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Kent H. Jones

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DILUTE SOLUTION CHEMISTRY OF ANTIMONY - JONES

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

This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

E F Castetter
DEAN

DATE June 16, 1960

Committee

Milton Kahn
CHAIRMAN

E. L. Martin

J. V. Lewis

Guido H. Daub

J. L. Riebsomer

ACKNOWLEDGMENT

The author expresses his appreciation to Dr. Milton Kahn for helpful suggestions and direction throughout this work.

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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

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 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(2). 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, 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.

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

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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 F 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 F 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 F 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 (Stannochlor 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

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.

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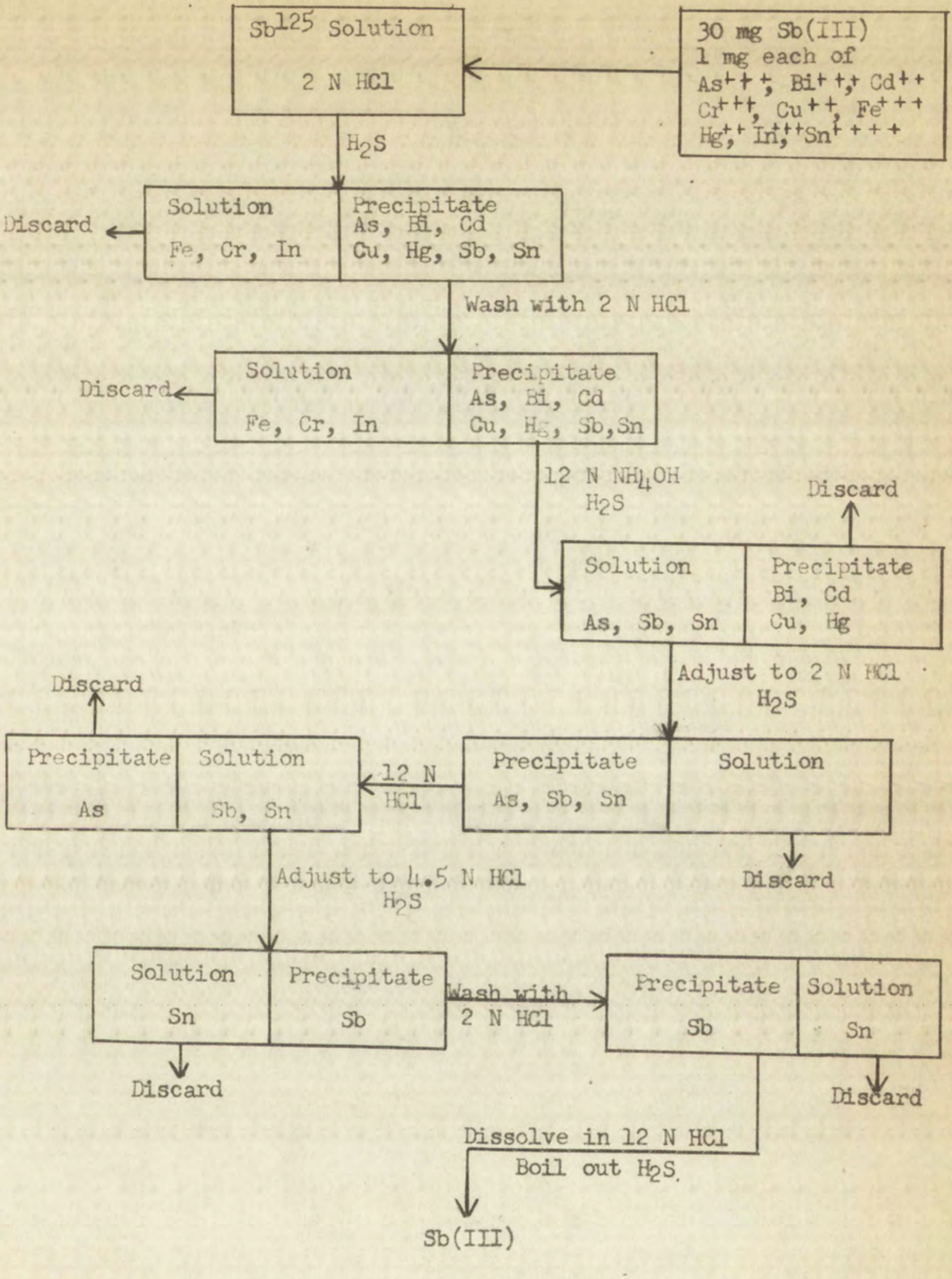
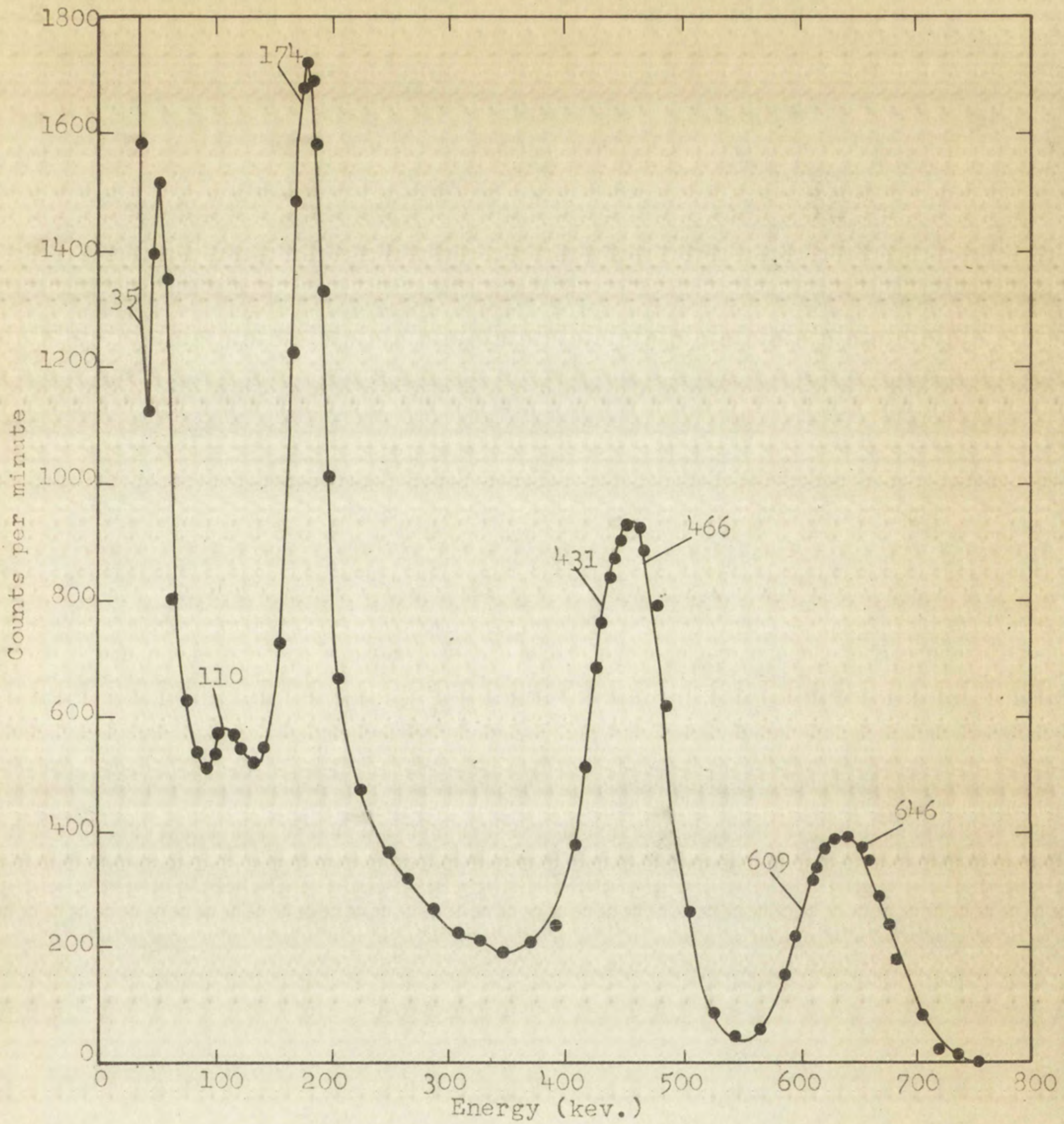


Figure 1

Procedure for Proof of Radioactive Purity of Sb^{125}



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}.

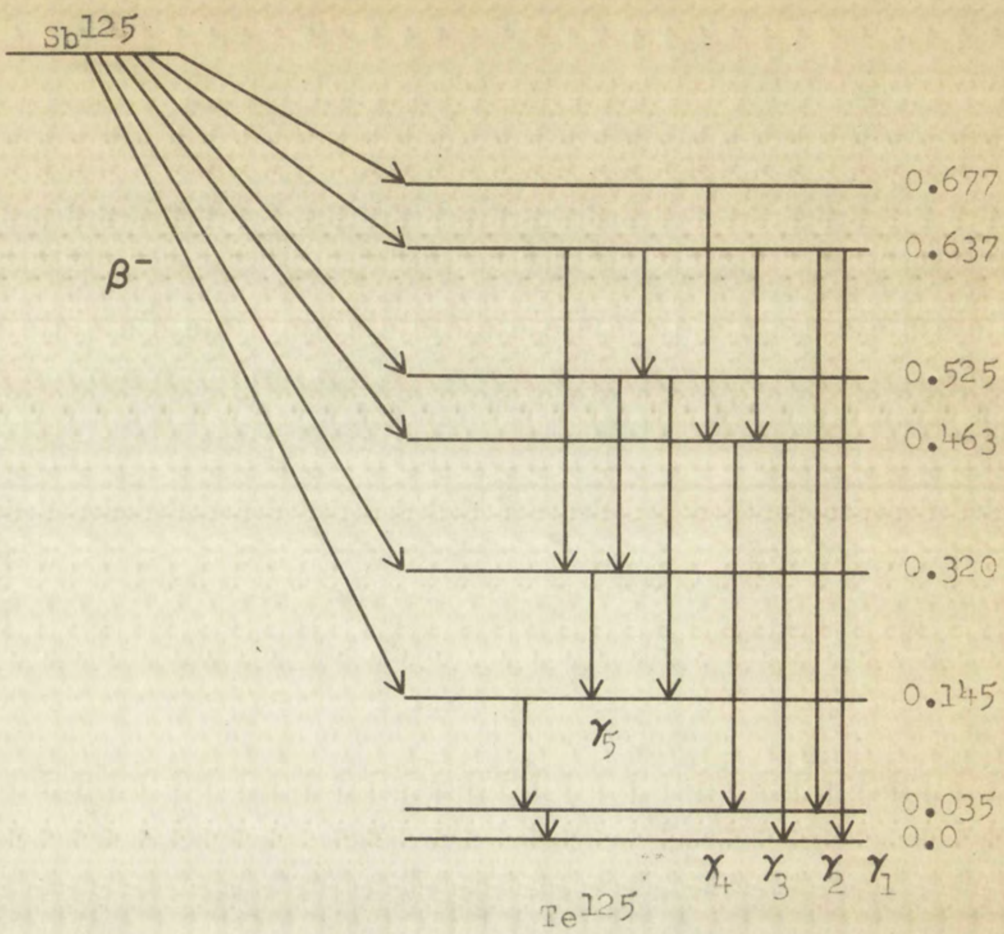
TABLE 1

Activities Resulting from an Assumed Thermal Neutron Irradiation of Tin[a]

Nuclide	Atoms produced	Half-life	Mode of decay
Sn^{113}	2.25×10^9	112d	EC(to In^{113m})
Sn^{117m}	1.55×10^8	14.0d	IT(to stable Sn^{117})
Sn^{119m}	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

*



*Level energies are in Mev.

The relative intensities of the five most prominent gamma radiations are γ_1: 0.23, γ_2: 0.38, γ_3: 0.31, γ_4: 1.0, γ_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 Te^{125m}, 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

Detection [illegible]

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decay of the [illegible]

thallium-activated [illegible] crystal [illegible]

with an RCA 5819 photomultiplier tube. [illegible]

components which [illegible]

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All counting [illegible]

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and reproducible geometry [illegible] sodium iodide

crystal. The [illegible]

each an equal amount of [illegible]

height, counting and [illegible]

within 1% of the [illegible] at the [illegible]

Inherent in all [illegible] is the [illegible]

day daughter [illegible], and [illegible]

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To a two-month [illegible] hydrochloric

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antimony(III) and tellurium(IV). [illegible]

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dioxide was passed into [illegible]

tellurium [illegible] centrifuged, washed with water, and

finally dissolved [illegible]

registered 10 c/m. [illegible] that

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.

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

III. PREPARATION OF CARRIER-FREE SOLUTIONS OF Sb-125

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Bio-Rad Laboratories supply AG1 [illegible] Dowex-1 in chloride form, 100 to 200 mesh, 8% cross-linkage, was 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 [illegible] was 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 for chloride with acidified silver nitrate. The resin was dried for 24 hours in an oven at 40° 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 0.200 or 0.250 gm. of dried resin in 18 mm. Pyrex tubes. The initial concentration of antimony(III) in the reaction solution was 0.00457 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 F hydrochloric acid.

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TABLE 2

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

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

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

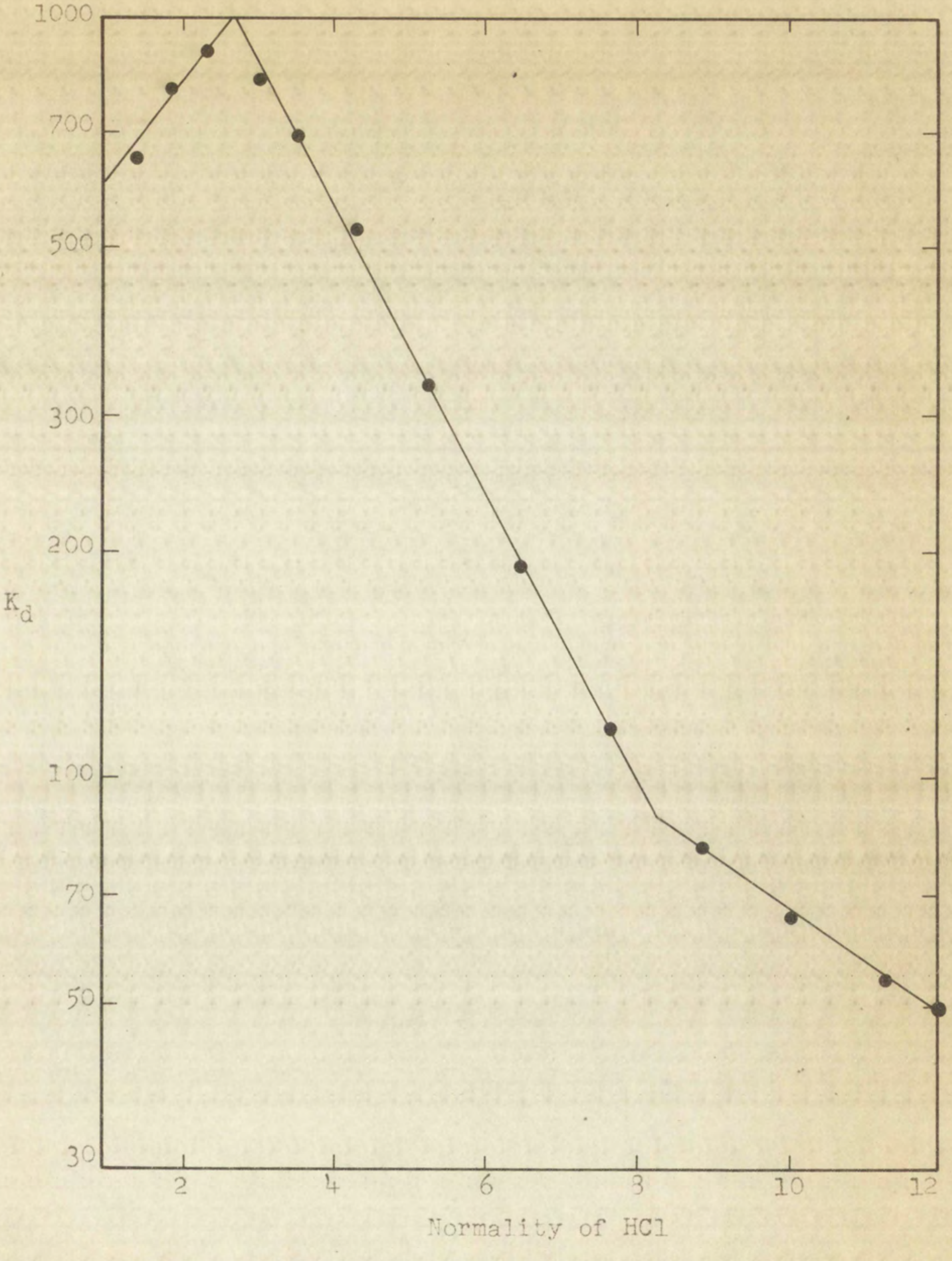

Figure 4

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]

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

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

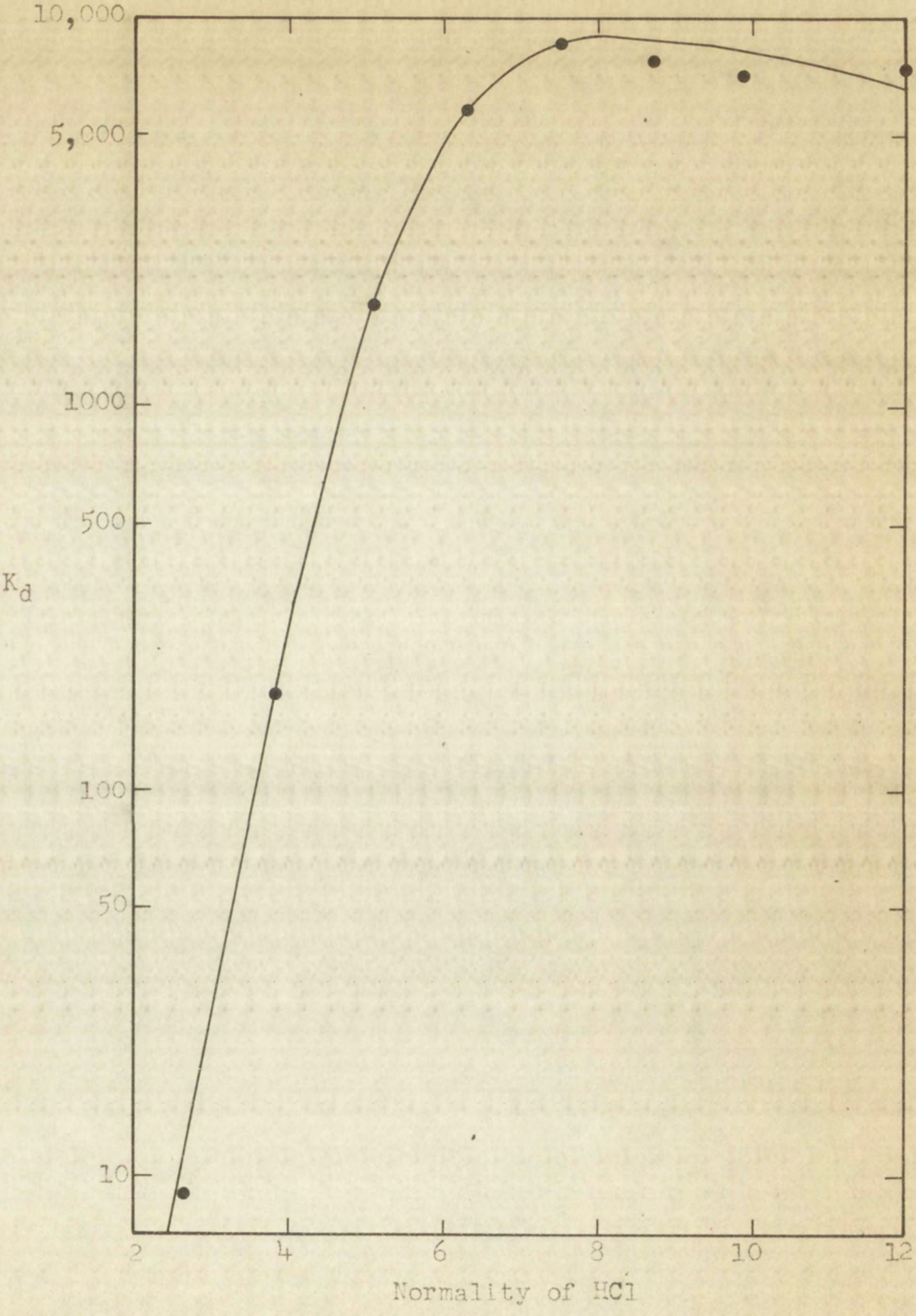

Figure 5

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

An examination [illegible]

that there is [illegible] refinements

on resin which [illegible]

is obtained in the [illegible]

distribution [illegible]

the higher distribution [illegible]

the relatively [illegible]

in solution for [illegible] considered.

For instance with 9.10% [illegible] distribution coef-

ficient is about [illegible] the antimony [illegible]

but if 99% is [illegible] coefficient rises

to nearly 10,000 [illegible]

Subsequent to the completion of [illegible]

similar information [illegible] was

published[14] [illegible]

distribution coefficient curve [illegible]

in shape to the curve in Figure [illegible]

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latter it does not rise above [illegible]

ed information for [illegible] results of

this work.

An Attempt to [illegible]

Neutron-irradiated [illegible]

Considering [illegible] results of a study

by Kraus, Moore, and [illegible] 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/cm^2. 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 concentrated hydrochloric acid using antimony(III) or in 2 to 3 N hydrochloric acid using antimony(V). Other workers(27, 28) 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 2 N hydrochloric acid from Dowex-1 resin with tin(IV) remaining on the column.

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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 4% of the activity appeared in the first 3 ml. of eluate; essentially no activity was removed by 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 are 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 0.13 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 4-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 0.2% 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 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 5½-cm. resin column. The dissolved stannous chloride solution was treated with chlorine and diluted to 25 ml. One 10-ml. aliquot was boiled to expel 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 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 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}, prepared as described above, is not readily removed from Dowex-1 resin by 2 N hydrochloric acid. Because of the difficulty in preparing carrier-free Sb^{125} no further attempt was made to separate it from neutron-irradiated tin through the use of the 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(29) (see p. 5). Their method was investigated by employing a metallic copper spiral of #18 B & S gauge wire of approximately 5 sq. cm. area. This spiral was rotated in 5 ml. of 6 N hydrochloric acid containing a 0.5-gm. sample of neutron-irradiated stannous chloride; the spiral served both as stirrer and reductant. After 30 minutes of stirring the spiral was removed, rinsed in 5 N hydrochloric soln., and then immersed in 6 N nitric acid for 5 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 quantitatively separated 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 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.

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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

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 nitrate. A slight test for chlorides was observed when vacuum was applied for 30 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.

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TABLE 4

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

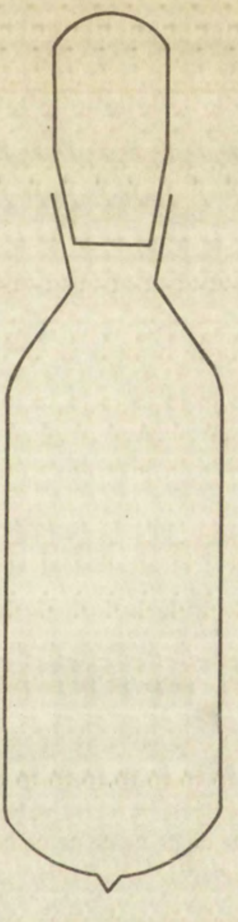
Sample	HCl concentration, (N)	Solvent	Dissolving time, min.	Sb^{125} recovered, %
1	2	2 N H_2SO_4	1	85
2	2	2 N H_2SO_4	60	85
3	2	2 N H_2SO_4	120	85
4	10	2 N H_2SO_4	15	96
5	10	2 N H_2SO_4	15	80
6	10	2 N H_2SO_4	15	75
7	2	2 N $HClO_4$	1	81
8	2	2 N $HClO_4$	60	81
9	2	2 N $HClO_4$	120	70
10	10	2 N $HClO_4$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

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



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 [illegible] with isopropyl ether. The [illegible] extracted into [illegible] and 92%. [illegible] stock solution [illegible] hydro- chloric acid [illegible] chloride was removed by [illegible] chloric acid [illegible] ether. The [illegible] other phase were [illegible] indicate that in [illegible] oxidation state [illegible] dioxide the [illegible] Because the radioactivity [illegible] one of the phases in [illegible] ^{125} [illegible] exclusively in one [illegible] carrier-free [illegible] that reported [illegible]

This system was [illegible] in order to [illegible] ^{125} [illegible] of liquid bromine [illegible] solution in 20 ml [illegible] The solution was [illegible] excess bromine. [illegible] acid concentration of [illegible] 11% of the [illegible] Apparently [illegible] 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;

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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 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; 88% and 89% of the remainder of the sample in each instance was used for the next step in the procedure. Duplicate results, which were obtained by extracting 1 ml. of 3 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.

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TABLE 5

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

Procedure	Per cent extracted
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

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 entered the other phase. In order to check the extent of exchange between the valence states of 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 that 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 2.17 M in magnesium chloride and 6.0 M in hydrochloric acid. Bonner found that 98% of the antimony(V) went into the isopropyl ether and 97% 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 heating to remove excess hydrogen sulfide. After equilibration the aqueous phase was extracted with 2 ml. of isopropyl ether. Ninety-nine per cent was extracted into the ether phase in all four samples of antimony(V) tested and 98% in the two samples of antimony(III) tested.

However when this system was used with carrier-free Sb127 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

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 ½ ml. of 6 N perchloric extracted [illegible] For three [illegible] samples [illegible] cally boiled [illegible] previous [illegible] percentage [illegible] with 99% [illegible] ples of boiled [illegible]

The extract [illegible] oxidation of [illegible] tions. [illegible] chloride, sulfur [illegible] change the [illegible] several tests [illegible] stock solution [illegible] to a certain [illegible] 2 ml. of 2 [illegible] ether phase [illegible] chloric acid [illegible] with 1 ml. of [illegible] solutions of [illegible] tested. [illegible] was extracted [illegible] Also sulfuric [illegible] extraction mixture [illegible] affected by [illegible] evident [illegible] 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.

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

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

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Solutions of antimony(III) in sulfuric acid, perchloric acid, or water were obtained on dissolving the residues which remained after the hydrochloric acid had been evaporated from 10 M 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 M hydrochloric acid, an average of 90% of the Sb^{125} was reduced to the lower oxidation state, whereas the fraction reduced was considerably 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-Al mercury lamp having light of wave lengths greater than 3300 Angstrom units. Quantitative oxidation occurred within one hour.

Stability of Sb^{125}(III)

Table 6 contains the results of a set of experiments designed to yield information concerning the stability of Sb^{125}(III) in various solutions. Into an 8 mm Pyrex tube was placed 1 ml. of the solution containing Sb^{125}(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 Sb^{125}(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 Sb^{125}(III) under certain conditions lower than 2 N hydrochloric acid solutions (see Figure 6). Solutions of antimony(V) were obtained by exposing the antimony(III) solutions, contained in Pyrex tubes, to a General Electric H85-A3 mercury lamp having lines of wave lengths greater than 3000 Angstrom units. Quantitative oxidation occurred in less than one hour.

Stability of Sb^{125}(III)

Table 6 contains the results of a set of experiments designed to yield information concerning the stability of Sb^{125}(III) in various solutions. Into an 8 mm Pyrex tube was placed 1 ml. of the solution containing Sb^{125}(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 7 hours, 48 hours, or 1 week after which time the per cent oxidation was determined.

The results of other experiments showing the stability of Sb^{125}(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 then 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 Sb^{125}(III) under certain conditions

TABLE 6

Stability of Sb^{125}(III) in

HCl, H_2SO_4, $HClO_4$, and H_2O at Room Temperature

Acid	Normality	Oxidation, %					
		5 hrs.		40 hrs.		1 week	
		light present	light absent	light present	light absent	light present	light absent
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 7

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

Normality range	Oxidation, %			
	Stoppered, oxygen not removed, light present			
	2 wks.	3 wks.		
0.5	19	21		
3	5	5		
6	7	9		
9	8	21		
11	56	90		
	Stoppered, oxygen removed			
	48 hrs.		72 hrs.	
	light present	light absent	light present	light absent
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
	Sealed, oxygen removed			
	72 hrs, light present	1 wk, light absent		
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		

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 Sb^{125}(III) to Sb^{125}(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. Sb^{125}(III) is quite unstable in neutral and basic solutions (see Tables 6 and 9).

Stability of Sb^{125}(V)

Experiments to determine the stability of Sb^{125}(V) were performed by sealing 1 ml. of various solutions containing Sb^{125}(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 Sb^{125}(V) in hydrochloric acid in the presence of fluorescent lights, and Table 12 contains the results of similar experiments with sodium hydroxide solutions.

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and Table 12 [illegible]
with sodium [illegible].

TABLE 8

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

Acid	Time, hrs.	Oxidation, %
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]

Conditions	Oxidation, %
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 10

Stability of $Sb^{125}(V)$ in HCl, H_2SO_4,

$HClO_4$, and H_2O at Room Temperature

Acid	Normality	Reduction, %					
		5 hrs.		40 hrs.		1 week	
		light present	light absent	light present	light absent	light present	light absent
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 11

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

Normality range	Reduction, %				
	40 hrs.	72 hrs.	1 wk.	2 wks.	3 wks.
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 $Sb^{125}(V)$ in 10^{-4} N NaOH[a]

Conditions	Reduction, %
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.

In general, Sb^{125}(V) appears to be relatively stable in the solutions examined. However, the tables indicate that occasionally a significantly large fraction of Sb^{125}(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 Sb^{125}(III), it was noted that Sb^{125}(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.

VI. OXIDATION AND REDUCTION

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

A considerable number of experiments were done in attempting to define the conditions under which Sb^{125}(V) is reduced to Sb^{125}(III) in hydrochloric acid. Inasmuch as quantitative reduction occurred upon boiling solutions of concentrated hydrochloric acid containing Sb^{125}(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 Sb^{125}(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 Sb^{125}(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

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 Sb^{125}(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 8-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 sucking; 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 $Sb^{125}(V)$ 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 causes 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

TABLE 13

Reduction of Sb^{125}(V) in Hydrochloric Acid[a]

Room temperature 40 hours		100° 1 hour		Room temperature 1 hour	
Normality of HCl	Reduction, %	Normality of HCl	Reduction, %	Normality of HCl	Reduction, %
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				

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[a] Light and oxygen were excluded.

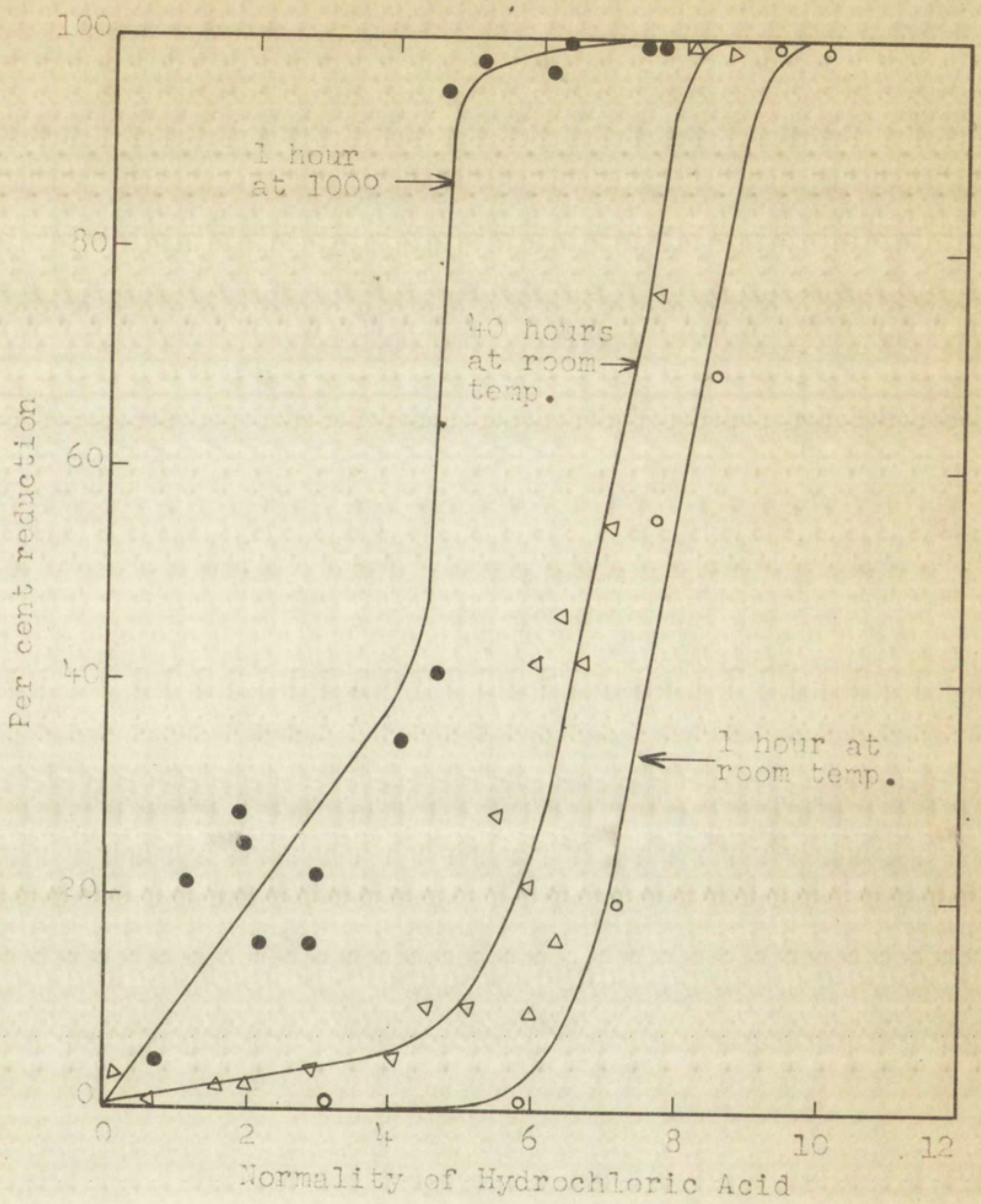


Figure 7

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

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

$$Sb(V) + 2Cl^- = Sb(III) + Cl_2$$

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 $Sb^{125}(V)$]. Also the reverse reaction is favored for normal concentrations of antimony by the oxidation potentials of the two reactions involved.

$$2Cl^- = Cl_2(g) + 2e \qquad E^o = -1.36^{(9)}$$

$$Sb(III) = Sb(V) + 2e \qquad E^1 = -0.83^{(2)}$$

$$HCl = 6 \text{ to } 10 \text{ N}$$

$$Sb(III) = Sb(V) = 0.005 \text{ M}$$

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,

$$2\ Sb(III) = Sb_2(V) + 4e$$

$$E = E^1 - \frac{0.059}{4} \log[Sb_2(V)] / [Sb(III)]^2$$

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

$$E = -0.83 - 0.015 \log 5 \times 10^{-13}/(.99 \times 10^{-10})^2$$

$$= -0.83 - 0.015 \times 7.3 = -0.83 - 0.08 = -0.91.$$

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-acid where [illegible]

The reduction [illegible]

reaction.

$$Sb(V) + 2I^- = Sb(III) + I_2$$

However, [illegible]

reaction [illegible]

when [illegible]

Table 17 for [illegible] Sb(V)). [illegible]

action is favoured for [illegible]

the oxidation potentials of the [illegible]

$$2I^- = I_2 + 2e \quad [illegible]$$

$$Sb(III) = Sb(V) + 2e \quad [illegible]$$

[illegible]

If antimony(V) is [illegible]

half-reaction would [illegible]

the forward reaction [illegible]

For example, [illegible]

$$2\ Sb(III) = [illegible]$$

$$E = E^0 + 0.029 \log [illegible] [Sb(III)]^2$$

if the total [illegible]

the Sb(V) is reduced, [illegible]

$$E = [illegible]$$

$$= [illegible]$$

However other workers [illegible]

zation in aqueous [illegible].

A more likely [illegible]

associated with the [illegible]

chlorine reaction,

$$2\ Cl^- = Cl_2(g) + 2e$$

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

[illegible]

becoming more positive for lower partial pressures of chlorine. The amount of chloride formed in the reaction of carrier-free Sb^{125}(V) is very small; therefore partly the chlorine pressure may be sufficiently low to allow for the reduction of Sb^{125}(V) by [illegible].

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 M hydrochloric acid was [illegible] after flushing [illegible] with [illegible] oxygen-free nitrogen. The sample was sealed and heated at 100° for 1 hour after which the oxidation state of the antimony was determined. The results are presented in Table 14 and Figure 14. Under the conditions of this experiment, reduction of antimony(V) does not occur until the antimony concentration is lowered to about [illegible] M, and the reduction becomes quantitative for concentrations between 10^{-7} and 10^{-9} M.

This experiment provides a basis for understanding the antimony(V) reduction in solutions containing carrier-free Sb^{125}. As mentioned in [illegible], antimony(V) is not quantitatively reduced in 1 hour in 10 M hydrochloric

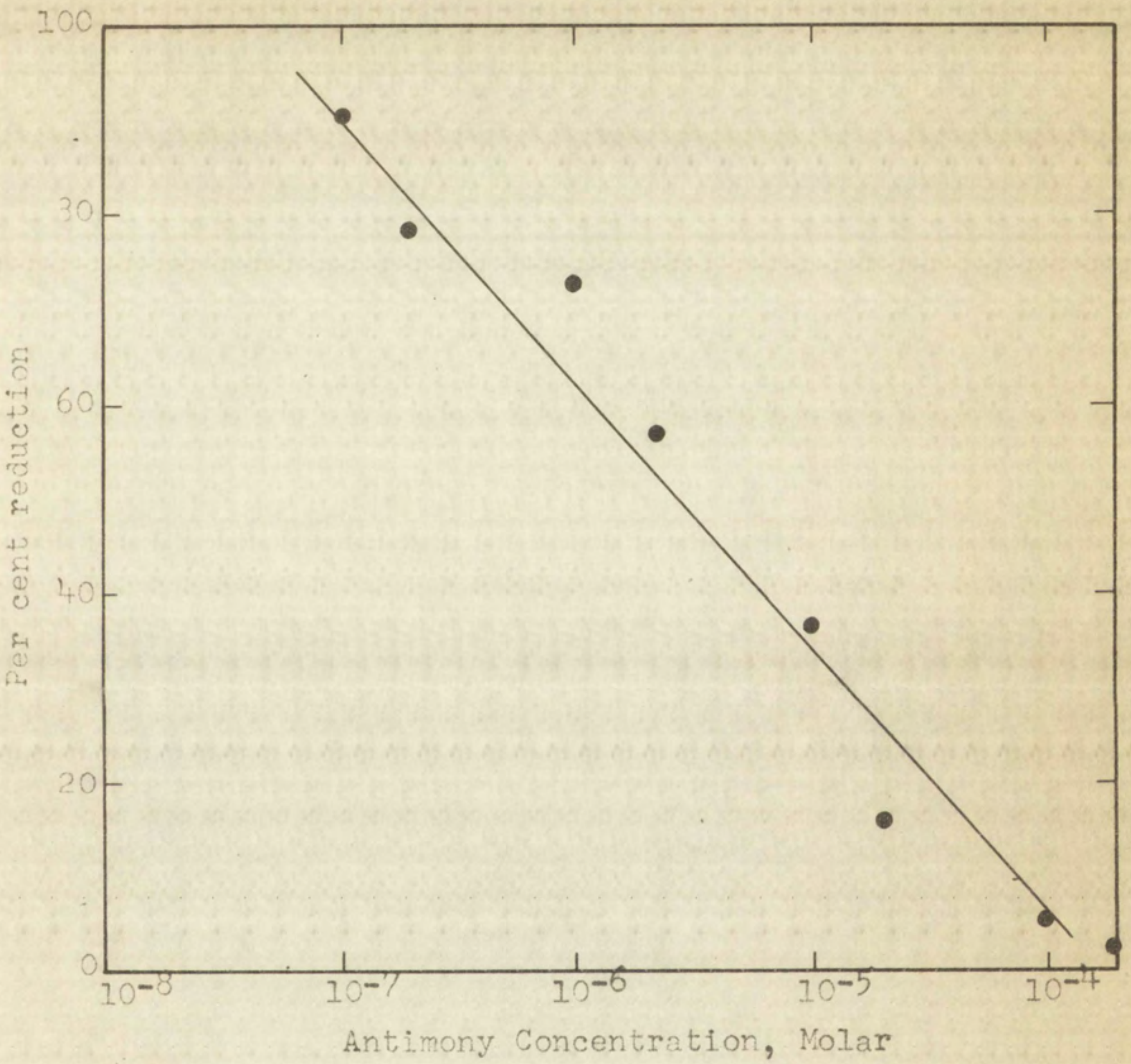


Figure 8

Reduction of Carrier Antimony(V)

TABLE 14

Reduction of Carrier Antimony(V)[a]

Antimony concentration (M)	Reduction, %	Average
2×10^{-4}	3, 4	3
10^{-4}	0, 5, 6, 9, 10	6
2×10^{-5}	16, 17	16
10^{-5}	26, 41, 44	37
2×10^{-6}	52, 58	55
10^{-6}	64, 75, 79	73
2×10^{-7}	79	79
10^{-7}	91	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 Sb^{125}(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

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.

carrier-free Sb^{125} [illegible] in this [illegible] by [illegible].

Reduction of [illegible]

Various Reducing Agents

Several solutions of [illegible]

Each was calculated to [illegible]

to 1 ml. [illegible]

any appreciable [illegible]

extraction [illegible]

antimony with these [illegible]

be reduced during the extraction [illegible]

dioxide solution [illegible]

in 1N [illegible]

water, and a 0.07 [illegible] solution of [illegible] sul-

furic acid were [illegible]

sulfuric, or perchloric [illegible] carrier-free

Sb^{125}(V) or 5x10^{-5} M [illegible] Sb(V) was added

0.01 ml. of [illegible]

tion was [illegible]

for 1 hour [illegible]

than the oxidation [illegible] antimony [illegible]

The results are [illegible]

ments iodide [illegible]

three [illegible]

fraction [illegible]

concent[illegible]

acid.

TABLE 15

Reduction of Antimony(V)[a]

Reducing Agent	Antimony concentration	Normality of acid	Reduction, %					
			HCl		H_2SO_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	-	-
	5×10^{-5} M	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	-	-
	5×10^{-5} M	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	-	-
	5×10^{-5} M	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	-	-
	5×10^{-5} M	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	-	-
	5×10^{-5} M	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 Sb^{125}

Reduction of Sb^{125}(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 Sb^{125}(III)

A series of experiments was performed to investigate the oxidation of carrier-free Sb^{125}(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 Sb^{125}(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

Reduction of Sb^{+5} (?) [illegible]

From Table 15, it is observed that carrier-free [illegible] is partially reduced [illegible] carrier-free Sb^{124} in [illegible] acids at 100°C. The per cent reduced is [illegible]% for hydrochloric acid, 30% 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. Identification was done in the same manner as that previously described except that the reaction times were varied.

Table 16 and Figure 9 indicate the results of these rate studies. A leveling off of reduction is noted for hydrochloric acid solutions, but no apparent decrease in the per cent reduction was observed for sulfuric and perchloric acids. No attempt was made to exclude oxygen from these solutions; therefore, the decrease in reduction may be caused by a competing reaction, presumably with the oxygen dissolved in the solutions.

Oxidation of [illegible]

A series of experiments was undertaken to investigate the oxidation of carrier-free Sb^{124} (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 Sb^{124}(III) was added 0.01 ml. of either bromine or chlorine solution. Thus the concentration of the oxidizing agent in the mixture was [illegible] M. The mixture, contained in a [illegible]

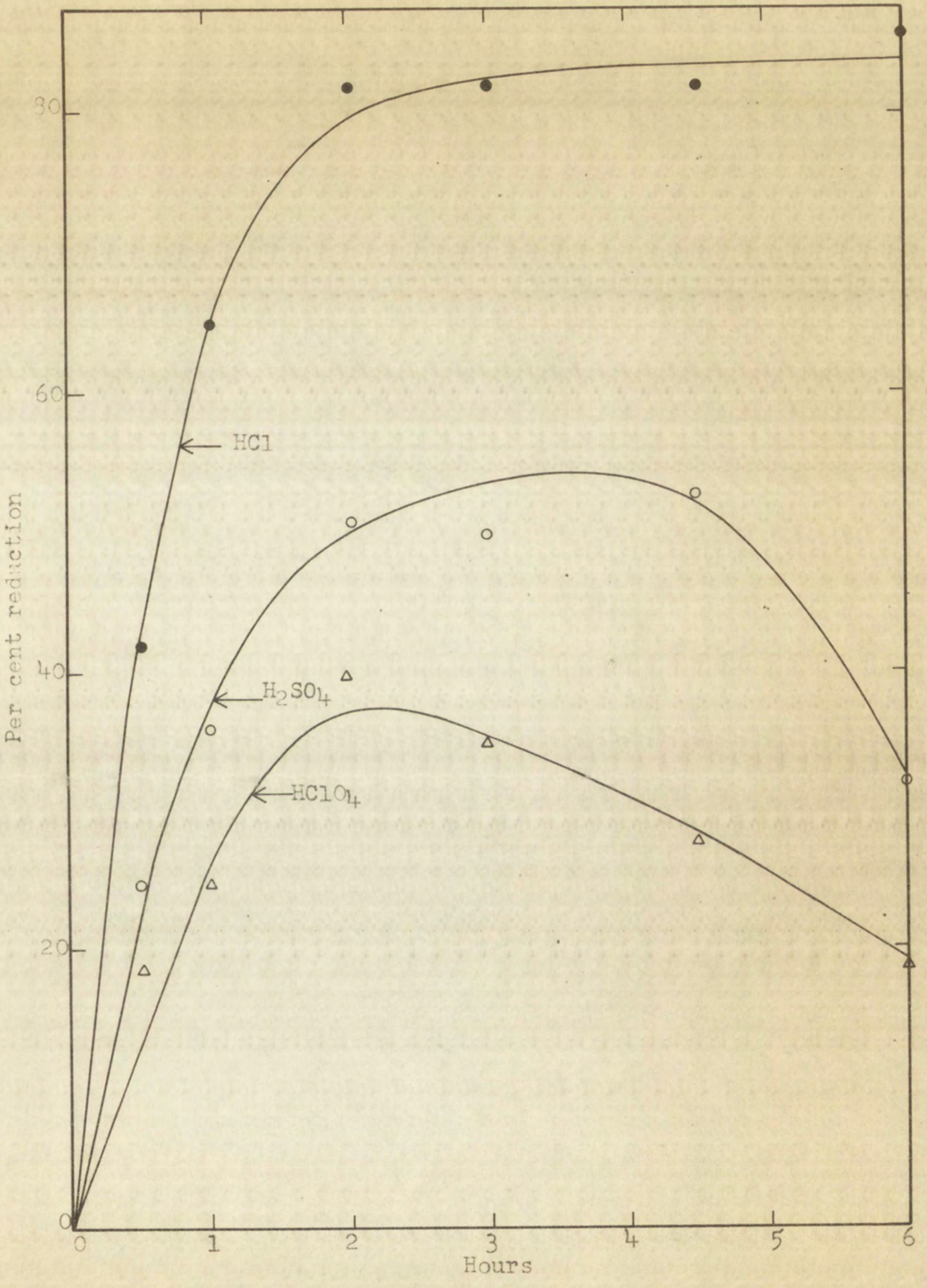


Figure 9

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

TABLE 16

Reduction of Sb^{125}(V) by Sulfur Dioxide[a]

Reduction time, hrs.	Reduction, %		
	HCl	H_2SO_4	$HClO_4$
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 Sb^{125}(III). In this investigation 1 ml. of solution in a stoppered Pyrex tube containing Sb^{125}(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 Sb^{125}(V) tends to be more stable than Sb^{125}(III).

TABLE 17

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

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 $Sb^{125}(III)$ 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

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. Baüll(1) attributes the oxidation of carrier amounts of antimony(III) by direct sunlight or by was tested. In [illegible] and heating [illegible] tested for the oxidation [illegible] instances it [illegible] the samples [illegible] exposure to the light [illegible] I^{131} [illegible] to be oxidized; in the three instances of [illegible] 9%, 6%, and 7% [illegible] ment indicates that [illegible] reversible.

Further tests were made [illegible] mechanism of the light-induced oxidation reaction. Two 1-ml. samples of concentrated [illegible] were exposed to light from the [illegible] for 1 hour [illegible] to 0.1 ml. of I^{131} [illegible] acid. After 30 minutes [illegible] In both instances the I^{131} had been [illegible] oxidized. In another [illegible] chloric acid [illegible] and stored in the dark [illegible] added to 0.1 ml. [illegible] I^{131} [illegible] 30 minutes [illegible] no oxidation occurred [illegible].

These experiments indicate that [illegible] oxidase [illegible] ondary reaction. [illegible] which [illegible] on irradiation with light. [illegible] of carrier [illegible] light from a mercury lamp to the formation of some intermediate peroxide.

VII. ADSORPTION AND COPRECIPITATION

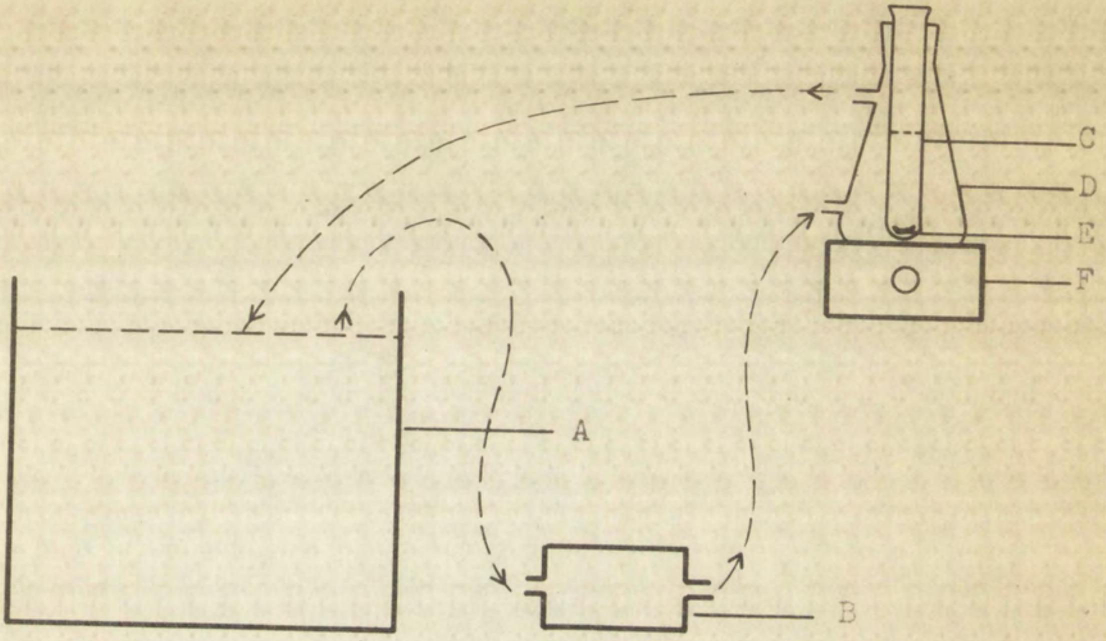
Adsorption of Sb^{125} on Pyrex

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 thermoregulated 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°.

VII. [illegible]

Adsorption of [illegible] in Flasks

The loss of a small amount of substance from a solution may not be significant for substances in macroscopic concentrations, whereas the same amount could represent a sizable fraction or all of the substance at concentrations on the order of 10^{-10} [illegible]. Thus [illegible] knowledge of the adsorption of carrier-free [illegible] 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 agitated, and the atmosphere was excluded. Also the samples [illegible] easily [illegible] after stirring either by transferring [illegible] centrifuge cones or by centrifuging in the original test tube. [illegible] in this work was done at high speed [illegible] by [illegible] centrifuge. The temperature was maintained at [illegible] temperature bath with a [illegible] of [illegible] the thermo-regulated water [illegible] a 5-liter Erlenmeyer flask which had an inlet tube near the bottom and an outlet tube near the top. The flask [illegible] of a [illegible] stirrer, and in the flask was placed a [illegible] test tube containing the sample solution and [illegible] the [illegible]. The atmosphere was excluded by [illegible] a [illegible] stopper or [illegible]. For all experiments with this apparatus the temperature was maintained at [illegible].



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 Sb^{125}(III) and Sb^{125}(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 Sb^{125}(III) is rather unstable in sodium hydroxide solutions. However, experiments for both Sb^{125}(III) and Sb^{125}(V) were performed on the basis of

A [illegible]
of both Rb^{86} [illegible]
The acids were [illegible] hydrochloric acid;
2 N, 6 N, 3 N, [illegible] and [illegible] per-
chloric acid. [illegible]
10 ml. of solution [illegible]
was transferred [illegible]
10 minutes, and then the [illegible] remaining in solution
was determined. [illegible]
activity [illegible] by solution.

In a similar manner the [illegible]
was demonstrated [illegible] adjusted by
adding small amounts of [illegible] sodium hydroxide
solution to water solutions of [illegible] activity the
samples [illegible] deter-
mination with a [illegible] ml.
was centrifuged 10 minutes, [illegible]
through [illegible] filter paper [illegible]
from each sample was [illegible] residual
activity [illegible]
tube was also [illegible]
was removed from solution [illegible] initial
1 hour stirring period.

The results of [illegible] in Table 1.
It was previously [illegible]
in sodium hydroxide [illegible]
both Rb^{86}(III) and Ce^{144}(IV) [illegible]

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 miximum 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 Sb^{125}(III) and of Sb^{125}(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, %	
	Sb^{125}(III)	Sb^{125}(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.

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 Sb^{125}(III) or Sb^{125}(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 $Fe(OH)_3$ as Function of pH[a]

pH	Coprecipitation, %	
	Sb^{125}(III)	Sb^{125}(V)
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 20

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

Oxidation state of Sb^{125}	Type of filter	Total Sb^{125} Adsorbed, %	Residual Sb^{125} in solution retained by filter,%
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 $Sb^{125}(V)$ 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 $Sb^{125}(V)$ 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 Bi(III), Cu(II), As(III), or As(V) and either $Sb^{125}(III)$ or $Sb^{125}(V)$, was added 5 ml. of hydrogen sulfide-saturated water. The tubes were closed and the samples stirred at 29.2° for 5 minutes

TABLE 21

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

Experiment	Centrifugation time, min.	Sb^{125} removed from solution, %
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.

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 Sb^{125}(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 Sb^{125}(III) and Sb^{125}(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 Sb^{125}(III) or Sb^{125}(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 Sb^{125}(III) and Sb^{125}(V) except, perhaps, for the sodium chloride solution.

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

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 & Cd^{++} 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 Sb^{125}(III) and Sb^{125}(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 Sb^{125}(III) and Sb^{125}(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 Sb^{125}(III) and Sb^{125}(V) deposited on the copper after stirring 1 hour at 29.2° and 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 Sb^{125}(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

TABLE 23

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

Antimony concentration, M	Stirring time, min.	Antimony removed from solution, %
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

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resin was used for removing copper from Sb^{125}. The Sb^{125} eventually eluted from the resin column was in the higher oxidation state. Some experiments were performed to help identify the oxidation state of the Sb^{125} during the preparation procedure. In this procedure after removing the electrochemically-deposited Sb^{125} from the copper surface with nitric acid, the solution was boiled with excess

hydrochloric acid to destroy the nitric acid. Inasmuch as reduction of $Sb^{125}(V)$ 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 $Sb^{125}(V)$ 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 $Sb^{125}(III)$, $Sb^{125}(V)$, or $Sb^{125}(V)$ 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 $Sb^{125}(III)$ and $Sb^{125}(V)$ seems to be that water elutes a considerable portion of $Sb^{125}(III)$, whereas a much smaller

TABLE 24

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

Experiment	Oxidation state of Sb^{125}	Eluant (10 ml portions)	Sb^{125} eluted, %
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

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

There is again (see p. 25) the unusual behavior of $Sb^{125}(V)$ 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 $Sb(OH)_2Cl_4^-$ and that $Sb(OH)_3Cl_3^-$ or more hydrolyzed species are the most important in lower acid concentrations. The ion exchange resin reactions might be represented as follows,

$$R\text{-}Sb(OH)_2Cl_4 + Cl^- = R\text{-}Cl + Sb(OH)_2Cl_4^- \qquad (1)$$

$$R\text{-}Sb(OH)_2Cl_4 + H_2O = R\text{-}Sb(OH)_3Cl_3 + HCl \qquad (2)$$

$$R\text{-}Sb(OH)_3Cl_3 + Cl^- = R\text{-}Cl + Sb(OH)_3Cl_3^- \qquad (3)$$

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. Therefor 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, $R\text{-}Sb(OH)_2Cl_4$, 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.

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

Thus, assuming the hypothesis [illegible], [illegible] that the number of [illegible] this essentially [illegible].[117] hypothesis, it would explain [illegible] apparent difference between the behavior of [illegible] with [illegible] carrier-type sub[illegible].[107]

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 Sb^{125}(III) and Sb^{125}(V) under various conditions, the factors that cause oxidation of Sb^{125}(III) and reduction of Sb^{125}(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 Sb^{125}(V) were prepared directly by this method; Sb^{125}(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

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 Sb^{125}(III) were obtained. Sb^{125}(V) was readily obtained by irradiating the solutions of Sb^{125}(III) with a General Electric H400-A1 mercury lamp.

Distinguishing between Sb^{125}(III) and Sb^{125}(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}; Sb^{125}(V) entered the ether phase and Sb^{125}(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 Sb^{125}(V) was more stable than Sb^{125}(III). For instance, only in hydrochloric acid in the absence of light and oxygen could Sb^{125}(III) be maintained without oxidation for a long period, whereas stock solutions of Sb^{125}(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 Sb^{125}(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 Sb^{125}(III). Reduction of Sb^{125}(V) occurred mostly in

80% to 95% of the Sb^{125} [illegible] when the evaporation [illegible] solutions, [illegible] Sb^{125}(III) were obtained. Sb^{125}(V) [illegible] solutions of Sb^{125}(III) [illegible] mercury lamp.

Distinguishing [illegible] Sb^{125} [illegible] and Sb^{125}(V) [illegible] accomplished by [illegible] containing of 8 ml. of isopropyl [illegible] chloric acid and [illegible], and 1 ml. of solution 6 N in hydrochloric [illegible] antimony(III) and antimony(V). [illegible] 1 ml. of solution [illegible] other phase the Sb^{125}(III) [illegible]

The stability [illegible] Sb^{125}(III) was measured in different [illegible] In general Sb^{125}(V) [illegible] instance, only [illegible] and oxygen until Sb^{125} [illegible] for a long period [illegible] 2 N hydrochloric [illegible] tion occurring [illegible] light and oxygen. [illegible] Sb^{125}(III) was considerably [illegible] in the absence of light. It [illegible] ments that both [illegible] oxidation of Sb^{125}(III). [illegible] 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 $Sb^{125}(V)$ 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 $Sb^{125}(V)$ 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 $Sb^{125}(V)$ 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 $Sb^{125}(III)$. 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 [illegible] and [illegible] [illegible] decomposition was [illegible] the limited [illegible] been due to [illegible]).

A specific study of the reduction of $Sb^{125}(V)$ in hydrochloric acid revealed that the reduction of antimony produced is increased by [illegible] hydrochloric acid [illegible]. [illegible] earlier studies of [illegible] that [illegible] reduction does not occur in [illegible] 10^{-4} [illegible]. The study also [illegible]. The antimony concentration in the solutions [illegible] in this work. The [illegible] of 10^{-8} to 10^{-10} M. Several [illegible] ([illegible], Sn^{++}, Fe^{++}, and I^-) were [illegible] the reduction of carrier-free $Sb^{125}(V)$ with [illegible] in various solutions (HCl, [illegible]). Very little difference in reduction was [illegible] with [illegible] dioxide in hydrochloric acid [illegible] the carrier-free $Sb^{125}(V)$ was more effectively [illegible] was observed to be the most effective reducing agent. [illegible], heat, and light from the mercury lamp were all [illegible] effective in oxidizing $Sb^{125}(III)$. It was concluded that oxidation by light proceeds indirectly through an unstable intermediate, probably a peroxide.

It was shown that [illegible] Sb^{125} [illegible] acid solutions [illegible] 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.

vessels. A maximum of about 1% [illegible] 1 hour from solution of pH [illegible] adsorbed on the glassware from these [illegible] [illegible] Pediococcis [illegible] which could be [illegible] fide precipitate [illegible] ferric hydroxide in the [illegible] precipitated by [illegible] carrier Sb^{125}, whereas with no [illegible] the amount of antimony removed from solution by [illegible] as the antimony concentration [illegible] carrier-free Sb^{125}. [illegible]

The behavior of carrier-free Sb^{125} on Dowex-1 resin was found to be different from that of [illegible] antimony in at least one respect. [illegible] the distribution coefficient in 2.5 N [illegible] is [illegible] low, and after placing antimony(V) in [illegible] on a Dowex-1 resin column, the antimony [illegible] eluted with 2.5 N hydrochloric acid. However, for carrier-free Sb^{125}(V) [illegible] column, it was only with difficulty [illegible] 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 Sb^{125}(V) on Dowex-1 anion exchange resin. Distribution coefficients for Sb^{125} could be determined by performing batch experiments

IX. POSSIBLE FURTHER INVESTIGATIONS

This section of the dissertation is devoted to suggesting a few of the problems in the solvent extraction chemistry of antimony that would be interesting for investigation and study. No attempt is made to list [illegible] possible areas of research [illegible] in connection with these problems [illegible] out by this work.

Although as there are typical forms [illegible] exist in hydrochloric acid [illegible] amounts of antimony, as well as [illegible] if similar [illegible] [illegible] extraction of [illegible] solutions by isopropyl ether, and [illegible] been observed(4) in the extraction of [illegible] amounts of antimony. In the latter case, [illegible] Various forms of antimony [illegible] coefficients and [illegible] tant in determining [illegible] might be further elucidated by solvent extraction studies of hydrochloric acid solutions [illegible] carrier-free [illegible].

Some evidence [illegible] advanced for [illegible] on Dowex-1 anion exchange resin. [illegible] for Sb^{+5} [illegible] as was done for carrier antimony, and elution of $Sb^{125}(V)$ 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 $Sb^{125}(V)$ by 2 N hydrochloric acid.

In the oxidation of $Sb^{125}(III)$ 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 $Sb^{125}(III)$. The amount of intermediate which is formed may depend on the length of the irradiation, and, in turn, the amount of $Sb^{125}(III)$ which is oxidized would depend on the amount of intermediate formed. Hence, the oxidation of $Sb^{125}(III)$ 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 $Sb^{125}(V)$ by hydrochloric acid merits further investigation. This reduction should be investigated electrolytically as a function of antimony concentration and cathode potential.

as was done [illegible] (17) from the neutralization of [illegible] salt could be [illegible] sites as suggested [illegible] obtained by [illegible] hydrochloric acid [illegible]. Also it might be possible [illegible] amount of some material [illegible] than is antimony(V) [illegible] by 2 N hydrochloric acid.

In the [illegible] light, evidence [illegible] stable intermediate, [illegible] undertaken by [illegible]. The [illegible] length of the [illegible] $Sb^{124}(V)$ which [illegible] intermediate [illegible] this [illegible] to measure light [illegible] is formed on [illegible] oxidation [illegible] dosimeter.

The phenomenon [illegible] chloric acid [illegible] should be investigated [illegible] antimony [illegible].

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 [illegible]

carry Sb^{125}, but [illegible]

the mechanism by which [illegible]

could be designed [illegible]

to adsorption on the surface [illegible]

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and, if the latter, [illegible]

Vaporization, [illegible]

electrolytic deposit [illegible]

studies involving the [illegible]

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