frac{1}{2}}$ = 118 hrs.	48.53	0.516	86
	51.09	0.490	97
	53.58	0.465	110
	100.18	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	19.06	0.770	20
1.30×10^{-3} $\underline{M}$ Sb(V)	27.97	0.662	45
$\mu = 10.7$	36.63	0.557	75
9.75 $\underline{M}$ H^+	40.25	0.513	95
2.57 $\underline{M}$ HSO_4^-	47.66	0.424	115
0.20 $\underline{M}$ Cl^-	50.15	0.394	140
0.83 $\underline{M}$ $SO_4^=$	50.94	0.384	152
5.44 $\underline{M}$ ClO_4^-	55.22	0.332	170
0.12 $\underline{M}$ Li^+	59.38	0.282	195
$t_{\frac{1}{2}}$ = 111 hrs.	65.56	0.207	215
	66.20	0.200	240
	68.67	0.170	265
	82.71	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	18.65	0.771	20
1.30×10^{-3} $\underline{M}$ Sb(V)	28.41	0.652	45
$\mu = 10.7$	42.02	0.485	75
9.75 $\underline{M}$ H^+	43.27	0.470	95
2.87 $\underline{M}$ HSO_4^-	46.60	0.429	115
0.20 $\underline{M}$ Cl^-	54.78	0.328	170
0.93 $\underline{M}$ $SO_4^=$	60.26	0.261	195
4.82 $\underline{M}$ ClO_4^-	61.35	0.248	215
$t_{\frac{1}{2}}$ = 124 hrs.	63.74	0.219	240
	81.57	---	∞

Original Data from Table VI - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	18.01	0.788	20
1.30×10^{-3} $\underline{M}$ Sb(V)	27.27	0.679	45
$\mu = 11.0$	37.38	0.561	75
9.75 $\underline{M}$ H^+	43.52	0.488	95
3.44 $\underline{M}$ HSO_4^-	45.09	0.470	115
0.20 $\underline{M}$ Cl^-	48.42	0.431	140
1.06 $\underline{M}$ $SO_4^=$	51.12	0.399	152
4.19 $\underline{M}$ ClO_4^-	53.67	0.369	170
0.20 $\underline{M}$ Li^+	59.02	0.306	195
$t_{\frac{1}{2}}$ = 136 hrs.	63.08	0.259	215
	64.25	0.245	240
	65.32	0.232	265
	85.08	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	17.52	0.800	20
1.30×10^{-3} $\underline{M}$ Sb(V)	26.25	0.700	45
$\mu = 11.0$	35.43	0.595	75
9.75 $\underline{M}$ H^+	40.62	0.535	95
3.66 $\underline{M}$ HSO_4^-	44.13	0.495	115
0.20 $\underline{M}$ Cl^-	52.27	0.402	152
1.14 $\underline{M}$ $SO_4^=$	53.65	0.386	170
3.72 $\underline{M}$ ClO_4^-	60.48	0.308	195
0.11 $\underline{M}$ Li^+	61.92	0.292	215
$t_{\frac{1}{2}}$ = 127 hrs.	67.03	0.233	240
	69.20	0.209	265
	87.44	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	16.34	0.813	20
1.30×10^{-3} $\underline{M}$ Sb(V)	25.06	0.714	45
$\mu = 11.0$	32.50	0.629	75
9.75 $\underline{M}$ H^+	37.50	0.572	95
3.88 $\underline{M}$ HSO_4^-	40.55	0.537	115
0.20 $\underline{M}$ Cl^-	44.02	0.497	140
1.20 $\underline{M}$ $SO_4^=$	46.54	0.468	152
3.32 $\underline{M}$ ClO_4^-	49.48	0.435	170
0.05 $\underline{M}$ Li^+	55.84	0.362	195
$t_{\frac{1}{2}}$ = 156 hrs.	58.03	0.337	215
	61.35	0.299	240
	87.52	---	∞

Original Data from Table VI - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	16.98	0.806	20
1.30×10^{-3} $\underline{M}$ Sb(V)	23.50	0.732	45
$\mu = 11.0$	30.76	0.649	75
9.75 $\underline{M}$ H^+	35.20	0.598	95
4.05 $\underline{M}$ HSO_4^-	38.55	0.560	115
0.20 $\underline{M}$ Cl^-	41.96	0.521	140
1.25 $\underline{M}$ $SO_4^=$	44.03	0.497	152
3.00 $\underline{M}$ ClO_4^-	48.22	0.450	170
$t_{\frac{1}{2}}$ = 181 hrs.	52.01	0.406	195
	59.85	0.317	265
	87.60	---	∞

ORIGINAL DATA FROM TABLE VII
(page 60)

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	18.66	0.787	1
1.30×10^{-3} $\underline{M}$ Sb(V)	24.65	0.718	2
$\mu = 10.1$	30.19	0.655	3
9.75 $\underline{M}$ H^+	37.62	0.570	4
6.00 $\underline{M}$ Cl^-	40.75	0.535	5
0.20 $\underline{M}$ $SO_4^=$	49.98	0.429	6.5
0.60 $\underline{M}$ HSO_4^-	52.35	0.402	8
2.70 $\underline{M}$ ClO_4^-	57.83	0.340	9.5
0.15 $\underline{M}$ Li^+	62.39	0.287	11
$t_{\frac{1}{2}}$ = 7.02 hrs.	65.10	0.257	12.5
	87.56	---	∞

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	18.57	0.791	1
1.30×10^{-3} $\underline{M}$ Sb(V)	25.29	0.716	2
$\mu = 10.5$	32.75	0.632	3
9.75 $\underline{M}$ H^+	42.15	0.526	4
6.00 $\underline{M}$ Cl^-	45.46	0.489	5
0.52 $\underline{M}$ $SO_4^=$	49.56	0.443	6.5
1.58 $\underline{M}$ HSO_4^-	55.30	0.379	8
1.36 $\underline{M}$ ClO_4^-	56.01	0.371	9.5
0.23 $\underline{M}$ Li^+	62.35	0.299	11
$t_{\frac{1}{2}}$ = 7.65 hrs.	64.88	0.271	12.5
	89.00	---	∞

Original Data from Table VII - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	18.53	0.793	1
1.30×10^{-3} $\underline{M}$ Sb(V)	25.48	0.715	2
$\mu = 10.5$	33.25	0.628	3
9.75 $\underline{M}$ H^+	38.21	0.572	4
6.00 $\underline{M}$ Cl^-	42.05	0.529	5
0.74 $\underline{M}$ $SO_4^{=}$	47.78	0.465	6.5
2.27 $\underline{M}$ HSO_4^-	52.52	0.412	8
$t_{\frac{1}{2}}$ = 7.62 hrs.	57.54	0.356	9.5
	63.00	0.295	11
	65.20	0.270	13
	89.35	---	∞

ORIGINAL DATA FROM TABLE VIII
(page 60)

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	11.38	0.880	7
1.30×10^{-3} $\underline{M}$ Sb(V)	14.29	0.849	14
$\mu = 9.00$	14.52	0.847	21
8.00 $\underline{M}$ H^+	16.94	0.821	28
0.74 $\underline{M}$ $SO_4^{=}$	17.02	0.820	35
1.86 $\underline{M}$ HSO_4^-	18.64	0.803	44
0.20 $\underline{M}$ Cl^-	21.18	0.776	51
0.26 $\underline{M}$ Li^+	23.88	0.748	58
4.72 $\underline{M}$ ClO_4^-	26.28	0.723	71
$t_{\frac{1}{2}}$ = 255 hrs.	26.93	0.716	82
	28.33	0.701	93
	94.71	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	14.74	0.850	7
1.30×10^{-3} $\underline{M}$ Sb(V)	15.85	0.838	14
$\mu = 9.00$	17.31	0.824	21
8.25 $\underline{M}$ H^+	19.02	0.806	28
0.20 $\underline{M}$ Cl^-	19.91	0.797	35
0.74 $\underline{M}$ $SO_4^{=}$	24.11	0.755	46
1.92 $\underline{M}$ HSO_4^-	26.46	0.730	53
4.65 $\underline{M}$ ClO_4^-	27.44	0.720	59
$t_{\frac{1}{2}}$ = 201 hrs.	31.62	0.678	71
	33.14	0.662	82
	34.73	0.646	93
	98.13	---	∞

Original Data from Table VIII - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} M Sb(III)	16.38	0.834	8
1.30×10^{-3} M Sb(V)	18.02	0.818	14
$\mu = 9.50$	21.36	0.784	22
8.50 M H^+	23.55	0.762	29
0.20 M Cl^-	26.26	0.734	38
0.74 M $SO_4^=$	28.75	0.709	46
1.94 M HSO_4^-	34.68	0.649	54
[illegible].14 M ClO_4^-	36.82	0.628	62
0.26 M Li^+	38.75	0.608	71
$t_{\frac{1}{2}}$ = 134 hrs.	42.65	0.569	81
	44.74	0.547	94
	48.49	0.510	106
	98.87	---	∞
1.31×10^{-3} M Sb(III)	13.95	0.832	10
1.30×10^{-3} M Sb(V)	20.46	0.754	25
$\mu = 10.1$	25.88	0.689	35
8.75 M H^+	32.21	0.612	50
0.74 M $SO_4^=$	36.91	0.556	60
2.00 M HSO_4^-	40.05	0.518	74
0.20 M Cl^-	47.20	0.432	98
5.68 M ClO_4^-	53.56	0.355	111
0.61 M Li^+	57.47	0.308	125
$t_{\frac{1}{2}}$ = 91.7 hrs.	58.29	0.298	145
	59.64	0.282	155
	61.67	0.258	175
	83.09	---	∞
1.31×10^{-3} M Sb(III)	13.23	0.841	10
1.30×10^{-3} M Sb(V)	21.19	0.745	25
$\mu = 10.1$	23.88	0.713	35
9.00 M H^+	30.29	0.636	50
0.74 M $SO_4^=$	33.21	0.601	60
2.06 M HSO_4^-	33.48	0.597	75
0.20 M Cl^-	46.76	0.438	98
5.62 M ClO_4^-	53.28	0.359	110
0.36 M Li^+	57.64	0.307	125
$t_{\frac{1}{2}}$ = 87.7	[illegible]5.05	0.338	145
	61.01	0.267	155
	63.73	0.234	175
	83.18	---	∞

Original Data from Table VIII - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	18.41	0.817	8
1.30×10^{-3} $\underline{M}$ Sb(V)	22.02	0.781	15
$\mu = 10.1$	26.36	0.738	23
9.00 $\underline{M}$ H^+	30.37	0.698	31
0.20 $\underline{M}$ Cl^-	31.89	0.683	39
0.74 $\underline{M}$ $SO_4^=$	41.21	0.590	49
2.06 $\underline{M}$ HSO_4^-	44.53	0.557	60
5.62 $\underline{M}$ ClO_4^-	50.64	0.496	71
0.36 $\underline{M}$ Li^+	54.04	0.463	80
$t_{\frac{1}{2}}$ = 91.3 hrs.	55.20	0.451	86
	58.97	0.413	97
	60.22	0.401	109
	100.54	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	14.62	0.824	12
1.30×10^{-3} $\underline{M}$ Sb(V)	21.59	0.740	27
$\mu = 10.1$	24.50	0.705	39
9.25 $\underline{M}$ H^+	31.45	0.622	54
0.74 $\underline{M}$ $SO_4^=$	37.92	0.527	72
2.11 $\underline{M}$ HSO_4^-	42.02	0.495	87
0.20 $\underline{M}$ Cl^-	48.49	0.417	102
5.66 $\underline{M}$ ClO_4^-	46.47	0.441	120
0.11 $\underline{M}$ Li^+	53.68	0.354	135
$t_{\frac{1}{2}}$ = 114 hrs.	54.65	0.343	156
	58.88	0.292	177
	61.01	0.266	199
	83.13	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	16.44	0.816	10
1.30×10^{-3} $\underline{M}$ Sb(V)	21.37	0.761	24
$\mu = 10.5$	29.86	0.666	40
9.25 $\underline{M}$ H^+	37.96	0.575	61
0.75 $\underline{M}$ $SO_4^=$	44.52	0.502	79
2.15 $\underline{M}$ HSO_4^-	49.62	0.445	99
0.20 $\underline{M}$ Cl^-	51.11	0.428	109
5.93 $\underline{M}$ ClO_4^-	54.30	0.393	130
0.51 $\underline{M}$ Li^+	59.39	0.336	150
$t_{\frac{1}{2}}$ = 118 hrs.	62.00	0.307	170
	65.66	0.266	195
	71.62	0.199	250
	89.41	---	∞

Original Data from Table VIII - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	15.67	0.828	10
1.30×10^{-3} $\underline{M}$ Sb(V)	21.46	0.764	24
$\mu = 10.5$	38.19	0.580	61
9.50 $\underline{M}$ H^+	43.68	0.520	79
0.74 $\underline{M}$ $SO_4^=$	48.90	0.462	99
2.20 $\underline{M}$ HSO_4^-	50.22	0.448	109
0.20 $\underline{M}$ Cl^-	52.98	0.417	130
5.88 $\underline{M}$ ClO_4^-	56.85	0.375	150
0.26 $\underline{M}$ Li^+	60.59	0.334	170
$t_{\frac{1}{2}}$ = 124 hrs.	62.34	0.314	195
	71.00	0.219	219
	71.14	0.218	250
	90.92	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	17.48	0.810	10
1.30×10^{-3} $\underline{M}$ Sb(V)	20.53	0.777	24
$\mu = 10.7$	30.27	0.671	40
10.00 $\underline{M}$ H^+	37.02	0.598	61
0.74 $\underline{M}$ $SO_4^=$	40.69	0.558	79
2.36 $\underline{M}$ HSO_4^-	46.90	0.490	99
0.20 $\underline{M}$ Cl^-	48.57	0.472	109
5.96 $\underline{M}$ ClO_4^-	53.17	0.422	130
$t_{\frac{1}{2}}$ = 141 hrs.	53.41	0.420	150
	57.85	0.371	170
	61.15	0.335	195
	66.58	0.276	219
	69.96	0.240	250
	92.02	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	16.37	0.820	10
1.30×10^{-3} $\underline{M}$ Sb(V)	20.55	0.774	24
$\mu = 11.0$	26.87	0.705	40
10.25 $\underline{M}$ H^+	35.24	0.613	61
0.74 $\underline{M}$ $SO_4^=$	38.98	0.572	79
2.51 $\underline{M}$ HSO_4^-	45.64	0.499	109
0.20 $\underline{M}$ Cl^-	46.68	0.488	130
6.06 $\underline{M}$ ClO_4^-	52.66	0.422	150
$t_{\frac{1}{2}}$ = 155 hrs.	54.64	0.400	170
	58.45	0.359	195
	66.32	0.272	250
	91.13	---	∞

Original Data from Table VIII - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	14.48	0.846	15
1.30×10^{-3} $\underline{M}$ Sb(V)	16.41	0.825	36
$\mu = 11.7$	20.42	0.783	56
11.00 $\underline{M}$ H^+	24.14	0.743	76
0.74 $\underline{M}$ $SO_4^=$	26.88	0.714	96
3.13 $\underline{M}$ HSO_4^-	27.80	0.704	111
0.20 $\underline{M}$ Cl^-	30.68	0.673	132
6.19 $\underline{M}$ ClO_4^-	32.84	0.650	150
$t_{\frac{1}{2}}$ = 367 hrs.	34.69	0.631	171
	36.71	0.609	196
	93.91	---	∞

ORIGINAL DATA FROM TABLE IX
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	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	24.44	0.725	1.5
1.30×10^{-3} $\underline{M}$ Sb(V)	33.15	0.627	3
$\mu = 10.5$	39.44	0.556	4.5
8.00 $\underline{M}$ H^+	45.96	0.483	6
0.74 $\underline{M}$ $SO_4^=$	52.80	0.406	7.5
1.86 $\underline{M}$ HSO_4^-	56.30	0.367	9
6.00 $\underline{M}$ Cl^-	58.23	0.345	10.5
0.42 $\underline{M}$ ClO_4^-	88.92	---	∞
1.76 $\underline{M}$ Li^+			
$t_{\frac{1}{2}}$ = 8.06 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	21.82	0.750	1.5
1.30×10^{-3} $\underline{M}$ Sb(V)	31.05	0.645	3
$\mu = 10.5$	39.31	0.550	4.5
8.50 $\underline{M}$ H^+	44.53	0.490	6
0.74 $\underline{M}$ $SO_4^=$	48.98	0.439	7.5
1.86 $\underline{M}$ HSO_4^-	53.94	0.383	9
6.00 $\underline{M}$ Cl^-	59.21	0.322	10.5
0.30 $\underline{M}$ ClO_4^-	87.37	---	∞
1.26 $\underline{M}$ Li^+			
$t_{\frac{1}{2}}$ = 7.66 hrs.			

Original Data from Table IX - cont.

	c/s	(1-F)	t(hrs.)
$1.31 \times 10^{-3}\ \underline{M}$ Sb(III)	18.53	0.793	1
$1.30 \times 10^{-3}\ \underline{M}$ Sb(V)	25.48	0.715	2
$\mu = 10.5$	33.25	0.628	3
$9.75\ \underline{M}\ H^+$	38.21	0.572	4
$6.00\ \underline{M}\ Cl^-$	42.05	0.529	5
$0.74\ \underline{M}\ SO_4^=$	47.78	0.465	6.5
$2.27\ \underline{M}\ HSO_4^-$	52.52	0.412	8
$t_{\frac{1}{2}} = 7.62$ hrs.	57.54	0.356	9.5
	63.00	0.295	11
	65.20	0.270	13
	89.35	---	∞
$1.31 \times 10^{-3}\ \underline{M}$ Sb(III)	22.18	0.758	1.5
$1.30 \times 10^{-3}\ \underline{M}$ Sb(V)	30.51	0.667	3
$\mu = 11.0$	36.64	0.600	4.5
$10.25\ \underline{M}\ H^+$	43.12	0.529	6
$0.74\ \underline{M}\ SO_4^=$	47.78	0.478	7.5
$2.09\ \underline{M}\ HSO_4^-$	52.95	0.422	9
$6.00\ \underline{M}\ Cl^-$	57.15	0.376	10.5
$0.26\ \underline{M}\ ClO_4^-$	91.54	---	∞
$t_{\frac{1}{2}} = 8.96$ hrs.			
$1.31 \times 10^{-3}\ \underline{M}$ Sb(III)	20.53	0.773	1.5
$1.30 \times 10^{-3}\ \underline{M}$ Sb(V)	28.30	0.688	3
$\mu = 11.7$	34.17	0.623	4.5
$11.00\ \underline{M}\ H^+$	39.89	0.560	6
$0.74\ \underline{M}\ SO_4^=$	46.89	0.483	7.5
$3.13\ \underline{M}\ HSO_4^-$	50.62	0.441	9
$6.00\ \underline{M}\ Cl^-$	53.14	0.414	10.5
$0.39\ \underline{M}\ ClO_4^-$	56.02	0.382	12
$t_{\frac{1}{2}} = 10.1$ hrs.	90.63	---	∞

ORIGINAL DATA FROM TABLE X
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	c/s	(1-F)	t(hrs.)
$1.31 \times 10^{-3}\ \underline{M}$ Sb(III)	3.84	0.886	10
$1.29 \times 10^{-3}\ \underline{M}$ Sb(V)	5.79	0.827	25
$\mu = 10.5$	8.18	0.756	45
$9.75\ \underline{M}\ H^+$	10.98	0.665	71
$0.74\ \underline{M}\ SO_4^=$	14.67	0.563	97
$2.27\ \underline{M}\ HSO_4^-$	18.09	0.461	147
$5.80\ \underline{M}\ ClO_4^-$	22.51	0.329	196
$0.20\ \underline{M}\ Cl^-$	27.03	0.194	290
$t_{\frac{1}{2}} = 123$ hrs.	33.54	---	∞

Original Data from Table X - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} $\underline{M}$ Sb(III)	7.77	0.778	29
1.29×10^{-3} $\underline{M}$ Sb(V)	13.41	0.617	60
$\mu = 10.5$	18.36	0.475	100
9.75 $\underline{M}$ H^+	21.35	0.389	145
0.74 $\underline{M}$ $SO_4^=$	27.21	0.222	220
2.27 $\underline{M}$ HSO_4^-	28.47	0.186	268
5.80 $\underline{M}$ ClO_4^-	34.97	---	∞
0.20 $\underline{M}$ Cl^-			
$t_{\frac{1}{2}}$ = 115 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	6.71	0.811	20
1.29×10^{-3} $\underline{M}$ Sb(V)	12.51	0.647	50
$\mu = 10.5$	19.60	0.447	100
9.75 $\underline{M}$ H^+	22.13	0.375	140
5.80 $\underline{M}$ ClO_4^-	24.86	0.298	190
0.20 $\underline{M}$ Cl^-	27.58	0.222	240
0.74 $\underline{M}$ $SO_4^=$	30.48	0.140	296
2.27 $\underline{M}$ HSO_4^-	35.43	---	∞
$t_{\frac{1}{2}}$ = 118 hrs.			
1.31×10^{-3} $\underline{M}$ Sb(III)	16.69	0.826	13
1.30×10^{-3} $\underline{M}$ Sb(V)	23.00	0.760	25
$\mu = 10.5$	27.78	0.710	40
9.75 $\underline{M}$ H^+	33.76	0.648	55
0.74 $\underline{M}$ $SO_4^=$	39.08	0.593	73
2.27 $\underline{M}$ HSO_4^-	44.91	0.532	87
0.20 $\underline{M}$ Cl^-	48.31	0.496	100
5.80 $\underline{M}$ ClO_4^-	51.02	0.468	120
$t_{\frac{1}{2}}$ = 121 hrs.	56.91	0.407	135
	59.54	0.379	155
	65.24	0.320	173
	72.04	0.249	220
	95.91	---	∞
1.31×10^{-3} $\underline{M}$ Sb(III)	17.45	0.791	20
1.30×10^{-3} $\underline{M}$ Sb(V)	28.93	0.653	45
$\mu = 10.7$	37.22	0.554	75
9.75 $\underline{M}$ H^+	44.63	0.465	95
0.74 $\underline{M}$ $SO_4^=$	47.97	0.425	115
2.30 $\underline{M}$ HSO_4^-	51.00	0.388	140
0.20 $\underline{M}$ Cl^-	53.08	0.363	152
5.97 $\underline{M}$ ClO_4^-	55.40	0.336	170
0.20 $\underline{M}$ Li^+	60.52	0.274	195
$t_{\frac{1}{2}}$ = 115 hrs.	63.44	0.239	215
	69.47	0.167	265
	83.38	---	∞

Original Data from Table X - cont.

	c/s	(1-F)	t(hrs.)
1.31 x 10^{-3} $\underline{M}$ Sb(III)	16.71	0.797	20
1.30 x 10^{-3} $\underline{M}$ Sb(V)	24.71	0.699	45
μ = 11.0	35.56	0.567	75
9.75 $\underline{M}$ H^+	39.43	0.520	95
2.39 $\underline{M}$ HSO_4^-	45.46	0.447	115
0.20 $\underline{M}$ Cl^-	49.80	0.394	140
0.74 $\underline{M}$ $SO_4^=$	57.59	0.299	195
6.18 $\underline{M}$ ClO_4^-	61.99	0.246	215
0.50 $\underline{M}$ Li^+	68.43	0.168	265
$t_{\frac{1}{2}}$ = 112 hrs.	82.21	---	∞
1.31 x 10^{-3} $\underline{M}$ Sb(III)	4.98	0.861	12
1.29 x 10^{-3} $\underline{M}$ Sb(V)	7.22	0.798	27
μ = 10.5	9.98	0.721	45
9.75 $\underline{M}$ H^+	12.94	0.638	60
0.74 $\underline{M}$ $SO_4^=$	14.17	0.604	76
2.27 $\underline{M}$ HSO_4^-	17.16	0.520	97
5.80 $\underline{M}$ ClO_4^-	20.31	0.432	122
0.20 $\underline{M}$ Cl^-	35.76	---	∞
$t_{\frac{1}{2}}$ = 111 hrs.			
1.31 x 10^{-3} $\underline{M}$ Sb(III)	5.31	0.851	12
1.29 x 10^{-3} $\underline{M}$ Sb(V)	7.02	0.803	27
μ = 10.5	9.27	0.740	45
9.75 $\underline{M}$ H^+	12.20	0.657	60
0.74 $\underline{M}$ $SO_4^=$	13.75	0.614	76
2.27 $\underline{M}$ HSO_4^-	17.14	0.519	96
5.80 $\underline{M}$ ClO_4^-	18.94	0.468	122
0.20 $\underline{M}$ Cl^-	35.62	---	∞
$t_{\frac{1}{2}}$ = 122 hrs.			
1.31 x 10^{-3} $\underline{M}$ Sb(III)	15.49	0.827	10
1.30 x 10^{-3} $\underline{M}$ Sb(V)	17.28	0.807	21
μ = 10.5	22.91	0.745	39
9.75 $\underline{M}$ H^+	29.05	0.676	50
0.74 $\underline{M}$ $SO_4^=$	33.90	0.622	60
2.27 $\underline{M}$ HSO_4^-	36.45	0.594	69
5.80 $\underline{M}$ ClO_4^-	39.19	0.563	80
0.20 $\underline{M}$ Cl^-	45.39	0.494	96
$t_{\frac{1}{2}}$ = 121 hrs.	47.01	0.476	108
	48.02	0.465	122
	89.73	---	∞

Original Data from Table X - cont.

	c/s	(1-F)	t(hrs.)
1.31×10^{-3} M Sb(III)	15.25	0.835	10
1.30×10^{-3} M Sb(V)	18.88	0.795	21
$\mu = 10.5$	21.27	0.769	30
9.75 M H^+	24.42	0.735	39
0.74 M $SO_4^{=}$	27.97	0.697	50
2.27 M HSO_4^-	33.46	0.637	60
5.80 M ClO_4^-	35.69	0.613	69
0.20 M Cl^-	36.70	0.602	80
$t_{\frac{1}{2}}$ = 123 hrs.	43.37	0.530	95
	45.31	0.509	107
	52.21	0.434	122
	92.24	---	∞
1.31×10^{-3} M Sb(III)	15.84	0.843	10
1.30×10^{-3} M Sb(V)	22.34	0.779	20
$\mu = 10.5$	27.21	0.731	29
9.75 M H^+	28.58	0.717	37
0.20 M Cl^-	33.42	0.669	47
0.74 M $SO_4^{=}$	39.11	0.613	60
2.27 M HSO_4^-	43.71	0.567	72
5.80 M ClO_4^-	45.80	0.546	83
$t_{\frac{1}{2}}$ = 122 hrs.	48.24	0.522	95
	54.14	0.464	108
	55.61	0.449	120
	61.31	0.391	142
	100.99	---	∞