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The Dilute Solution Chemistry of Antimony

Kent H. Jones

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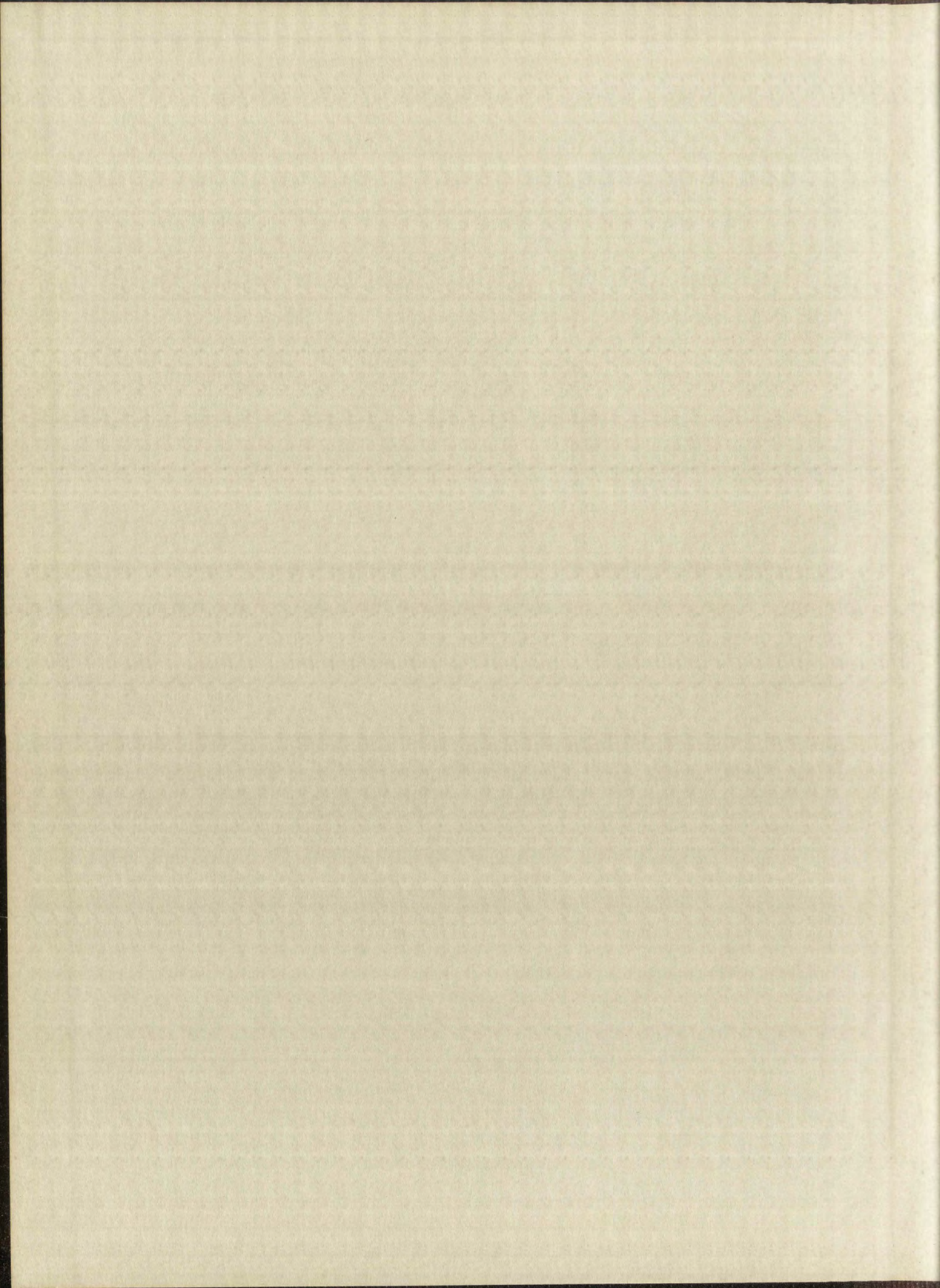


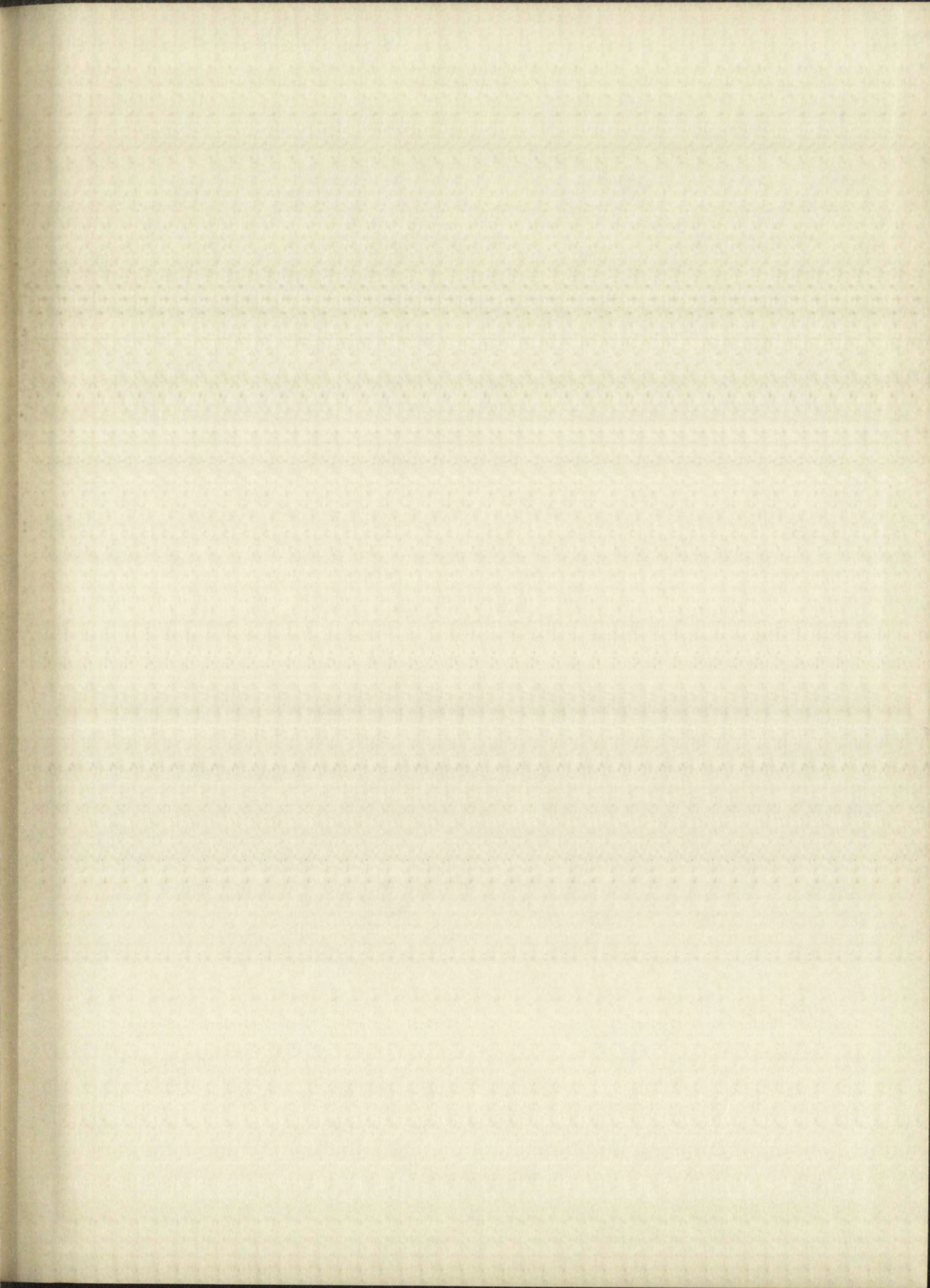
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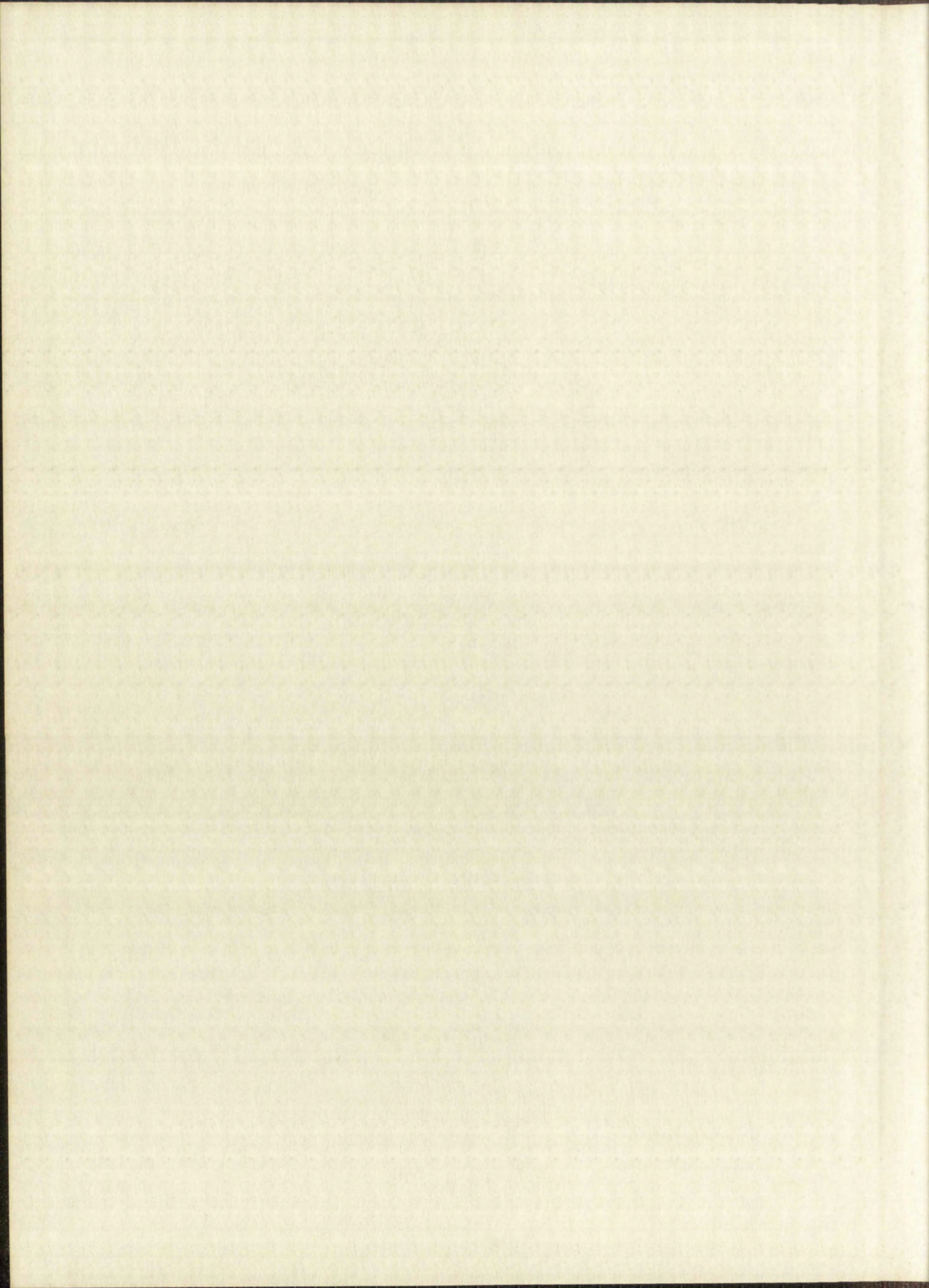
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THE DILUTE SOLUTION CHEMISTRY OF ANTIMONY

by
Kent H. Jones



A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Chemistry

The University of New Mexico

1960



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I. INTRODUCTION

Investigation of the chemistry of the elements by conventional methods is generally limited to concentrations on the order of 10^{-5} M or higher. The discovery of radioactivity opened new fields in chemistry among which is the obtaining of information concerning chemical behavior of elements at very low concentrations. For many years after the initial discovery of radioactivity in 1896 by Becquerel, the study of low-concentration chemistry was limited to about ten naturally occurring radioactive elements. A renewed interest in this field was generated after 1934 when it was discovered by Curie and Joliot that radioactive elements could be artificially produced.

The use of radioactivity to study low-concentration chemistry is based upon the ability to detect very small amounts of a substance; the detection actually consists of measuring the radiation (α , β , or γ) which is emitted by the radioactive substance. The amount of material that can be detected depends largely on the half-life of the nuclide. For example, the amounts of three radioactive nuclides undergoing 10,000 d/m, an easily measurable rate, are listed below:

1622-year	Ra ²²⁶	2×10^{-11} gram-atom
2.0-year	Sb ¹²⁵	2.5×10^{-14} gram-atom
10.6-hour	Pb ²¹²	1.5×10^{-17} gram-atom.

Thus it is seen that the chemical behavior of substances in

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Half-life	Activity	Amount
10.6-hour	$2.1 \times 10^{12} \text{ d}^{-1}$	$1.2 \times 10^{-12} \text{ gram-atom}$
5.0-year	$2.1 \times 10^7 \text{ d}^{-1}$	$2.2 \times 10^{-16} \text{ gram-atom}$
1669-year	2.1 d^{-1}	$2 \times 10^{-12} \text{ gram-atom}$

Thus it is seen that the chemical behavior of substances in

extremely low concentrations can be studied. In experiments involving carrier-free tracers, measurements are in terms of the fraction of the radioactive nuclide that is affected by the process under investigation rather than in terms of absolute amounts. The absolute amount involved may be the same at high concentrations as at low concentrations but the fraction involved may be quite different. For instance, trace impurities in a solution may change the oxidation state of an amount of a substance in high concentrations that would not be possible to detect, whereas the same amount may represent essentially all of the substance in low concentrations.

Preparations of radioactive nuclides which contain no added or detectable isotopic carrier are referred to as carrier-free. An excellent summary of the type of work done in the past with carrier-free tracers is contained in the book edited by Wahl and Bonner⁽²⁴⁾. Included in this summary is information about coprecipitation, deposition on preformed, non-metallic solids, radiocolloidal formation, solvent extraction, vaporization, oxidation-reduction, and diffusion and electrical migration.

Primarily, dilute solution chemistry studies are of value because of their intrinsic interest and because they add to the general fund of scientific knowledge. Fission product yield determinations are dependent upon an understanding of the peculiar chemical behavior that may be exhibited by fission products at low concentrations. Likewise

extremely low concentrations can be studied. In experiments involving carrier-free species, measurements are in terms of the fraction of the radioactive nuclei that is affected by the process under investigation rather than in terms of absolute amounts. The absolute amount involved may be the same at high concentrations as at low concentrations and the fraction involved may be quite different. For instance, trace quantities in a solution may change the oxidation state of an amount of a substance in high concentrations that would not be possible to detect, whereas the same amount may represent essentially all of the substance in low concentrations.

Preparations of radioactive materials which contain no added or detectable radioactive carrier are referred to as carrier-free. An excellent summary of the facts of work done in the past with carrier-free isotopes is contained in the book edited by Wahl and Berger. Included in this summary is information about coprecipitation, deposition on preferred, non-retentive solids, radiocolloidal formation, solvent extraction, vaporization, oxidation-reduction, and diffusion and electrical migration.

Primarily, dilute solution chemistry studies are of value because of their inherent simplicity and because they add to the general fund of scientific knowledge. A typical product yield determination is dependent upon an accurate standing of the better chemical carrier that may be exhibited by the process at low concentrations. Likewise

studies in the field of "hot-atom" chemistry rely upon an understanding of the behavior of atoms in the low concentrations encountered in this field of study. Biological systems are often strongly affected by trace quantities of substances, and a better understanding of this effect may be obtained through dilute solution chemistry studies.

Several elements exist only as short-lived nuclides and, consequently, their behavior is only known in carrier-free concentrations. Some knowledge of their behavior at ordinary concentrations is suggested from comparing the behavior of other elements at ordinary and carrier-free concentrations; often there is a marked difference in behavior at the two concentrations. For instance, I^{131} in carrier-free concentrations forms new species which are not known to be stable at ordinary concentrations⁽¹¹⁾.

The purpose of the work contained in this dissertation was to contribute some information to the limited supply of knowledge available concerning the chemistry of antimony in very low concentrations. To date the published literature on this subject includes procedures for preparing carrier-free Sb^{125} by Robinson and Kahn⁽¹⁹⁾ and $Sb^{122,124}$ by Maxwell⁽¹⁶⁾ and some absorption studies by Schweitzer and Jackson⁽²¹⁾ in which the antimony concentration was 10^{-7} M.

studies in the field of "hot-atom" chemistry rely upon an understanding of the behavior of atoms in the low concentration regions encountered in this field of study. Biological systems are often strongly affected by trace quantities of substances, and a better understanding of this effect may be obtained through these scientific chemistry studies.

Several elements exist only as short-lived nuclides and, consequently, their behavior is only known in certain trace concentrations. Some knowledge of their behavior at ordinary concentrations is suggested from comparing the behavior of other elements at ordinary and carrier-free concentrations; often there is a marked difference in behavior at the two concentrations. For instance, ^{131}I is known to be stable at ordinary concentrations (11).

The purpose of the work contained in this dissertation was to contribute some information to the limited supply of knowledge available concerning the chemistry of actinium in very low concentrations. To date the published literature on this subject includes procedures for preparing carrier-free Ac^{227} by Robinson and Kahn (12) and Ac^{227} , Ac^{228} by Maxwell (13) and some absorption studies by Schweitzer and Jackson (14).

In which the actinium concentration was 10^{-5} M.

II. RADIOACTIVITY AND CHEMICALS

Preparation of Radioactivity

The antimony radioactivities used in the determination of distribution coefficients for antimony(III) and antimony(V) between Dowex-1 ion exchange resin and hydrochloric acid solutions were Sb^{122} and Sb^{124} . These nuclides were prepared by irradiating C.P. twice-distilled antimony trichloride in a thermal neutron column of a reactor at Los Alamos Scientific Laboratory.

In preparing antimony(III) solutions consideration was given to the possibility that neutron irradiation may produce different oxidation states of antimony. Therefore, before the irradiated antimony trichloride was used in the equilibration experiments, it was subjected to oxidation and reduction treatments. The irradiated sample was dissolved in 3 N hydrochloric acid and heated. Antimony(III) was oxidized to antimony(V) by passing chlorine into the hot solution. After the chlorine was removed by boiling, the antimony(V) was reduced to antimony(III) with sulfur dioxide which was subsequently expelled by boiling. Concentrated ammonium hydroxide was next added to the solution in order to precipitate antimony oxychloride. This precipitate was washed with hot 1.5 N ammonium hydroxide until no test for chloride ion was obtained with acidified silver nitrate. The precipitate was dried at 110° and then dissolved in 12.0 N hydrochloric acid. Solutions of

II. RADIOACTIVITY AND CHEMISTRY

Preparation of Radioactivity

The primary radioisotopes used in the determination of distribution coefficients for antimony(III) and antimony(V) between Dovers-I for exchange resin and hydrochloric acid solutions were ^{125}Sb and ^{124}Sb . These radioisotopes were prepared by irradiating D.V. water-soluble antimony trioxide in a thermal neutron column at a reactor at Los Alamos Scientific Laboratory.

In preparing antimony(III) solutions consideration was given to the possibility that neutron irradiation may produce different oxidation states of antimony. Therefore, before the irradiated antimony trioxide was used in the equilibrium experiments, it was subjected to oxidation and reduction treatments. The irradiated sample was dissolved in 5 N hydrochloric acid and heated. Antimony(III) was oxidized to antimony(V) by passing chlorine into the hot solution. After the chlorine was removed by boiling, the antimony(V) was reduced to antimony(III) by passing carbon dioxide which was subsequently expelled by boiling. Concentrated ammonia hydroxide was then added to the solution in order to precipitate antimony oxychloride. This precipitate was washed with hot 1.5 N ammonia hydroxide until no test for chloride ion was obtained with acidified silver nitrate. The precipitate was dried at 110°C and then dissolved in 12.0 N hydrochloric acid. Solutions of

antimony(III) in hydrochloric acid of various concentrations were prepared from this stock solution.

Antimony(V) solutions were prepared by dissolving radioactive antimony trichloride in cold concentrated nitric acid and heating. A precipitate formed which was separated from the nitric acid by centrifugation. The precipitate was then dissolved in concentrated hydrochloric acid and residual nitric acid was consumed by boiling for eight hours. At this point the solution, which was less than 1 ml. in volume, was diluted to 50 ml. with 12.0 N hydrochloric acid. Solutions of antimony(V) in hydrochloric acid of various concentrations were prepared from this stock solution.

The radioactivity for other studies included in this work was Sb^{125} which was obtained from two sources. The chemical behavior of Sb^{125} from both of these sources was identical in all experiments performed.

(1) Stannous chloride was irradiated with neutrons at Los Alamos and Sb^{125} formed in the process was separated by an electrochemical process⁽¹⁹⁾ discussed in more detail in a later section (see p.23). Stannous chloride (Stanno-chlor from Metal and Thermit Corporation) was processed for irradiation by dissolving 50 gm. of stannous chloride in 75 ml. of 6 N hydrochloric acid and stirring the solution in the presence of 10 gm. of copper wire for one hour. The purpose of the copper was to remove traces of stable antimony and thus to insure a carrier-free concentration of

antimony(III) in hydrochloric acid solution were prepared from this source. The antimony(V) solution was prepared by dissolving radioactive antimony trisulfide in concentrated hydrochloric acid and heating. A small amount of antimony(III) was added from the nitric acid by adding the antimony(III) solution. The solution was then dissolved in concentrated hydrochloric acid and the residual nitric acid was removed by boiling for 24 hours. At this point the solution was diluted to 100 ml. in volume, and diluted to 200 ml. with distilled water. Solutions of antimony(III) in hydrochloric acid of various concentrations were prepared from this stock solution.

The radioactivity for each solution included in this work was 50^{125} which was checked from the source. The chemical behavior of ^{125}Sb in the above solution was identical in all experimental observations.

(1) Stannous chloride was prepared with hydrochloric acid from stannous chloride. The process was repeated by an electrochemical process. Stannous chloride was a later section (see p. 10). Stannous chloride was prepared from metal and Thorell's compound. The process was repeated by irradiation by dissolving stannous chloride in hydrochloric acid. 75 ml. of 6 N hydrochloric acid was added to the solution in the presence of 10 g. of copper. The purpose of the copper was to prevent the formation of stannous ions and thus to have a more uniform solution.

Sb^{125} in the final preparation. After removing the copper the stannous chloride was recrystallized and 5-gm. samples were sent to Los Alamos in quartz vials for irradiation. A stock solution of Sb^{125} in 2 N hydrochloric acid was prepared by employing the electrochemical separation mentioned above. The radioactive purity was determined by addition of carrier antimony and other selected ions and by following the chemical separation outlined in Figure 1. The final solution containing the separated antimony was counted and analyzed for per cent antimony recovered; 99.4% of the radioactivity was associated with antimony.

(2) One millicurie of Sb^{125} in 2 ml. of 1 N hydrochloric acid was obtained from Oak Ridge National Laboratory. This radioactivity was subjected to the same electrochemical separation procedure as used for separating Sb^{125} from tin. Again a stock solution of Sb^{125} in 2 N hydrochloric acid was prepared. A gamma ray spectrum for this radioactive nuclide was obtained by using a Model 132 Nuclear Chicago Corporation single channel analyzer with a Model DS5-1 scintillation probe. The spectrum is plotted in Figure 2 and corresponds to the gamma spectrum of the same nuclide published by N. H. Lazar⁽¹⁵⁾.

Six radioactive nuclides (Cl^{36} , Cl^{38} , Sb^{122} , Sb^{124} , Sb^{124m_1} , and Sb^{124m_2}) are formed when antimony trichloride is irradiated with thermal neutrons. However, the chlorine nuclides do not interfere with gamma radiation detection after a few days "cooling off" period.

Sp¹³⁷ in the final preparation. After removing the copper
the stannous chloride was recrystallized and 5-10% samples
were sent to Los Alamos in quartz vials for irradiation.

A stock solution of Sp¹³⁷ in 2 N hydrochloric acid was pre-
pared by applying the electrochemical separation mentioned
above. The radioactive purity was estimated by addition

of carrier activity and other selected ions and by following
the chemical separation outlined in Figure 1. The final
solution containing the separated activity was counted and

analyzed for pure activity recovery. 97% of the
radioactivity was associated with activity.
(2) One milliliter of Sp¹³⁷ in 2 ml. of 1 N hydrochloric
acid was obtained from Oak Ridge National Laboratory. This

radioactivity was subjected to the same electrochemical
separation procedure as used for separation Sp¹³⁷ from the

Again a stock solution of Sp¹³⁷ in 2 N hydrochloric acid
was prepared. A gamma ray spectrum for this radioactivity
was obtained by using a Model 132 NaI scintillation
counter single channel analyzer with a Model 135-1

scintillation probe. The spectrum is plotted in Figure 2
and corresponds to the gamma spectrum of the same nuclide
published by N. H. Larsen (12).

Six radioactive nuclides (Cl³⁶, Cl³⁸, Sp¹³², Sp¹³⁴,
Sp¹³⁶, and Sp¹³⁸) are known to form stable chlorides
in contrast with the other halogens. However, the chlorine
nuclides do not interact with gamma radiation detection

after a few days "cooling off" period.

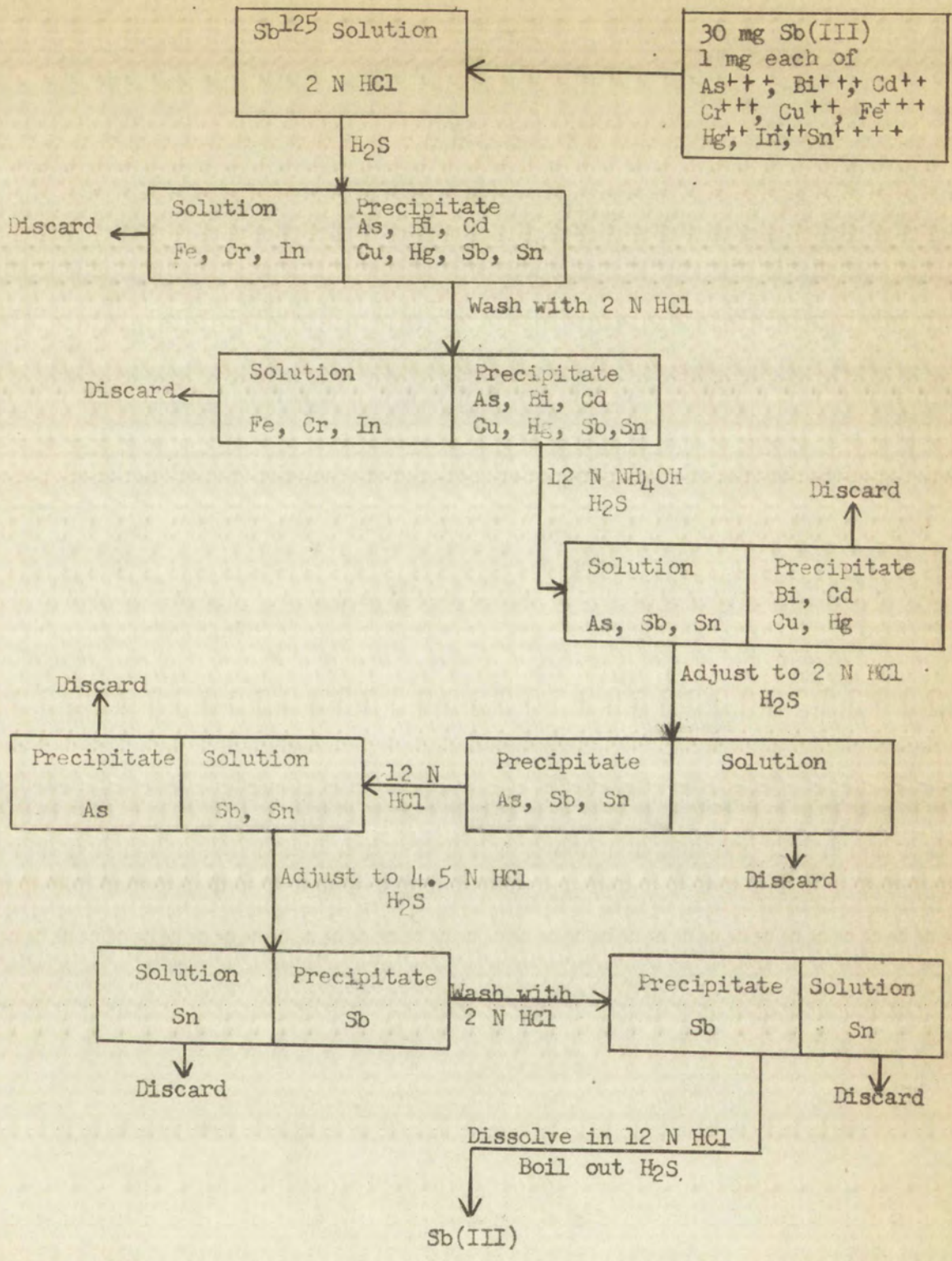
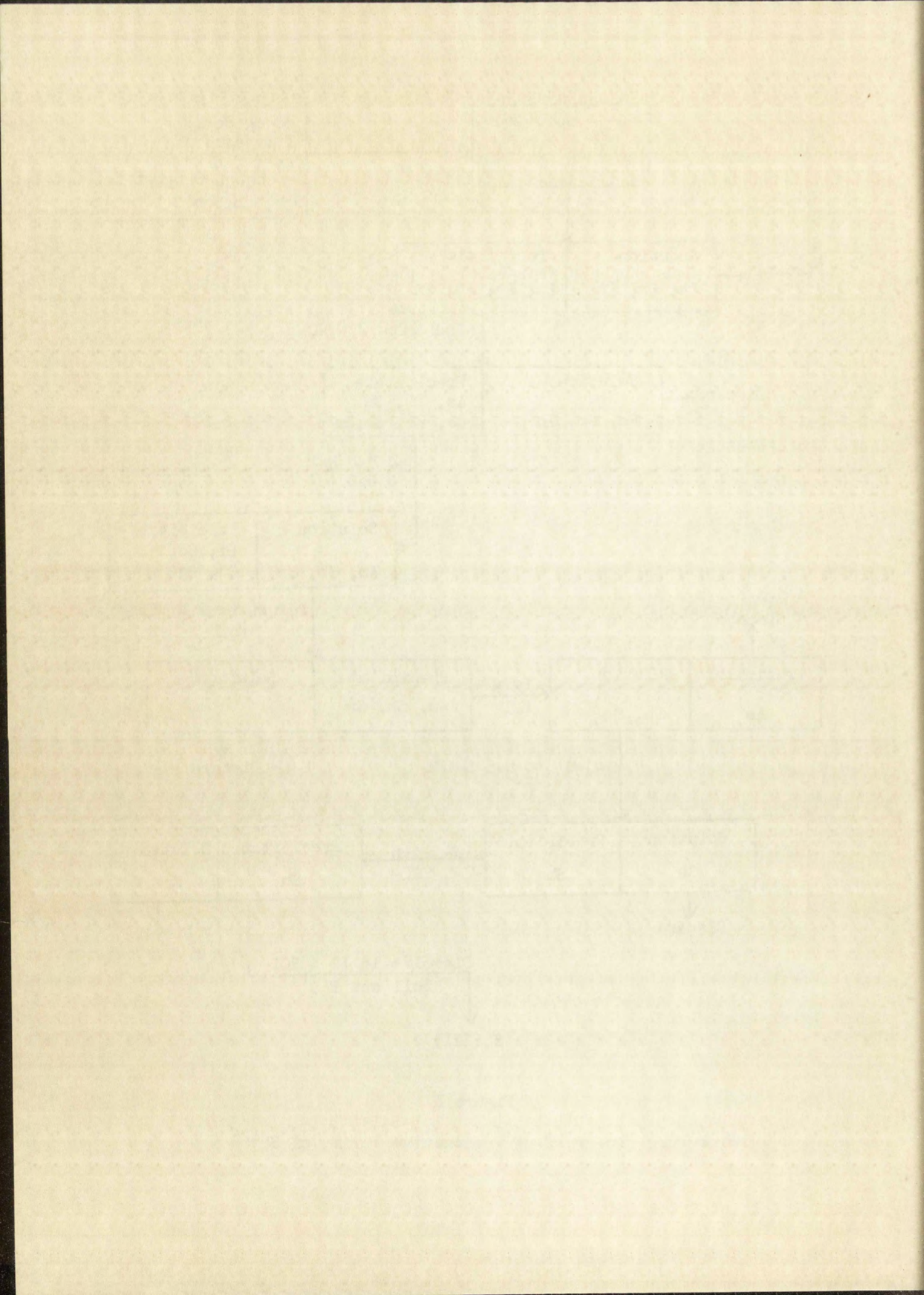
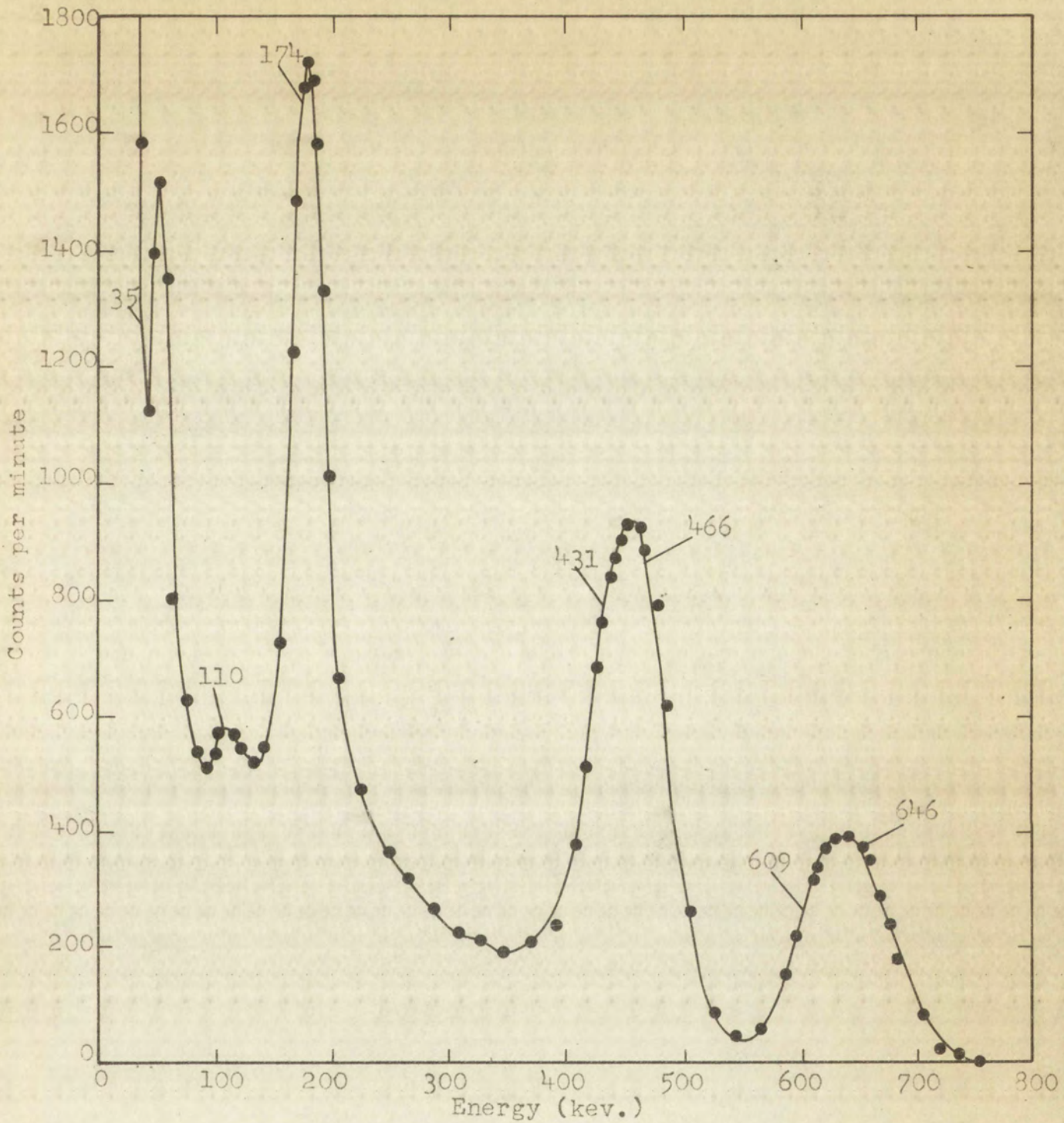


Figure 1

Procedure for Proof of Radioactive Purity of Sb¹²⁵





High voltage setting = 744 v.
 Gain = 8
 Window = 1 v.
 Counting time per point = 1 minute

Figure 2

Gamma Ray Spectrum for Sb^{125}

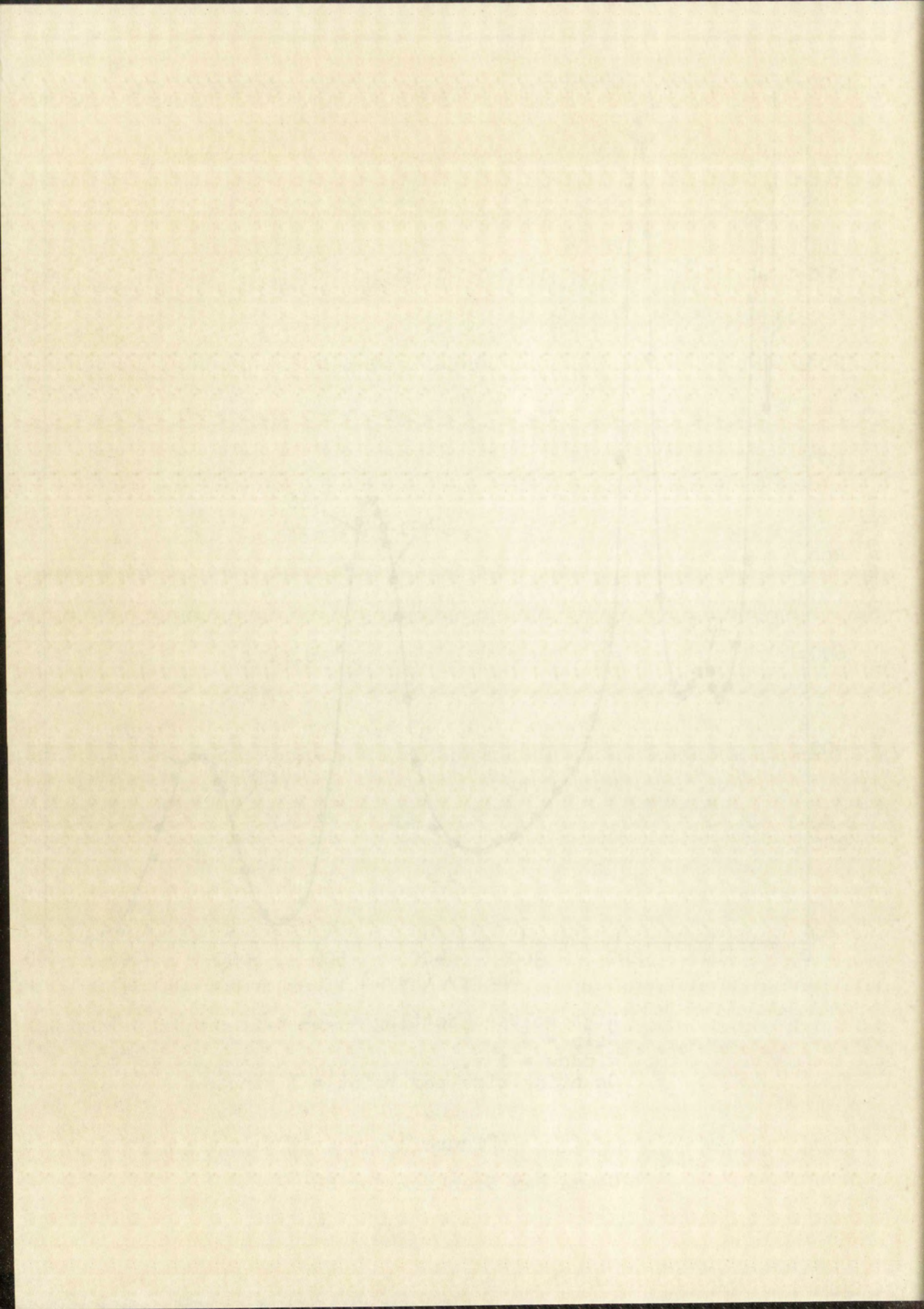


Table 1 lists the tin nuclides formed when tin is irradiated in a thermal neutron flux. Sb^{125} is produced by the beta decay of Sn^{125} which is formed through radiative capture of Sn^{124} . The decay scheme of Sb^{125} is given in Figure 3. In addition to Sb^{125} formed through neutron irradiation of tin, two stable antimony nuclides are also formed. It can be calculated from the data in Table 1 that the ratio of radioactive antimony atoms to total antimony atoms will not exceed 0.2 if a few days "cooling off" period is allowed before separation of Sb^{125} from the irradiated tin. Thus an upper limit is set on the specific radioactivity of Sb^{125} .

TABLE 1

Activities Resulting from an Assumed
Thermal Neutron Irradiation of Tin^a

<u>Nuclide</u>	<u>Atoms produced</u>	<u>Half-life</u>	<u>Mode of decay</u>
Sn^{113}	2.25×10^9	112d	EC(to $\text{In}^{113\text{m}}$)
$\text{Sn}^{117\text{m}}$	1.55×10^8	14.0d	IT(to stable Sn^{117})
$\text{Sn}^{119\text{m}}$	4.35×10^8	250d	IT(to stable Sn^{119})
Sn^{121}	8.40×10^9	27.5h	beta(to stable Sb^{121})
Sn^{123}	1.38×10^9	39.5m	beta & gamma (to stable Sb^{123})
Sn^{123}	8.60×10^6	136d	beta(to stable Sb^{123})
Sn^{125}	2.10×10^9	9.5m	beta & gamma(to Sb^{125})
Sn^{125}	4.20×10^7	9.4d	beta & gamma(to Sb^{125})

a. Weight of tin = 1 gram; neutron flux = 10^{10} neutrons/
 cm^2/sec ; irradiation time = 1 hour

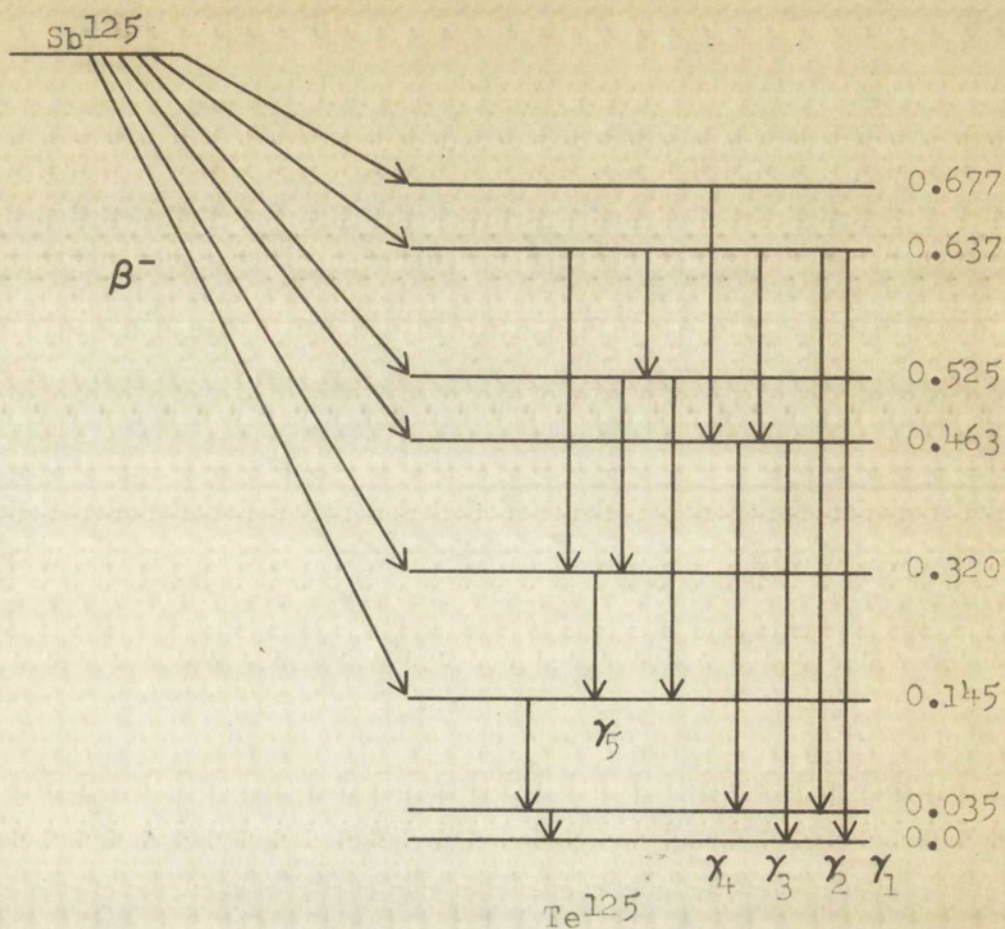
Table 1. Data for the various samples used in this study.

The samples were irradiated in a thermal neutron flux of 10^{15} neutrons/cm² by the hot beam of the TRIGA reactor at the University of Wisconsin-Madison. The irradiation dose was approximately 10^{20} neutrons/cm². In addition to the thermal neutron irradiation, the samples were also irradiated with a ⁶⁰Co source. The dose rate from the ⁶⁰Co source was approximately 1000 rad/hr. The total dose from both sources was approximately 10^6 rad. The samples were then analyzed by the method of Kohn and Fink (1962). The results are given in Table 1. The error in the determination of the cross-section is approximately 5%.

Table 2. Comparison of the results of this study with those of Kohn and Fink (1962).

Sample	Present Study	Kohn and Fink (1962)
²⁰³ Pb	0.28×10^{-24}	0.28×10^{-24}
²⁰⁵ Pb	1.87×10^{-24}	1.87×10^{-24}
²⁰⁷ Pb	4.32×10^{-24}	4.32×10^{-24}
²⁰⁹ Pb	8.40×10^{-24}	8.40×10^{-24}
²¹¹ Pb	1.33×10^{-24}	1.33×10^{-24}
²¹³ Pb	3.60×10^{-24}	3.60×10^{-24}
²¹⁵ Pb	2.19×10^{-24}	2.19×10^{-24}
²¹⁷ Pb	0.20×10^{-24}	0.20×10^{-24}

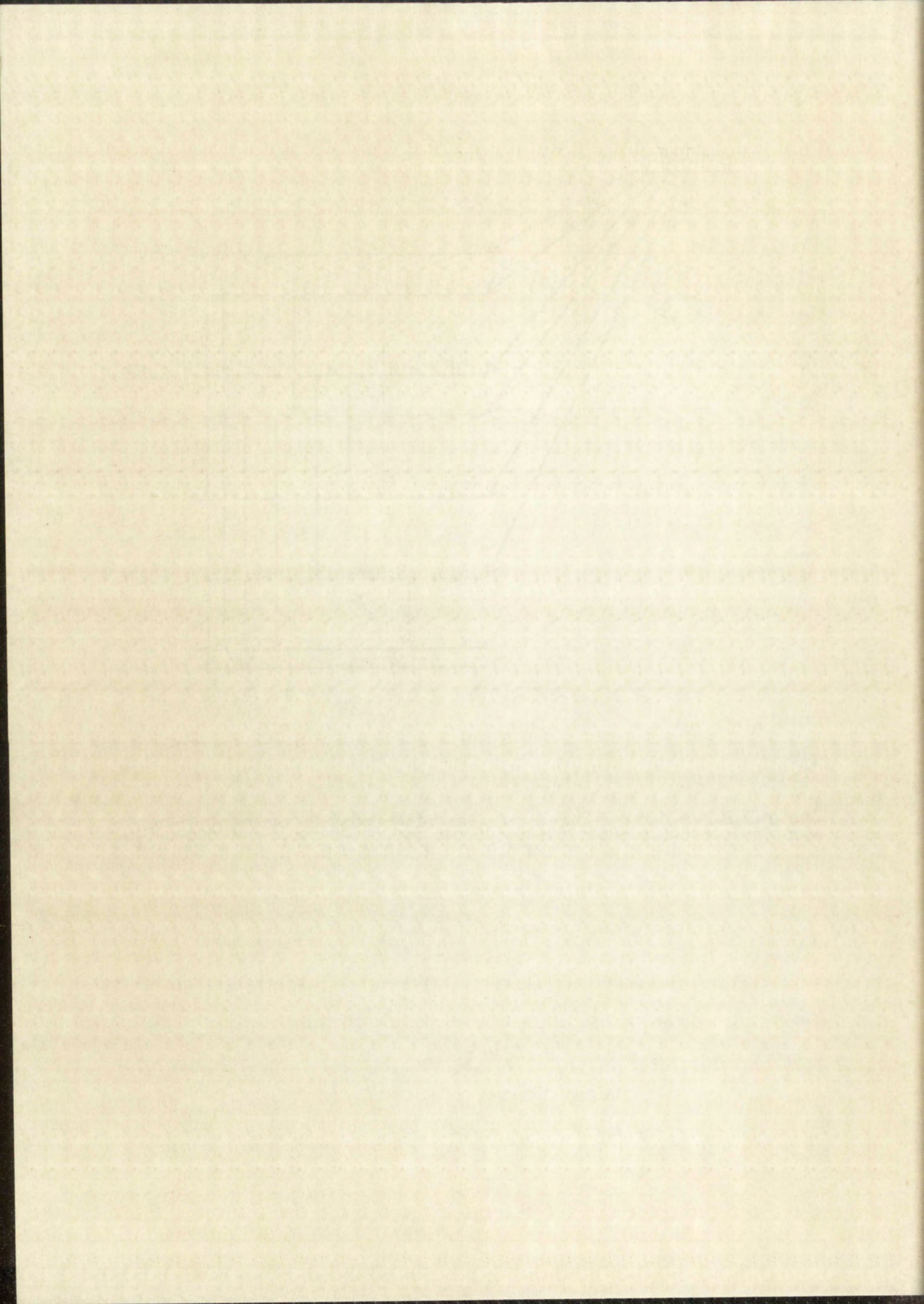
The error in the determination of the cross-section is approximately 5%.



*Level energies are in Mev.

The relative intensities of the five most prominent gamma radiations are $\gamma_1: 0.23, \gamma_2: 0.39, \gamma_3: 0.31, \gamma_4: 1.0, \gamma_5: 0.19$.

Figure 3
Decay Scheme of Sb^{125} (15)



Detection of Radioactivity

The energetic gamma radiation associated with the decay of the antimony nuclides was detected by means of a thallium-activated sodium iodide crystal in conjunction with an RCA 5819 photomultiplier tube. The electronic components which consisted of a preamplifier, discriminator, and scaler were designed, constructed, and supplied by Los Alamos Scientific Laboratory.

All counting was done with liquid samples contained in 18 x 150 mm. Pyrex tubes which were placed in a fixed and reproducible geometry in front of the sodium iodide crystal. The counting tubes were calibrated by adding to each an equal amount of radioactivity, diluting to a standard height, counting and discarding the tubes with rates not within 1% of the rate given by a tube chosen as the standard.

Inherent in all solutions containing Sb^{125} is the 58-day daughter $\text{Te}^{125\text{m}}$, and thus there is the possibility of detecting the two weak gammas associated with its decay. To a two-month old solution of Sb^{125} in 3 N hydrochloric acid which registered 8000 c/m were added 10 mg. each of antimony(III) and tellurium(IV). This solution sat overnight and the next day was heated with the addition of liquid bromine. After expelling the bromine by boiling, sulfur dioxide was passed into the hot solution. The precipitated tellurium metal was centrifuged, washed with water, and finally dissolved in dilute aqua regia and counted. It registered 10 c/m. However, in order to be certain that

The majority of the specimens were found in a
mass of the same material, which was
shattered into small pieces, and was
with an HCA 1919 specimen, which was
exposed to the air for a few days,
and under these conditions, the material
was found to be very soft and
plastic. All specimens were found in a
mass of the same material, which was
shattered into small pieces, and was
with an HCA 1919 specimen, which was
exposed to the air for a few days,
and under these conditions, the material
was found to be very soft and
plastic. The majority of the specimens
each an equal amount of the material,
height, counting and other data, which
within 15 of the specimens, which were
found in all specimens, which were
day before the specimens, which were
deposited in the same material, which
to a two-month period, which were
solid which contained the same material,
antimony (III) and other elements,
right and the same material, which were
found. After the specimens, which were
oxide was found in the same material,
which was found in the same material,
finally dissolved in the same material,
registered in the same material, which

tellurium activity was not being counted, a lead shield (thickness of 1 gm/cm^2) was placed between the sample and the sodium iodide crystal. This thickness of lead was calculated⁽⁷⁾ to adsorb at least 99% of any gamma radiations of energies as high as 0.110 Mev.

Reagents and Glassware

Eastman Kodak practical grade isopropyl ether was purified according to the method by Vogel⁽²³⁾. In distilling one liter of ether the first 150 ml. of distillate was discarded, and the last 150 ml. was not distilled. During the process the reflux ratio was 4:1. The purified isopropyl ether was stored over acidified ferrous sulfate in order to remove any traces of peroxides.

Compressed gases were used from tanks as supplied. All water was redistilled from alkaline permanganate solution and stored in Pyrex containers. Other chemicals employed were of analytical reagent grade.

The glassware used for experiments with carrier-free Sb^{125} had no previous history of use with carrier antimony. All glassware was cleaned by washing with an Alconox solution followed by chromic acid-sulfuric acid cleaning solution and finally rinsing with distilled water.

Calcium activity was not being counted, a lead shield
(thickness of 1 g/cm²) was placed between the source and
the sodium iodide crystal. This thickness of lead was
calculated (?) to absorb at least 99% of any gamma radiation
of energies as high as 0.119 Mev.

Reagents and Materials

Eastman Kodak practical grade spectrograph ether was
purified according to the method by Vogel⁽²³⁾. In distil-
ling one liter of ether the lower 250 ml. of distillate was
discarded, and the last 150 ml. was not distilled. During
the process the reflux ratio was 1:1. The purified spectrograph
ether was stored over reduced pressure sulfate in order to
remove any traces of peroxide.
Compressed gases were used from tanks as supplied. All
water was redistilled from alkaline permanganate solution
and stored in Pyrex containers. Other chemicals employed
were of analytical reagent grade.
The glassware used for experiments with carrier-free
Sp¹³² had no previous history of use with carrier activity.
All glassware was cleaned by washing with an alkaline solution
followed by chromic acid-sulfuric acid cleaning solution and
finally rinsing with distilled water.

III. PREPARATION OF CARRIER-FREE SOLUTIONS OF Sb^{125}

Determination of Distribution Coefficients for Antimony(III) and Antimony(V) between Dowex-1 Resin and Hydrochloric Acid Solutions

It was desired to develop a suitable method for the preparation of carrier-free solutions of Sb^{125} . This nuclide is formed as a result of thermal neutron irradiation of tin; the problem thus developed to one of finding a way to separate carrier-free quantities of Sb^{125} from conventional concentrations of tin. The first approach to this problem concerned itself with the possible use of an ion exchange resin to effect this separation. An anion exchange resin was selected because in hydrochloric acid solutions both antimony and tin form anion complexes, and by accumulating data concerning the distribution coefficients of these complexes as a function of acid concentration it seemed that one might determine an acid concentration which would allow a suitable separation of Sb^{125} from tin. With this purpose in mind a series of experiments was performed to determine distribution coefficients between Dowex-1 anion exchange resin and hydrochloric acid solutions.

Bio-Rad Laboratories analytical grade Dowex-1 in chloride form, 100 to 200 mesh, 8% cross-linkage, was twice alternately treated with 2 N hydrochloric acid and 2 N sodium hydroxide. It was subsequently treated with 2 N hydrochloric acid and then washed with water until no test was

Determination of the... for Addition... Lower-1 Resin and... It was desired to develop... preparation of... is formed as a result... the system... rate... concentrations of... concerned itself with... resin to effect... was selected because... anion and the... data concerning... complexes as a... that one might... allow a suitable... purpose in mind... determine... exchange resin... Bio-Rad Laboratories... Total, 100 to 200... nately treated... hydroxide. It was... chloride acid...

obtained for chloride with acidified silver nitrate. The resin was dried for 14 hours in an oven at 80° and then stored over Drierite where it lost less than 0.1% weight over a two-week period.

Ten-milliliter volumes of antimony(III) or antimony(V) solutions of various hydrochloric acid concentrations were sealed with 0.100 or 0.200 gm. of dried resin in 18 mm. Pyrex tubes. The initial concentration of antimony(III) in the reaction solution was 0.00197 M as determined by titration with standard bromate⁽¹⁷⁾, and the initial concentration of antimony(V) in the reaction solution was 0.00218 as determined by the procedure of Willard and Diehl⁽²⁵⁾ using standard thiosulfate. Because preliminary experiments had shown that the amount of antimony adsorbed by the resin was not increased by increasing the reaction time beyond 16 hours, this length of time was selected as the standard reaction time for all subsequent experiments. The samples were mechanically agitated in a constant temperature bath at 32°. The quantity of antimony adsorbed by the resin was calculated from the loss in activity by the solution. Due to hydrolysis of antimony in low acid concentrations, distribution coefficients were not determined in concentrations below 1.4 N hydrochloric acid.

The results of these experiments are shown in Tables 2 and 3 and Figures 4 and 5. The distribution coefficient (K_d) is defined as follows:

$$K_d = \frac{\text{fraction of antimony adsorbed by resin}}{\text{fraction of antimony remaining in liquid}} \times \frac{\text{liquid volume, ml.}}{\text{resin mass, gm.}}$$

obtained low viscosity with solidified silver nitrate. The resin was dried for 24 hours in a vacuum at 30° and then stored over silica gel where it lost less than 0.1% weight over a two-week period.

Low-viscosity solutions of styrene (II) or acrylonitrile (V) solutions of various hydrochloric acid concentrations were sealed with 0.100 or 0.200 gm. of dried resin in 15 ml. Pyrex tubes. The initial concentration of styrene (II) or

the reaction solution was 0.0010 M as determined by titration with standard potassium permanganate (17) and the initial concentration of styrene (V) in the reaction solution was

0.0010 as determined by the procedure of Willard and Bright (18) using standard thioacetamide. Because preliminary experiments had shown that the amount of styrene absorbed

by the resin was not increased by increasing the reaction time beyond 16 hours, this length of time was selected as the standard reaction time for all subsequent experiments.

The samples were repeatedly extracted in a constant temperature bath at 30°. The quantity of styrene extracted by the resin was calculated from the loss in weight by the spin-

tion. Due to hydrolysis of styrene in low acid concentrations, dissociation coefficients were not determined in concentrations below 1.0 x 10⁻² hydrochloric acid.

The results of these experiments are shown in Tables 1 and 2 and Figures 1 and 2. The distribution coefficient (K_d) is defined as follows:

$$K_d = \frac{\text{fraction of styrene absorbed by resin}}{\text{fraction of styrene remaining in liquid resin medium}}$$

TABLE 2

Adsorbtion of Antimony (III) from
Hydrochloric Acid Solutions by Dowex-1 Resin^a

<u>Experiment no.</u>	<u>Normality of HCl Solution</u>	<u>Weight of Resin, (gm)</u>	<u>Distribution coefficient, (K_d)</u>	<u>Average K_d</u>
1, 2, 3 4, 5	1.4	0.100 0.200	620, 620, 663 707, 710	664
6, 7 8, 9	1.9	0.100 0.200	814, 829 790, 805	809
10, 11, 12 13, 14, 15	2.4	0.100 0.200	897, 920, 996 812, 820, 1000	907
16, 17, 18 19, 20	3.1	0.100 0.200	786, 800, 887 856, 856	837
21, 22, 23 24, 25	3.6	0.100 0.200	680, 693, 713 702, 704	698
26, 27, 28 29, 30	4.3	0.100 0.200	513, 517, 525 538, 540	527
31, 32, 33 34, 35	5.3	0.100 0.200	311, 320, 345 324, 328	326
36 37	6.5	0.100 0.200	190 191	190
38 39	7.7	0.100 0.200	116 114	115
40 41	8.9	0.100 0.200	79 82	80
42 43	10.1	0.100 0.200	62 65	64
44 45	11.3	0.100 0.200	53 53	53
46 47	12.0	0.100 0.200	49 47	48

a. Temperature = 32°, reaction time = 16 hours, volume of solution = 10.0 ml., initial antimony concentration = 0.00197 M

Advertisement of the ...

Hydrochloric acid solution of ...

Experiment no.	Temperature of solution	Volume of solution	...
1, 2, 3
4, 5
6, 7, 8
9, 10, 11, 12
13, 14, 15
16, 17, 18
19, 20
21, 22, 23
24, 25
26, 27, 28
29, 30
31, 32, 33
34, 35
36
37
38
39
40
41
42
43
44
45
46

Temperature = ... solution = 10.0 ml. ...

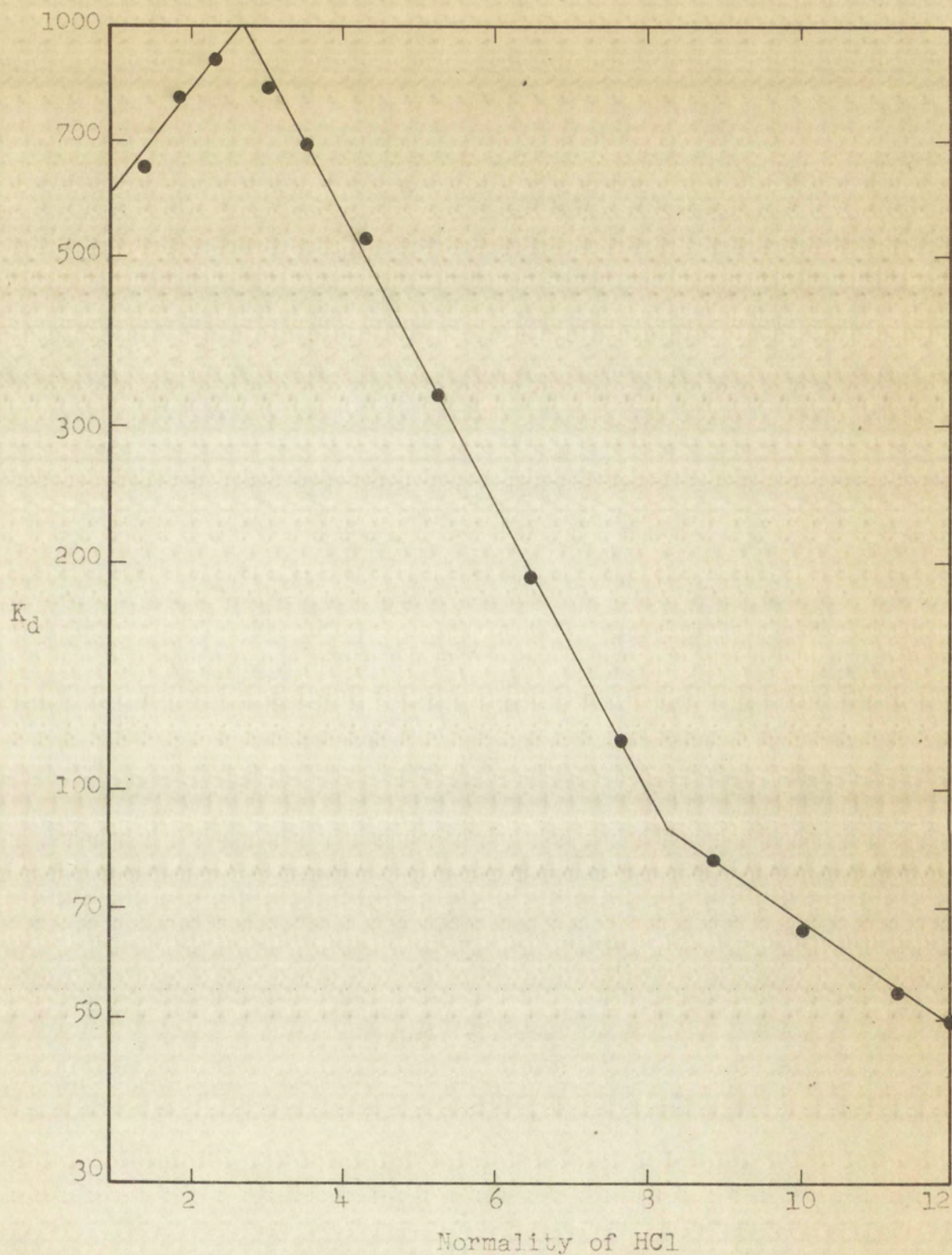


Figure 4

Adsorption of Antimony(III) from Hydrochloric Acid

Solutions by Dowex-1 Resin

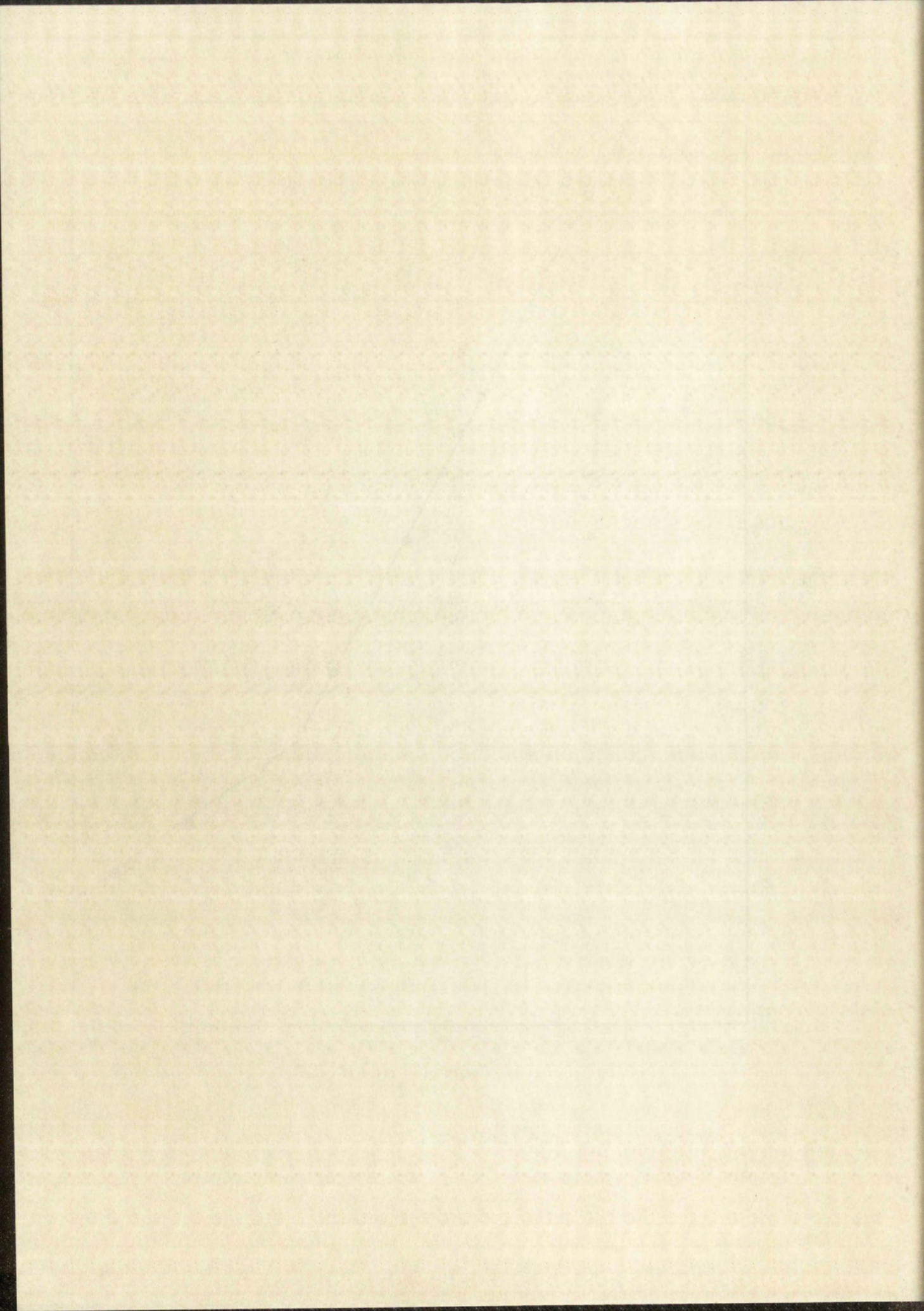


TABLE 3

Adsorption of Antimony(V) from
Hydrochloric Acid Solutions by Dowex-1 Resin^a

<u>Experiment no.</u>	<u>Normality of HCl solution</u>	<u>Weight of resin, (gm)</u>	<u>Distribution coefficient, (K_d)</u>	<u>Average K_d</u>
1	2.6	0.100	9	9
2, 3		0.200	8, 11	
4	3.9	0.100	157	180
5, 6		0.200	177, 205	
7	5.1	0.100	1810	1830
8, 9		0.200	1830, 1850	
10	6.3	0.100	5650	5800
11, 12		0.200	5400, 6350	
13, 14, 15	7.5	0.100	4670, 11200, 11400	8830
16, 17, 18		0.200	7900, 8600, 9200	
19, 20	8.7	0.100	4660, 7900	7770
21, 22, 23		0.200	5500, 9700, 11100	
24	9.9	0.100	6800	7070
25, 26		0.200	6700, 7700	
27, 28, 29	12.0	0.100	8500, 11500, 11900	7400
30, 31, 32		0.200	3700, 4150, 4900	
33			7200	

a. Temperature = 32°, reaction time = 16 hours, volume of solution = 10.0 ml., initial antimony concentration = 0.00218 M

EXPERIMENTAL

Report on the results of the experiments conducted during the year 1900.

No.	Date	Time	Temperature	Remarks
1	3/1	10:00	15.0	Normal
2	3/1	11:00	15.0	Normal
3	3/1	12:00	15.0	Normal
4	3/1	13:00	15.0	Normal
5	3/1	14:00	15.0	Normal
6	3/1	15:00	15.0	Normal
7	3/1	16:00	15.0	Normal
8	3/1	17:00	15.0	Normal
9	3/1	18:00	15.0	Normal
10	3/1	19:00	15.0	Normal
11	3/1	20:00	15.0	Normal
12	3/1	21:00	15.0	Normal
13	3/1	22:00	15.0	Normal
14	3/1	23:00	15.0	Normal
15	3/1	24:00	15.0	Normal
16	3/1	25:00	15.0	Normal
17	3/1	26:00	15.0	Normal
18	3/1	27:00	15.0	Normal
19	3/1	28:00	15.0	Normal
20	3/1	29:00	15.0	Normal
21	3/1	30:00	15.0	Normal
22	3/1	31:00	15.0	Normal
23	3/1	32:00	15.0	Normal

* Temperature = 15.0 C. in all experiments. * Solution = 10.0 C. in all experiments.

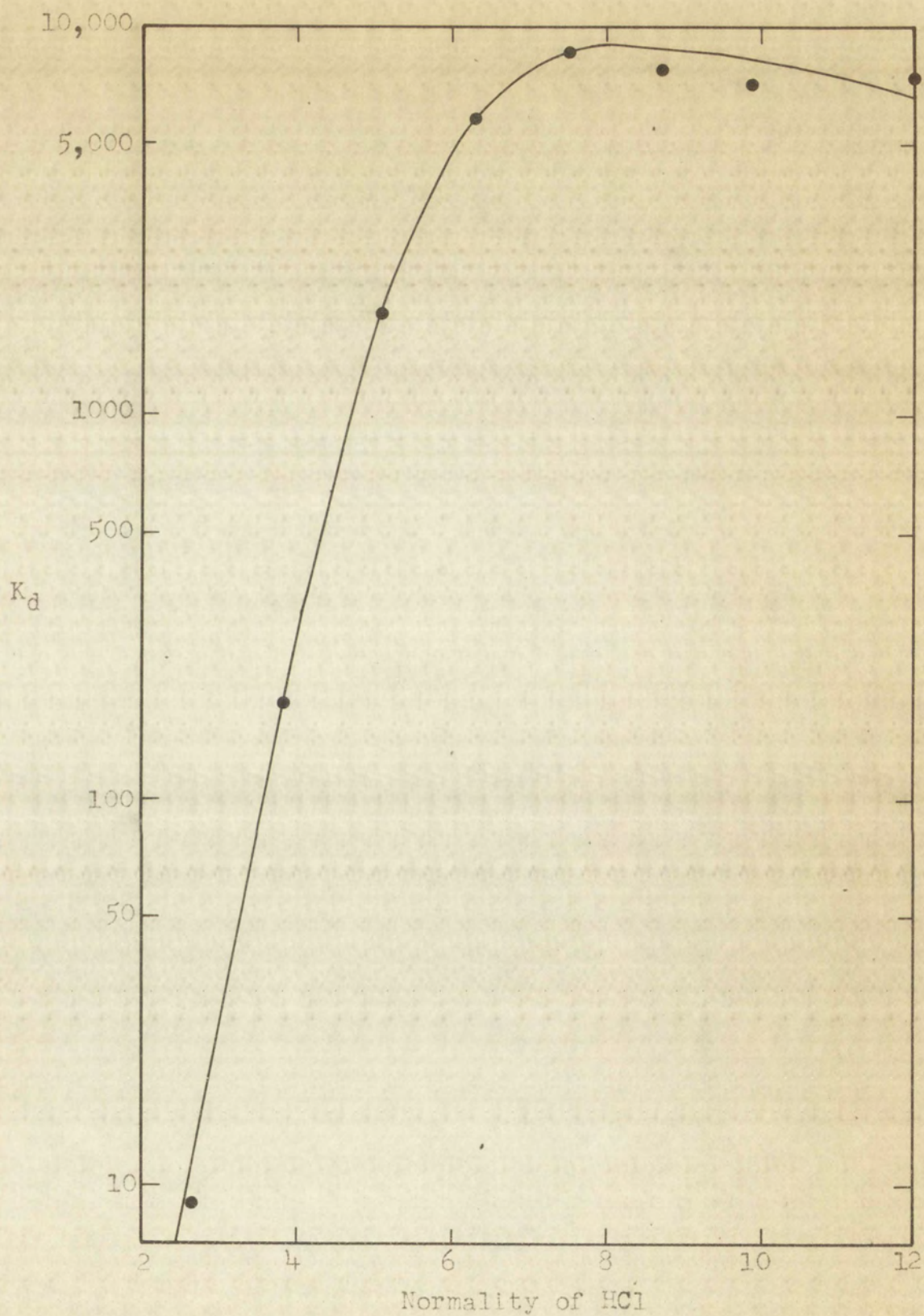
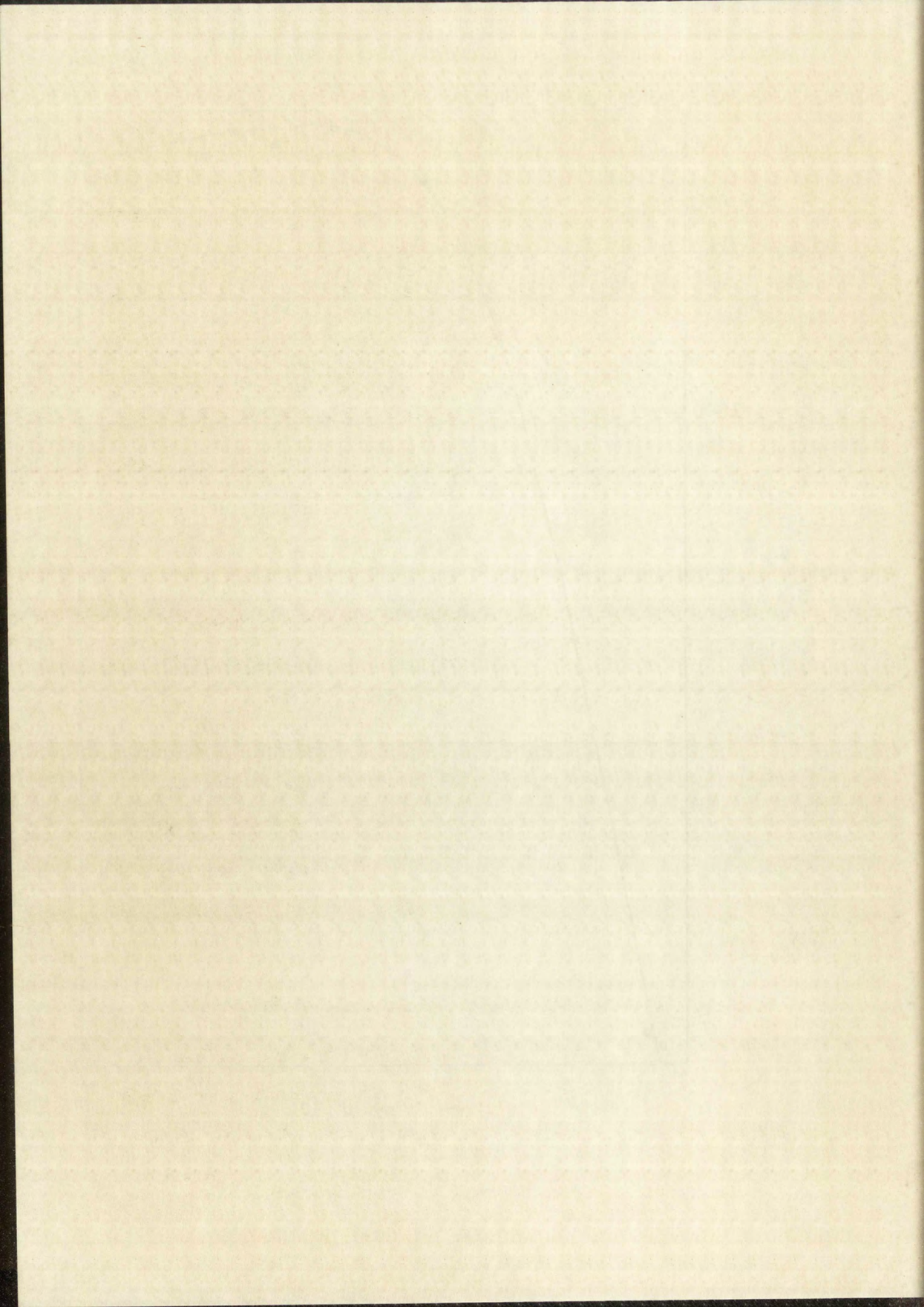


Figure 5

Adsorption of Antimony(V) from Hydrochloric
Acid Solutions by Dowex-1 Resin



An examination of the results in Tables 2 and 3 reveals that there is no dependence of the distribution coefficients on resin weight. It is also evident that greater precision is obtained in the determination of the numerically lower distribution coefficients. The variations in the values of the higher distribution coefficients are possibly due to the relatively low counting rate of the residual antimony in solution for large values of the distribution coefficient. For instance with 0.100 gm. of resin the distribution coefficient is about 5000 if 98% of the antimony is adsorbed, but if 99% is adsorbed the distribution coefficient increases to nearly 10,000.

Subsequent to the completion of these experiments similar information about antimony(III) and antimony(V) was published⁽¹⁴⁾ in graphical form. Although the published distribution coefficient curve for antimony(V) is similar in shape to the curve in Figure 5, the distribution coefficient in the former rises above 100,000 whereas in the latter it does not rise above 10,000. However, the published information for antimony(III) agrees with the results of this work.

An Attempt to Separate Carrier-free Sb^{125} from Neutron-irradiated Tin on an Anion Exchange Column

Considering the above data and the results of a study by Kraus, Moore, and Nelson⁽¹³⁾ concerning the adsorption of tin(IV) from hydrochloric acid solutions, it appeared

practicable to separate antimony from tin either in concentrated hydrochloric acid using antimony(III) or in 2 to 3 N hydrochloric acid using antimony(V). Other workers^(20, 22) had already used anion exchange resins to effect such a separation. The essential difference is that their separations involve carrier amounts of both antimony and tin in contrast to the proposed separation of carrier-free antimony. Smith and Reynolds⁽²²⁾ added oxalic acid to assist in eluting antimony. It was hoped to avoid addition of further reagents in preparation of hydrochloric acid solutions of Sb^{125} ; therefore this technique in the separation was not studied. Sasaki⁽²⁰⁾ demonstrated that antimony(V) could be preferentially eluted with 3 N hydrochloric acid from Dowex-1 resin with tin(IV) remaining on the column.

The separation of antimony(V) from tin(IV) in 2 N hydrochloric acid was studied using a Dowex-1 resin column (54 cm. x 3.3 mm. i.d.). The flow rate was 5.8 ml/min/cm². In this system the distribution coefficient for antimony(V) is 10 whereas the value for tin(IV) is 4000. Thus the preferential elution of antimony(V) in 2 N hydrochloric acid was expected.

The capacity of the resin column for tin(IV) was investigated using 112-day Sn^{113} as tracer. When 1 gm. of tin(IV) was put on the column, 61% of the tin was eluted with 81 ml. of 2 N hydrochloric acid; about 50% of the tin was present in the first 27 ml. of eluate. Similar experiments were conducted with 0.33 and 0.17 gm. of tin(IV). In both instances,

practicable to separate antimony from tin either in common
treated hydrochloric acid using antimony(III) or in 2 N
hydrochloric acid using antimony(V). Other workers (20, 21)
had already used such exchange resins to effect such a
separation. The essential difference is that their separa-

tions involve earlier amounts of both antimony and tin in
contrast to the proposed separation of carrier-free antimony.
Guth and Hevovick (22) added oxalic acid to assist in eluting
antimony. It was hoped to avoid addition of further reagents
in preparation of hydrochloric acid solutions of 10^{-12} M
therefore this technique in the separation was not adopted.
Baker (23) demonstrated that antimony(V) could be separated
fairly easily with 2 N hydrochloric acid from Dowex-1 resin
with tin(IV) remaining on the column.

The separation of antimony(V) from tin(IV) in 2 N
hydrochloric acid was studied using a Dowex-1 resin column
(5.4 cm. x 3.3 mm. i.d.). The flow rate was 2.8 ml/min.
In this system the distribution coefficient for antimony(V)
is 10 whereas the value for tin(IV) is 1000. Thus the
preferential elution of antimony(V) in 2 N hydrochloric
acid was expected.

The capacity of the resin column for tin(IV) was investi-
gated using 115-day ^{113m}Sn as tracer. When 1 μg . of tin(IV)
was put on the column, 61% of the tin was eluted with 61 ml.
of 2 N hydrochloric acid; about 30% of the tin was present
in the first 57 ml. of eluate. Similar experiments were
conducted with 0.33 and 0.17 μg . of tin(IV). In both instances,

about 4% of the activity appeared in the first 8 ml. of eluate; essentially no activity was removed with further elution. These results suggest that when no more than 0.33 gm. of tin is put on a column of the above dimensions, the tin is not readily eluted with 2 N hydrochloric acid. On the basis of the tin complex having a single charge and from the information supplied by the manufacturer of the resin, 0.75 gm. of tin was the column's capacity. The small amount of activity which initially appeared in the eluate was probably a long-lived impurity in the approximately one year old sample of Sn^{113} which was the source of tracer for these experiments.

The elution of small amounts of antimony(V) with 2 N hydrochloric acid in the presence of 0.33 gm. of inactive tin(IV) was studied using high-specific activity Sb^{124} as tracer. Two solutions, each containing 0.33 gm. of tin(IV) and a trace of high-specific activity Sb^{124} in 2 N hydrochloric acid, were oxidized with chlorine gas and boiled to remove excess chlorine. These solutions in 6 N hydrochloric acid were added to 54-cm. columns which were subsequently eluted with 2 N hydrochloric acid. It was found that 94% and 100% of the antimony activity appeared in the first 15 ml. of the eluates.

The eluted solutions were tested for the presence of tin according to the method of Charlot⁽⁵⁾. Tin(IV) was first reduced to tin(II) with iron powder and added to an iodine-iodide-starch paste mixture. Less than 0.3% of the total

about 1/2 of the activity appeared in the first 3 ml. of eluate; essentially no activity was observed in the subsequent elution. These results suggest that when no more than 0.33 gm. of tin is put on a column of the above dimensions, the tin is not readily eluted with 2 N hydrochloric acid. On the basis of the tin complex having a slight charge and from the information supplied by the measurement of the resin, 0.75 gm. of tin was the column's capacity. The small amount of activity which failed to elute is probably due to the fact that the resin was probably a low-activity resin in the amount of resin per year old sample of Sn¹¹³ which was the source of tracer for these experiments.

The elution of small amounts of activity (V) with 2 N hydrochloric acid in the presence of 0.33 gm. of inactive tin(IV) was studied using high-specific activity Sn¹¹³ as tracer. The solutions, each containing 0.55 gm. of tin(IV) and a trace of high-specific activity Sn¹¹³ in 2 N hydrochloric acid, were added with eluting acid and eluted to remove excess chlorine. These solutions in 2 N hydrochloric acid were added to 5-ml. columns which were subsequently eluted with 2 N hydrochloric acid. It was found that 90% and 100% of the activity activity appeared in the first 15 ml. of the eluate.

The eluted solutions were tested for the presence of tin according to the method of Harlow (2). Tin(IV) was first reduced to tin(II) with zinc powder and added to an iodine-iodide-starch paste mixture. Less than 0.5% of the total

tin was found in the eluate. These results suggest that small amounts of antimony(V) can be separated from large amounts of tin. However the amount of tin remaining with the antimony would still be large in comparison to carrier-free antimony.

This separation was further studied by dissolving 0.5 gm. of neutron-irradiated stannous chloride in 2 N hydrochloric acid and using the solution for experiments with the 54-cm. resin column. The dissolved stannous chloride solution was treated with chlorine and diluted to 25 ml. One 10-ml. aliquot was boiled to expell excess chlorine and analyzed for antimony activity as outlined in the flow sheet shown in Figure 1 except that after adding 30 mg. of antimony carrier, the bulk of the tin present was removed by twice precipitating the antimony with hydrogen sulfide in 4.5 N hydrochloric acid and discarding the supernatant liquid containing the tin. A second 10-ml. aliquot of the solution was boiled to remove chlorine and then put on the resin column which was subsequently washed with 2 N hydrochloric acid. Most of the eluted activity was contained in the first 10 ml. of eluate which was analyzed for antimony activity as before. According to the analysis only 7% of the antimony was eluted.

The small per cent of antimony appearing in the eluate in the preceding experiment is in contrast to the elution of essentially all the antimony when the concentration was not carrier-free. Also this behavior is not consistent with

tin was found in the eluate. These results suggest that
 small amounts of anthony(V) can be separated from large
 amounts of tin. However the extent of tin remaining with
 the anthony would still be large in comparison to earlier
 runs.

This separation was further studied by dissolving
 0.5 gm of reagent-grade tin in 10 ml of 10% HCl
 hydrochloric acid and using the solution for experiments
 with the 20-cc resin column. The dissolved tin was eluted
 with the solution was treated with chlorine and added to 20 ml
 10-ml aliquots were boiled to expel excess chlorine and
 analyzed for anthony activity as outlined in the first part
 shown in Figure 1 except that after adding 50 ml of anti-
 mony carrier, the bulk of the tin present was removed by
 eluting with the anthony with hydrogen sulfide in
 4.5 N hydrochloric acid and discarding the supernatant
 liquid containing the tin. A second 10-ml aliquot of the
 solution was boiled to remove chlorine and then put on the
 resin column which was subsequently treated with 5 N hydro-
 chloric acid. Most of the eluted activity was contained in
 the first 10 ml of eluate which was analyzed for anthony
 activity as before. According to the analysis only 5% of
 the anthony was eluted.

The small percent of anthony appearing in the eluate
 in the preceding experiment is in contrast to the eluate
 of essentially all the anthony when the concentration was
 not carrier-free. Also this behavior is not consistent with

the results of the adsorption studies which showed a low affinity of carrier antimony(V) for Dowex-1 resin in 2 N hydrochloric acid. Subsequent experiments verified that carrier-free Sb^{125} , produced as described above, is not readily removed from Dowex-1 resin by 2 N hydrochloric acid. Because of the difficulty in desorbing carrier-free Sb^{125} no further attempt was made to separate it from neutron-irradiated tin through the use of ion exchange resin.

Preparation of Carrier-free Sb^{125} from Neutron-irradiated
Tin by Electrochemical Deposition on Copper
and Subsequent Use of Dowex-1 Resin

A successful study of the preparation of carrier-free Sb^{125} from neutron-irradiated tin had been reported by Robinson and Kahn⁽¹⁹⁾ (see p. 3). Their method was investigated by employing a metallic copper spiral of #18 B & S gauge wire of approximately 5 cm^2 surface area. This spiral was rotated in 4 ml. of 6 N hydrochloric acid containing a 0.5-gm. sample of neutron-irradiated stannous chloride; the spiral served both as stirrer and reactant. After 90 minutes of stirring the spiral was removed, rinsed in 3 N hydrochloric acid, and then immersed in 6 N nitric acid for 2 minutes. This nitric acid solution contained 95% of the Sb^{125} activity according to the Robinson-Kahn study previously cited.

The antimony activity was now successfully separated

The results of the experiments...
activity of...
neuron-...
rest.

Preparation of Carotid-Tissue... in by Electrochemical... and subsequent use of (carotid) tissue

A successful study of the preparation of carotid-tissue...
Robinson and Kahn (1957) (see p. 21). Their method was...
gated by employing a special...
gauge wire of approximately 5...
was rotated in 5...
0.5-gram sample of neuron-tissue...
spiral served both as...
of exiting the spiral was...
chloric acid, and then...
minutes. This...
spiral activity...
ated.

The activity... was...
The activity... was...
The activity... was...

from tin and contained in a nitric acid solution with macro amounts of copper. The next step was to separate this activity from the copper. This separation was partially achieved by Robinson and Kahn by precipitating the copper with sodium hydroxide, but then the antimony activity was left in solution with macro amounts of sodium. A more satisfactory method using Dowex-1 resin was developed.

According to a study by Kraus and Moore⁽¹²⁾ dealing with the adsorption of copper on Dowex-1 resin from hydrochloric acid solutions, copper was only slightly adsorbed on the resin over the entire acid range. Because carrier-free Sb^{125} was not readily eluted from Dowex-1 resin by 2 N hydrochloric acid, it was hoped that the solution containing copper and Sb^{125} could be placed on a resin column, the copper completely eluted, and finally Sb^{125} eluted by some suitable eluting agent. About 50 ml. of concentrated hydrochloric acid was added to the nitric acid solution containing copper and Sb^{125} . The solution was boiled to a volume of 5 ml. and then placed on an ion-exchange column (5.5 cm x 0.5 cm. i.d.) containing Dowex-1 resin. The column was washed with 6 N hydrochloric acid until a total volume of 150 ml. of eluate was collected. Copper appeared in the first part of this eluate and gradually decreased until none was detected in the last 60 ml. The column was next washed with 25 ml. of water and finally with 2 N hydrochloric acid. The first 13 ml. of eluate from the 2 N hydrochloric acid wash contained 85% of the activity originally in the nitric

first and contained in a nitric acid solution with known
 amounts of copper. The next step was to separate this
 activity from the copper. This separation was partially
 achieved by Robinson and Kahn by precipitating the copper
 with sodium hydroxide, but then the activity was
 left in solution with known amounts of sodium. A more
 satisfactory method using Dowex-1 resin was developed.
 According to a study by Kohn and Moore (1957) dealing
 with the adsorption of copper on Dowex-1 resin from hydro-
 chloric acid solutions, copper was only slightly adsorbed
 on the resin over the entire acid range. Because copper-
 free ^{64}Cu was not readily eluted from Dowex-1 resin by
 2 N hydrochloric acid, it was hoped that the solution con-
 taining copper and ^{64}Cu could be placed on a resin column,
 the copper completely eluted, and finally ^{64}Cu eluted by
 some suitable eluting agent. About 50 ml. of concentrated
 hydrochloric acid was added to the nitric acid solution
 containing copper and ^{64}Cu . The solution was diluted to a
 volume of 5 ml. and then placed on an ion-exchange column
 (2.5 cm x 0.5 cm, i.d.) containing Dowex-1 resin. The column
 was washed with 6 N hydrochloric acid until a total volume
 of 150 ml. of eluate was collected. Copper appeared in the
 first part of this eluate and gradually decreased until none
 was detected in the last 60 ml. The column was then washed
 with 2 N water and finally with 2 N hydrochloric acid.
 The final 15 ml. of eluate from the 2 N hydrochloric acid
 wash contained 82% of the activity originally in the eluate

acid solution. A check for radioactive purity according to the flow sheet outlined in Figure 1 revealed that 99.4% of the radioactivity was associated with antimony. Thus a solution of carrier-free Sb^{125} in hydrochloric acid free from other metal ions was prepared. It is important to note that 2 N hydrochloric acid did not effectively remove the activity when applied directly following the 6 N hydrochloric acid wash but was effective only after the column had been washed with water.

Preparation of Chloride-free Solutions of Carrier-free Sb^{125}

In addition to investigating some of the behavior of Sb^{125} in hydrochloric acid it was felt desirable to prepare solutions of Sb^{125} in sulfuric and perchloric acids and to investigate the behavior of Sb^{125} in these solutions. Two methods for preparing these solutions were developed; both of which could be extended to other solvents.

The first method consisted of vaporizing the hydrochloric acid under vacuum and leaving the dry carrier-free Sb^{125} on the walls of the vessel from which it was then removed with the desired solution. A vacuum pump, vacuum desiccator, and liquid nitrogen trap were used. In order to test the effectiveness in vaporizing hydrochloric acid, 2 ml. of 2 N hydrochloric acid was placed in a 10-ml. Erlenmeyer flask in the vacuum desiccator. After applying vacuum, 1 ml. of water was added to the flask and a test made with acidified silver

acid solution. The first effect of the acid was to dissolve the solid and the resulting solution was filtered. The residue was washed with water and the filtrate was concentrated. The residue was washed with water and the filtrate was concentrated. The residue was washed with water and the filtrate was concentrated.

In addition to the above, the following experiments were conducted. The first was to determine the effect of the acid on the solid. The second was to determine the effect of the acid on the solution. The third was to determine the effect of the acid on the residue. The fourth was to determine the effect of the acid on the filtrate. The fifth was to determine the effect of the acid on the concentrate. The sixth was to determine the effect of the acid on the residue. The seventh was to determine the effect of the acid on the filtrate. The eighth was to determine the effect of the acid on the concentrate. The ninth was to determine the effect of the acid on the residue. The tenth was to determine the effect of the acid on the filtrate. The eleventh was to determine the effect of the acid on the concentrate. The twelfth was to determine the effect of the acid on the residue. The thirteenth was to determine the effect of the acid on the filtrate. The fourteenth was to determine the effect of the acid on the concentrate. The fifteenth was to determine the effect of the acid on the residue. The sixteenth was to determine the effect of the acid on the filtrate. The seventeenth was to determine the effect of the acid on the concentrate. The eighteenth was to determine the effect of the acid on the residue. The nineteenth was to determine the effect of the acid on the filtrate. The twentieth was to determine the effect of the acid on the concentrate.

nitrate. A slight test for chlorides was observed when vacuum was applied for 90 minutes; however there was no test after 3 hours under vacuum. During this process a Pyrex "ebullition tube" was placed in the solution to eliminate bumping.

The same technique was applied to 0.1-ml. samples of Sb^{125} of known activity in 2 N or 10 N hydrochloric acid. After evaporation under vacuum for 3 hours, 1 ml. of either 2 N sulfuric acid or 2 N perchloric acid was added. The samples stood for 1 minute to 2 hours and were then counted for Sb^{125} recovered based on the activity initially present. The results are in Table 4. The average per cent recovered for sulfuric acid was 84% and for perchloric acid it was 80%. This per cent recovery is apparently independent of the hydrochloric acid concentration and of the dissolving time if greater than 1 minute. Up to 10% additional activity was recovered upon the addition of hydrofluoric acid. Although only about 50% of the Sb^{125} dissolved in water, solutions prepared with water as the solvent were used when other reagents were not desired.

The second method consisted of passing dry nitrogen gas into a hydrochloric acid solution of Sb^{125} until all the hydrochloric acid was evaporated and then dissolving the residual Sb^{125} in the desired solvent. Tank nitrogen was dried by passing it through sulfuric acid. After evaporation of 0.1-ml. samples of 2 N hydrochloric acid solutions of Sb^{125} for 24 hours with nitrogen gas, several milliliters

After 2 hours under vacuum, the solution in the solution to Pyrex "distillation tube" was placed in the solution to eliminate pumping.

The same technique was applied to 0.1-ml. samples of

Sp¹³² of known activity in 2 N or 10 N hydrochloric acid.

After evaporation under vacuum for 3 hours, 1 ml. of 2 N

hydrochloric acid or 2 N perchloric acid was added. The

samples stood for 2 hours and were then counted

for Sp¹³² recovered based on the activity initially present.

The results are in Table II. The average per cent recovered

for hydrochloric acid was 84% and for perchloric acid it was

80%. This per cent recovery is apparently independent of

the hydrochloric acid concentration and of the dissolving

time if greater than 1 minute. If no 10% additional activity

was recovered upon the addition of hydrochloric acid, Al-

though only about 5% of the Sp¹³² dissolved in water, this

element prepared with water as the solvent were used when

other reagents were not desired.

The second method consisted of passing dry nitrogen gas

into a hydrochloric acid solution of Sp¹³² until all the

hydrochloric acid was evaporated and then dissolving the

residual Sp¹³² in the desired solvent. This technique was

tried by passing it through sulfuric acid. After evapora-

tion of 0.1-ml. samples of 2 N hydrochloric acid solutions

of Sp¹³² for 2 hours with nitrogen gas, several milligrams

of solvent were used to dissolve the residual activity. After a 2-hour dissolving period, 95% was recovered with 2 N sulfuric acid and 83% with 2 N perchloric acid. No chloride was detected with acidified silver nitrate.

TABLE 4

Removal of Sb^{125} from Pyrex Vessels after Vaporization of Hydrochloric Acid under Vacuum for Three Hours at Room Temperature

<u>Sample</u>	<u>HCl</u> <u>concentration,</u> <u>(N)</u>	<u>Solvent</u>	<u>Dissolving</u> <u>time, min.</u>	<u>Sb^{125}</u> <u>recovered,</u> <u>%</u>
1	2	2 N H_2SO_4	1	85
2	2	2 N H_2SO_4	60	85
3	2	2 N H_2SO_4	120	85
4	10	2 N H_2SO_4	15	96
5	10	2 N H_2SO_4	15	80
6	10	2 N H_2SO_4	15	75
7	2	2 N HClO_4	1	81
8	2	2 N HClO_4	60	81
9	2	2 N HClO_4	120	70
10	10	2 N HClO_4	15	94
11	10	2 N HClO_4	15	81
12	10	2 N HClO_4	15	74

of solvent were used to dissolve the residual activity. After a 2-hour standing period, the solution was filtered with 2 N sodium hydroxide and the filtrate was dried over calcium chloride and deposited with distilled water.

TABLE I

Removal of ^{235}U from Pyrex by means of a Hydrochloric Acid-NaOH System in Three Hours at Room Temperature

Run No.	Initial ^{235}U Concentration (%)	Solvent	Final ^{235}U Concentration (%)
1	2	2 N HCl	0.5
2	2	2 N HCl	0.5
3	2	2 N HCl	0.5
4	10	2 N HCl	0.5
5	10	2 N HCl	0.5
6	10	2 N HCl	0.5
7	2	2 N HCl	0.5
8	2	2 N HCl	0.5
9	2	2 N HCl	0.5
10	10	2 N HCl	0.5
11	10	2 N HCl	0.5
12	10	2 N HCl	0.5

IV. DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF THE OXIDATION STATE OF CARRIER-FREE Sb^{125}

In order to determine the oxidation state of an element in very low concentrations it is necessary to develop a procedure for the separation of the possible oxidation states. Solvent extraction is a convenient process for this purpose. For instance, if two oxidation states of an element are present in an aqueous solution, a suitable solvent might be found that extracts only one of the oxidation states. Such is the case with antimony in conventional concentrations. Isopropyl ether extracts antimony(V) from hydrochloric acid solutions but does not extract antimony(III). An investigation was conducted to determine whether or not the same behavior would occur with carrier-free Sb^{125} .

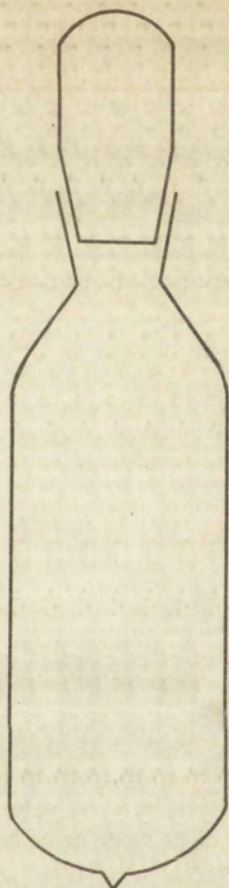
Edwards and Voigt⁽⁶⁾ reported that isopropyl ether quantitatively extracts antimony(V) from 8 N hydrochloric acid while antimony(III) is not extracted. A series of experiments was performed to determine the distribution of carrier-free Sb^{125} between isopropyl ether and 8 N hydrochloric acid. Into a glass-stoppered extraction vessel (see Figure 6) were placed 8 ml. of isopropyl ether and 8 ml. of 8 N hydrochloric acid containing the Sb^{125} . The vessel was shaken for 3 minutes and centrifuged for 5 minutes. The two phases were then separated and each counted for radioactivity.

Six samples of Sb^{125} from the 2 N hydrochloric acid stock solution mentioned in the previous section were adjusted

IV. DEVELOPMENT OF A METHOD FOR THE DETERMINATION

OF THE OXIDATION STATE OF CARBON-14

In order to determine the oxidation state of an element in very low concentrations it is necessary to develop a procedure for the separation of the possible oxidation states. Solvent extraction is a convenient process for this purpose. For instance, if two oxidation states of an element are present in an aqueous solution, a suitable solvent might be found that extracts only one of the oxidation states. Such is the case with uranium in conventional concentrations. Isopropyl ether extracts uranium(V) from hydrochloric acid solutions but does not extract uranium(III). An investigation was conducted to determine whether or not the same behavior would occur with carbon-14. Edwards and Vogt⁽⁶⁾ reported that isopropyl ether quantitatively extracts uranium(V) from 2 N hydrochloric acid while uranium(III) is not extracted. A series of experiments was performed to determine the distribution of carbon-14 between isopropyl ether and 2 N hydrochloric acid. Into a glass-stoppered extraction vessel (see Figure 6) were placed 8 ml. of isopropyl ether and 8 ml. of 2 N hydrochloric acid containing the ^{14}C . The vessel was shaken for 5 minutes and centrifuged for 5 minutes. The two phases were then separated and each counted for radioactivity. Six samples of ^{14}C from the 2 N hydrochloric acid stock solution mentioned in the previous section were analyzed

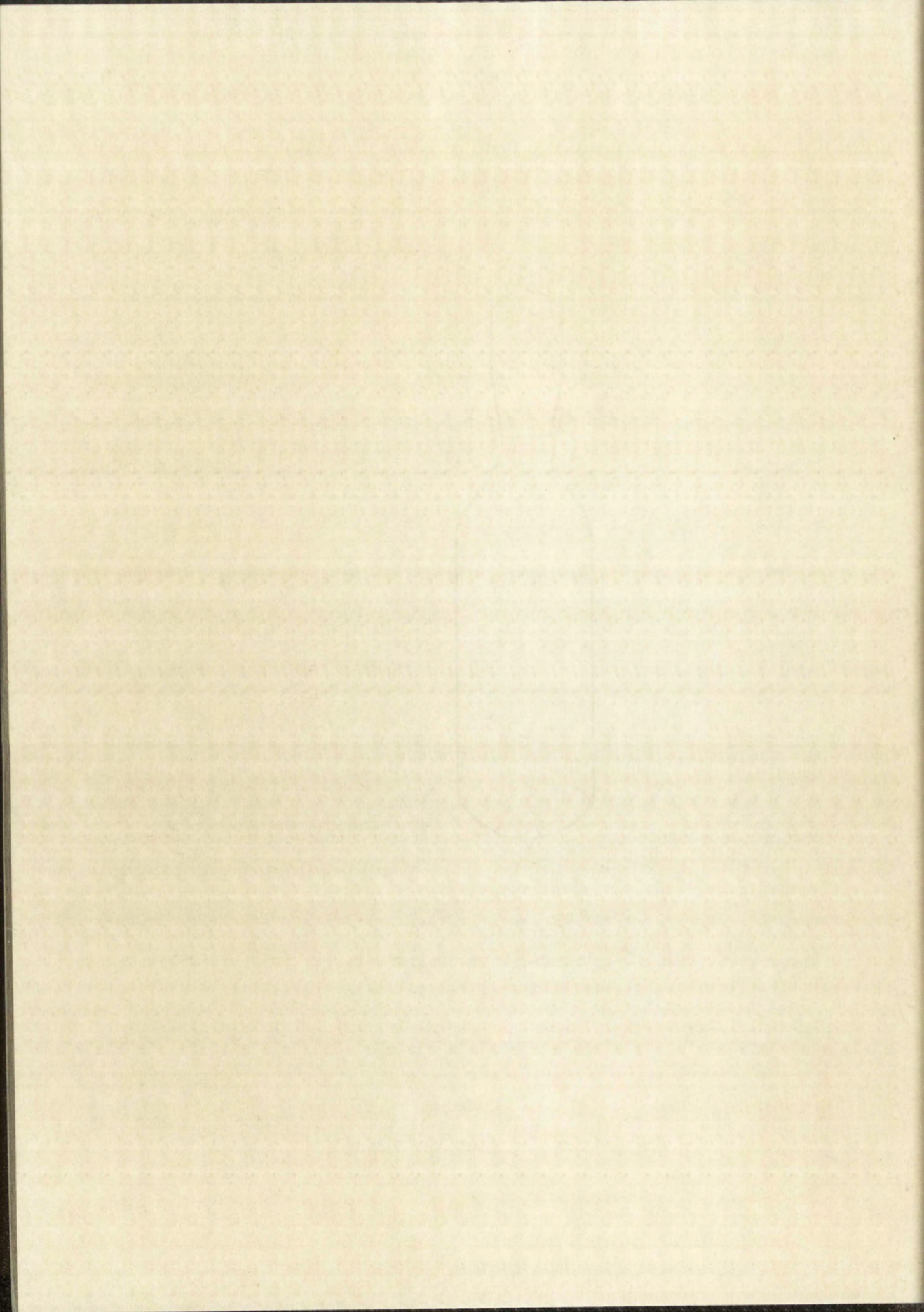


Capacity = 25 ml.

14/20 ground-glass joint

Figure 6

Pyrex Extraction Vessel



to a hydrochloric acid concentration of 8 N and extracted with isopropyl ether. The percentages of radioactivity extracted into the ether phase were 85%, 88%, 90%, 90%, 93%, and 93%. Sulfur dioxide was passed into 2 ml. of the Sb^{125} stock solution combined with 20 ml. of concentrated hydrochloric acid for 30 minutes; excess sulfur dioxide was removed by boiling. Four samples were adjusted to a hydrochloric acid concentration of 8 N and extracted with isopropyl ether. The percentages of radioactivity extracted into the ether phase were 15%, 17%, 22%, and 22%. These results indicate that in the initial stock solution the predominant oxidation state is antimony(V); after treatment with sulfur dioxide the antimony(V) is largely reduced to antimony(III). Because the radioactivity did not quantitatively collect in one of the phases in either case, the Sb^{125} was either not exclusively in one oxidation state or the distribution of carrier-free Sb^{125} between the two phases was different from that reported for conventional concentrations of antimony.

This system was further investigated by adding bromine in order to oxidize the Sb^{125} more completely. About 1.5 ml. of liquid bromine was added to 3 ml. of the Sb^{125} stock solution in 20 ml. of concentrated hydrochloric acid. The solution was heated for 30 minutes and then boiled to remove excess bromine. Two samples were adjusted to a hydrochloric acid concentration of 8 N and, unexpectedly, only 10% and 11% of the radioactivity extracted into isopropyl ether. Apparently considerable reduction of the Sb^{125} occurred in

to a hydrochloric acid solution of the substance
with hydrochloric acid. The substance
extracted into the ether. The ether
and 95% alcohol. The ether extract
stock solution was prepared by
chloroform and 95% alcohol. The
removed by washing with water. The
chloroform and 95% alcohol. The
ether. The ether extract was
ether phase was dried with
indicate that in the ether phase
oxidation state is not very different
chloride the substance is highly soluble in
Because the substance is highly soluble
one of the phases in ether and 95%
exclusively in the ether phase and
ether-phase of the substance is highly
that reported for ether and 95%
This system was further investigated by
in order to obtain the substance in
of liquid phase the ether and 95%
solution in 95% alcohol. The
solution was prepared by the
excess amount. The substance
salt concentration of 1 M. The
1% of the substance in the ether phase
apparently completely soluble in the ether phase

the process of adding bromine and boiling the solution to remove excess bromine. Because the reduction probably occurred during the boiling, 1 ml. of the Sb^{125} stock solution in 20 ml. of concentrated hydrochloric acid was vigorously boiled for 20 minutes. Two samples were extracted with isopropyl ether; 5% and 6% entered the ether phase. Hence reduction did occur during the boiling process.

The percentage of Sb^{125} extracted by isopropyl ether was increased by adding sufficient bromine to the extraction mixture to give the ether a light brown color. In four samples of the stock solution of Sb^{125} the percentages extracted were 94%, 96%, 96%, and 97%. Also 95% and 96% of the radioactivity extracted when a similar excess of bromine was added to samples of Sb^{125} which had been boiled in concentrated hydrochloric acid. In addition, a 2-ml. sample of the Sb^{125} stock solution in 20 ml. of concentrated hydrochloric acid was boiled for 2 hours with the periodic addition of concentrated hydrochloric acid to keep the volume above 10 ml. Two samples were tested with isopropyl ether; 10% and 11% extracted. Liquid bromine was added to the rest of the boiled solution. Eight samples were removed at various times from 1 minute to 72 hours and extracted with ether. The amounts extracted in all instances were between 86% and 90%.

Two samples of Sb^{125} stock solution were subjected to experiments in which portions of the samples were periodically removed and tested for extraction into isopropyl ether;

the process of adding bromine and boiling the solution to remove excess bromine. Because the reduction probably occurred during the boiling, 1 ml. of the Sp^{125} stock solution in 20 ml. of concentrated hydrochloric acid was vigorously boiled for 30 minutes. Two samples were extracted with isopropyl ether; 75 and 85 entered the ether phase. Hence reduction did occur during the boiling process. The percentage of Sp^{125} extracted by isopropyl ether was increased by adding sufficient bromine to the extraction mixture to give the ether a light brown color. In four samples of the stock solution of Sp^{125} the percentages extracted were 94%, 96%, 98%, and 97%. Also 95% and 96% of the radioactivity extracted when a similar excess of bromine was added to samples of Sp^{125} which had been boiled in concentrated hydrochloric acid. In addition, a 2-ml. sample of the Sp^{125} stock solution in 20 ml. of concentrated hydrochloric acid was boiled for 2 hours with the periodic addition of concentrated hydrochloric acid to keep the volume above 10 ml. Two samples were tested with isopropyl ether; 10% and 15% extracted. Liquid bromine was added to the rest of the boiled solution. Eight samples were removed at various times from 1 minute to 75 hours and extracted with ether. The amounts extracted in all instances were between 85% and 90%.

Two samples of Sp^{125} stock solution were subjected to experiments in which portions of the samples were periodically removed and tested for extraction into isopropyl ether;

the remainder of the sample in each instance was used for the next step in the procedure. Duplicate results, which were obtained by extracting 8 ml. of 8 N hydrochloric acid containing Sb^{125} with 8 ml. of isopropyl ether, are shown in Table 5. Although these results do not establish that the oxidation states of Sb^{125} can be suitably determined by the extraction mixture employed, they do indicate some interesting behavior of carrier-free Sb^{125} which will be discussed in a later section. For example, a greater fraction of antimony(V) was reduced in concentrated hydrochloric acid than in dilute hydrochloric acid. The reduction occurs even after the solution has been treated with bromine.

An examination of the results of all the extraction experiments reveals that in no case was 100% of the radioactivity extracted into isopropyl ether nor did 100% remain in the aqueous phase. Because the distribution of carrier-free Sb^{125} between isopropyl ether and 8 N hydrochloric acid appeared to be different from that reported for carrier concentrations of antimony, the distribution of carrier antimony(V) was briefly investigated. A 0.03 M antimony(V) solution was prepared by adding a known amount of antimony trichloride and 2 ml. of Sb^{125} stock solution to 75 ml. of 2 N hydrochloric acid, reducing with sulfur dioxide, and oxidizing with liquid bromine. The excess bromine was removed by boiling. Two samples of this carrier antimony(V) solution were adjusted to a hydrochloric acid concentration of 8 N and extracted with isopropyl ether; 83% and 89% of

the remainder of the sample in each instance was used for the next step in the procedure. The results are given in Table I. Although these results do not indicate that the oxidation states of Sp^{125} can be readily determined by the extraction mixture employed, they do indicate some interesting behavior of carrier-free Sp^{125} which will be discussed in a later section. For example, a greater fraction of antimony(V) was reduced in concentrated hydrochloric acid than in dilute hydrochloric acid. The reduction occurs even after the solution has been treated with bromine.

An examination of the results of all the extraction experiments reveals that in no case was 100% of the radioactivity extracted into hydrochloric acid nor did 100% remain in the aqueous phase. Because the distribution of carrier-free Sp^{125} between hydrochloric acid and 5 N hydrochloric acid appeared to be different from that reported for carrier concentrations of antimony, the distribution of carrier antimony(V) was briefly investigated. A 0.03 N antimony(V) solution was prepared by adding a known amount of antimony trichloride and 5 ml. of 50% stock solution to 75 ml. of 5 N hydrochloric acid, reducing with stannous chloride, and oxidizing with liquid bromine. The excess bromine was removed by boiling. Two samples of this carrier antimony(V) solution were adjusted to a hydrochloric acid concentration of 5 N and extracted with hydrochloric acid; 88% and 92% of

TABLE 5

Extraction of Sb^{125} by Isopropyl
Ether from 8 N Hydrochloric Acid

<u>Procedure</u>	<u>Per cent extracted</u>
Experiment A	
Step no. (1) 2 ml. of stock solution was boiled in 20 ml. of 12 N HCl to a volume of 12 ml.	7, 17
(2) Bromine was added and the solution remained at room temperature for 25 minutes	84, 89
(3) Nitrogen was passed into the solution for 25 minutes in order to remove excess bromine	79, 81
(4) 10 ml. of 6 N HCl was added and the solution was boiled 15 minutes to a volume of 4.5 ml.	8, 9
(5) Bromine was added and the solution remained at room temperature for 25 minutes. 20 ml. of 2 N HCl was added and the solution was boiled 15 minutes to a volume of 3.5 ml.	5, 8
Experiment B	
(1) 2 ml. of solution was boiled in 20 ml. of water for 15 minutes to a volume of 8.5 ml.	76, 76
(2) The boiling was continued to a volume of 1 ml. 6 ml. of water was added	55, 62
(3) The solution was diluted to 10 ml. of 6 N HCl and boiled 4 minutes.	53, 54
(4) 3 ml. of the remaining solution in 10 ml. of 12 N HCl was boiled for 20 minutes to a volume of 1.5 ml.	9, 10

TABLE 2

Reaction of 2,4-DNP with
Sulfur from 2-Hydroxybutanoic acid

EXPERIMENTAL

Procedure

Experiment A

- (1) 1 ml. of fresh solution was added to 20 ml. of 2% HCl solution and the volume of 2% HCl was 21 ml.
- (2) Solution was added and the volume of 2% HCl was 22 ml. for 25 minutes.
- (3) Solution was added and the volume of 2% HCl was 23 ml. for 25 minutes.
- (4) 10 ml. of 2% HCl was added and the solution was boiled for 25 minutes at a volume of 24 ml.
- (5) Solution was added and the volume of 2% HCl was 25 ml. for 25 minutes. HCl was added and the solution was boiled for 25 minutes at a volume of 26 ml.

Experiment B

- (1) 2 ml. of solution was added to 20 ml. of water. 15 minutes at a volume of 21 ml.
- (2) The boiling was continued to a volume of 1 ml. 5 ml. of water was added.
- (3) The solution was diluted to 10 ml. of 2% HCl and boiled for 25 minutes.
- (4) 2 ml. of the remaining solution in 10 ml. of 2% HCl was added for 25 minutes to a volume of 12 ml.

the radioactivity entered the ether phase. In order to check the extent of exchange between the active and inactive antimony, another extraction was conducted as before. After the phases were separated, chromous chloride was added to the aqueous phase to precipitate any remaining antimony as metal. On the basis of the weight of the precipitate, 12% of the antimony remained in the aqueous phase; this result indicated the isotopic exchange was complete. These experiments show a deviation in behavior, even with carrier antimony, from those results reported in the literature⁽⁶⁾ for antimony.

A different extraction mixture was used by Bonner⁽³⁾ for separating antimony(V) from antimony(III). The aqueous solution was 2.14 M in magnesium chloride and 6.0 N in hydrochloric acid. Bonner found that 98% of the antimony(V) went into the isopropyl ether and 98% of the antimony(III) remained in the aqueous phase. These reported results were checked by using a portion of the previous carrier antimony(V) solution and a carrier antimony(III) solution prepared by precipitating antimony with hydrogen sulfide, dissolving the precipitate in concentrated hydrochloric acid, and boiling to remove excess hydrogen sulfide. Eight milliliters of the aqueous phase was extracted with 8 ml. of isopropyl ether. Ninety-nine per cent was extracted into the ether phase in all four samples of antimony(V) tested and 1% in the two samples of antimony(III) tested.

However when this system was used with carrier-free Sb^{125}

The radioactivity showed the same pattern. In order to check the extent of the reaction, the samples were analyzed and the phases were separated, the phases were analyzed and the amount of the phases was determined. On the basis of the weight of the precipitate, the amount of the precipitate in the reaction phase, this result indicated that the reaction was complete. These experiments show a substantial increase in the amount of anti- body, from about 10% to 100% in the reaction phase. antibody.

A different experiment was used to determine the for separating antibody (V) from antibody (III). The reaction solution was 2.1% in an aqueous solution and 0.5% in hydrochloric acid. The reaction was 100% of the antibody (V) went into the precipitate and 50% of the antibody (III) remained in the aqueous phase. These results were checked by using a method of the reaction phase and antibody (III) solution and a carrier antibody (III) solution. The precipitate was separated with hydrochloric acid, the precipitate is concentrated by hydrochloric acid, the precipitate to remove excess sugar on solids. The precipitate of the aqueous phase was extracted with 2% of the reaction phase. Ninety-nine per cent was extracted into the aqueous phase. All four samples of antibody (V) tested and 50% in the two samples of antibody (III) tested. However when the reaction was used with carrier-free antibody

the results were not as consistent nor as quantitative. Five samples of the Sb^{125} stock solution were tested and the amount extracted into the ether phase ranged from 68% to 98% with an average of 84%. Five samples of Sb^{125} boiled in concentrated hydrochloric acid gave percentages extracted from 7% to 34% with an average of 19%. It is possible that the difference between the distribution of carrier antimony and carrier-free Sb^{125} is due to substances in the extraction mixture which partially oxidize or reduce the very small amounts of Sb^{125} .

Bonner's (3) work also demonstrated that the exchange between antimony(III) and antimony(V) in hydrochloric acid solutions is slow in comparison to the duration of an extraction experiment. It was hoped that this observation could be exploited by adding an extraction mixture containing both oxidation states of carrier antimony to the Sb^{125} solution under investigation. Isotopic exchange was not expected to occur between the radioactive antimony in one oxidation state and the carrier antimony in another oxidation state. An extraction mixture was used which consisted of 8 ml. of isopropyl ether, 7 ml. of a solution 6 N in hydrochloric acid and 2.14 M in magnesium chloride, and 1 ml. of a solution 6 N in hydrochloric acid and 0.05 M in both antimony(III) and antimony(V). The aqueous active solution to be tested was added to this mixture. Two samples of carrier antimony(III) were tested and in both cases 1% was extracted into isopropyl ether; 99% was

the results were as follows: ...
Five samples of ...
amount ...
982 with an ...
in comparison ...
from 75 to ...
the difference ...
and ...
amount ...
between ...
solution ...
extraction ...
could be ...
the ...
solution ...
expected ...
oxidation ...
tion ...
of 8 ml. of ...
hydrochloric ...
1 ml. of a ...
in both ...
solution ...
samples ...
cases ...

extracted in both cases when carrier antimony(V) was tested. For three months samples of the stock solution of Sb^{125} and samples of Sb^{125} boiled in hydrochloric acid were periodically tested with the extraction mixture described in the previous paragraph. Nine samples of the stock solution gave percentages extracted into the ether phase from 96% to 99% with 98% as the average; 1% to 4% was extracted in 18 samples of boiled solutions with 2.5% as the average.

The extraction mixture was used to determine the oxidation state of Sb^{125} in solutions of various compositions. In order to verify that certain amounts of hydrochloric, sulfuric, and perchloric acids would not appreciably change the distribution of antimony between the two phases, several tests were performed. In each test one drop of the stock solution of Sb^{125} in 2 N hydrochloric acid was added to a certain amount of the solution to be tested. With 2 ml. of 2 N hydrochloric acid 93% was extracted into the ether phase; with 2 ml. and 1 ml. of concentrated hydrochloric acid 96% and 99%, respectively, were extracted; and with 1 ml. of water 96% was extracted. Similarly, boiled solutions of Sb^{125} in concentrated hydrochloric acid were tested. With 1 ml. of concentrated hydrochloric acid 2% was extracted and with 1 ml. of water 1% was extracted. Also sulfuric acid and perchloric acid were tested in the extraction mixture. The distribution of Sb^{125} was not affected by 1 ml. of 12 N sulfuric acid and no effect was evident when 1 ml. of 2 N or less than $\frac{1}{2}$ ml. of 6 N perchloric

extracted with ether and dried over anhydrous calcium chloride
for three days. The residue was then distilled under reduced
pressure and the fraction boiling at 100-110°C was collected
and analyzed. The yield was 1.5 g (10%). The boiling point was
100-110°C at 10 mm Hg. The refractive index was 1.4500.
The specific gravity was 0.8500. The density at 20°C was
0.8500. The molecular weight was 100. The analysis was
calculated for C₁₀H₁₆ and found C, 85.63%; H, 14.37%.
The infrared spectrum showed a strong absorption at 1640 cm⁻¹
and a weak absorption at 3000 cm⁻¹. The ultraviolet
spectrum showed a maximum at 210 mμ. The compound was
found to be a diene and was identified as 1,3-cyclohexadiene.
The compound was prepared by the reaction of cyclohexane
with a mixture of sulfuric acid and phosphoric acid. The
reaction was carried out at 100°C for 24 hours. The
product was then distilled and the fraction boiling at
100-110°C was collected. The yield was 1.5 g (10%).
The boiling point was 100-110°C at 10 mm Hg. The
refractive index was 1.4500. The specific gravity was
0.8500. The density at 20°C was 0.8500. The molecular
weight was 100. The analysis was calculated for C₁₀H₁₆
and found C, 85.63%; H, 14.37%. The infrared spectrum
showed a strong absorption at 1640 cm⁻¹ and a weak
absorption at 3000 cm⁻¹. The ultraviolet spectrum
showed a maximum at 210 mμ. The compound was found
to be a diene and was identified as 1,3-cyclohexadiene.

acid was used. Greater amounts of perchloric acid caused the two-phase extraction mixture to separate into three phases.

In analyzing the results of the extraction experiments performed it was concluded that the Sb^{125} in the stock solution of 2 N hydrochloric acid was antimony(V) and that it was quantitatively reduced to antimony(III) by boiling in concentrated hydrochloric acid. A standard procedure was developed for determining the oxidation state of carrier-free Sb^{125} . It consisted of adding 1 ml. or less of the sample to be tested to an extraction mixture of the composition indicated on page 35, shaking the mixture for 3 minutes, centrifuging for 5 minutes, separating the phases and finally counting the amount of activity in each phase. The amount of each oxidation state was calculated on the basis of 98% of antimony(V) entering the ether phase and 98% of antimony(III) remaining in the aqueous phase.

acid was used. Greater amounts of perchloric acid caused the two-phase extraction system to separate into three phases.

In analyzing the results of the extraction experiments performed it was concluded that the UO_2^{2+} in the stock solution of 2 M hydrochloric acid was antimony(V) and that it was quantitatively reduced to antimony(III) by boiling in concentrated hydrochloric acid. A standard procedure was developed for determining the oxidation state of antimony in the sample. It consisted of adding 1 ml. or less of the sample to be tested to an extraction mixture of the composition indicated on page 37, shaking the mixture for 5 minutes, centrifuging for 5 minutes, separating the phases and finally counting the amount of activity in each phase. The amount of each oxidation state was calculated on the basis of 98% of antimony(V) entering the ether phase and 98% of antimony(III) remaining in the aqueous phase.

V. PREPARATION AND STABILITY OF $\text{Sb}^{125}(\text{III})$ AND $\text{Sb}^{125}(\text{V})$

Preparation in Hydrochloric Acid

In the process of developing a method for determining the oxidation state of carrier-free Sb^{125} as outlined in the previous section, suitable methods were found for the preparation of both oxidation states of antimony in hydrochloric acid. Antimony(V) was quantitatively obtained when stock solutions of Sb^{125} were prepared by eluting the Sb^{125} from Dowex-1 anion exchange resin with 2 N hydrochloric acid (see pp. 36-37). Antimony(III) was quantitatively obtained upon the boiling of concentrated hydrochloric acid solutions containing Sb^{125} (see pp. 36-37). In both instances the only chemical reagent added to the Sb^{125} was hydrochloric acid. Therefore the eventual problem of removing the excess of some special oxidizing or reducing reagent was avoided.

Preparation in Sulfuric and Perchloric

Acids and Water

Solutions of antimony(III) in sulfuric acid, perchloric acid, or water were obtained on dissolving the residue which remained after the hydrochloric acid had been evaporated from 10 N hydrochloric acid solutions containing carrier-free Sb^{125} as outlined in a previous section (see pp. 24-26). On treatment of 14 samples in 10 N hydrochloric acid, an average of 96% of the Sb^{125} was reduced to the lower oxidation state, whereas the fraction reduced was considerably

Preparation in Hydrochloric Acid

In the process of developing a method for determining

the oxidation state of carrier-free Sp^{127} as obtained in

the previous section, suitable methods were found for the

preparation of both oxidation states of interest in hydro-

chloric acid. Antimony(V) was quantitatively obtained when

stock solutions of Sp^{127} were prepared by eluting the Sp^{127}

from Dowex-1 anion exchange resin with 2 N hydrochloric

acid (see pp. 25-27). Antimony(III) was quantitatively

obtained upon the boiling of concentrated hydrochloric

acid solutions containing Sp^{127} (see pp. 30-32). In some

instances the only chemical reagent added to the Sp^{127} was

hydrochloric acid. Therefore the general problem of

removing the excess of some special oxidizing or reducing

reagent was avoided.

Preparation in Sulfuric and Perchloric

Acids and Water

Solutions of antimony(III) in sulfuric acid, perchloric

acid, or water were obtained on eluting the carrier which

remained after the hydrochloric acid had been evaporated

from 10 N hydrochloric acid solutions containing carrier-

free Sp^{127} as obtained in a previous section (see pp. 25-27).

On treatment of 14 samples in 10 N hydrochloric acid, an

average of 90% of the Sp^{127} was reduced to the lower oxida-

tion state, whereas the fraction reduced was quantitatively

lower when 2 N hydrochloric acid solutions were vaporized. Solutions of antimony(V) were obtained by exposing the antimony(III) solutions, contained in Pyrex tubes, to a general Electric H400-A1 mercury lamp having light of wave lengths greater than 3300 Angstrom units. Quantitative oxidation occurred within one hour.

Stability of $\text{Sb}^{125}(\text{III})$

Table 6 contains the results of a set of experiments designed to yield information concerning the stability of $\text{Sb}^{125}(\text{III})$ in various solutions. Into an 8 mm Pyrex tube was placed 1 ml. of the solution containing $\text{Sb}^{125}(\text{III})$, the tube was closed with a rubber stopper, and the sample was then placed either in the dark or exposed to ordinary laboratory fluorescent lighting conditions for 5 hours, 40 hours, or 1 week after which time the per cent oxidation was determined.

The results of other experiments showing the stability of $\text{Sb}^{125}(\text{III})$ in hydrochloric acid are recorded in Table 7. As indicated, the vessels were either closed by stoppering or by sealing with an oxygen torch and either stored in the dark or exposed to the light. Oxygen was removed by flushing the solution for 15 minutes with nitrogen that had been passed through chromous chloride solution. The acid concentration and per cent oxidation were determined after the samples stood for the length of time indicated.

The stability of $\text{Sb}^{125}(\text{III})$ under certain conditions

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Stability of ^{125}I (III)

Table 6 contains the results of a set of experiments designed to yield information concerning the stability of ^{125}I (III) in various solutions. Each in 5 ml. vial was placed in 1 ml. of the solution containing ^{125}I (III), the tube was closed with a rubber stopper, and the sample was then placed in the dark or exposed to ordinary laboratory fluorescent lighting (15 minutes for 2 hours, 15 hours, or 1 week after which time the per cent oxidation was determined.

The results of other experiments showing the stability of ^{125}I (III) in hydrochloric acid are reported in Table 7. As indicated, the vessels were either closed by stoppering or by sealing with an oxygen cover and the stored in the dark or exposed to the light. Oxygen was removed by treating the solution for 15 minutes with nitrogen that had been passed through calcium chloride solution. The cold solution and per cent oxidation were determined after the samples stood for the length of time indicated. The stability of ^{125}I (III) under various conditions

TABLE 6

Stability of $\text{Sb}^{125}(\text{III})$ in
 HCl , H_2SO_4 , HClO_4 , and H_2O at Room Temperature

Acid	Normality	Oxidation, %					
		5 hrs.		40 hrs.		1 week	
		<u>light present</u>	<u>light absent</u>	<u>light present</u>	<u>light absent</u>	<u>light present</u>	<u>light absent</u>
HCl	2	0	1	2	0	11	0
	6	0	0	1	0	0	0
	9	1	0	2	0	19	0
	12	37	58	7	13	11	5
H_2SO_4	2	0	0	2	0	10	1
	6	0	1	2	12	14	16
	9	0	1	5	3	34	11
	12	1	2	5	5	33	14
HClO_4	2	5	4	12	12	97	46
	6	2	6	16	11	91	40
H_2O	-	56	71	94	97	97	98

TABLE 2

Stability of ^{137}Cs (III) in

HCl , H_2SO_4 , HClO_4 , and H_2O at Room Temperature

Acid	Normality	Oxidation, %			
		1 hr.		2 hrs.	
		Loss	Gain	Loss	Gain
HCl	2	0	1	0	0
	6	0	1	0	0
	9	1	2	0	0
	12	32	7	28	2
H_2SO_4	2	0	2	0	1
	6	0	2	1	16
	9	0	2	1	11
	12	1	2	2	14
HClO_4	2	2	12	4	16
	6	2	12	6	10
H_2O	-	26	21	24	23

TABLE 7

Stability of $\text{Sb}^{125}(\text{III})$ in HCl at Room Temperature

<u>Normality</u> <u>range</u>	<u>Oxidation, %</u>			
	<u>Stoppered, oxygen not removed, light present</u>			
	<u>2 wks.</u>		<u>3 wks.</u>	
0.5	19		21	
3	5		5	
6	7		9	
9	8		21	
11	56		90	
	<u>Stoppered, oxygen removed</u>			
	<u>48 hrs.</u>		<u>72 hrs.</u>	
	<u>light present</u>	<u>light absent</u>	<u>light present</u>	<u>light absent</u>
1.6 - 2.0	11, 16	0, 0	23	2
5.0 - 6.0	28, 38	0, 0	29	1
8.0 - 10.0	59, 84	0, 0	29, 60	0, 12
	<u>Sealed, oxygen removed</u>			
	<u>72 hrs, light present</u>		<u>1 wk, light absent</u>	
1.0 - 3.0	40		31, 32	
3.5 - 5.0	3		13, 33	
6.0 - 7.5	7		0, 0	
8.0 - 8.9	0		0, 0	
9.0 - 10.0	16		0, 0	

Stability of Ca^{2+} (ppm) in water from temperature

Exposure, oxygen removed		Sealed, oxygen removed	
Temp. (°C)	Ca ²⁺ (ppm)	Temp. (°C)	Ca ²⁺ (ppm)
11	90	1.0 - 3.0	40
9	81	3.5 - 5.0	3
7	7	6.0 - 7.5	7
5	5	8.0 - 8.5	0
3	3	9.0 - 10.0	15
2	2		
1	1		
0	0		

in sulfuric acid, perchloric acid, and sodium hydroxide is recorded in Tables 8 and 9.

These experiments suggest that oxygen and light lead to oxidation of $\text{Sb}^{125}(\text{III})$ to $\text{Sb}^{125}(\text{V})$. For instance, Table 7 shows that in hydrochloric acid no oxidation occurs in the dark with the oxygen removed except in a few instances when the vessels were sealed with an oxygen torch. In those instances, the intense light used in the sealing process may have promoted some oxidation. The variations in the amount of oxidation that occurred may be due to variations in light exposure and the amount of oxygen in the solution. However, the absence of light and oxygen from sulfuric and perchloric acid solutions did not prevent oxidation as indicated in Table 8. $\text{Sb}^{125}(\text{III})$ is quite unstable in neutral and basic solutions (see Tables 6 and 9).

Stability of $\text{Sb}^{125}(\text{V})$

Experiments to determine the stability of $\text{Sb}^{125}(\text{V})$ were performed by sealing 1 ml. of various solutions containing $\text{Sb}^{125}(\text{V})$ in Pyrex tubes and allowing these tubes to stand either in the dark or exposed to fluorescent lights for certain lengths of time. The results are recorded in Table 10. Table 11 gives the results of additional experiments designed to determine the stability of $\text{Sb}^{125}(\text{V})$ in hydrochloric acid in the presence of fluorescent lights, and Table 12 contains the results of similar experiments with sodium hydroxide solutions.

in animals subjected to the same treatment as recorded in Table 7.

These experiments were conducted under conditions to oxidation of 5% (10% and 15% in some cases). Table 7 shows that in the first 10 minutes after the vessel was cut, the amount of oxygen in the blood was 10% higher than in the control. However, the amount of oxygen in the blood decreased rapidly and by 30 minutes it was only 5% higher than in the control. The amount of oxygen in the blood was 10% higher than in the control at 10 minutes after the vessel was cut. The amount of oxygen in the blood was 10% higher than in the control at 10 minutes after the vessel was cut. The amount of oxygen in the blood was 10% higher than in the control at 10 minutes after the vessel was cut.

Experiments were conducted to determine the effect of hydrochloric acid on the rate of oxygen consumption in animals subjected to the same treatment as recorded in Table 10. Table 10 shows that the rate of oxygen consumption was 10% higher than in the control at 10 minutes after the vessel was cut. The rate of oxygen consumption was 10% higher than in the control at 10 minutes after the vessel was cut. The rate of oxygen consumption was 10% higher than in the control at 10 minutes after the vessel was cut. The rate of oxygen consumption was 10% higher than in the control at 10 minutes after the vessel was cut.

TABLE 8

Stability of Sb^{125} (III) in H_2SO_4 and HClO_4 ^a

<u>Acid</u>	<u>Time, hrs.</u>	<u>Oxidation, %</u>
2 N HClO_4	1	5
2 N HClO_4	48	12
2 N HClO_4	168	34
6 N HClO_4	1	6
6 N HClO_4	48	15
6 N HClO_4	168	29
2 N H_2SO_4	168	6
6 N H_2SO_4	168	5
9 N H_2SO_4	168	22
9 N H_2SO_4	168	21

a. Vessels were stoppered and stored in the absence of light and oxygen at room temperature.

TABLE 9

Stability of Sb^{125} (III) in 10^{-4} N NaOH ^a

<u>Conditions</u>	<u>Oxidation, %</u>
light present, 15 min	52
light present, 1 hr	61
light present, 18 hr	41
light absent, 15 min	56
light absent, 1 hr	60
light absent, 18 hr	30

a. Vessels were stoppered and stored in presence of oxygen at room temperature.

TABLE 8

Stability of ^{135}I (III) in H_2O and HClO_4

Acid	Time, hrs.	Yield, %
HClO_4	1	7
HClO_4	48	12
HClO_4	168	34
HClO_4	1	6
HClO_4	48	14
HClO_4	168	20
H_2SO_4	168	6
H_2SO_4	168	7
H_2SO_4	168	22
H_2SO_4	168	21

Vessels were stoppered and stored in the absence of light and oxygen at room temperature.

TABLE 9

Stability of ^{135}I (III) in 10^{-4} M NaOH

Yield, %	Conditions
22	Light present, 15 min
61	Light present, 1 hr
41	Light present, 18 hr
76	Light absent, 15 min
60	Light absent, 1 hr
50	Light absent, 18 hr

Vessels were stoppered and stored in presence of oxygen at room temperature.

TABLE 10

Stability of $\text{Sb}^{125}(\text{V})$ in HCl , H_2SO_4 ,
 HClO_4 , and H_2O at Room Temperature

Acid	Normality	Reduction, %					
		5 hrs.		40 hrs.		1 week	
		<u>light present</u>	<u>light absent</u>	<u>light present</u>	<u>light absent</u>	<u>light present</u>	<u>light absent</u>
HCl	2	1	2	1	4	1	3
	6	2	22	0	1	0	12
	9	0	1	0	13	1	0
	12	6	2	2	2	80	27
H_2SO_4	2	2	3	3	3	2, 7	14
	6	3	2	3	4	13	11
	9	2	4	2	0	2	6
	12	1	4	1	1	1, 1, 2	2
HClO_4	2	4	2	3	1	0, 3	2
	6	10	16	2	12	0, 2	5
H_2O	-	4	2	2	3	3	4

TABLE 10

Stability of ^{135}I in HCl , H_2SO_4 , HClO_4 , and H_2O at Room Temperature

Acid Normality	Retention, %			
	1 hr.		30 hrs.	
	Present	Missing	Present	Missing
HCl	2	1	2	4
	6	2	22	1
	9	0	1	13
	12	2	2	80
H_2SO_4	2	2	3	3
	6	3	3	4
	9	2	2	2
	12	1	4	1, 1, 2
HClO_4	2	4	2	1
	6	10	16	12
H_2O	-	4	2	3

TABLE 11

Stability of $\text{Sb}^{125}(\text{V})$ in HCl at Room Temperature

<u>Normality range</u>	<u>Reduction, %</u>				
	<u>40 hrs.</u>	<u>72 hrs.</u>	<u>1 wk.</u>	<u>2 wks.</u>	<u>3 wks.</u>
0.5 - 2.0	0, 43	1, 7	0,1,1,1	1, 5	1, 6
2.5 - 4.0	-	0, 13	0,0,1,1	-	-
4.5 - 6.0	0, 2	10	1,1,5	4	8
6.5 - 7.5	-	0, 2	1,1	-	-
8.0 - 9.5	33	0, 32	0,0,0,31	23	0
10.0 - 11.0	0, 0, 0	0, 32	-	4	7

TABLE 12

Stability of $\text{Sb}^{125}(\text{V})$ in 10^{-4} N NaOH^a

<u>Conditions</u>	<u>Reduction, %</u>
light present, 15 min	8
light present, 1 hr	6
light present, 18 hr	4
light absent, 15 min	13
light absent, 1 hr	4
light absent, 18 hr	4

a. Vessels were stoppered and stored in presence of oxygen at room temperature.

TABLE 11

Stability of sp^{132} (V) in 10% X medium at room temperature

Reduction, %			Potentially viable		
40 hrs.	24 hrs.	1 hr.	40 hrs.	24 hrs.	1 hr.
0.2 - 2.0	0.13	0.1, 1, 1, 1	0.2	0.13	0.1, 1, 1, 1
2.2 - 4.0	0.13	0.1, 1, 1, 1	-	-	-
4.2 - 6.0	0.2	1, 1, 2	0.2	0.2	1, 1, 2
6.2 - 7.2	-	1, 1	-	-	-
8.0 - 9.2	0.33	0.1, 0.1, 0.1	0.33	0.33	0.1, 0.1, 0.1
10.0 - 11.0	0.1, 0.1, 0.1	-	0.1, 0.1, 0.1	0.1, 0.1, 0.1	-

TABLE 12

Stability of sp^{132} (V) in 10% X medium

Reduction, %	Conditions
0	light present, 15 min
0	light present, 1 hr
4	light present, 18 hr
13	light absent, 15 min
4	light absent, 1 hr
4	light absent, 18 hr

a. Vessels were stoppered and stored in presence of oxygen at room temperature.

In general, $\text{Sb}^{125}(\text{V})$ appears to be relatively stable in the solutions examined. However, the tables indicate that occasionally a significantly large fraction of $\text{Sb}^{125}(\text{V})$ was reduced. These large fractions occurred mostly with the hydrochloric acid solutions. In a previous section (see p. 38) dealing with the preparation of $\text{Sb}^{125}(\text{III})$, it was noted that $\text{Sb}^{125}(\text{V})$ is reduced by boiling in hydrochloric acid. Reduction may also occur at room temperature. At any rate, the oxidation state of Sb^{125} was periodically checked during the investigation of its chemical behavior in order to be assured of the initial oxidation state for each experiment.

In general, $sp^{132}(V)$ appears to be relatively stable in the solutions examined. However, the results indicate that essentially a slightly larger fraction of $sp^{132}(V)$ was reduced. These large fractions occurred only with the hydrochloric acid solutions. In a previous section (see p. 38) dealing with the preparation of $sp^{132}(III)$, it was noted that $sp^{132}(V)$ is reduced by boiling in hydrochloric acid. Reduction may also occur at room temperature. At any rate, the oxidation state of sp^{132} was periodically checked during the investigation of its chemical behavior in order to be assured of the initial oxidation state for each experiment.

VI. OXIDATION AND REDUCTION

Reduction of $\text{Sb}^{125}(\text{V})$ in Hydrochloric Acid

A considerable number of experiments were done in attempting to define the conditions under which $\text{Sb}^{125}(\text{V})$ is reduced to $\text{Sb}^{125}(\text{III})$ in hydrochloric acid. Inasmuch as quantitative reduction occurred upon boiling solutions of concentrated hydrochloric acid containing $\text{Sb}^{125}(\text{V})$ and a lesser amount of reduction occurred in hydrochloric acid of lesser concentrations under the same conditions, a study of the reduction as a function of acid concentration was made. Incidentally, no radioactivity was lost when samples of Sb^{125} in 50 ml. of concentrated hydrochloric acid were boiled to a volume of 1 ml. Initially the experiments consisted of sealing 2-ml. samples of hydrochloric acid containing $\text{Sb}^{125}(\text{V})$ in 9-mm Pyrex tubes, placing them in metal tubes containing oil for transfer of heat, and heating them in a constant temperature bath for certain lengths of time. After removal the Pyrex tubes were opened by scratching with a file and touching a hot rod to the wetted surface. Part of the sample was used for determination of the oxidation state of Sb^{125} and part for determination of the acid concentration. The results of these experiments were not reproducible. Under the same conditions the fraction of $\text{Sb}^{125}(\text{V})$ reduced varied from zero to more than one-half.

Three modifications in the experiments yielded results that were reproducible. A constriction was made in the neck

VI. OXIDATION AND REDUCTION

Reduction of $Sp^{132}(V)$ in Hydrochloric Acid

A considerable number of experiments were done in attempting to define the conditions under which $Sp^{132}(V)$ is reduced to $Sp^{132}(III)$ in hydrochloric acid. Inasmuch as quantitative reduction occurred upon boiling solutions of concentrated hydrochloric acid containing $Sp^{132}(V)$ and a lesser amount of reduction occurred in hydrochloric acid of lesser concentrations under the same conditions, a study of the reduction as a function of acid concentration was made. Incidentally, no radioactivity was lost from samples of Sp^{132} in 50 ml. of concentrated hydrochloric acid when boiled to a volume of 1 ml. Initially the experiments consisted of sealing 5-ml. samples of hydrochloric acid containing $Sp^{132}(V)$ in 9-mm Pyrex tubes, placing them in metal tubes containing oil for transfer of heat, and heating them in a constant temperature bath for certain lengths of time. After removal the Pyrex tubes were opened by sawing with a file and touching a hot rod to the wetted surface. Part of the sample was used for determination of the oxidation state of Sp^{132} and part for determination of the acid concentration. The results of these experiments were not reproducible. Under the same conditions the fraction of $Sp^{132}(V)$ reduced varied from zero to more than one-half. Three modifications in the experiment yielded results that were reproducible. A construction was made in the work

of the 9-mm Pyrex tube to allow its being opened by a slight scratch and thus to avoid the use of intense light in the opening process; the Pyrex tube was attached to a wire for the purpose of promptly removing it without shaking; and oxygen-free nitrogen was used to flush the solution for 15 minutes prior to sealing the Pyrex tube. Oxygen-free nitrogen was prepared by passing tank nitrogen into chromous chloride solution containing amalgamated zinc to keep the chromium in a lower oxidation state.

Results of the experiments using the described modifications are recorded in Table 13 and Figure 7. All samples were stored in the dark for the length of time indicated either at 100° or at room temperature. The per cent reduction of $\text{Sb}^{125}(\text{V})$ as a function of hydrochloric acid concentration is plotted in Figure 7. The three sets of experiments (1 hour at 100°, 1 hour at room temperature, and 40 hours at room temperature) indicate that increased temperature increases the fraction of antimony reduced, that a large increase in reaction time does not appreciably increase the fraction reduced, and that the fraction reduced increases with increasing hydrochloric acid concentration.

When sulfuric acid or perchloric acid was used in the place of hydrochloric acid, no significant reduction occurred. Therefore the chloride ion or some reducing impurity in the hydrochloric acid caused the reduction. The possibility of a reducing impurity was essentially eliminated by the results of the experiments in which solutions of Sb^{125} in hydrochloric

of the D-V... was able to allow its being covered by a slight
separator and thus to avoid the use of infrared light in the
opening process; the D-V tube was attached to a wire for
the purpose of practically removing it without shaking; and
oxygen-free nitrogen was used to flush the solution from
it minutes prior to sealing the lower tube. Oxygen-free
nitrogen was prepared by passing through nitrogen and phosphorus
chloride solution containing anhydrous calcium chloride to keep the
chromium in a lower oxidation state.
Results of the experiments using the described cell
cations are recorded in Table I and Figure 7. All samples
were stored in the dark for the length of time indicated
either at 100° or at room temperature. The per cent reduc-
tion of $^{137}\text{Ce}(\text{IV})$ as a function of hydrochloric acid concen-
tration is plotted in Figure 7. The time sets of experi-
ments (1 hour at 100°, 1 hour at room temperature, and 20
hours at room temperature) indicate that increased tempera-
ture increases the fraction of cerium reduced, that a
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the fraction reduced, and that the fraction reduced increases
with increasing hydrochloric acid concentration.
When sulfuric acid or perchloric acid was used in the
place of hydrochloric acid, no significant reduction occurred.
Therefore the chloride ion or some reducing impurity in the
hydrochloric acid causes the reduction. The possibility of
a reducing impurity was essentially eliminated by the results
of the experiments in which solutions of $^{137}\text{Ce}(\text{IV})$ in hydrochloric

TABLE 13

Reduction of $\text{Sb}^{125}(\text{V})$ in Hydrochloric Acid^a

<u>Room temperature</u> <u>40 hours</u>		<u>100°</u> <u>1 hour</u>		<u>Room temperature</u> <u>1 hour</u>	
<u>Normality</u> <u>of HCl</u>	<u>Reduction, %</u>	<u>Normality</u> <u>of HCl</u>	<u>Reduction, %</u>	<u>Normality</u> <u>of HCl</u>	<u>Reduction, %</u>
0.2	3	0.1	0	3.2	0
0.7	1	0.6	5	5.9	1
1.6	2	1.1	21	7.1	20
2.0	2	1.8	28	7.7	56
2.9	4	1.9	26	8.5	69
4.0	5	2.1	16	9.4	100
4.5	10	2.9	16	9.6	100
5.1	10	3.0	22	10.2	100
5.5	28	4.2	35	11.0	94
5.8	21	4.6	41		
6.0	9	4.6	96		
6.0	42	5.2	98		
6.3	17	6.2	97		
6.3	47	6.4	100		
6.6	42	7.5	100		
7.0	55	7.6	100		
7.6	77	9.7	99		
8.1	100				
8.7	99				
9.1	100				
9.2	100				
9.3	100				
9.6	99				
9.8	100				
10.1	100				
10.4	100				
10.7	100				

a. Light and oxygen were excluded.

TABLE 13

Reduction of SO_2 in Hydrochloric Acid

Room temperature 10 hours	100° 1 hour	Room temperature 1 hour
Normality of HCl	Reduction, %	Normality of HCl
0.2	0.2	0.2
0.3	0.3	0.3
0.4	0.4	0.4
0.5	0.5	0.5
0.6	0.6	0.6
0.7	0.7	0.7
0.8	0.8	0.8
0.9	0.9	0.9
1.0	1.0	1.0
1.1	1.1	1.1
1.2	1.2	1.2
1.3	1.3	1.3
1.4	1.4	1.4
1.5	1.5	1.5
1.6	1.6	1.6
1.7	1.7	1.7
1.8	1.8	1.8
1.9	1.9	1.9
2.0	2.0	2.0
2.1	2.1	2.1
2.2	2.2	2.2
2.3	2.3	2.3
2.4	2.4	2.4
2.5	2.5	2.5
2.6	2.6	2.6
2.7	2.7	2.7
2.8	2.8	2.8
2.9	2.9	2.9
3.0	3.0	3.0
3.1	3.1	3.1
3.2	3.2	3.2
3.3	3.3	3.3
3.4	3.4	3.4
3.5	3.5	3.5
3.6	3.6	3.6
3.7	3.7	3.7
3.8	3.8	3.8
3.9	3.9	3.9
4.0	4.0	4.0
4.1	4.1	4.1
4.2	4.2	4.2
4.3	4.3	4.3
4.4	4.4	4.4
4.5	4.5	4.5
4.6	4.6	4.6
4.7	4.7	4.7
4.8	4.8	4.8
4.9	4.9	4.9
5.0	5.0	5.0
5.1	5.1	5.1
5.2	5.2	5.2
5.3	5.3	5.3
5.4	5.4	5.4
5.5	5.5	5.5
5.6	5.6	5.6
5.7	5.7	5.7
5.8	5.8	5.8
5.9	5.9	5.9
6.0	6.0	6.0
6.1	6.1	6.1
6.2	6.2	6.2
6.3	6.3	6.3
6.4	6.4	6.4
6.5	6.5	6.5
6.6	6.6	6.6
6.7	6.7	6.7
6.8	6.8	6.8
6.9	6.9	6.9
7.0	7.0	7.0
7.1	7.1	7.1
7.2	7.2	7.2
7.3	7.3	7.3
7.4	7.4	7.4
7.5	7.5	7.5
7.6	7.6	7.6
7.7	7.7	7.7
7.8	7.8	7.8
7.9	7.9	7.9
8.0	8.0	8.0
8.1	8.1	8.1
8.2	8.2	8.2
8.3	8.3	8.3
8.4	8.4	8.4
8.5	8.5	8.5
8.6	8.6	8.6
8.7	8.7	8.7
8.8	8.8	8.8
8.9	8.9	8.9
9.0	9.0	9.0
9.1	9.1	9.1
9.2	9.2	9.2
9.3	9.3	9.3
9.4	9.4	9.4
9.5	9.5	9.5
9.6	9.6	9.6
9.7	9.7	9.7
9.8	9.8	9.8
9.9	9.9	9.9
10.0	10.0	10.0

a. Light and oxygen were excluded.

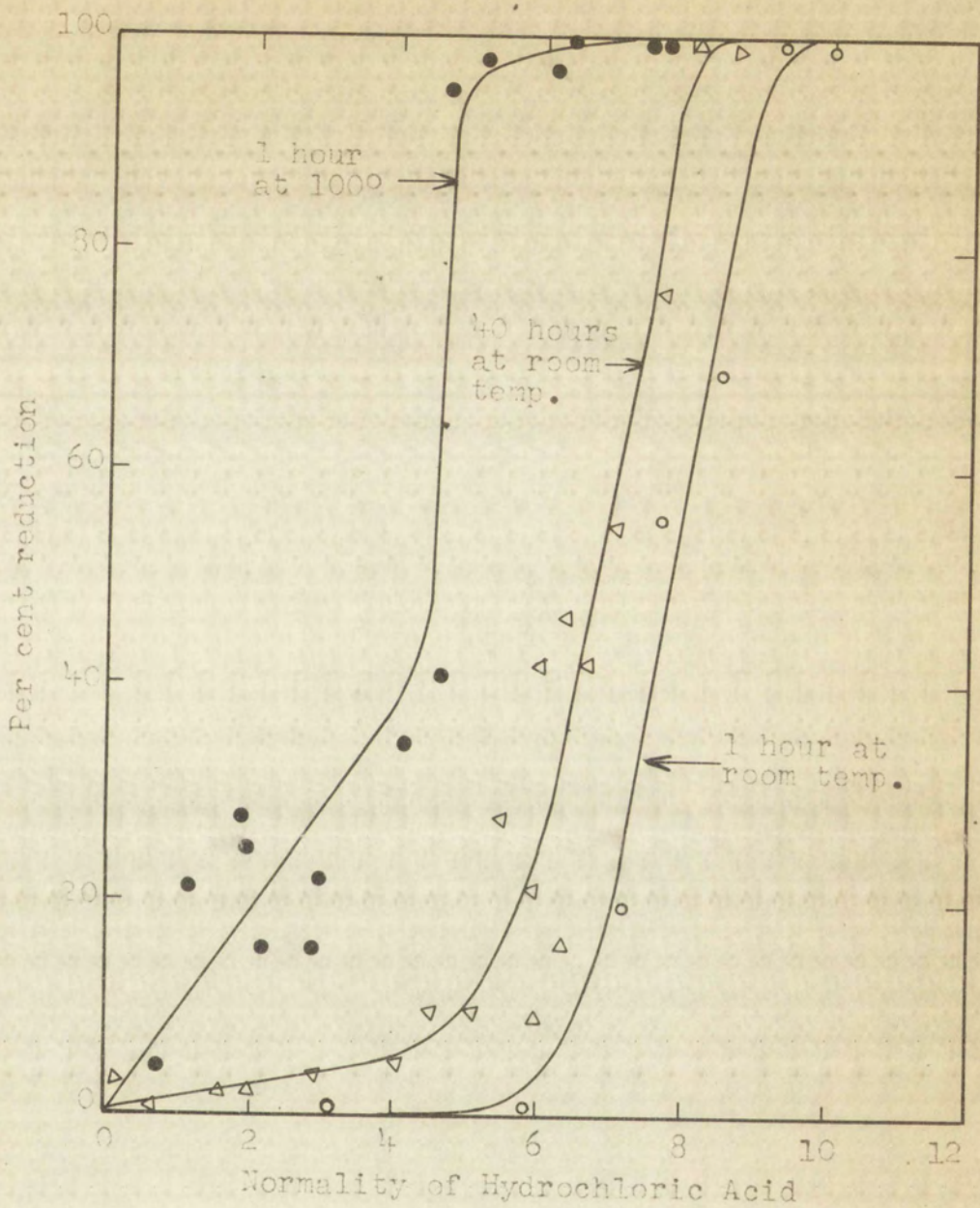
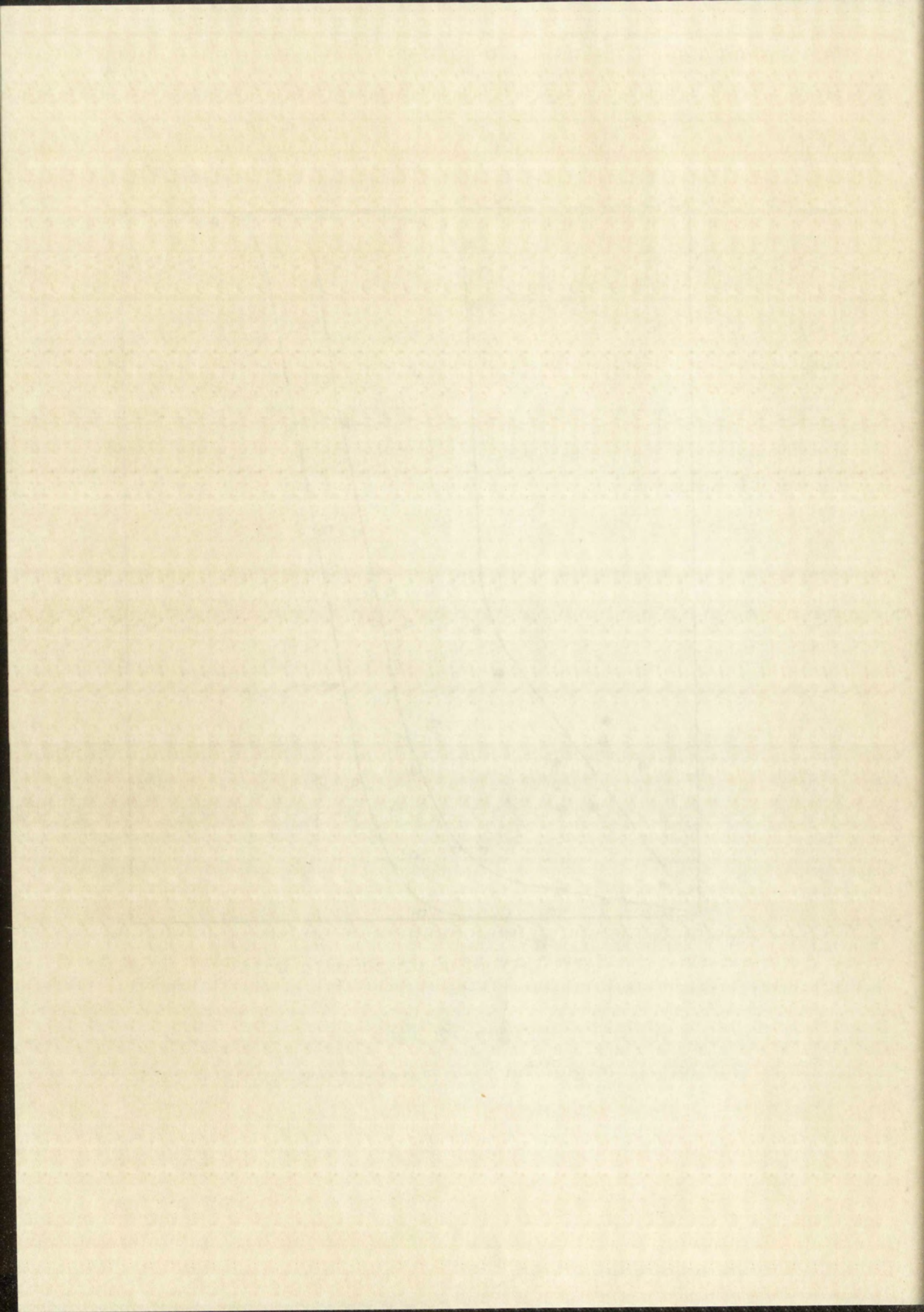
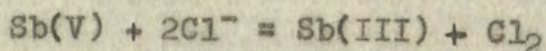


Figure 7

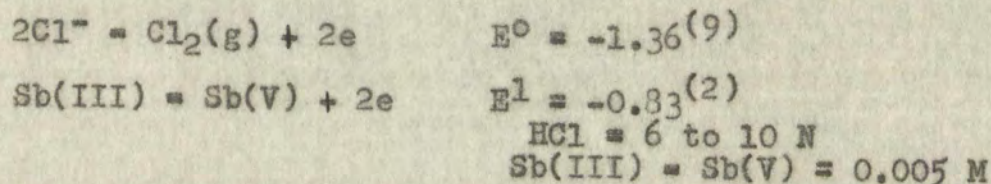
Reduction of $\text{Sb}^{125}(\text{V})$ in Hydrochloric Acid



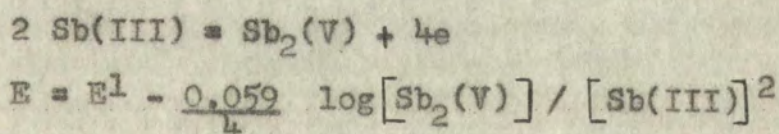
acid were boiled after the addition of chlorine or bromine. The reduction probably occurs according to the following reaction.



However, it has been shown experimentally that the reverse reaction takes place for all concentrations of antimony when any appreciable amount of chlorine is present [see Table 17 for carrier-free $\text{Sb}^{125}(\text{V})$]. Also the reverse reaction is favored for normal concentrations of antimony by the oxidation potentials of the two reactions involved.



If antimony(V) formed dimers the potential of the antimony half-reaction would become more negative (which would favor the forward reaction) at lower total antimony concentrations. For example, employing the following equations,



if the total antimony concentration is 10^{-10} M and 99% of the Sb(V) is reduced, then

$$\begin{aligned} E &= -0.83 - 0.015 \log 5 \times 10^{-13} / (.99 \times 10^{-10})^2 \\ &= -0.83 - 0.015 \times 7.3 = -0.83 - 0.08 = -0.91. \end{aligned}$$

However other workers⁽⁴⁾ with antimony do not report dimerization in aqueous solutions.

A more likely explanation for the forward reaction is associated with the oxidation potential of the chloride-

self...
the...
reaction...

$$20(Y) + 20(Z) = 20(X) + 20(W)$$

However...
reaction...
when...
Table...
action...
the...
20(Y) + 20(Z) = 20(X) + 20(W)

$$20(Y) + 20(Z) = 20(X) + 20(W)$$

soluble...
If...
half...
the...
for...
20(Y) + 20(Z) = 20(X) + 20(W)

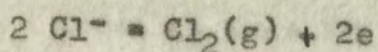
$$20(Y) + 20(Z) = 20(X) + 20(W)$$

if...
the...
20(Y) + 20(Z) = 20(X) + 20(W)

$$20(Y) + 20(Z) = 20(X) + 20(W)$$

However...
action...
A...
associated...

chlorine reaction,



becoming more positive for lower partial pressures of chlorine. The amount of chlorine formed through reduction of carrier-free $\text{Sb}^{125}(\text{V})$ is very small and consequently the chlorine pressure may be sufficiently low to allow for the reduction of $\text{Sb}^{125}(\text{V})$ by chloride.

Reduction of Antimony(V) in Hydrochloric Acid as a Function of Antimony Concentration

The reduction of antimony(V) in hydrochloric acid as a function of antimony concentration was investigated. A known quantity of radioactive carrier antimony(V) in 1 ml. of 10 N hydrochloric acid was sealed in a 9-mm Pyrex tube after flushing the solution for 15 minutes with oxygen-free nitrogen. The sample was then heated in the dark at 100° for 1 hour after which time the oxidation state of the antimony was determined. The results are recorded in Table 14 and Figure 8. Under the conditions of the experiment, reduction of antimony(V) does not begin until the antimony concentration is lowered to about 10^{-4} M, and the reduction becomes quantitative for antimony concentrations between 10^{-7} and 10^{-8} M.

This experiment provides a method for estimating the antimony concentration in solutions containing carrier-free Sb^{125} . As mentioned in the previous paragraph, antimony(V) is not quantitatively reduced in 1 hour in 10 N hydrochloric

absolute resolution

of the white...

becoming... The amount of... free sp... pressure... of sp...

Reduction of...

the reaction of... a function of... known quantity... of 10... after... nitrogen... for... many was... and Figure... tion of... reaction... quantities...

10-8 M.

This... another... sp... is not...

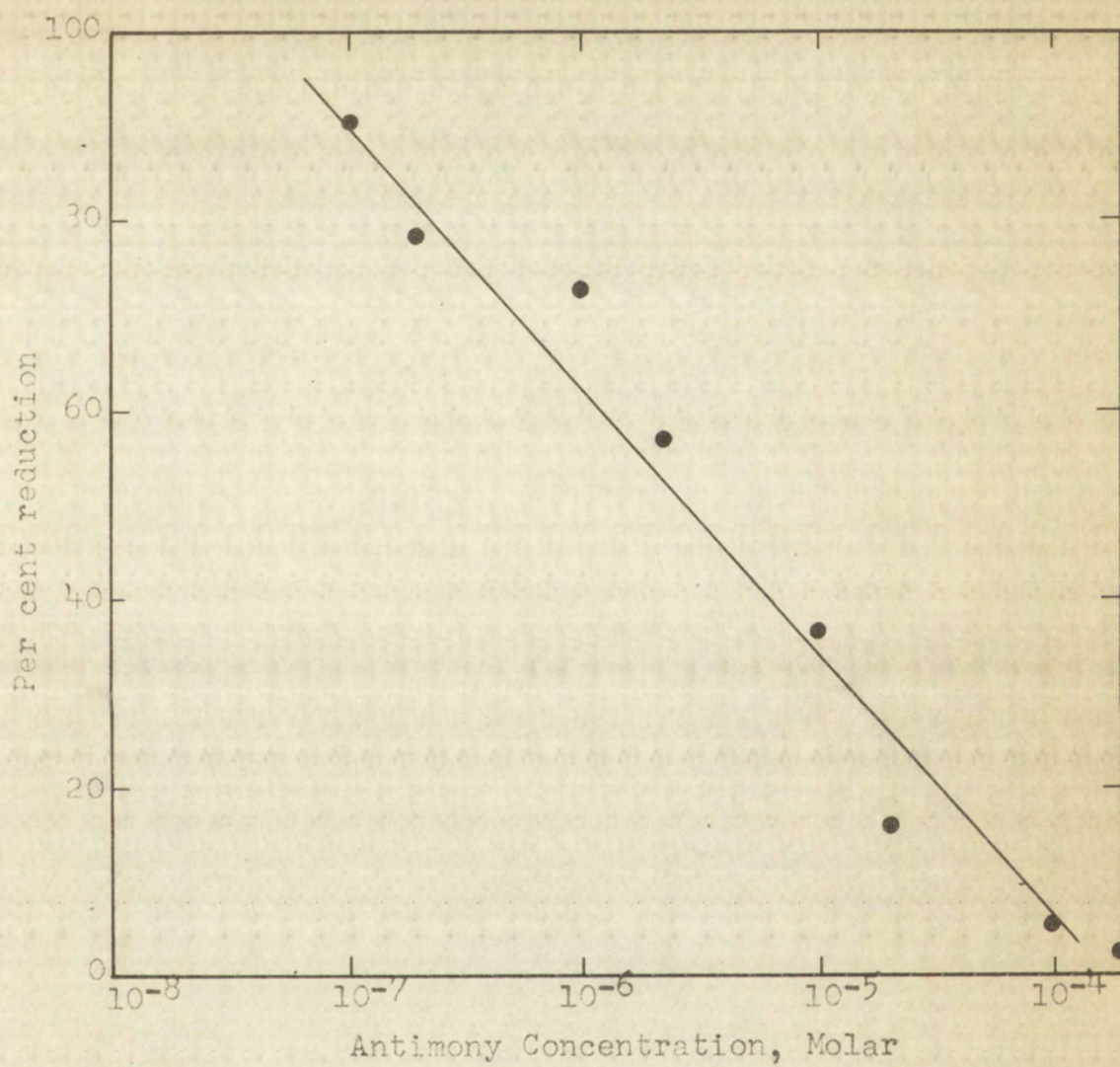


Figure 8
Reduction of Carrier Antimony(V)

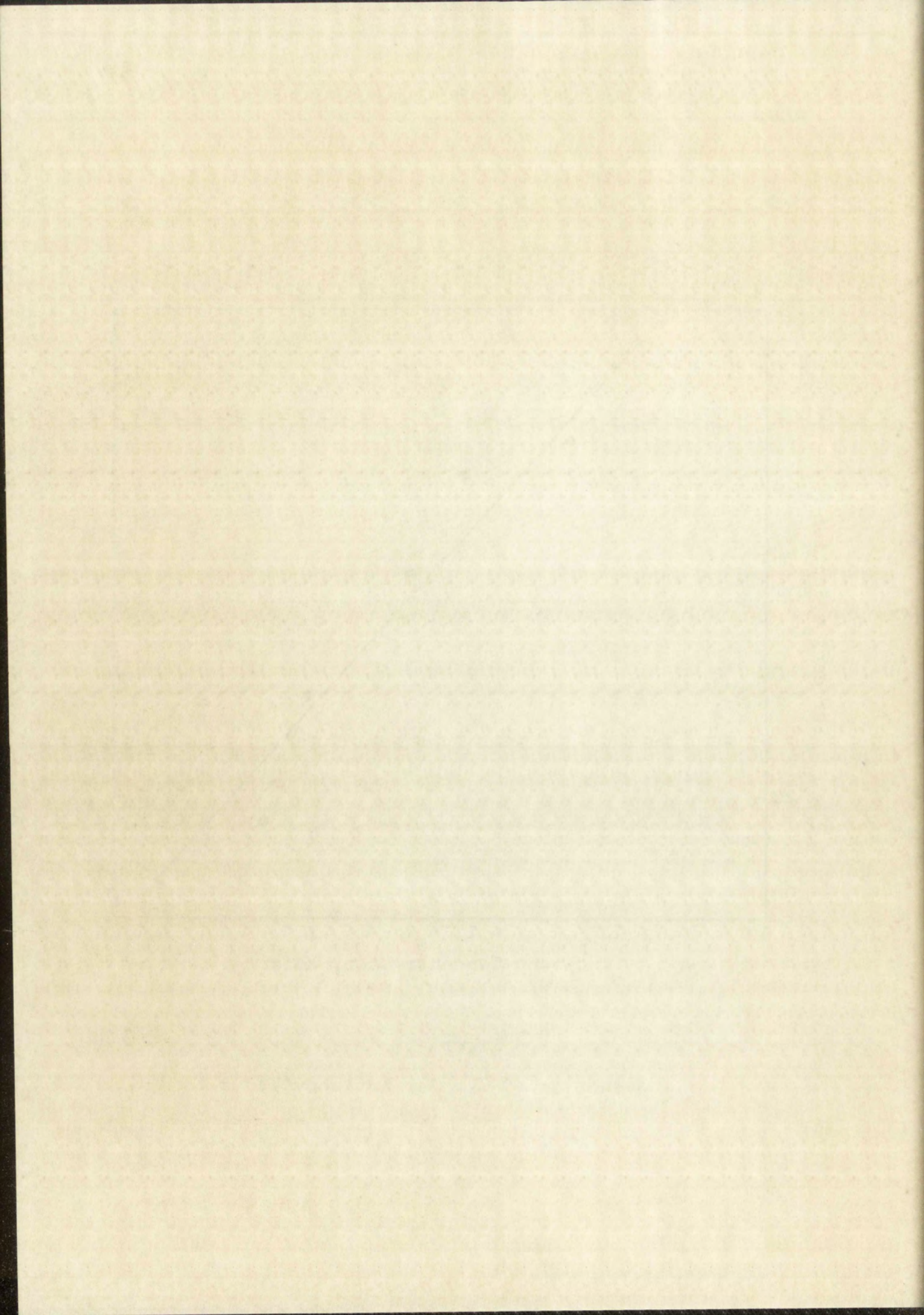


TABLE 14

Reduction of Carrier Antimony(V)^a

<u>Antimony concentration (M)</u>	<u>Reduction, %</u>	<u>Average</u>
2×10^{-4} 10^{-4}	0, 5, 6, 9, 10 3, 4	3 6
2×10^{-5} 10^{-5}	26, 41, 44 16, 17	16 37
2×10^{-6} 10^{-6}	64, 75, 79 52, 58	55 73
2×10^{-7} 10^{-7}	79 91	79 91
2×10^{-8}	98, 99, 100	99

a. Light and oxygen were excluded from the 10 N HCl solutions which were heated at 100° for 1 hour.

acid at 100° until the antimony concentration becomes as low as about 10^{-8} M. Carrier-free $\text{Sb}^{125}(\text{V})$ is quantitatively reduced under the same conditions, and, hence, the upper limit to the concentration of carrier-free Sb^{125} is 10^{-8} M. The lower limit is obtained from consideration of the radioactivity of the 2-year Sb^{125} . A 1-ml. solution of Sb^{125} giving 10,000 d/m contains 2.5×10^{-14} gram atoms of Sb^{125} and is 2.5×10^{-11} M with respect to antimony. Inasmuch as a counting rate of more than 1000 c/m was used in each experiment and since the counting efficiency of the scintillation counter used to detect the radioactivity was less than 10%, the minimum concentration of antimony was about 10^{-10} M. Therefore the antimony concentration in the solutions of

PROPERTIES OF POLYMER SOLUTIONS

Concentration (g/100 ml)	Viscosity (poise)	Intrinsic Viscosity (dl/g)
0.5	1.2×10^{-2}	1.2×10^{-2}
1.0	2.4×10^{-2}	1.2×10^{-2}
2.0	4.8×10^{-2}	1.2×10^{-2}
3.0	7.2×10^{-2}	1.2×10^{-2}
4.0	9.6×10^{-2}	1.2×10^{-2}

It is observed that the intrinsic viscosity remains constant at 1.2×10^{-2} dl/g across the concentration range studied, indicating that the polymer chains are in a random coil configuration and do not undergo significant conformational changes upon dilution.

The lower limit of the concentration range is determined by the onset of precipitation, which occurs at approximately 0.5 g/100 ml. Above this concentration, the solution becomes turbid and the viscosity increases sharply, suggesting the formation of aggregates or cross-links between polymer chains. The constant intrinsic viscosity in the dilute region is characteristic of a good solvent, where the polymer chains are fully solvated and their hydrodynamic volume is proportional to the square of the degree of polymerization. The observed behavior is consistent with the theoretical predictions for a random coil polymer in a good solvent, where the intrinsic viscosity is independent of concentration.

carrier-free Sb^{125} used in this work was 10^{-8} to 10^{-10} M.

Reduction of Antimony(V) by Various Reducing Agents

Several solutions of reducing agents were prepared. Each was calculated to be 10^{-3} N when 0.01 ml. was diluted to 1 ml. This concentration was selected in order to avoid any appreciable reduction of the 0.05 M antimony(V) in the extraction mixture used to determine the oxidation state of antimony; with these concentrations no more than 1% would be reduced during the extraction process. A 0.05 M sulfur dioxide solution in water, a 0.1 M ferrous sulfate solution in 1% sulfuric acid, a 0.1 M potassium iodide solution in water, and a 0.05 M stannous chloride solution in 1% sulfuric acid were prepared. To 1 ml. of either hydrochloric, sulfuric, or perchloric acid containing either carrier-free Sb^{125} (V) or 5×10^{-5} M radioactive antimony(V) was added 0.01 ml. of one of the prepared reducing agents. The solution was sealed in a 9-mm Pyrex tube and stored in the dark for 1 hour either at room temperature or at 100° after which time the oxidation state of the antimony was determined.

The results are recorded in Table 15. In these experiments iodide is considerably more effective than the other three reagents in reducing antimony(V). In general the fraction reduced does not appear to depend on the antimony(V) concentration but rather on the type and concentration of acid.

carboxylic acid in the presence of a catalyst.

Experimental

General procedure: A solution of 1.0 g (0.01 mole) of the acid in 10 ml of water was placed in a 25 ml beaker.

To this was added 0.5 g of the catalyst and the mixture was stirred for 10 minutes.

The reaction mixture was then poured into 50 ml of water and the solid product was filtered off.

The solid was washed with water and dried in a vacuum oven at 50°C for 24 hours.

The yield of the product was 0.8 g, which corresponds to an 80% conversion of the acid.

The melting point of the product was found to be 120°C, which is in good agreement with the literature value.

The infrared spectrum of the product showed a strong absorption at 1710 cm⁻¹, characteristic of a carbonyl group.

The ¹H NMR spectrum of the product showed a singlet at 7.2 ppm, which is characteristic of an aromatic proton.

For a more detailed description of the experimental procedure, see the full report.

The results are summarized in the following table:

Table 1. Reaction conditions and yields for the synthesis of the product.

Reaction conditions: 1.0 g acid, 0.5 g catalyst, 10 ml water, 25 ml beaker, 10 min stirring.

Yield: 0.8 g (80% conversion).

TABLE 15

Reduction of Antimony(V)^a

Reducing Agent	Antimony concentration	Normality of acid	Reduction, %						
			HCl		H ₂ SO ₄		HClO ₄		
			RT ^b	100°	RT	100°	RT	100°	
Fe ⁺⁺	CF ^c	2	1	6	3	8	2	11	
		6	13	99	1	10	1	1	
		9	98	96	0	4	-	-	
		12	98	99	1	4	-	-	
		2	9	7	0	0	3	0	
		6	22	98	1	7	19	2	
	9	94	99	0	4	-	-		
	12	100	100	0	1	-	-		
	I ⁻	CF	2	98	97	28	6	6	3
			6	100	100	100	54	99	99
			9	100	100	99	97	-	-
			12	100	100	98	100	-	-
2			91	92	25	2	2	3	
6			97	100	90	40	98	100	
9		99	100	100	99	-	-		
12		99	100	99	100	-	-		
Sn ⁺⁺		CF	2	1	3	2	15	4	90
			6	3	2	1	16	5	97
			9	97	99	2	13	-	-
			12	99	99	2	14	-	-
	2		4	3	3	22	3	93	
	6		26	2	1	15	4	60	
	9	72	89	2	18	-	-		
	12	97	100	1	19	-	-		
	SO ₂	CF	2	3	65	1	36	2	25
			6	1	100	2	10	1	3
			9	67	98	1	3	-	-
			12	45	99	0	1	-	-
2			10	66	0	58	0	22	
6			3	32	2	21	0	3	
9		4	46	0	18	-	-		
12		1	47	0	2	-	-		
None		CF	2	2	15	2	7	2	1
			6	0	57	2	4	3	3
			9	2	82	1	3	-	-
			12	0	89	1	1	-	-
	2		-	4	-	-	-	-	
	6		-	5	-	-	-	-	
	9	-	3	-	-	-	-		
	12	-	7	-	-	-	-		

a. Light was excluded from the samples in sealed Pyrex tubes for 1 hour
 b. Room temperature
 c. Carrier-free Sb¹²⁵

Reduction of $\text{Sb}^{125}(\text{V})$ by Sulfur Dioxide

From Table 15, it is observed that sulfur dioxide only partially reduces carrier-free Sb^{125} in 2 N acids at 100° . The per cent reduced is 65% for hydrochloric acid, 36% for sulfuric acid, and 25% for perchloric acid. A brief investigation was made to determine the rate at which the reduction occurred under these conditions. Experiments were done in the same manner as just previously described except that the reaction times were varied.

Table 16 and Figure 9 contain the results of these rate studies. A leveling off at about 80% is noted for hydrochloric acid solutions, and an apparent decrease in the per cent reduction is observed for sulfuric and perchloric acids. No attempt was made to exclude oxygen from these solutions, and, hence, the decrease in reduction may be caused by a competing oxidation reaction due to the oxygen dissolved in the solutions.

Oxidation of $\text{Sb}^{125}(\text{III})$

A series of experiments was performed to investigate the oxidation of carrier-free $\text{Sb}^{125}(\text{III})$ in hydrochloric, sulfuric, and perchloric acids. Aqueous solutions of 0.05 M chlorine and bromine were prepared. To 1 ml. of solution containing carrier-free $\text{Sb}^{125}(\text{III})$ was added 0.01 ml. of either bromine or chlorine solution. Thus the concentration of the oxidizing agent in the sample was 10^{-3} N. The sample, contained in a stoppered Pyrex tube, stood for 1 hour at room

partially reduced counter-ions... The rate of reduction is... A first-order... reaction was found to... than occurred under... done in the same... that the reaction... Table in the... rate studies... hydrochloric acid... the per cent... chloric acids... these solutions... be assessed by... oxygen dissolved... A series of... the oxidation... nitric, and... chlorine and... contains... either... of the oxidant... contained in...

Table in the... rate studies... hydrochloric acid... the per cent... chloric acids... these solutions... be assessed by... oxygen dissolved... A series of... the oxidation... nitric, and... chlorine and... contains... either... of the oxidant... contained in...

A series of... the oxidation... nitric, and... chlorine and... contains... either... of the oxidant... contained in...

of the oxidant... contained in...

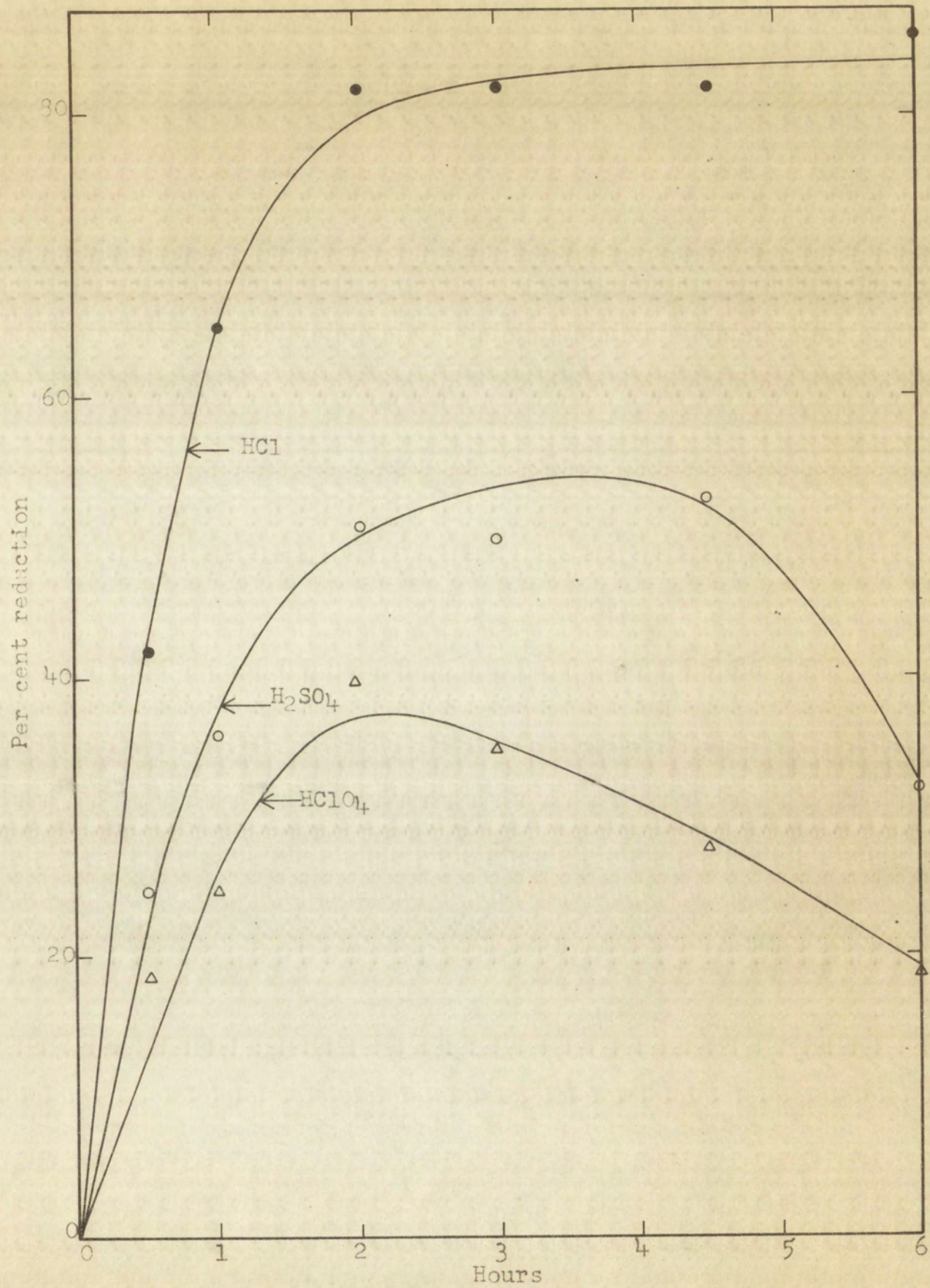


Figure 9
Reduction of $Sb^{125}(V)$ by Sulfur Dioxide

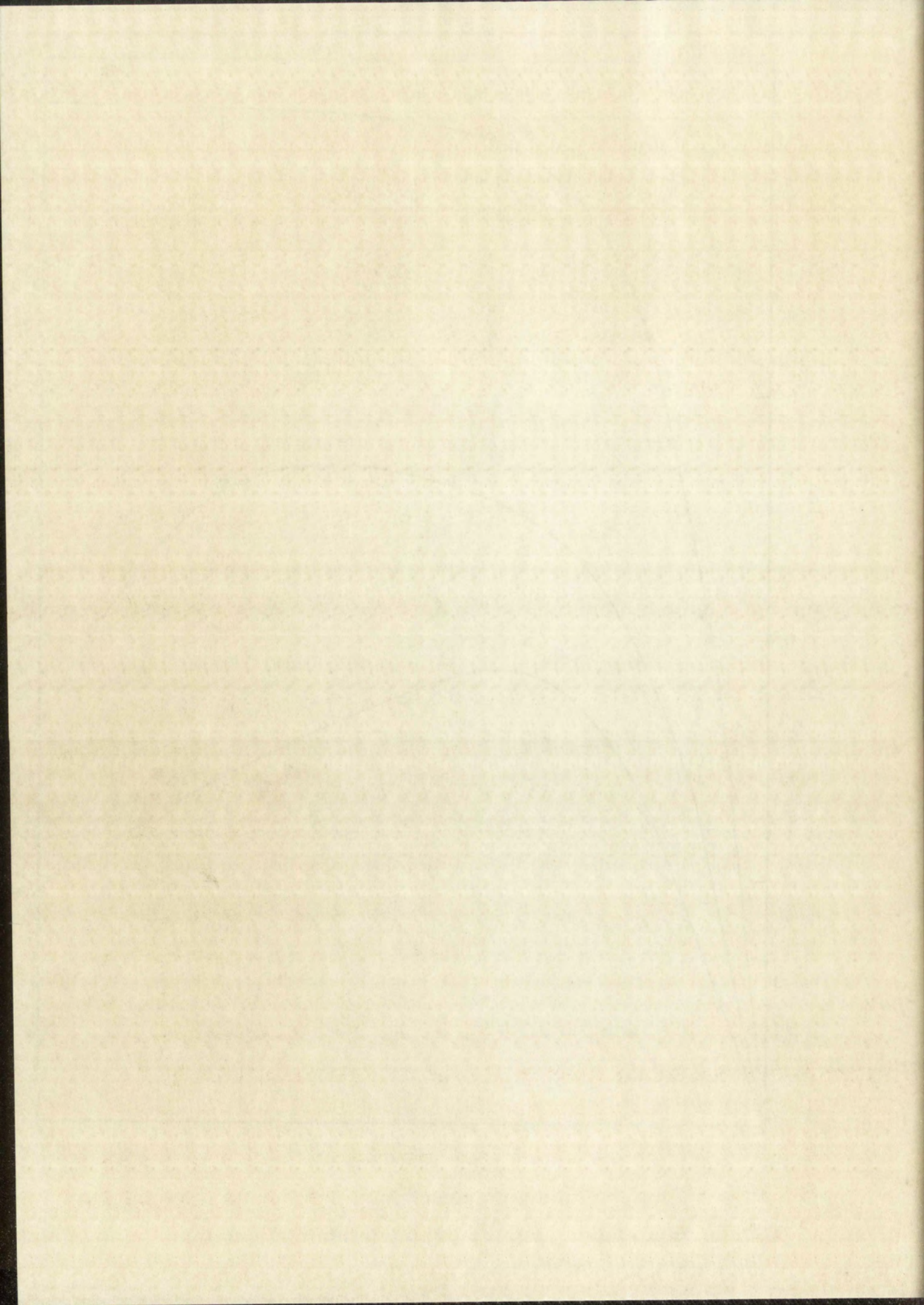


TABLE 16

Reduction of $\text{Sb}^{125}(\text{V})$ by Sulfur Dioxide^a

<u>Reduction time,</u> <u>hrs.</u>	<u>Reduction, %</u>		
	<u>HCl</u>	<u>H₂SO₄</u>	<u>HClO₄</u>
1/2	42	24	18
1	65	36	25
2	82	51	40
3	82	50	35
4 1/2	82	53	28
6	86	82	18

a. Samples were at 100° in 2 N acid with SO_2 concentration of 10^{-3} N.

temperature after which time the oxidation state was determined. In addition to the oxidation experiments with chlorine and bromine, an investigation was made of the oxidizing effect of the light of a General Electric H400-A1 mercury lamp on $\text{Sb}^{125}(\text{III})$. In this investigation 1 ml. of solution in a stoppered Pyrex tube containing $\text{Sb}^{125}(\text{III})$ was placed 1 inch from the mercury lamp for 1 hour; during this time the sample was cooled by an electric fan. The per cent oxidation for this investigation and for the experiments with chlorine and bromine is recorded in Table 17. It is noted that nearly quantitative oxidation occurred in all of the experiments. This behavior supports the observation in the previous section that $\text{Sb}^{125}(\text{V})$ tends to be more stable than $\text{Sb}^{125}(\text{III})$.

TABLE 17

Oxidation of $\text{Sb}^{125}(\text{III})^a$

Acid	Normality	Oxidation, %		
		Chlorine	Bromine	Hg lamp
HCl	2	93	99	94
	6	100	100	100
	9	99	100	100
	12	94	100	100
H_2SO_4	2	99	99	95
	6	98	100	99
	9	100	100	100
	12	100	100	99
HClO_4	2	96	100	99
	6	99	99	83

a. Samples were in stoppered vessels for 1 hour with 10^{-3} N oxidizing agents.

Another experiment consisted of alternately exposing samples to light from the mercury lamp and heating them at 100° in the dark. Six samples of $\text{Sb}^{125}(\text{III})$ in 10 N hydrochloric acid were sealed in Pyrex tubes without removing the oxygen from the solution. All six samples were exposed to the light for 30 minutes after which time one sample was tested for the oxidation state of the Sb^{125} . The remaining five samples were heated for 1 hour and then another sample

Sample No.	Weight (g)	Volume (ml)	Concentration (%)	Notes
1	100	100	100	
2	100	100	100	
3	100	100	100	
4	100	100	100	
5	100	100	100	
6	100	100	100	
7	100	100	100	
8	100	100	100	
9	100	100	100	
10	100	100	100	

a. Samples were prepared by adding a certain amount of oxidizing agent.

Another experiment was conducted to determine the effect of the amount of oxidizing agent on the rate of reaction. Five samples were prepared, each containing a different amount of oxidizing agent. The reaction was carried out at 100°C in the dark. The rate of reaction was determined by measuring the volume of gas evolved at regular intervals. The results are shown in the following table:

was tested. In this way the alternate exposure to light and heating was continued until all the samples had been tested for the oxidation state of the Sb^{125} . In the three instances in which the samples were tested immediately after exposure to the light 100% of the Sb^{125} was found to be oxidized; in the three instances of testing after heating 94%, 60%, and 71%, respectively, were reduced. This experiment indicates that the oxidation-reduction reaction is reversible.

Further tests were made to determine the nature of the mechanism of the light-induced oxidation reaction. Two 1-ml. samples of concentrated hydrochloric acid were exposed to light from the mercury lamp for 1 hour and then were added to 0.1 ml. of Sb^{125} (III) in 6 N hydrochloric acid. After 30 minutes the oxidation state of the Sb^{125} was checked. In both instances the Sb^{125} (III) had been quantitatively oxidized. In another test 1 ml. of concentrated hydrochloric acid was exposed to the mercury lamp for 1 hour and stored in the dark for 24 hours after which time it was added to 0.1 ml. of Sb^{125} (III) solution and allowed to stand 30 minutes as before. No oxidation occurred in this instance.

These experiments indicate that light does not directly oxidize antimony(III) but that the oxidation occurs as a secondary reaction. Thus a relatively unstable intermediate which is capable of oxidizing Sb^{125} (III) to Sb^{125} (V) is formed on irradiation with light. Baüli⁽¹⁾ attributes the oxidation of carrier amounts of antimony(III) by direct sunlight or by

was tested. In the first instance, the reaction was carried out in a sealed tube for the purpose of determining the amount of gas evolved. The results showed that the reaction was reversible. The amount of gas evolved was found to be proportional to the amount of the substance oxidized. In the second instance, the reaction was carried out in an open vessel. The results showed that the reaction was also reversible. The amount of gas evolved was found to be proportional to the amount of the substance oxidized.

Further experiments were carried out to determine the mechanism of the reaction. It was found that the reaction was first order with respect to the concentration of the substance oxidized. The rate of reaction was found to be independent of the concentration of the gas evolved. This suggests that the reaction is a simple oxidation reaction. The results of these experiments are summarized in the following table:

Concentration of substance oxidized (M)	Rate of reaction (M/min)
0.1	0.01
0.2	0.02
0.3	0.03
0.4	0.04
0.5	0.05

These results show that the reaction is a simple oxidation reaction. The rate of reaction is first order with respect to the concentration of the substance oxidized. The results of these experiments are summarized in the following table:

Concentration of substance oxidized (M)	Rate of reaction (M/min)
0.1	0.01
0.2	0.02
0.3	0.03
0.4	0.04
0.5	0.05

light from a mercury lamp to the formation of some intermediate peroxide.

Light from a nearby lamp is reflected by the surface of the water.

medias de agua.

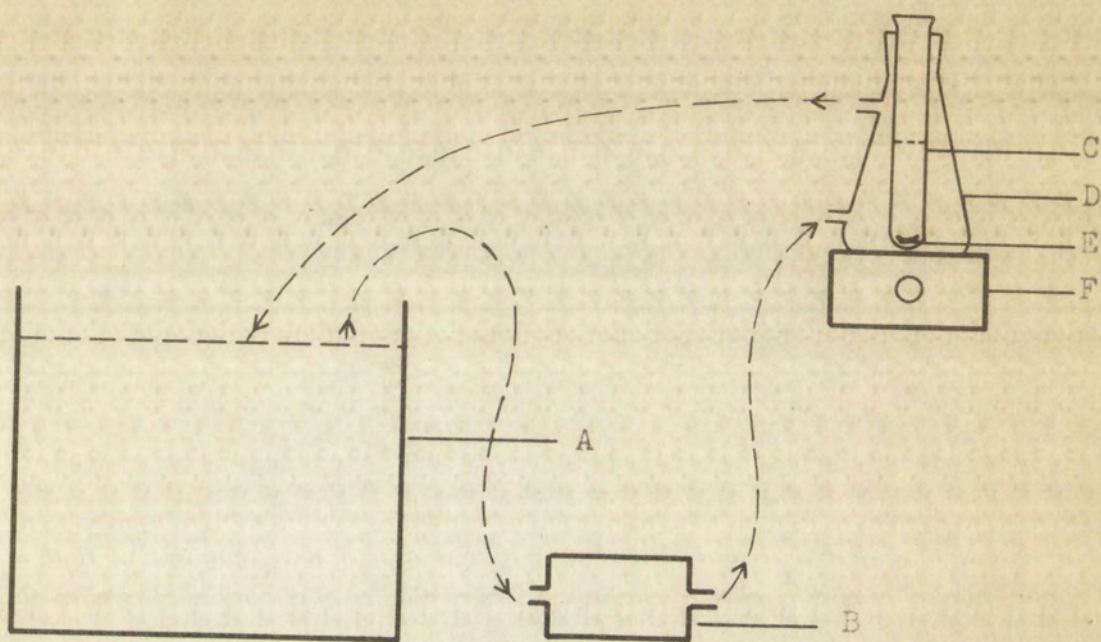
VII. ADSORPTION AND COPRECIPITATION

Adsorption of Sb^{125} on Pyrex

The loss of a small amount of material from solution may not be significant for substances in conventional concentrations, whereas the same amount could represent a sizable fraction or all of the material in concentrations on the order of 10^{-10} M. Therefore a knowledge of the adsorption of carrier-free substances on the walls of containing vessels is of special interest. In order to investigate this problem the apparatus outlined in Figure 10 was assembled. With this apparatus, constant temperature was maintained, the solutions were stirred, and the atmosphere was excluded. Also the samples were easily centrifuged after stirring either by transferring to a centrifuge cone or by centrifuging the original test tube. All centrifuging in this work was done at high speed in an ordinary clinical centrifuge. The apparatus consisted of a constant temperature bath with a centrifugal pump to circulate the thermostated water through a 250-ml. Erlenmeyer flask which had an inlet tube near the bottom and an outlet tube near the top. The flask rested on a magnetic stirrer, and in the flask was placed a Pyrex test tube which contained the sample solution and a small magnetic stirring bar. The atmosphere was excluded by closing the test tube with a stopper or with parafilm. For all experiments with this apparatus the temperature was maintained at 29.2° .

[Faint, illegible title]

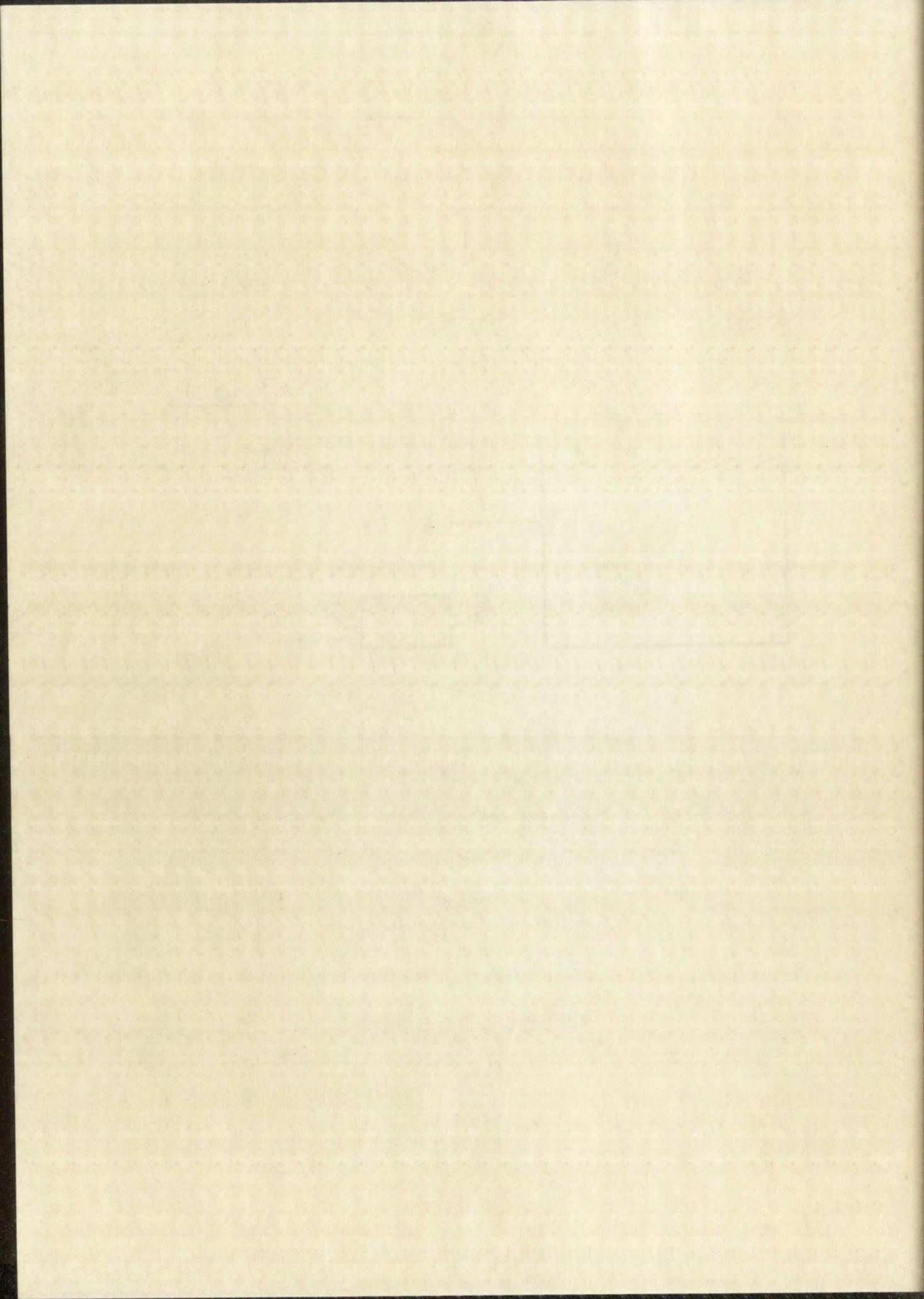
The loss of a small amount of material... may not be critical... conventional, whereas the... stable... on the order of... absorption of... taking... please... assembled... maintained... was... after... or by... in this way... centrifuge... tube... regulated... had an... the top... the flask... sample... atmosphere... stopped... apparatus...



- A Constant temperature bath
- B Centrifugal pump
- C Adsorption tube
- D Erlehmeyer flask
- E Magnetic stirring bar
- F Magnetic stirrer

Figure 10

Adsorption Apparatus



A measure was made of the extent of adsorption on Pyrex of both $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ from various acid solutions. The acids were 2 N, 6 N, 9 N, and 12 N hydrochloric acid; 2 N, 6 N, 9 N, and 12 N sulfuric acid; and 2 N and 6 N perchloric acid. Samples of Sb^{125} of known radioactivity in 10 ml. of solution were stirred for 1 hour, the solution was transferred to a centrifuge cone and centrifuged for 10 minutes, and then the radioactivity remaining in solution was determined. In all instances 97% to 100% of the radioactivity remained in solution.

In a similar manner the adsorption of Sb^{125} on Pyrex was determined as a function of pH. The pH was adjusted by adding small amounts of freshly prepared sodium hydroxide solution to water solutions of Sb^{125} . After stirring the samples 1 hour, 3 ml. of each sample was used for pH determination with a Beckman pH meter, and the remaining 7 ml. was centrifuged 10 minutes. The samples were then filtered through Whatman 42 filter paper and 5 ml. of the filtrate from each sample was counted for radioactivity. The residual activity on the centrifuge cone and on the original test tube was also counted. Essentially all of the Sb^{125} that was removed from solution was removed during the initial 1 hour stirring period.

The results of these experiments are recorded in Table 18. It was previously observed that $\text{Sb}^{125}(\text{III})$ is rather unstable in sodium hydroxide solutions. However, experiments for both $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ were performed on the basis of

the oxidation state of the Sb^{125} at the beginning of the experiment. The data of Table 18 indicate that adsorption of Sb^{125} on Pyrex reaches a maximum in the pH region 7.9 to 9.2. A plot of the data would yield a bell-shaped curve with a peak at a pH of about 8.7. No essential difference was observed between the behavior of $\text{Sb}^{125}(\text{III})$ and of $\text{Sb}^{125}(\text{V})$ as was quite often the case for adsorption and coprecipitation studies in this work.

TABLE 18

Adsorption of Sb^{125} on Pyrex as Function of pH^a

pH	Adsorption, %	
	$\text{Sb}^{125}(\text{III})$	$\text{Sb}^{125}(\text{V})$
4.0	-	2
4.2	-	2
4.4	-	5
5.5	-	1
6.0	6	3, 4
6.2	-	9
6.6	-	6
6.8	8	-
7.1	-	4
7.5	-	7
7.9	-	12
8.3	14	10
8.4	-	9
8.6	6	14
8.8	8	9
9.2	12	-
9.3	-	3, 5
10.6	4	3
10.7	-	5, 12
11.5	-	1, 2
11.6	3	-
11.8	-	0

a. NaOH solutions; stirring time = 1 hour; temperature = 29.2°; volume = 10 ml.

The ordinary state of the atmosphere is such that the
 experiment. The total amount of water vapor in the air
 of 60% of the total weight of the air. A rise of temperature
 a peak at a point which is not necessarily the same as
 observed when the air is cooled. It is also observed
 as was also shown in the case of the other experiments
 tion studies in this case.

Table 1. Absorption of water vapor in the atmosphere.

Temperature (°C)	Relative Humidity (%)	Water Vapor (g/m³)
12.8	100	10.0
11.5	100	9.5
11.0	100	9.0
10.7	100	8.8
10.0	100	8.0
9.0	100	7.0
8.0	100	6.0
7.0	100	5.0
6.0	100	4.0
5.0	100	3.0
4.0	100	2.0
3.0	100	1.5
2.0	100	1.0
1.0	100	0.8
0.0	100	0.6
-1.0	100	0.4
-2.0	100	0.3
-3.0	100	0.2
-4.0	100	0.15
-5.0	100	0.1
-6.0	100	0.08
-7.0	100	0.06
-8.0	100	0.04
-9.0	100	0.03
-10.0	100	0.02
-11.0	100	0.015
-12.0	100	0.01

Coprecipitation of Sb^{125} with Ferric Hydroxide

Because ferric hydroxide is known to carry many radioactive species⁽⁸⁾, the coprecipitation of Sb^{125} with ferric hydroxide was studied as a function of pH. A solution containing 1 mg. of ferric ion per ml. of 0.1 N hydrochloric acid was prepared. To 5 ml. of this solution containing either $\text{Sb}^{125}(\text{III})$ or $\text{Sb}^{125}(\text{V})$ of known radioactivity was added 5 ml. of sodium hydroxide solution. After stirring 5 minutes and centrifuging 10 minutes, an aliquot was counted for radioactivity and a portion was used for a pH determination. The results are summarized in Table 19. Essentially quantitative coprecipitation occurred from a pH of 5.4 to a pH of 9.3. The incomplete coprecipitation of Sb^{125} at higher pH values is probably due to the amphoteric nature of antimony. Again, the results for the two oxidation states are similar.

Adsorption, Centrifugation,

Filtration, and Coprecipitation of Sb^{125}

Although antimony trisulfide is relatively soluble in water (1.7×10^{-6} gm/ml)⁽¹⁰⁾, some experiments were performed in which hydrogen sulfide was added to hydrochloric acid solutions of carrier-free Sb^{125} was removed from solution. The removal of Sb^{125} was probably due to radiocolloidal formation. Table 20 contains the results of experiments performed by passing hydrogen sulfide into 10 ml. of 0.05 N hydrochloric acid solutions of Sb^{125} for 10 minutes. Some

TABLE 19

Coprecipitation of Sb^{125} with $\text{Fe}(\text{OH})_3$
as Function of pH^a

<u>pH</u>	<u>Coprecipitation, %</u>	
	<u>$\text{Sb}^{125}(\text{III})$</u>	<u>$\text{Sb}^{125}(\text{V})$</u>
2.6	18	-
4.0	-	88
5.4	99	-
7.0	99	-
7.2	-	99
8.7	-	97
9.3	99	-
11.1	-	64, 70
11.3	68	-

a. pH adjusted with NaOH; stirring time = 5 min; centrifugation time = 10 min; temperature = 29.2° ; volume = 10 ml; 5 mg. of Fe^{+++} in each sample.

solutions contained a 1-inch diameter filter paper (either Whatman No. 50 or a millipore filter, type PH) which had been cut into 50 pieces and was present to test the adsorption of Sb^{125} . After addition of hydrogen sulfide the sample, contained in a 15-ml. Pyrex centrifuge cone, was then either centrifuged for 10 minutes or filtered through either a Whatman No. 50 or a type PH millipore filter.

The oxidation state of Sb^{125} for the experiments in Tables 20 and 21 was not determined at the time of the experiments but was inferred from the treatment of the Sb^{125} solutions. No difference in the behavior of the of the two oxidation states is noted as is also the case for similar experiments recorded in Table 22. The data of

TABLE I

Reaction of ...

Sample
1	...	5.5
2	...	4.0
3	...	5.4
4	...	7.3
5	...	7.2
6	...	8.7
7	...	9.3
8	...	11.1
9	...	11.3

... adjusted with ...

... contained a ...

... No. 30 or ...

... into 50 ...

... of ...

... in a ...

... for 10 ...

... No. 30 or ...

... The oxidation ...

... Table 50 and 51 ...

... experiments ...

... solutions ...

... of the two ...

... for similar ...

TABLE 20

Adsorption and Filtration of Sb^{125} from
Hydrogen Sulfide-Hydrochloric Acid Solutions^a

<u>Oxidation state</u> <u>of Sb^{125}</u>	<u>Type of</u> <u>filter</u>	<u>Total Sb^{125}</u> <u>Adsorbed, %</u>	<u>Residual Sb^{125}</u> <u>in solution</u> <u>retained by filter, %</u>
III	none	35, 36, 39, 40 41, 42, 48, 52	- -
V	none	38, 39, 42, 46 46	- -
III	Whatman No. 50 ^b	74, 78, 80, 83	-
V	Whatman No. 50 ^b	67, 81	-
III	Millipore Filter ^b	57, 67	-
V	Millipore Filter ^b	49	-
III	Whatman No. 50 ^c	-	40, 45, 47, 48
V	Whatman No. 50 ^c	-	42, 49
III	Millipore Filter ^c	-	78, 98
V	Millipore Filter ^c	-	99

a. Hydrochloric acid concentration = 0.05 N; volume = 10 ml.; H_2S was added for 10 minutes.

b. These samples contained bits of filter paper during the addition of H_2S and subsequent centrifugation.

c. These samples were not centrifuged.

Table 20 indicate that removal of Sb^{125} from solution is largely by adsorption when filtered through Whatman No. 50 filter paper but is largely by filtration when filtered through a millipore filter, type PH. The pore size of this type millipore filter is 0.3 microns and since very little Sb^{125} filters through the paper, one may conclude that the

radiocolloidal particles are somewhat larger than 0.3 microns if the filtration is purely mechanical.

Table 21 contains the results of experiments in which the per cent $\text{Sb}^{125}(\text{V})$ removed from a hydrogen sulfide-hydrochloric acid solution was determined as a function of centrifugation time. The experiments were performed as before by passing hydrogen sulfide for 10 minutes into 10 ml. of 0.09 N hydrochloric acid solutions of $\text{Sb}^{125}(\text{V})$ in 15-ml. Pyrex centrifuge cones and then centrifuging for various lengths of time. Due to the long centrifuging time about one-half of the solution evaporated in experiments 9 and 10; this loss by evaporation was avoided in the remaining experiments by covering the centrifuge cones with parafilm. For centrifugation times of 1 hour or less the amount of Sb^{125} removed from solution was not increased by covering the tubes with parafilm. Although most of the Sb^{125} could be removed from solution by centrifuging for 6 hours, very little of the adsorbed activity would dissolve in either water or perchloric acid. For instance, only 25% would dissolve in 70% perchloric acid which was heated at 200° for 1 hour.

The coprecipitation of Sb^{125} with various insoluble sulfides was investigated. To 5 ml. of 4 N hydrochloric acid in Pyrex tubes, containing 5 mg. of $\text{Bi}(\text{III})$, $\text{Cu}(\text{II})$, $\text{As}(\text{III})$, or $\text{As}(\text{V})$ and either $\text{Sb}^{125}(\text{III})$ or $\text{Sb}^{125}(\text{V})$, was added 5 ml. of hydrogen sulfide-saturated water. The tubes were closed and the samples stirred at 29.2° for 5 minutes

Table 25 reports the results of the experiments
conducted by heating hydroxy acids and their
pyrene carboxylic esters and their carboxylic
lengths of time. The carboxylic acids
one-half of the relative rate of evaporation
this loss by evaporation was due to the
results by covering the carboxylic acids
centrifugation times of 1 hour and 2 hours
removed from solution and the amount of
tubes with parallel. Although the amount
removed from solution by centrifugation
little of the adsorbed acid. The amount
water or hydroxy acids. For example, only 0.1%
dissolve in 10% hydroxy acid and 0.1%
for 1 hour.

The sorption of hydroxy acids and their
esters was investigated. The results are
given in Table 26, containing the results
As(III), or As(V) and other acids. The
added 5 ml. of hydrogen peroxide solution
were closed and the samples were analyzed

TABLE 21

Removal of $\text{Sb}^{125}(\text{V})$ from Hydrogen
Sulfide-Hydrochloric Acid
Solutions as a Function of
Centrifugation Time^a

<u>Experiment</u>	<u>Centrifugation time,</u> <u>min.</u>	<u>Sb^{125} removed</u> <u>from solution, %</u>
1	0	16
2	0	20
3	10	46
4	10	46
5	60	55
6	60	59
7	60	63
8	60	74
9 ^b	360	24
10 ^b	360	32
11 ^c	240	86
12 ^c	240	89
13 ^c	360	92
14 ^c	360	97

a. Volume = 10 ml. of 0.09 N hydrochloric acid, H_2S was added for 10 min.

b. One-half of solution was lost during centrifugation due to evaporation.

c. Centrifuge cone was covered with parafilm during centrifugation.

TABLE I

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Run	Time (min)	Temperature (°C)	Pressure (mm Hg)
1	10	100	10
2	20	100	10
3	30	100	10
4	40	100	10
5	50	100	10
6	60	100	10
7	70	100	10
8	80	100	10
9	90	100	10
10	100	100	10
11	110	100	10
12	120	100	10
13	130	100	10
14	140	100	10
15	150	100	10

a. Volume = 10 ml. of 10% solution of sodium acetate in water.
 b. The rate of evolution of gas was measured by a gas syringe.
 c. The pressure was measured by a manometer.

and then centrifuged for 10 minutes. In seven of the samples, 100% of the Sb^{125} was carried with the precipitate. In the eighth sample [As(V) and $\text{Sb}^{125}\text{(III)}$], 91% was carried. Only an estimated 5% of the As(V) precipitated during the experiment.

Adsorption, centrifugation, and filtration measurements were made from four different solutions for both $\text{Sb}^{125}\text{(III)}$ and $\text{Sb}^{125}\text{(V)}$. The solutions were (1) 5 ml. of 6 N hydrochloric acid and 5 ml. of Oxorbent, (2) 5 ml. of 4 N hydrochloric acid and 5 ml. of hydrogen sulfide-saturated water, (3) 5 ml. of 4 N hydrochloric acid containing 5 mg. of Cd(II) and 5 ml. of hydrogen sulfide-saturated water, and (4) 10 ml. of 0.1 N sodium chloride solution. The solutions, containing either $\text{Sb}^{125}\text{(III)}$ or $\text{Sb}^{125}\text{(V)}$, were stirred for 1 hour in a closed Pyrex tube at 29.2° , transferred to a centrifuge cone and centrifuged for 10 minutes, and finally filtered through Whatman 42 filter paper. The Sb^{125} removed by each step was determined and the results are recorded in Table 22. Although no visible cadmium sulfide precipitated from the solution containing cadmium, it is interesting that considerably more Sb^{125} was removed from solution than when no cadmium was present. No significant difference is noted between $\text{Sb}^{125}\text{(III)}$ and $\text{Sb}^{125}\text{(V)}$ except, perhaps, for the sodium chloride solution.

No $\text{Sb}^{125}\text{(V)}$ and only 2% of the $\text{Sb}^{125}\text{(III)}$ coprecipitated with silver chloride from a solution 0.1 N in sodium chloride containing 5 mg. of silver ion. The solution was stirred

and than centrifuged for 10 minutes. The supernatant was
evaporated, 100% of the ^{135}I was recovered in the
in the original solvent. The ^{135}I was then
yield. Only an insignificant amount of ^{135}I was found in
the extractant.

Absorption coefficients for ^{135}I in various
solvents were determined. The absorption coefficients
and $\text{sp}^{135}\text{I}(\text{V})$. The absorption coefficients for ^{135}I in
chloroform and $\text{sp}^{135}\text{I}(\text{V})$ were determined.

(3) 5 ml. of 5% potassium iodide solution and 5 ml.
of 5% sodium chloride solution were added to 5 ml.
of 5% potassium iodide solution and 5 ml. of 5% sodium
chloride solution and 5 ml. of 5% potassium iodide
solution.

(4) 10 ml. of 0.1% sodium chloride solution and 10 ml.
of 0.1% potassium iodide solution were added to 10 ml.
of 0.1% sodium chloride solution and 10 ml. of 0.1%
potassium iodide solution.

1 hour in a closed system. The solution was then
centrifuged and the supernatant was analyzed for ^{135}I .
The results are shown in Table 2. The ^{135}I was
detected through absorption in the supernatant.

by each case was determined and the results are shown
Table 2. Although no visible change was observed in
from the solution containing ^{135}I and ^{135}I was
considerably more ^{135}I was recovered than when
no solution was present.

between $\text{sp}^{135}\text{I}(\text{III})$ and $\text{sp}^{135}\text{I}(\text{V})$ was determined.
sodium chloride solution.

So $\text{sp}^{135}\text{I}(\text{V})$ and $\text{sp}^{135}\text{I}(\text{III})$ were determined
with silver chloride. The results are shown in Table 2.
containing 5 ml. of 5% potassium iodide solution.

TABLE 22

Adsorption, Centrifugation, and Filtration
of Sb^{125} from Various Solutions^a

Solution	Oxidation state of Sb^{125}	Sb removed, %			Sb not removed, %
		Adsorption	Centrif.	Filtrat.	
Oxorbent in 3 N HCl	III	28	26	13	33
	V	18	18	38	26
H_2S in 2 N HCl	III	10	10	13	67
	V	11	10	19	60
H_2S & Ca^{++} in 2 N HCl	III	14	31	33	22
	V	17	24	29	30
0.1 N NaCl in H_2O	III	3	2	17	78
	V	0	0	0	100

a. Volume = 10 ml.; temperature = 29.2° ; stirring time = 1 hour; centrifugation time = 10 min.; Whatman 42 filter paper used for filtration.

5 minutes at 29.2° and centrifuged 10 minutes. On the other hand, 100% of both $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ coprecipitated with arsenic metal when 5 ml. of Oxorbent was added to 5 ml. of 6 N hydrochloric acid containing 4 mg. of As(III) and the sample was stirred 1 hour at 29.2° and centrifuged 10 minutes. No difference between $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ was noted in electrochemical deposition on copper powder; from 10 ml. of 6 N hydrochloric acid mixed with 10 mg. of copper powder, 55% and 54%, respectively, of $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ deposited on the copper after stirring 1 hour at 29.2° and centrifuging 10 minutes.

Association of ...
 of ...

 Solution

Label	Solution
...	0.1 M HCl in H ₂ O
...	H ₂ S & Ca ⁺⁺ in 2 N HCl
...	H ₂ S in 2 N HCl
...	0.1 M HCl in H ₂ O

a. Volume = 10 ml.
 centrifugation time = 5 min.
 filtration.

5 minutes at 2500 rpm and centrifuged 10 minutes. In the other
 hand, 100% of both ...
 with stable ...
 of 5 N hydrochloric acid ...
 the sample was stirred ...
 minutes. No difference ...
 noted in electrochemical ...
 10 ml. of 5 N hydrochloric acid ...
 powder, 5% and ...
 deposited on the ...
 centrifuging 10 minutes.

Antimonic oxide precipitates from hot concentrated nitric acid when antimony is present in conventional concentrations. However no evidence could be obtained for a similar behavior for carrier-free Sb^{125} although several experiments were tried. For instance, 10 ml. of concentrated nitric acid and 1 drop of $\text{Sb}^{125}(\text{V})$ in 2 N hydrochloric acid were heated on the steam bath for 1 hour and centrifuged 10 minutes. No radioactivity was removed from solution.

Removal of Antimony(V) from Solution as a Function of Antimony Concentration

A set of experiments using Oxorbent to precipitate antimony metal as a function of antimony(V) concentration was performed. To 5 ml. of 6 N hydrochloric acid containing a known concentration of antimony(V) was added 5 ml. of Oxorbent. The solution was stirred at 29.2° for a certain length of time and then filtered through Whatman 42 filter paper. The results are recorded in Table 23. Although in one instance only 65% of the antimony was removed from a 10^{-6} M solution and in another instance 82% was removed from a carrier-free solution, these results, in general, indicate that the concentration of carrier-free Sb^{125} in these solutions was less than 10^{-7} M. This finding is in agreement with the previous conclusion that the concentration of the carrier-free Sb^{125} was 10^{-8} to 10^{-10} M.

Resin Studies with Sb^{125}

In the process for preparing carrier-free Sb^{125} , Dowex-1

Anticatalytic effect of the...
where said when subjected to...
concentration, however, no...
analysis reported for...
experiment was...
nitric acid and I...
was stated on the...
to nitrous. The...
Removal of...
at a...
A set of...
antimony metal as a...
was performed. To...
a known concentration of...
Oxidant. The...
louch of...
paper. The...
one instance only...
10⁻⁵ M...
a carrier-free...
that the...
tion was less than...
with the...
carrier-free...
In the process...

TABLE 23

Removal of Antimony(V) from Solution
as a Function of Antimony Concentration^a

<u>Antimony concentration, M</u>	<u>Stirring time, min.</u>	<u>Antimony removed from solution, %</u>
10 ⁻⁴	30	95
10 ⁻⁴	60	93
10 ⁻⁵	30	94
10 ⁻⁵	60	93
10 ⁻⁶	30	65
10 ⁻⁶	60	86
10 ⁻⁷	30	81
10 ⁻⁷	60	78
C.F. ^b	0	52, 58
C.F.	30	50, 82
C.F.	60	50, 62

a. 5 ml. of Oxorbent; total volume = 10 ml. which was 3 N in HCl; temperature = 29.2°; Sb was removed from solution by filtration through Whatman 42 filter paper.

b. Carrier-free

resin was used for removing copper from Sb¹²⁵. The Sb¹²⁵ eventually eluted from the resin column was in the higher oxidation state. Some experiments were performed to help identify the oxidation state of the Sb¹²⁵ during the preparation procedure. In this procedure after removing the electrochemically-deposited Sb¹²⁵ from the copper surface with nitric acid, the solution was boiled with excess

Removal of Nickel (II) from solution
 as a function of the concentration of the

Concentration of Ni ²⁺ , M	Concentration of Ni ²⁺ , M	Concentration of Ni ²⁺ , M
10 ⁻⁴	10 ⁻⁴	10 ⁻⁴
10 ⁻⁵	10 ⁻⁵	10 ⁻⁵
10 ⁻⁶	10 ⁻⁶	10 ⁻⁶
10 ⁻⁷	10 ⁻⁷	10 ⁻⁷
10 ⁻⁸	10 ⁻⁸	10 ⁻⁸
10 ⁻⁹	10 ⁻⁹	10 ⁻⁹
10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰
10 ⁻¹¹	10 ⁻¹¹	10 ⁻¹¹
10 ⁻¹²	10 ⁻¹²	10 ⁻¹²
10 ⁻¹³	10 ⁻¹³	10 ⁻¹³
10 ⁻¹⁴	10 ⁻¹⁴	10 ⁻¹⁴
10 ⁻¹⁵	10 ⁻¹⁵	10 ⁻¹⁵
10 ⁻¹⁶	10 ⁻¹⁶	10 ⁻¹⁶
10 ⁻¹⁷	10 ⁻¹⁷	10 ⁻¹⁷
10 ⁻¹⁸	10 ⁻¹⁸	10 ⁻¹⁸
10 ⁻¹⁹	10 ⁻¹⁹	10 ⁻¹⁹
10 ⁻²⁰	10 ⁻²⁰	10 ⁻²⁰

Fig. 2. Dependence of the concentration of Ni²⁺ on the concentration of the reagent in the solution. The concentration of Ni²⁺ is expressed in M. The concentration of the reagent is expressed in M. The concentration of the reagent is expressed in M.

It is seen from the graph that the concentration of Ni²⁺ decreases as the concentration of the reagent increases. This is due to the fact that the reagent reacts with Ni²⁺ to form a complex. The concentration of Ni²⁺ is expressed in M. The concentration of the reagent is expressed in M.

hydrochloric acid to destroy the nitric acid. Inasmuch as reduction of $\text{Sb}^{125}(\text{V})$ occurs in boiling hydrochloric acid even after addition of chlorine or bromine, it was felt that the Sb^{125} would be in the lower oxidation state after boiling the nitric acid-hydrochloric acid solution. However a different behavior was observed. When a solution of $\text{Sb}^{125}(\text{V})$ in 10 ml. of concentrated nitric acid and 50 ml. of concentrated hydrochloric acid was boiled to a volume of 3 ml., no reduction of the antimony occurred.

A Dowex-1 resin column of about 2 ml. volume (5 cm. length and 7 mm. i.d.) was prepared. On the column was placed 1 ml. of 6 N hydrochloric acid solution containing $\text{Sb}^{125}(\text{III})$, $\text{Sb}^{125}(\text{V})$, or $\text{Sb}^{125}(\text{V})$ with a trace of nitric acid. The trace of nitric acid was the residual nitric acid remaining in solutions of boiled hydrochloric acid as described in the previous paragraph. The column was then washed with 10 ml. portions of various eluting agents as indicated in Table 24 and the amount of Sb^{125} eluted was noted. On testing the oxidation state of the eluted Sb^{125} , it was found that there was no significant change from the oxidation state placed on the column.

The results of Table 24 indicate that the Sb^{125} is in the higher oxidation state throughout the preparation procedure after the time it is dissolved from the copper surface by nitric acid. The big difference in the behavior of $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ seems to be that water elutes a considerable portion of $\text{Sb}^{125}(\text{III})$, whereas a much smaller

hydrochloric acid to which was added a small amount of
reduction of $Sp^{125}(V)$ (Table 1) and the amount of
even after addition of a small amount of sodium
that the Sp^{125} was in the form of a precipitate
forming the strata of a 3-4 week period of
over a 24-hour period. The amount of $Sp^{125}(V)$ in 10 ml. of
 $Sp^{125}(V)$ in 10 ml. of concentrated hydrochloric acid
of 3 ml., no reduction was observed during the
A lower-1 resin column was used for the separation of
length and 7 ml. 1.1% sodium hydroxide solution was
placed 3 ml. of 2% sodium hydroxide solution was added
 $Sp^{125}(V)$, $Sp^{125}(VI)$, and $Sp^{125}(VII)$ were separated
acid. The trace of nitric acid and sodium nitrate
acid remaining in solution was removed by washing
described in the previous section. The amount of
washed with 10 ml. portions of 2% sodium hydroxide
indicated in Table 2 and the results are given in
noted. On testing the residue which was left
it was found that there was no significant amount of
oxidation was placed on the column.
The results of Table 2 are given in Table 2 and
the higher oxidation state products were separated
either the size of the particles or the amount of
by nitric acid. The slight amount of sodium nitrate
 $Sp^{125}(V)$ and $Sp^{125}(VI)$ were separated from
considerable portion of the $Sp^{125}(V)$ and $Sp^{125}(VI)$

TABLE 24

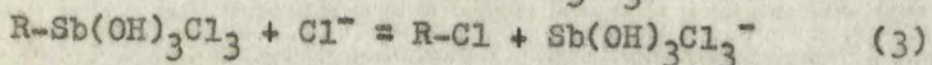
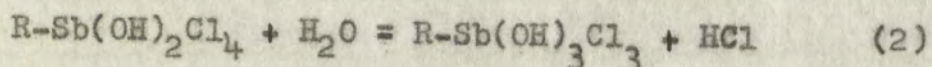
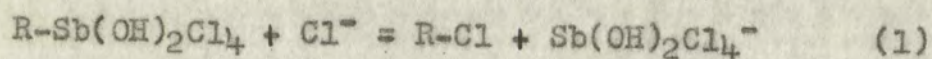
Elution of Sb^{125} from Dowex-1 Resin

<u>Experiment</u>	<u>Oxidation state of Sb^{125}</u>	<u>Eluant (10 ml portions)</u>	<u>Sb^{125} eluted, %</u>
1	III	6 N HCl	1
		2 N HCl	1
		H_2O	54
2	III	6 N HCl	0
		H_2O	82
		2 N HCl	3
3	III	6 N HCl	0
		H_2O	85
		2 N HCl	9
4	V	6 N HCl	0
		H_2O	22
		2 N HCl	78
5	V	6 N HCl	0
		H_2O	28
		2 N HCl	72
6	V	6 N HCl	0
		H_2O	32
		2 N HCl	67
7	V with trace of HNO_3	6 N HCl	0
		H_2O	4
		2 N HCl	91
8	V with trace of HNO_3	6 N HCl	2
		H_2O	12
		2 N HCl	47
9	V with trace of HNO_3	6 N HCl	0
		H_2O	13
		2 N HCl	83
10	V with trace of HNO_3	6 N HCl	0
		H_2O	19
		2 N HCl	81
11	V with trace of HNO_3	6 N HCl	0
		2 N HCl	10
		H_2O	2
		2 N HCl	88

Experiment	Time	Temperature	Pressure	Volume	Mass	Notes
1	10:00	20.0	101.3	100.0	100.0	Initial conditions
2	10:15	20.5	101.5	100.5	100.5	Small increase in T and P
3	10:30	21.0	101.8	101.0	101.0	Continuing to rise
4	10:45	21.5	102.1	101.5	101.5	Steady increase
5	11:00	22.0	102.4	102.0	102.0	Approaching 22°C
6	11:15	22.5	102.7	102.5	102.5	Temperature 22.5°C
7	11:30	23.0	103.0	103.0	103.0	Temperature 23.0°C
8	11:45	23.5	103.3	103.5	103.5	Temperature 23.5°C
9	12:00	24.0	103.6	104.0	104.0	Temperature 24.0°C
10	12:15	24.5	103.9	104.5	104.5	Temperature 24.5°C
11	12:30	25.0	104.2	105.0	105.0	Temperature 25.0°C

portion of $\text{Sb}^{125}(\text{V})$ is eluted with water particularly if a trace of nitric acid is present.

There is again (see p. 25) the unusual behavior of $\text{Sb}^{125}(\text{V})$ in that its effective elution by 2 N hydrochloric acid only occurred after the resin column had been treated with water. In order to discuss this phenomenon it is noted that Neumann⁽¹⁸⁾ postulates that the predominant form of antimony in 6 N hydrochloric acid is $\text{Sb}(\text{OH})_2\text{Cl}_4^-$ and that $\text{Sb}(\text{OH})_3\text{Cl}_3^-$ or more hydrolyzed species are the most important in lower acid concentrations. The ion exchange resin reactions might be represented as follows,



where R represents the resin. It has been experimentally observed (see pp. 14-19, 21) that the affinity of Dowex-1 resin for antimony(V) decreases rapidly from 6 N to 2 N hydrochloric acid and that carrier antimony(V) is readily eluted from Dowex-1 resin by 2 N hydrochloric acid. Therefore the equilibrium for reaction (1) lies to the left, whereas for reaction (3) it lies to the right. Also, it is possible that the species, $\text{R-Sb}(\text{OH})_2\text{Cl}_4$, is located at a relatively few preferred sites on the resin at which reaction (2) does not readily occur in 2 N hydrochloric acid. Hence, in order to remove antimony(V) from these preferred sites, it would be necessary to convert the antimony species to the more easily eluted form by adding water.

portion of $2p^{1/2}(V)$ is about 10% of the total
trace of nitric acid is present.

There is also a small amount of $2p^{1/2}(V)$
 $2p^{1/2}(V)$ in that the $2p^{1/2}(V)$ is about 10% of the total

acid only occurred. In other words, the $2p^{1/2}(V)$ is about 10% of the total
with water. In other words, the $2p^{1/2}(V)$ is about 10% of the total

that is, the $2p^{1/2}(V)$ is about 10% of the total
antimony in a 5% solution with a $2p^{1/2}(V)$ of 10%.

$2p^{1/2}(V)$ or more is present in the water. The $2p^{1/2}(V)$ is about 10% of the total
that is lower acid concentration. The $2p^{1/2}(V)$ is about 10% of the total

reactions might be expected to be
 $2p^{1/2}(V) + 2p^{1/2}(V) \rightarrow 2p^{1/2}(V) + 2p^{1/2}(V)$ (1)

$2p^{1/2}(V) + 2p^{1/2}(V) \rightarrow 2p^{1/2}(V) + 2p^{1/2}(V)$ (2)

where $2p^{1/2}(V)$ represents the $2p^{1/2}(V)$ in the water. The $2p^{1/2}(V)$ is about 10% of the total
observed (see $2p^{1/2}(V)$).

reactions for antimony(V) are expected to be
hydrochloric acid and lead. The $2p^{1/2}(V)$ is about 10% of the total

eluted from Dowex-1 resin. The $2p^{1/2}(V)$ is about 10% of the total
for the equilibrium between the $2p^{1/2}(V)$ and the $2p^{1/2}(V)$.

whereas for reaction (2) the $2p^{1/2}(V)$ is about 10% of the total
is possible that the $2p^{1/2}(V)$ is about 10% of the total

a relatively low $2p^{1/2}(V)$ is about 10% of the total
reaction (2) does not occur. The $2p^{1/2}(V)$ is about 10% of the total

acid. Hence, in order to obtain a $2p^{1/2}(V)$ of 10% of the total
preferred sites, it is necessary to have a $2p^{1/2}(V)$ of 10% of the total
many species to the $2p^{1/2}(V)$ is about 10% of the total.

Thus, assuming this hypothesis is true, one concludes that the number of preferred resin sites is sufficient to contain essentially all the carrier-free $\text{Sb}^{125}(\text{V})$. This hypothesis then would explain this apparent difference between the behavior of carrier antimony(V) and that of carrier-free $\text{Sb}^{125}(\text{V})$.

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VIII. SUMMARY

Solutions of carrier-free Sb^{125} in hydrochloric, sulfuric, and perchloric acids and in water were prepared, and some observations were made concerning the chemical behavior of Sb^{125} in these solutions. These observations consisted of determining the stability of $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ under various conditions, the factors that cause oxidation of $\text{Sb}^{125}(\text{III})$ and reduction of $\text{Sb}^{125}(\text{V})$, the extent of adsorption and coprecipitation of Sb^{125} from different solutions and with different substances, and the relationship between the behavior of carrier-free Sb^{125} and the behavior of antimony at conventional concentrations.

Hydrochloric acid solutions of Sb^{125} were prepared by electrochemically depositing Sb^{125} on copper from a 6 N hydrochloric acid solution containing neutron-irradiated tin, dissolving the Sb^{125} in nitric acid, and finally separating the Sb^{125} from copper by use of Dowex-1 anion exchange resin. An overall yield of greater than 80% of the Sb^{125} in the irradiated tin was obtained from this procedure. Hydrochloric acid solutions of $\text{Sb}^{125}(\text{V})$ were prepared directly by this method; $\text{Sb}^{125}(\text{III})$ was prepared by boiling these solutions in concentrated hydrochloric acid. Other solutions of Sb^{125} were prepared by evaporating the hydrochloric acid, in which the Sb^{125} was dissolved, either under vacuum or with a stream of dry nitrogen and then dissolving the residual Sb^{125} with the desired solvent. From

Solutions of ...
 and some other ...
 behavior of Sp^{125} ...
 consisted of ...
 $Sp^{125}(V)$ under ...
 oxidation of $Sp^{125}(V)$...
 extent of ...
 different ...
 relationship ...
 and the ...
 hydrolysis ...
 electrochemically ...
 hydrolysis ...
 the ...
 separating ...
 exchange ...
 the Sp^{125} ...
 column. Hydrolysis ...
 given directly ...
 boiling ...
 other solutions ...
 hydrolysis ...
 under vacuum ...
 dissolving ...

50% to 95% of the Sb^{125} was recovered in these experiments. When the evaporation occurred from 10 N hydrochloric acid solutions, nearly quantitative yields of $\text{Sb}^{125}(\text{III})$ were obtained. $\text{Sb}^{125}(\text{V})$ was readily obtained by irradiating the solutions of $\text{Sb}^{125}(\text{III})$ with a General Electric H400-A1 mercury lamp.

Distinguishing between $\text{Sb}^{125}(\text{III})$ and $\text{Sb}^{125}(\text{V})$ was accomplished by use of an extraction mixture consisting of 8 ml. of isopropyl ether, 7 ml. of solution 6 N in hydrochloric acid and 2.14 M in magnesium chloride, and 1 ml. of solution 6 N in hydrochloric acid and 0.05 M in both antimony(III) and antimony(V). To this mixture was added 1 ml. of solution containing Sb^{125} ; $\text{Sb}^{125}(\text{V})$ entered the ether phase and $\text{Sb}^{125}(\text{III})$ remained in the aqueous phase.

The stability of the two oxidation states of Sb^{125} was measured in different solutions under various conditions. In general $\text{Sb}^{125}(\text{V})$ was more stable than $\text{Sb}^{125}(\text{III})$. For instance, only in hydrochloric acid in the absence of light and oxygen could $\text{Sb}^{125}(\text{III})$ be maintained without oxidation for a long period, whereas stock solutions of $\text{Sb}^{125}(\text{V})$ in 2 N hydrochloric acid were kept indefinitely without reduction occurring when no special precaution was made to remove light and oxygen. In basic and neutral solutions $\text{Sb}^{125}(\text{III})$ was considerably oxidized within 1 hour even in the absence of light. It appears from the data of the stability experiments that both oxygen and light contribute to the oxidation of $\text{Sb}^{125}(\text{III})$. Reduction of $\text{Sb}^{125}(\text{V})$ occurred mostly in

500 to 950 of the $sp^{125}(III)$...
when the evaporation ...
solutions, ...
obtained, ...
analysis of ...
battery ...
Identification of ...
accumulated ...
5 ml. of ...
chloride ...
of solution ...
analysis ...
1 ml. of ...
other phase ...
The stability ...
measured ...
in general ...
instance, ...
and oxygen ...
for a long ...
2 N hydrochloric ...
then ...
light and ...
was ...
of light. ...
made that ...
of $sp^{125}(III)$...

hydrochloric acid solutions and subsequent experiments demonstrated that this reduction was probably due to chloride; the limited amount of reduction in other solutions may have been due to traces of some reducing impurity.

A specific study of the reduction of $\text{Sb}^{125}(\text{V})$ in hydrochloric acid revealed that the fraction of antimony reduced is increased by increasing the temperature and the hydrochloric acid concentration. Extending this study to carrier amounts of antimony revealed that appreciable reduction does not occur in concentrations above 10^{-4} M, and the study also provided a means of estimating the antimony concentration in the solutions of carrier-free Sb^{125} used in this work. The concentration was estimated in the range of 10^{-8} to 10^{-10} M. Several reducing agents (SO_2 , Sn^{++} , Fe^{++} , and I^-) were used to compare the reduction of carrier-free $\text{Sb}^{125}(\text{V})$ with the reduction of 5×10^{-5} M antimony(V) in various solutions (HCl , H_2SO_4 , and HClO_4). Very little difference in reduction was observed except with sulfur dioxide in hydrochloric acid in which case the carrier-free $\text{Sb}^{125}(\text{V})$ was more effectively reduced. Iodide was observed to be the most effective reducing agent. Chlorine, bromine, and light from the mercury lamp were all very effective in oxidizing $\text{Sb}^{125}(\text{III})$. It was concluded that oxidation by light proceeds indirectly through an unstable intermediate, probably a peroxide.

It was shown that carrier-free Sb^{125} is not lost from acid solutions due to adsorption on the walls of Pyrex

hydrochloric acid and sodium hydroxide solutions
were used to adjust the pH of the solutions to 2.0 and 12.0
the initial amount of the metal ion was 1.0 x 10⁻³ M
been due to the formation of the metal hydroxide
A specific study of the reduction of Cr(VI) to
hydrochloric acid was also carried out in the presence of sodium
reduced in presence of sodium hydroxide and sodium hydroxide
hydrochloric acid solution. It was found that the reduction of
certain amount of sodium hydroxide was necessary for the
reaction to occur in the presence of sodium hydroxide.
The study also showed a marked increase in the rate of
concentration in the presence of sodium hydroxide. This was
in this work. The rate constant was found to be 1.5 x 10⁻³
of 10⁻⁸ to 10⁻¹⁰ M. The rate constant was found to be 1.5 x 10⁻³
Fe²⁺ and Cr(VI) ions. The rate constant was found to be 1.5 x 10⁻³
Cr(VI) ions was found to be 1.5 x 10⁻³ M. The rate constant
in various solutions (0.1 M, 0.2 M, 0.5 M, 1.0 M, 2.0 M, 5.0 M, 10.0 M)
difference in reduction was observed with the
oxide in various solutions. The rate constant was found to be 1.5 x 10⁻³
Cr(VI) ions was found to be 1.5 x 10⁻³ M. The rate constant
to be the most effective in the presence of sodium hydroxide.
and light from the mercury lamp were also used in the study.
oxidizing Cr(VI) ions. It was found that the rate constant
light produced in the presence of sodium hydroxide.
probably a peroxide.
It was found that the rate constant was 1.5 x 10⁻³ M.
acid solutions of sodium hydroxide.

vessels. A maximum of about 14% is adsorbed on Pyrex in 1 hour from solutions of pH 7.9 to 9.2. A decreasing amount is adsorbed as the pH varied from these values. Sb^{125} formed radiocolloids in hydrogen sulfide-hydrochloric acid solutions which could be centrifuged and filtered from solution. Sulfide precipitates quantitatively carried Sb^{125} as also did ferric hydroxide in the middle pH region. Arsenic metal, precipitated by Oxorbent, quantitatively carried Sb^{125} , whereas with no arsenic present the amount of antimony removed from solution by Oxorbent decreased to about 50% as the antimony concentration was reduced to carrier-free Sb^{125} . Essentially no Sb^{125} was carried with silver chloride.

The behavior of carrier-free Sb^{125} on Dowex-1 resin was found to be different from that of carrier antimony in at least one respect. With carrier antimony(V) the distribution coefficient in 2 N hydrochloric acid is quite low, and after placing antimony(V) in 6 N hydrochloric acid on a Dowex-1 resin column, the antimony could be readily eluted with 2 N hydrochloric acid. However when carrier-free Sb^{125} (V) in 6 N hydrochloric acid was added to the column, it was only effectively eluted with 2 N hydrochloric acid after first washing the column with water.

IX. PROPOSALS FOR FURTHER EXPERIMENTS

This section of the dissertation is devoted to suggesting a few of the areas in the dilute solution chemistry of antimony that would be interesting to investigate further. No attempt is made to include a comprehensive listing of all possible areas of research, but, in general, this discussion is concerned with those problems which seem to be pointed out by this work.

Inasmuch as there are various forms of antimony that exist in hydrochloric acid solutions which contain carrier amounts of antimony, it would be of interest to determine if similar species exist in very low concentrations. Discrepancies were observed in attempting to measure the extraction of carrier-free Sb^{125} from hydrochloric acid solutions by isopropyl ether, and similar problems have been observed⁽⁴⁾ in the extraction of carrier amounts of antimony. In the latter case it was suggested that the various forms of antimony(V) have different distribution coefficients and that the history of the antimony is important in determining which forms are present. This behavior might be further elucidated by solvent extraction studies of hydrochloric acid solutions of carrier-free Sb^{125} .

More evidence is needed to confirm the hypothesis advanced for explaining the peculiar behavior of $\text{Sb}^{125}(\text{V})$ on Dowex-1 anion exchange resin. Distribution coefficients for Sb^{125} could be determined by performing batch experiments

This section discusses the mechanism of free-radical polymerization. It begins with the initiation step, where a radical species (R•) attacks a monomer (M) to form a radical intermediate (RM•). The propagation step follows, where the radical intermediate reacts with more monomers to grow the polymer chain. The termination step occurs when two radical chains react, leading to a dead polymer chain. The overall rate of polymerization is dependent on the concentration of the initiator and the monomer.

The rate of polymerization is given by the equation: $R_p = k_p \frac{R_i^{1/2}}{k_t^{1/2}} [M]$. This equation shows that the rate of polymerization is proportional to the square root of the initiator concentration and the monomer concentration. The rate constants k_p and k_t are dependent on the specific monomer and reaction conditions.

The mechanism of free-radical polymerization involves the formation of a radical species, which then reacts with monomers to form a growing radical chain. The rate of polymerization is determined by the concentration of the radical species and the monomer. The overall reaction is exothermic, and the heat of polymerization is a function of the monomer and the degree of substitution.

The polymerization of vinyl monomers is a complex process that involves many steps. The initiation step is the most important, as it determines the rate and the molecular weight of the polymer. The propagation step is the most rapid, and the termination step is the slowest. The overall rate of polymerization is dependent on the concentration of the initiator and the monomer.

as was done for carrier antimony, and elution of $\text{Sb}^{125}(\text{V})$ from the resin column by neutral solutions of a chloride salt could be checked. If indeed there are preferred resin sites as suggested, an estimate of their extent might be obtained by determining the elution of antimony(V) by 2 N hydrochloric acid as a function of antimony concentration. Also it might be possible to occupy these sites with a small amount of some material that is much more strongly adsorbed than is antimony(V) and then to check the elution of $\text{Sb}^{125}(\text{V})$ by 2 N hydrochloric acid.

In the oxidation of $\text{Sb}^{125}(\text{III})$ by irradiation with light, evidence was presented for the formation of an unstable intermediate. A study of this intermediate might be undertaken by employing the oxidation of carrier-free $\text{Sb}^{125}(\text{III})$. The amount of intermediate which is formed may depend on the length of the irradiation, and, in turn, the amount of $\text{Sb}^{125}(\text{III})$ which is oxidized would depend on the amount of intermediate formed. Hence, the oxidation of $\text{Sb}^{125}(\text{III})$ in this manner might be investigated as a possible dosimeter to measure light irradiations. If a similar intermediate is formed on irradiation with subnuclear particles, this oxidation reaction could serve as the basis for a radiation dosimeter.

The phenomenon of the reduction of $\text{Sb}^{125}(\text{V})$ by hydrochloric acid merits further investigation. This reduction should be investigated electrolytically as a function of antimony concentration and cathode potential.

As was shown in the preceding section, the reaction of the
from the mechanism proposed, it is clear that the
this could be shown by the following experiment:
also as stated in the preceding section, the
obtained by heating the mixture of the
hydrochloric acid and the reaction mixture.
Also it might be possible to show that the
amount of some material is less than that
than its anion, by the following experiment:
by 2 N hydrochloric acid.

In the experiment described above, it was shown
that, even when a very small amount of the
stable intermediate, the amount of the
understood by the following experiment:
The amount of the reaction mixture is
length of the reaction mixture is
applied (1 liter) is shown in the
intermediate, the amount of the
this amount of the reaction mixture
to react with the reaction mixture
is formed on the reaction mixture.
oxidation reaction and the reaction
product.

The presence of the reaction mixture (V) in the
chloric acid solution and the reaction mixture
should be the same as the reaction mixture
and any other reaction mixture.

It was observed that a number of precipitates readily carry Sb^{125} , but detailed studies were not made to determine the mechanism by which this carrying occurred. Experiments could be designed to indicate whether the carrying is due to adsorption on the surface of the precipitate or due to incorporation into the crystal lattice of the precipitate and, if the latter, what kind of distribution law is followed.

Vaporization, diffusion, electrical migration, and electrolytic deposition should also be included in future studies involving the dilute solution chemistry of antimony.

It was observed that the rate of reaction was
very low, but it was found that the reaction
the reaction was very slow and it was found
could be obtained by the use of a catalyst
to accelerate the reaction. The reaction
incorporation into the polymer chain was
and in the case of the reaction, it was
Vaporized and the reaction was very slow
electrolytic deposit on the surface of the
studied by the use of the following method.

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