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SOME PROBLEMS IN THE CHEMISTRY OF URANIUM AND THORIUM OF INTEREST TO THE DEVELOPMENT OF ATOMIC POWER

by

Robert William Nottorf

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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In Charge of Major Work

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INTRODUCTION

The desire to develop and use atomic disintegration as a source of power had its earliest beginning with the discovery of naturally radioactive elements. Radioactive processes are accompanied by the release of very large quantities of energy in the form of high velocity beta and alpha particles and gamma rays, and the energy release per disintegration amounts to as much as 8 million electron volts. This is several million times as much as, for example, the energy released per carbon atom in its combustion to form carbon dioxide. However, the rate of this radioactive decay cannot be altered, and spontaneous radioactivity is unfeasable as a power source.

The beginning in the practical development of atomic power was made by Fermi and his collaborators (1) who discovered in 1934 that neutron irradiation of various elements produced beta-ray emitting isotopes. Shortly after this discovery they subjected uranium to neutron bombardment (2) in the expectation that beta-ray emission from an active uranium isotope would produce element 93. Radioactivities were produced and work was begun to characterize and identify them. In all previous experience, neutron bombardment had produced elements whose atomic numbers were equal to or greater than that of the bombarded element, and initial workers with the neutron-induced activities from uranium sought to identify them as transuranic elements. This identification was indirectly supported by the fact that the activities could not be definitely identified with any of the elements whose atomic numbers are immediately below that of uranium. The addition of new experimental evidence accentuated the inadequacy of suggested explanations until in 1939 Hahn and Strassmann (3) tried to separate activities which they called "Ra IV" and "Ra III" from barium by fractional crystallization. Although they could separate the radium isotopes $MsTh_1$ and ThX from barium without difficulty, they could not do so with "Ra III" and "Ra IV". Hahn and Strassmann thus reluctantly admitted that the activities which they had called radium, actinium, and thorium were really barium, lanthanum, and cerium.

It was immediately apparent to many physicists that a tremendous amount of energy would be liberated in the disintegration of a uranium atom into two medium weight atoms. The mass of the uranium atom is roughly 0.1 atomic mass unit greater than an integer, and the masses of the medium weight atoms are each about 0.05 mass units less than an integer. The energy difference, roughly 0.2 mass units or about 200 million electron volts (200 Mev), would be expected to appear largely as kinetic energy in the fission fragments. Physical experiments picked up the high energy fission fragments in cloud chambers and ionization chambers.

Chemical evidence proved that most of the "transuranics" were actually elements centered about the middle region of the periodic table.

Activities produced in fission are hurled from the fission site in the form of stripped nuclei possessing a very high kinetic energy of recoil, while the activities produced by neutron absorption receive only the relatively small kinetic energy of the neutron impact and thus show little or no recoil. The recoiling and non-recoiling activities were separated, showing in the non-recoiling fraction a 23-minute uranium and an activity of approximately 2-day half-life (4) which was later identified as the true transuranic element neptunium, ${}_{93}Np^{239}$(50). The emission of delayed neutrons was observed (5) following the fission process and later the emission of fast neutrons simultaneously with fission (6). The discovery that neutrons are given off in fission suggested the possibility of a self-sustaining chain reaction in which the neutrons produced by fission were in turn used to produce further fissions. For a detailed account of the rapid developments of this period, the reader is referred to thorough reviews and complete bibliographies of the subject written 6 months before (7) and 10 months after (8) the discovery of fission.

A knowledge of the fission process as it is applied to the practical production of atomic power is desirable for the evaluation of the work reported in this paper. The key to the whole fission process is the neutron, and any understanding of the fission process must begin with an understanding of the neutron itself. Since a neutron has no charge it is not influenced by atomic electrostatic forces but proceeds in a straight line according to its original momentum until it collides with an atomic nucleus. It may induce in the nucleus any of several reactions; for example, if Z is the atomic number of the original nucleus, an alpha particle may be emitted to produce the residual nucleus Z-2; a proton may be emitted to produce the residual nucleus Z-1; several processes may occur to produce no change in Z; and finally, with uranium, fission may occur. The processes which produce no change in Z are a) elastic scattering, which involves only a transfer of kinetic energy, b) inelastic scattering, in which a neutron enters the nucleus and a neutron of different energy leaves, c) neutron capture, in which case the mass number of the nucleus is raised one unit, and d) emission of two neutrons, in which case the mass number of the nucleus is lowered one unit.

For each energy of the bombarding neutron, an atomic nucleus shows a definite tendency to undergo each of these possible reactions. This tendency is measured in terms of the atomic cross section which the nucleus exhibits toward the neutron. Thus an atomic nucleus with a high capture cross section tends to capture the bombarding neutron and a nucleus with a high fission cross section tends to be fissioned by neutron bombardment. Collisions of a neutron with nuclei whose reaction cross sections are low normally result in elastic and possibly inelastic scattering and the slowing down of the neutron. Deuterium and helium neuclei are particularly effective in this regard.

The establishment of a chain fission process depends primarily on two factors--first, the production of more than one neutron by each fission and second, the arrangement of the fissionable material in space so that at least one of the neutrons produced per fission in turn produces a new fission. While natural uranium is the material originally used to support the fission process, only the U^{235} isotope fissions upon absorbing a slow neutron. The U^{238} isotope either captures the bombarding neutron or emits two neutrons, depending on the energy of the incident neutron. The neutrons emitted in fission are mostly fast neutrons and since the cross sections which nuclei exhibit toward fast neutrons are all relatively small the neutrons suffer little initial loss by capture or fission, but are gradually slowed down by elastic scattering.

It has been shown that the effective cross section for capture of slow neutrons is inversely proportional to the velocity of the neutrons, when the energy of the neutrons is not in the neighborhood of a resonance absorption band. This is true both for U^{238} and U^{235}, but U^{238} has several resonance absorption bands and exhibits a very high cross section for capture of neutrons which possess slightly more than thermal energy. Thus a neutron which is slowed down in uranium undergoes a considerable likelihood of capture by U^{238} before its energy has been dissipated to the point where the neutron is effective in producing fission in U^{235}. Therefore, with the use of natural uranium as a source of fissionable material it is necessary to utilize another material for the specific job of slowing down or "moderating" the neutrons to thermal energy.

The first "piles", or spacial arrangements of uranium and other materials for the propagation of the chain fission reaction, were those based on the slow neutron fission cycle using natural uranium as the fissionable material and graphite as the neutron moderator. The piles were constructed with a lattice of uranium or uranium oxide "slugs" arranged in a matrix of graphite extending nearly equally in three dimensions. The pile must be large enough to give a volume-surface ratio sufficient to prevent the loss of neutrons through the walls of the pile from stopping the fission cycle. The process was started by the small amount of spontaneous fission occurring without the capture of neutrons, and the fast neutrons formed by the fission escaped from the slug in which they were formed and started through the graphite moderator. By a process involving elastic scattering from the carbon atoms the neutrons lost their energy and attained thermal energy before they reached the nearest uranium slug, where they could produce fission in U^{235} or be captured by U^{238}.

Since so few extra neutrons are produced in fission above the number actually needed to maintain the cycle, elaborate precautions must be taken to insure that they are used efficiently. One of these precautions is the construction of the pile from materials whose capture cross sections are very small and which therefore show only a very small tendency to absorb neutrons. Another precaution is the establishment of extremely high purity requirements for the materials of construction, especially in freedom from elements such as boron or cadmium which have high cross sections for capture.

The power rate of the pile is controlled by regulating the neutron intensity therein. This is done by inserting into the pile rods containing elements of high capture cross section. These elements compete with uranium in the capture of neutrons, and keep the reproductive factor of the fission cycle at exactly one.

As the fission cycle continues, there are produced in the pile significant quantities of fission products ranging in atomic number from 30 (zinc) through 63 (europium). Many of these elements have high cross sections and thus can change the operating characteristics of the pile after it has been operated for some time. A knowledge of the yield, identity, and characteristics of every fission product is desirable for the anticipation of high cross-section radioactive poisons which may be produced in fission, and from the standpoint of the health hazard involved in handling these highly dangerous radioactivities. A complete knowledge of the fission products is also necessary for the full understanding of the fission process.

The high intensity radioactivities produced in the pile create a need for chemical schemes for their removal and isolation. Beyond certain concentrations they interfere with the operation of the pile; removed, they offer a source of radiation to be used in medicine or in scientific investigations.

While thorium itself is not fissionable by slow neutrons, it can be utilized in a fission cycle by first converting it through neutron capture to Th^{233}, which undergoes beta decay to U^{233}.

The specific requirements suggested above as well as a need for a fuller understanding of the chemistry of uranium and thorium have prompted these researches. The separate problems are widely different in nature, but all are alike in that they contribute to the development of atomic power.

PART I

STUDIES OF THE BARIUM AND STRONTIUM ISOTOPES PRODUCED IN FISSION

1.1 Historical Survey

The study of the barium isotopes produced in fission began earlier than the knowledge of fission itself, for it was the identification of barium activities in neutron-bombarded uranium (3) which gave the first accepted evidence that fission had occurred. At the time the studies reported in the present work were begun, the radioactive isotopes of barium and strontium listed in Tables 1 and 2 had been identified in the fission products (9). These activities, like most or all of those produced in fission, are the members of chains of active elements which, though resulting from the fission process, are not necessarily produced directly by fission. The production of the parent member in a radioactive chain insures the eventual production of all of its daughter activities, but the time of daughter production depends on the half-life of the parent. Since an activity which has a radioactive daughter constantly generates radioactive contamination within itself, knowledge of the entire radioactive chain is important and is included in the tables.

Table 1

Radioactive Fission Chains Involving Strontium Known at the Start of These Researches*

Mass Number	Kr	Rb	Sr	Y	Zr
89	2 m →	15 m →	55 d →	Stable	
91			10 h →	57 d →	Stable (10)
90			2.7 h →	3.5 h →	(10)
			7 m →		

* Items under elements are half-lives; s = second, m = minute h = hour, d = day.

Table 2

Radioactive Fission Chains Involving Barium Known at the Start of These Researches

Mass Number	Xe	Cs	Ba	La	Ce
139	0.5 m →	7 m →	86 m →	Stable	
140	0.5 →	40 s →	300 h →	44 h →	Stable
			14 m →	2.5 h →	Stable
			1 m →	30 m →	

The radiochemical techniques which were used previous to this time were mostly ones which had been developed in the study of artificial radioactivities produced by cyclotron bombardment, and usually applied gravimetric-developed separations on a microchemical scale. Activities of only a limited number of elements were encountered in any specific problem and these elements were of neighboring atomic numbers with widely different chemical properties so that the separation schemes required were usually rather simple.

Fission, however, yielded a very heterogeneous set of activities--of elements ranging from zinc through europium. The chemistry of some of these elements, such as columbium, molybdenum, antimony, the platinum metals, etc., is difficult enough alone without being complicated by the variety of others. Thus, previous chemical separations were often inadequate.

1.2 The Separation of Barium and Strontium from Fission Products

In a number of experiments determining the behavior of fission products in uranium oxide and metal, it became necessary to determine the fission activities present in a sample by means of a schematic separation. These samples were usually analyzed more than a day after bombardment, and on materials which made the use of aliquots impossible. After a preliminary investigation it was decided that the isolation of the elements Ba, Sr, Y, Te, I, Sb, Mo, Ce, Zr, mixed rare earths, and UX_1(Th) was justified, and 20-30 milligrams of carrier of each element were added to facilitate the process. The tracer activities of Cs, Ru, Rh, Re, and Cb were present in such small amounts that the recovery of these elements was not important. The problems involved in the isolation of pure barium and strontium carriers and activities from the above mixture, and final recommendations for this isolation, are the chief concern of this section.

As already mentioned, early techniques for activity separation were based primarily on the addition of a sufficient amount of carrier to a sample, isolation of the carrier by chemical techniques which gave correct gravimetric separation, and measurement of the activity of the isolated carrier. The difficulty with this practice was that small amounts of impurity in the sample which were undetected gravimetrically could bear enough radioactivity to ruin the value of activity measurements on the fraction. However, because there was little else to begin with, the first separation techniques were based on the common qualitative and quantitative schemes of analysis.

Following standard qualitative analytical procedures, a precipitation of Te, Sb, and Mo was made by H_2S in a dilute HCl solution. The H_2S was removed from the filtrate and the hydroxides of Ce, La, Y, Th, and Zr were precipitated by the addition of ammonium hydroxide. Lastly the sulfates of Ba and Sr were precipitated from the hydroxide filtrate by reducing it to a small volume, adding H_2SO_4, and making it 50% alcoholic with ethyl alcohol.

The gravimetric recovery of barium and strontium was not satisfactory with this scheme for a number of reasons. 1) Whenever the H_2S precipitation is made in air, some of the sulfide is oxidized to sulfate. This may precipitate the sulfates of barium and strontium prematurely and cause their loss to the final precipitation. 2) Barium and strontium form insoluble diuranates, and since there is usually some uranium present in the sample, some barium and strontium are always precipitated in the hydroxide group. 3) If the hydroxide is open to the air, absorption of carbon dioxide from the air may cause the precipitation of barium and strontium carbonates. 4) It is impossible to use the fluoride precipitation to separate YF_3, LaF_3, ThF_4, and CeF_3 from barium, strontium and zirconium because, although BaF_2 and ZrF_4 separately are soluble, together they form the insoluble $BaZrF_6$. Because of these limitations on this scheme of analysis, it was abandoned in favor of the one described below.

This scheme of separation is based on the fact that barium and strontium nitrates have a very small solubility in concentrated nitric acid and are practically insoluble in 80% HNO_3 (11) while the other nitrates involved in these studies are normally soluble. The solution of activities and the carriers Ba, Sr, Te, Mo, Y, La, Ce, Zr, Th, and sometimes Sb were boiled down with nitric acid to a small volume, perhaps 10 ml, until barium and strontium nitrates began to precipitate from the hot, concentrated nitric acid solution. This solution was cooled to room temperature and with constant stirring was treated with fuming nitric acid until the HNO_3 concentration was 80 to 85 percent. The nitrates were allowed to precipitate and then were centrifuged. The clear liquid was poured off and used for the schematic separation of the remaining carriers. The solid nitrates were washed with a small volume of 80% HNO_3 and again centrifuged and the wash decanted.

According to Willard and Goodspeed (11) this precipitation affords a quantitative separation of barium and strontium from the other elements present. However, from a radiochemical point of view such an efficient separation has not been obtained. While the amount of contamination is very erratic, a number of contaminations have been observed to occur frequently. Nearly always in boiling down the nitric acid solution for the initial precipitation of barium and strontium nitrates, antimony carrier is oxidized and precipitated as antimonic acid or hydrated oxide, contaminating the barium and strontium fraction. The amount of this precipitate is large, and it interferes with the efficient separation. To a lesser but usually significant extent, tellurium and cerium are also precipitated. This precipitation may occur as the higher oxide but no experimental evidence is at hand to indicate the chemical nature of the precipitate.

In the expectation that some barium and strontium might be held in the water-insoluble part of the nitric acid precipitate, the first treatment was to dissolve the entire precipitate in hot, concentrated hydrochloric acid and after dilution, to precipitate $BaSO_4$ and $SrSO_4$ by the addition of H_2SO_4 and alcohol. The conversion of the sulfates to carbonates by fusion with sodium carbonate, solution of carbonates in HCl and precipitation of barium as chromate and strontium as sulfate gave products whose decay curves indicated radioactive contamination (Figures 1 and 2). It was apparent that the combination of carbonate fusion and nitrate, sulfate, and chromate precipitations had yielded a product which was probably gravimetrically pure, but which was radioactively contaminated.

It was known from tests that the rare earths coprecipitated badly as sulfates, especially from alcoholic solution, and that this sulfate precipitation was ineffective in removing contamination; so it was tentatively replaced by the HCl-ether precipitation of barium chloride (12) and by the carbonate precipitation of strontium. The barium then was pure, but the strontium continued to be contaminated.

Since the attempts at precipitation of barium and strontium away from foreign activities had been rather unsuccessful and had become very tedious, a different

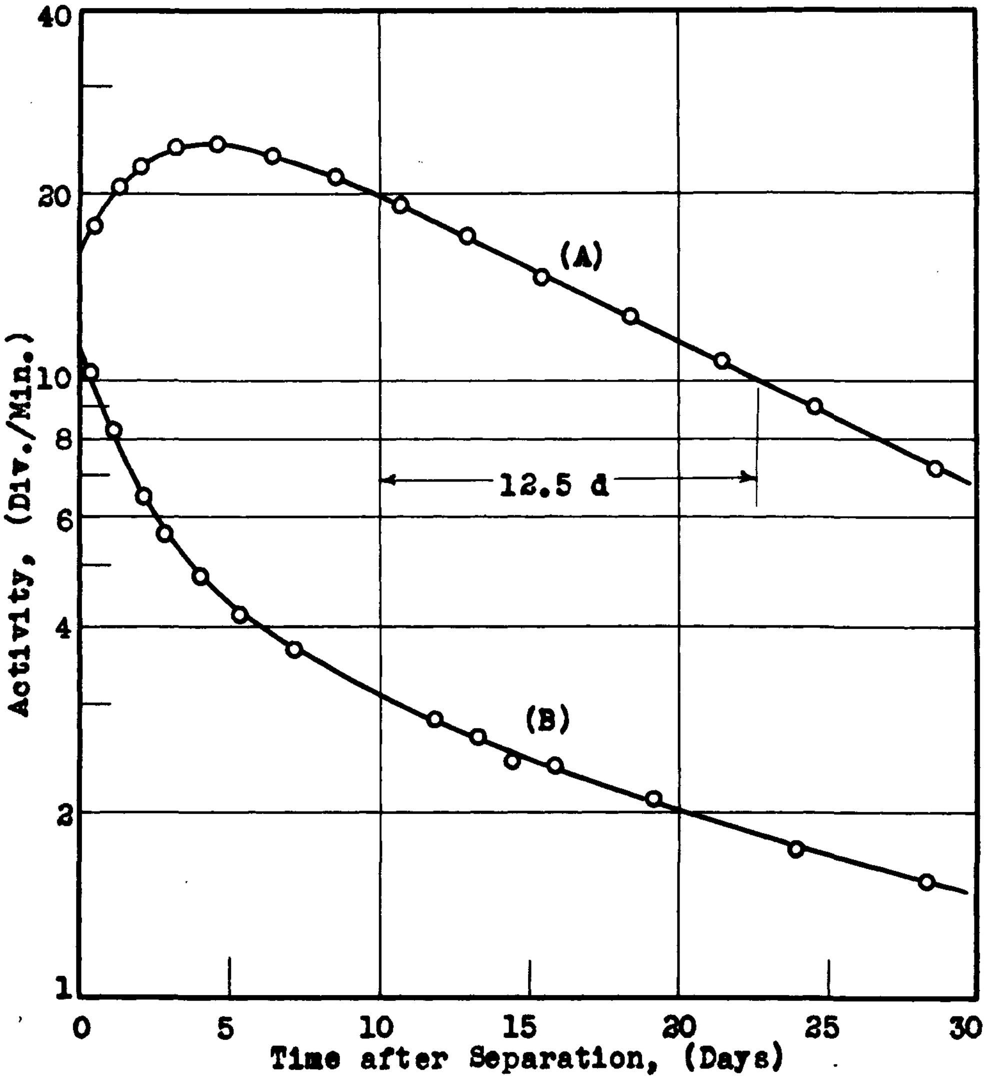

Figure 1. Decay Curves of Radioactive Barium Samples Separated from Uranium Fission Product Material. (A) Pure Ba^{140} activity at the time of separation, showing growth of daughter La^{140} (half-life 40 hours) and subsequent straight-line decay with the half-life of Ba^{140}, 300 hours (12.5 days). (B) An impure sample showing contamination by foreign activities of both short and long half-lives. If the plot of log activity versus time is a curved line, activities of more than a single half-life are indicated. If the line is straight, the decay is controlled by activity of a single half-life. The straight-line portion of (A) consists of barium in equilibrium with its daughter lanthanum, all decaying with an apparent half-life of 12.5 days.

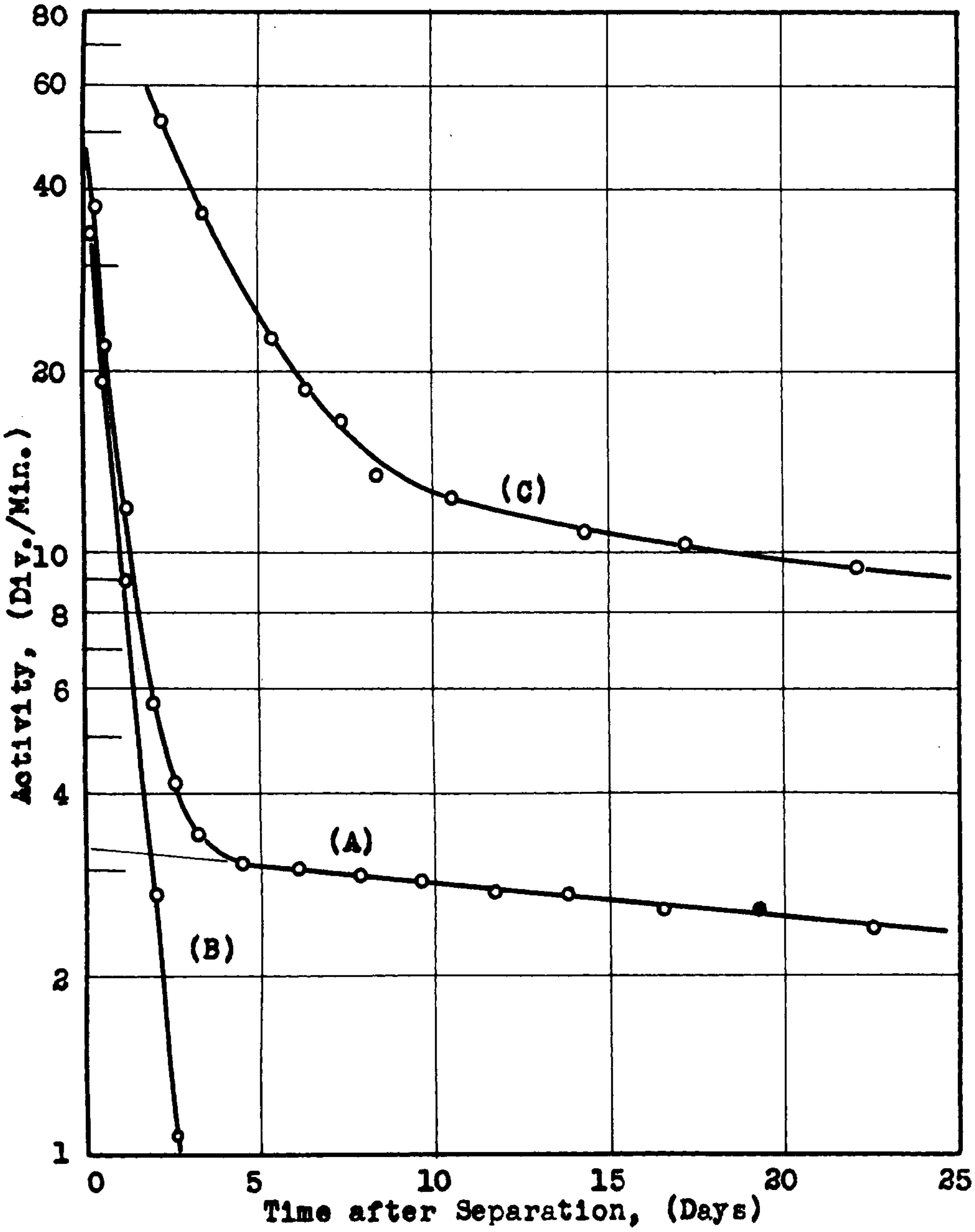

Figure 2. Decay Curves of Radioactive Strontium Samples Separated from Uranium Fission Product Material. (A) Pure strontium activities consisting of Sr^{91} (half-life 10 hours) and Sr^{89} (half-life 55 days). (B) Subtraction curve showing the decay of Sr^{91} alone, obtained by subtracting the activity of Sr^{89} from the total activity. (C) Impure strontium activity showing the effect on the decay curve of a foreign activity of medium half-life.

technique of purifying the barium and strontium was tried. This consisted of the removal of contaminating activities from the solution containing barium and strontium rather than the separation in the opposite order. For gravimetric analysis, complete precipitation of the desired constituent is the critical factor; for radioactive work, complete removal of all contaminants is usually more important.

When barium and strontium nitrates were first separated by the fuming nitric acid separation, about the only impurities still remaining were antimony, tellurium, and possibly some hydroxide-insoluble elements, so after the fuming nitric acid separation to remove barium and strontium from most of the rest of the carriers the nitrates were dissolved in water and immediately freed by centrifugation from the water-insoluble matter. The clear solution was evaporated with HCl to near dryness, diluted, treated first with metallic zinc to reduce antimony and tellurium, and then with a drop of ferric nitrate carrier and ammonium hydroxide to precipitate and carry down all hydroxide-insoluble elements. The precipitate of antimony, tellurium, and insoluble hydroxides was removed by filtration, and barium and strontium were precipitated from the filtrate by the addition of ammonium carbonate solution. The carbonates were dissolved in dilute HCl, and barium was separated by a double precipitation as chromate. In the filtrate, strontium was freed of the trace of barium and daughter lanthanum activity by the addition of a drop of barium carrier, a drop of ferric nitrate, and an excess of ammonium hydroxide. The solution was filtered and strontium was precipitated as carbonate by ammonium carbonate solution. By this scheme carrier separations free of radioactive contamination were reproducibly obtained.

Subsequent work has indicated that the zinc reduction of antimony and tellurium may usually be eliminated without serious contamination by these elements. Except for extreme purity requirements, the slight contamination remaining after the hydroxide scavenger purification does not usually interfere. The scavenger purification technique involves the use of an inactive carrier, in this case iron, to co-precipitate and carry down another material, here the insoluble hydroxides of lanthanum, yttrium and the rare earths. This shortened separation scheme proved very useful and reliable in the many activity analyses which other experiments required.

1.3 Some Tracer Studies of the Chromate Separation of Barium from Strontium

After the techniques had been developed for the separation of barium and strontium activities from the other fission products, attention was turned to the separation of barium and strontium from each other. Of the few methods for separating barium and strontium, the precipitation of barium as barium chromate by the addition of ammonium dichromate to a very slightly acid solution containing ammonium acetate is the recommended one (13). Also mentioned is a separation depending on the differential solubility of $BaCl_2$ and $SrCl_2$ in a solution composed of 4:1 HCl (33%) and ether. Although at least one reprecipitation of the $BaCrO_4$ is necessary in gravimetric procedures, and the solubility of $BaCrO_4$ in ammonium acetate solutions indicates that the procedure probably attains gravimetric acceptability by a combination of errors, the separation was accepted as the best one available. The combination of errors which permit gravimetric acceptance are the balancing of the solubility of $BaCrO_4$ by the amount of $SrCrO_4$ being carried as contamination in the precipitate.

Tracer technique offers excellent possibilities for the study of what actually happens in this separation, and since the tracer activities were available, a study was begun. The primary object of the research was to determine the number of steps necessary to prepare radioactive samples of a desired purity, and the technique used in the separations was devised with that in mind. However, the results are useful for interpreting gravimetric separations as well.

The radioactivities of nearly all of the samples described in this thesis were measured on a Lauritsen electroscope with a modified ionization chamber (14). The working part of the electroscope, the metal-sputtered quartz fiber arranged beside a condenser wire so that its displacement is proportional to its charge, was commercially made. The chamber consisted of a 2-inch diameter cylindrical cavity cut vertically through a block of aluminum 3¼ inches on each edge. The electroscope head was mounted in a hole cut through the front of this block, and at the back of the block was a ground glass window and a filament lamp for illuminating the electroscope fiber. The center chamber was sealed at the top by an aluminum foil of about 7 mg/cm^2 thickness held in place by a square, metal rim fastened by screws to the aluminum block. A similar aluminum foil 2.3 mg/cm^2 thick sealed the bottom of the chamber. The air inside the electroscope chamber was kept dry by two 1-inch diameter glass bulbs filled with Anhydrone and cotton. These bulbs were sealed with Apiezon-W wax into brass adapters screwed into holes in the side of the aluminum head. A sheet lead cover fitted just inside the metal rim on top of the electroscope, and beneath the aluminum block in front and back, grooved brass plates provided slots for brass shelves as low as 5 inches below the block. All of this was mounted on a wooden support so the telescope eyepiece came at natural eye level, and the charging connections were connected to a suitable source of potential, in this case a vacuum tube rectifier circuit. Mounted samples could be measured by placing them under the lid or on one of the brass stages below the chamber of the electroscope.

The carrier samples were mounted for measurement in onionskin paper packets. A weighed sample of the activity-bearing carrier was spread over a circular area one inch in diameter in the center of a 4-x 6-inch sheet of onionskin paper. The sample was carefully fastened into place with either a large gummed label or Scotch tape, and the four edges of the onionskin paper were folded up across the back of the label and fastened with another identifying label. The folded edges were spaced so the packet fitted snugly inside the fastener rim on the top of the electroscope. The one thickness of onionskin paper between the sample and the electroscope gave uniform results and there was only a small amount of absorption in the paper.

In the radiochemical work on the chromate separation of barium and strontium, gravimetric determinations indicated that with 20 mg of barium and 20 mg of strontium in a volume of 20 to 40 ml, a precipitation of the barium as chromate carried down from 6 to 10% of the strontium with the barium. When less strontium was present it was still important to know what percent of it was coprecipitated with the barium, but the amount could not be determined reliably by gravimetric means because its contribution to the final weight of $BaCrO_4$ was less than the degree of accuracy of the precipitation.

The technique of the tracer study was to precipitate barium as chromate from 20 ml of solution containing 20 mg of barium carrier, known amounts of pure 55-day strontium activity, and varying weights of strontium carrier. To the solution containing these materials and acidified with a drop of concentrated HCl were added 30 mg of $(NH_4)_2Cr_2O_7$. The solution was heated to boiling, and 2 ml of 20% ammonium acetate solution were added dropwise and with thorough stirring.

The precipitate of $BaCrO_4$ which formed was allowed to stand for several hours and was then filtered onto a weighed circular filter paper in a Gooch crucible. The weight of the precipitate was obtained by weighing the paper and sample after filtration and drying, and subtracting the original weight of the dry paper. The filter disc containing the precipitate was then mounted in the customary onionskin packet and its activity measured on the electroscope.

It is impossible to get 100% recovery by this technique of filtering since some precipitate falls off the edges of the filter disc, but recoveries of 95 to 97% are usual. The weight of strontium chromate in the mounted sample can be calculated from the weight of strontium in the solution and the percent of the total strontium activity found in the mounted sample. The weight of barium chromate can be obtained by difference, and the whole corrected to 100% recovery of the barium. It should be mentioned that in tracer studies it is seldom necessary to obtain 100 percent recovery of the carrier. If a known weight of carrier is used, any measureable recovery of the carrier permits calculation of the specific activity of the sample, and it is a simple matter to calculate the activity corresponding to 100 percent recovery of the carrier.

Table 3 gives the data which have been obtained in these precipitations of barium chromate from solutions containing strontium. These data have been plotted in several ways to find a regular behavior which can be expressed in a simple, useful equation, but the results have not been entirely successful. The earliest tests were on solutions containing strontium in amounts ranging from the weight of barium present down to amounts equal to only a few percent of the barium present. Throughout this range it was empirically found that the percent of total strontium carried down by the precipitation of barium chromate was a linear function of the log of the initial strontium concentration in the solution. However, later experiments with more widely varying strontium concentrations showed that this relationship is valid only over a limited range, and there is marked deviation at both higher and lower ranges of strontium concentration. Figure 3 is a plot of the percent of strontium carried down by the precipitation of 1 mg/ml of barium as chromate from a solution containing strontium concentrations of 10 mg to 26 grams per liter.

The weight percent $SrCrO_4$ contamination which a $BaCrO_4$ precipitate contains is a continuous but non-linear function

Table 3

The Coprecipitation of $SrCrO_4$ with $BaCrO_4$[a].

Wt. Sr in 20 ml soln (mg)	Wt. of Ppt. Mounted (mg)[a]	% Sr Activity Mounted %	Mg $SrCrO_4$ in Ppt. (X)	Mg $BaCrO_4$ in Ppt.[a] (M)	Percent Sr Co pptd. %[b]	Weight Ratio (X/M)	Concn. of Sr in Soln. (mg/liter)
524	57.0	1.12	13.6	43.4	1.12[c]	0.315	26200
524	55.2	1.29	15.7	39.5	1.29[c]	0.398	26200
106	45.9	3.35	8.25	37.6	3.35[c]	0.225	5300
106	47.6	4.20	10.6	37.0	4.24	0.285	5300
43.3	40.3	3.64	3.67	36.6	3.70	0.0995	2170
43.3	42.4	7.22	7.26	35.1	7.65	0.218	2170
22.3	39.8	6.68	3.46	36.3	6.85	0.0948	1115
22.3	39.5	7.97	4.13	35.3	8.40	0.1164	1115
11.9	38.6	10.56	2.92	35.7	11.0	0.0836	595
11.9	39.0	10.71	2.96	36.0	11.1	0.0843	595
6.65	38.0	13.70	2.15	35.9	14.2	0.0581	333
6.65	37.7	13.83	2.13	35.5	14.5	0.0598	333
3.5	38.2	15.85	1.29	36.9	16.0	0.0348	175
3.5	38.3	21.30	1.73	36.6	21.7	0.0467	175
1.40	36.8	22.8	0.74	36.1	23.5	0.0204	70
1.40	36.7	21.4	0.70	36.0	22.1	0.0195	70
0.70	36.6	25.5	0.41	36.2	26.2	0.012	35
0.70	36.0	22.6	0.37	35.6	23.6	0.0106	35
0.28	36.8	25.9	0.17	36.6	26.4	0.00458	14
0.28	37.0	23.8	0.15	36.8	24.0	0.00418	14
0.070	34.1	17.0	0.028	34.1	18.5	0.00079	3.5
0.070	34.3	15.8	0.026	34.3	17.2	0.00075	3.5
0.028	34.7	14.2	0.009	34.7	15.2	0.00027	1.4
0.028	34.2	20.8	0.013	34.2	22.6	0.00040	1.4

a $BaCrO_4$ = 37.2 mg in 20 ml solution. b Calculated to 100% $BaCrO_4$ precipitation.
c Assume 100% $BaCrO_4$ recovery.

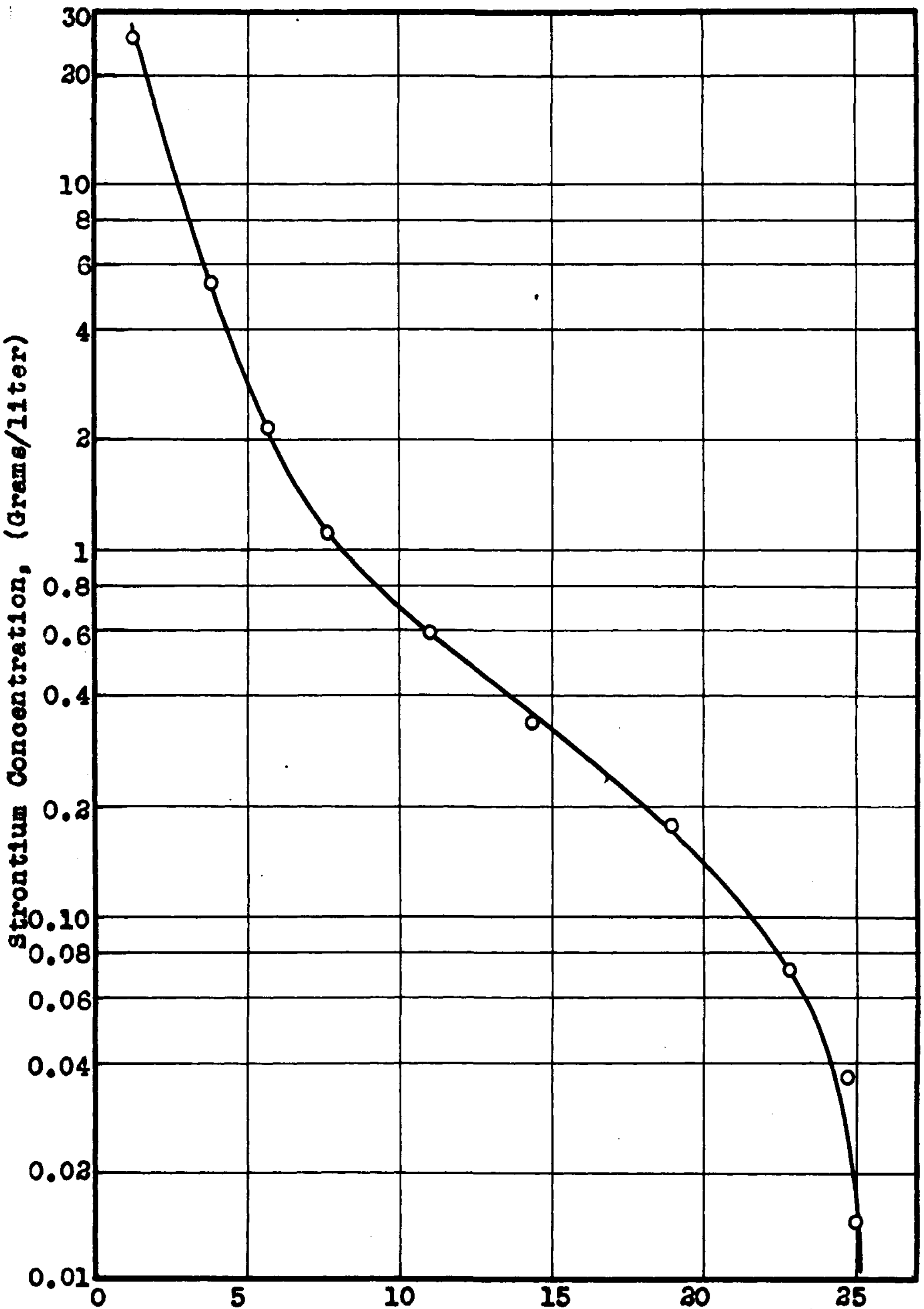

Figure 3. Coprecipitation of $SrCrO_4$ with $BaCrO_4$ from Solutions Containing 1 gram/liter Ba and Varying Amounts of Sr.

(Figure 4) of the strontium concentration of the solution from which it is precipitated. A curved line is also obtained when the log of the percent contamination is plotted instead of the percent itself. Any of these plots may be helpful in the estimation of the degree of purity of a chromate precipitate but they do not suggest a theoretical interpretation.

The data were plotted to see if the coprecipitation process follows Freundlich's isotherm, given by the expression

$\frac{X}{M} = K\ C^{1/n}$, in which

X = mg $SrCrO_4$ in a $BaCrO_4$ precipitate,

M = mg $BaCrO_4$ in the same precipitate,

K and n are constants,

C = concentration of Sr in the solution (mg/liter).

The plot of Log X/M against Log C should be a straight line. Figure 5 shows that this is approximately true only when C_{Sr} is less than 25 mg/liter. With strontium concentrations greater than this amount the deviation is very marked.

Newton (14) has shown that there is an extremely rapid recrystallization and interchange when aged silver bromide precipitates are placed in very dilute silver nitrate solution. The slight but appreciable solubility of $BaCrO_4$ in acetic acid solutions indicates that one should expect rather rapid interchange of atoms between the $BaCrO_4$ precipitate and the solution. Since precipitates digested for

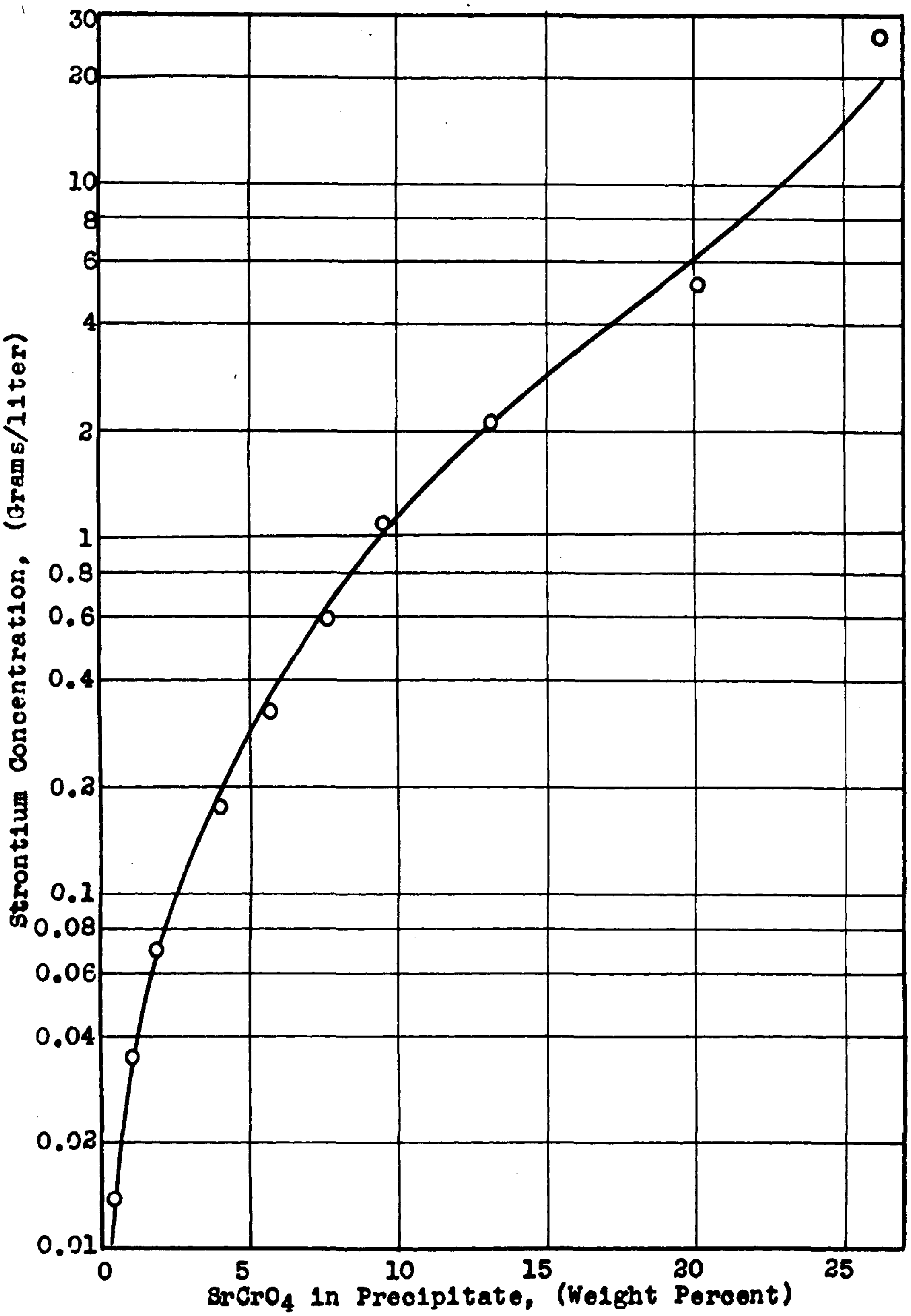

Figure 4. $SrCrO_4$ Contamination of $BaCrO_4$ Precipitated from Solutions Containing 1 gram/liter Ba and Varying Amounts of Sr.

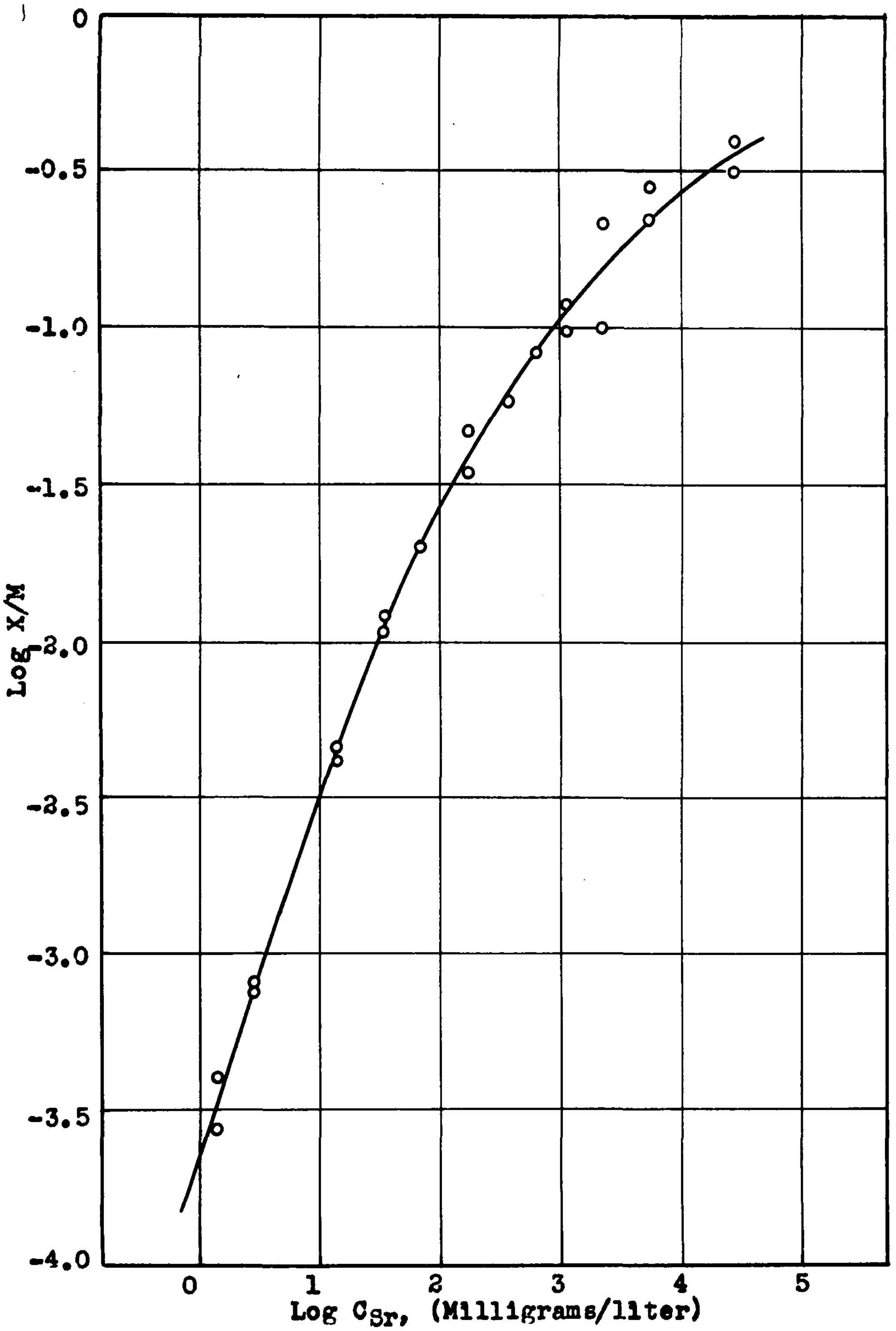

Figure 5. Plot of Freundlich's Absorption Isotherm as Applied to the Coprecipitation of $SrCrO_4$ with $BaCrO_4$.

several hours in solution still contain large amounts of strontium, it is likely that there is a dynamic interchange, perhaps with the attainment of equilibrium, between the strontium in the solution and the precipitate.

Rundle and Baenziger (47) have taken X-ray diagrams of $BaCrO_4$, $SrCrO_4$, and barium chromate which was precipitated from a solution containing a large amount of strontium and which, therefore, was strongly contaminated with strontium chromate. They have found that $BaCrO_4$ and $SrCrO_4$ have quite dissimilar structures. The sample containing coprecipitated strontium showed the barium chromate structure with a decided tightening of the lattice. Apparently when the coprecipitation occurs, the strontium atoms simply replace barium atoms in the $BaCrO_4$ crystal.

The existence of a reversible interchange between the strontium of the solution and the strontium contamination of a $BaCrO_4$ precipitate could be proved by placing an aged $BaCrO_4$ precipitate in a solution of radioactive strontium chromate buffered by ammonium acetate. If interchange does occur, the active strontium will appear in the precipitate. A measure of the strontium activity in the precipitate gives a measure of the degree of interchange, and if the process is followed for some time the rate can be calculated. When the system has become static, the degree of $SrCrO_4$ contamination of the $BaCrO_4$ indicates if the coprecipitation of $SrCrO_4$ with $BaCrO_4$ is a reversible equilibrium process or if the contamination is possible only by simultaneous precipitation from solution. While this is an interesting experiment from a scientific viewpoint, it was not carried out because it had little bearing on the problem which promoted these studies.

As a result of these studies it was concluded that a double precipitation of $BaCrO_4$ gave a separation of barium from strontium satisfactory for most of our requirements. It can be seen from Figure 3 that the precipitation of 20 mg of barium as chromate from 20 ml of solution containing 20 mg of strontium carries down about 8% of the strontium in the initial precipitate. After solution of the $BaCrO_4$ and reprecipitation about 2% of the original strontium still remains in the barium fraction. This is approximately the accuracy of the electroscope measurements, and was satisfactory for assay analyses. Since the strontium fraction usually had a specific activity only about one-fourth as great as that of the barium fraction, a 2% weight contamination corresponded to a 0.5% activity contamination. Each reprecipitation after the first one reduced the strontium in the precipitate by a factor of four to five.

1.4 The Identification of Y^{90} in Fission Product Material and the Discovery and Identification of Sr^{90}.

In connection with the work on the isolation of barium and strontium activities from fission product material, the activities of several samples of strontium were measured for a number of months to check the 55-day half-life (16), the longest reported previous to this work. It was observed that samples six to seven months old showed half-lives longer than 55 days, and a new or foreign activity was suspected.

The cerium activity then reported as having a 200-day half-life seemed the most likely contaminant, so an aged sample of active strontium carbonate was dissolved in nitric acid and treated with a few milligrams of cerium carrier. The cerium was precipitated by ammonium hydroxide, and strontium carbonate reprecipitated from the filtrate. The activity of both precipitates were followed. The hydroxide insoluble fraction showed a half-life of about 70 hours, tailing off in a small amount of long-lived background, and the strontium showed a scarcely measurable growth and a half-life longer than 55 days.

It was fairly certain that a long-lived strontium was at hand, but the short-lived activity could be either its daughter yttrium or granddaughter zirconium. Accordingly, the following experiments were performed to establish the identity and nature of the activities with certainty. A highly purified strontium carbonate sample isolated about a week after fission and allowed to stand until about 7 months after fission was dissolved in nitric acid and after the addition of 10 mg each of yttrium and zirconium carriers, strontium was reprecipitated as strontium nitrate by the use of fuming nitric acid. Following centrifugation and washing with 80% HNO_3, the product strontium nitrate was dissolved in water and strontium carbonate precipitated by the addition of ammonium carbonate solution. This pure sample exhibited an initial period of growth and a subsequent half-life of greater than 55 days. On the other hand, strontium activity separated a week after fission showed no growth and an initial half-life of nearly 55 days (Figure 6). This was later proved to be due to the fact that shortly after bombardment the activity of the long-lived Sr^{90} is relatively so small compared to the Sr^{89} activity that it was undetected. The detection of Sr^{90} in old samples depends on the fact that the Sr^{89} decays more rapidly and the relative contribution of Sr^{90} increases.

To identify the daughter activity, the solution from the fuming nitric acid separation was diluted, treated with 20 milligrams of inactive strontium carrier and again subjected to the fuming nitric acid precipitation of strontium nitrate to remove the trace of strontium activity remaining from the first separation. The fuming nitric acid solution was evaporated nearly dry, neutralized with ammonium hydroxide, and taken into solution with one drop of dilute hydrochloric acid. The solution was transferred to a lusteroid tube, and yttrium fluoride was precipitated with 6 N HF. The solution was centrifuged and decanted into a

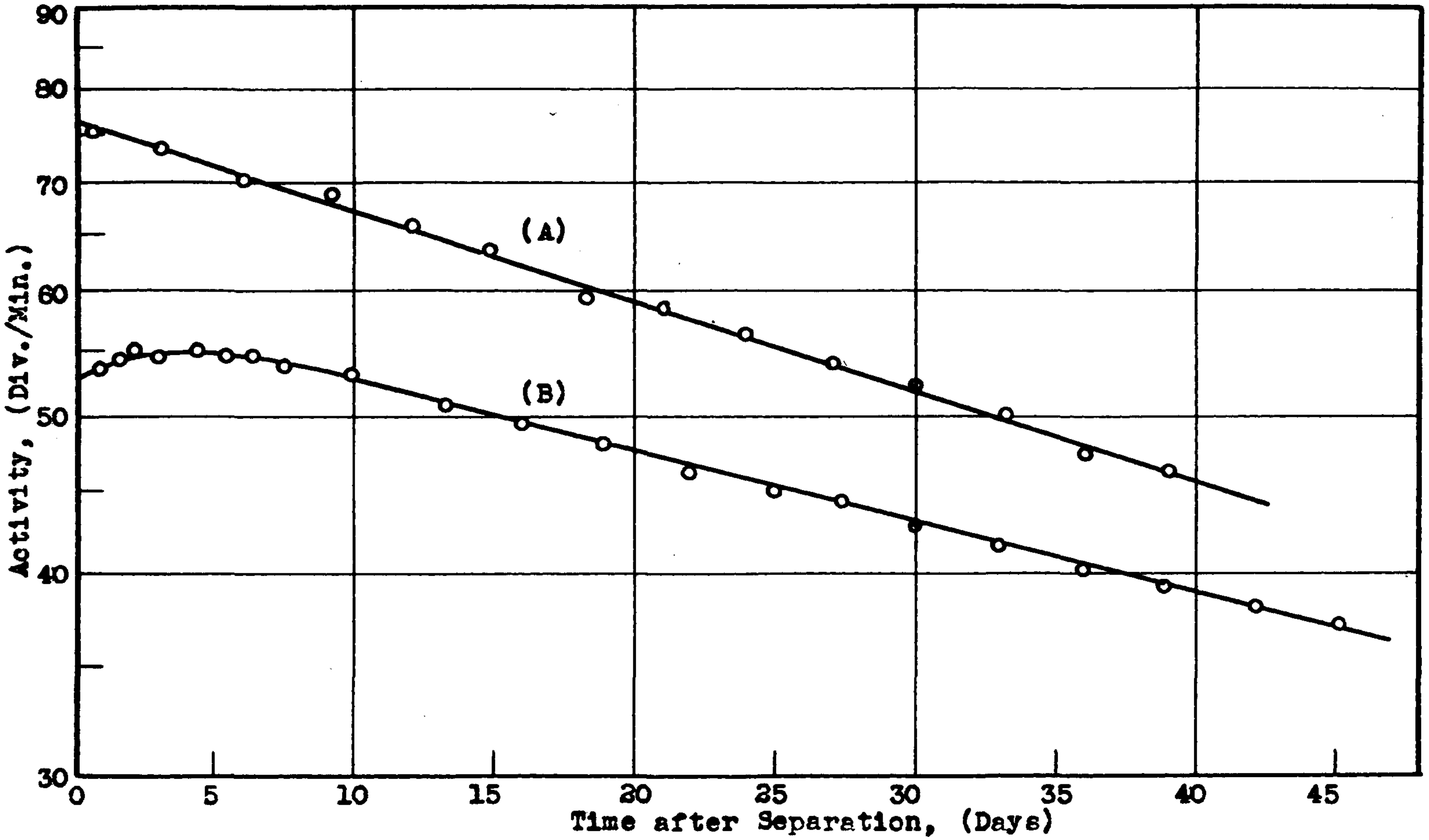

Figure 6. Decay Curves of Radio-strontium from Uranium Fission. (A) Activity separated 1 week after bombardment, showing nearly pure Sr^{89} decay. (B) Activity separated 7 months after bombardment, showing contribution of Sr^{90} and its daughter Y^{90}.

platinum dish, and the precipitate was washed with 6 N HF, centrifuged, and the wash solution decanted into the platinum dish.

The yttrium fluoride precipitate was washed from the centrifuge tube into a separate platinum dish. Both yttrium and zirconium fractions were fumed with H_2SO_4 to remove HF and, after fuming, the strong acid was diluted with water. The respective hydroxides were precipitated with ammonium hydroxide, filtered, ignited to oxides, weighed, and a weighed sample of each oxide mounted for activity measurements on the electroscope. All but a few percent of the activity appeared in the yttrium fraction, and what activity remained in the zirconium fraction decayed with the same half-life as the yttrium, indicating merely that the chemical separation was not complete.

A knowledge of the half-life and the radiation characteristics of the yttrium isotope was essential for its identification. For these determinations a sample of aged strontium activity with carrier was doubly purified by subjecting it to a fuming nitric acid separation to remove all elements but barium, adding inactive barium carrier and making a barium chromate precipitation, and then adding a few milligrams of ferric nitrate and precipitating ferric hydroxide with ammonium hydroxide. No filtration was made between the precipitation of barium chromate and the precipitation of ferric hydroxide, and the latter served to trap the chromate precipitate and insure its complete retention on the filter along with any hydroxide-insoluble matter which might have slipped through the fuming nitric acid separation. Pure strontium carbonate was precipitated from the filtrate by the addition of ammonium carbonate solution.

The purified strontium activity was allowed to stand a week after its purification to permit its daughter activity to grow to a useful concentration. Then the carbonate was dissolved in nitric acid and treated with 10 mg of yttrium carrier. A fuming nitric acid separation was made to precipitate most of the strontium from the yttrium, the centrifugate was diluted, treated with 20 mg inactive strontium carrier, and subjected to a second fuming nitric acid separation to remove still more of the strontium activity. The centrifugate of this separation was boiled to near dryness, diluted, and treated with ammonium hydroxide to precipitate yttrium hydroxide. The precipitate was filtered, ignited, and mounted as Y_2O_3. The decay and absorption curves of this material were measured on the electroscope, and are shown in Figures 7 and 8, respectively. The half-life was determined to be 65.5 hours, and the beta ray had a range of 1.250 grams Al/cm^2, which corresponds to a maximum energy of 2.6 Mev.

The energy was calculated from the range by the equation of Feather (48):

$$R = 0.543\, E_m - 0.160, \text{ where}$$

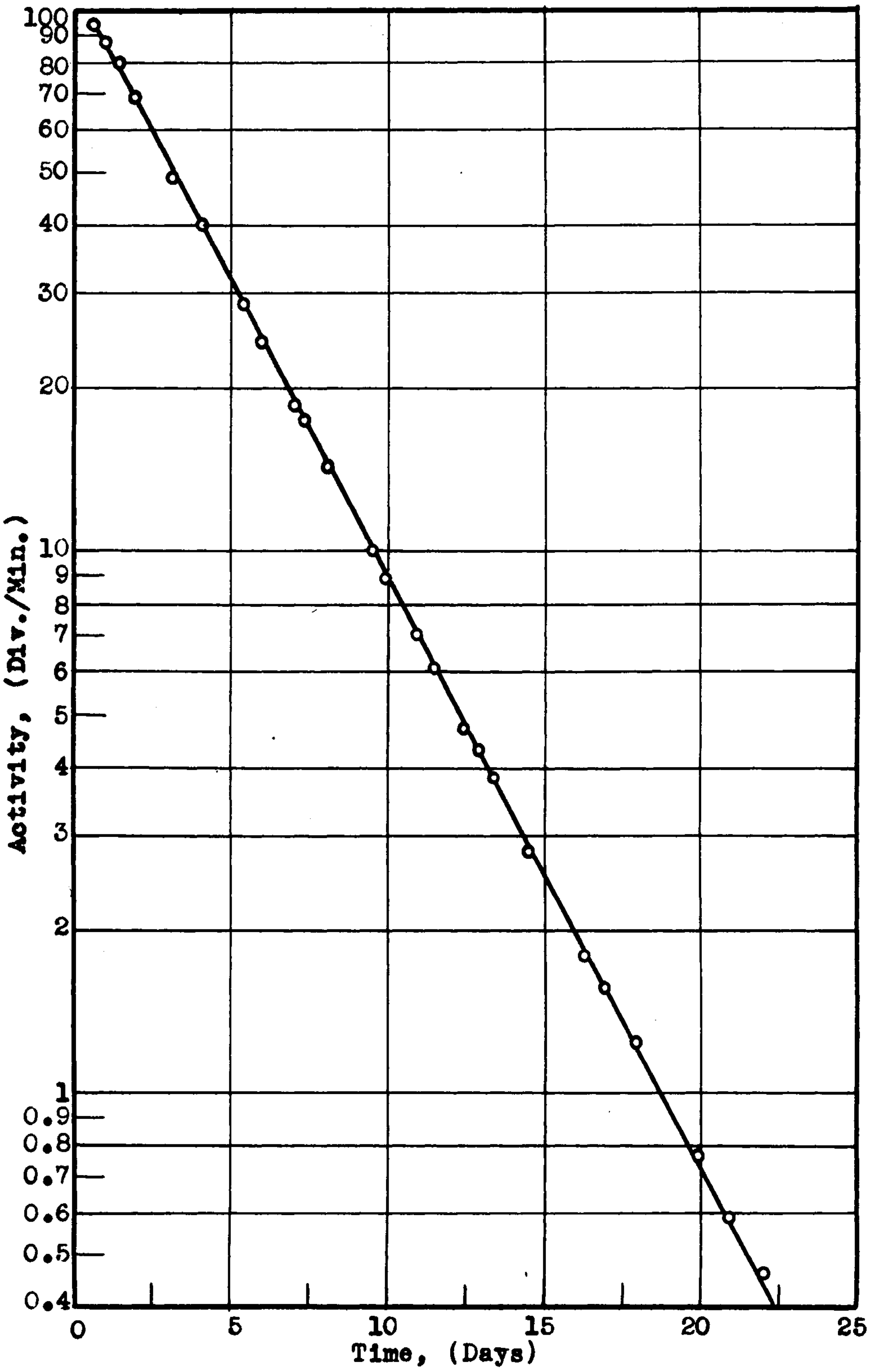

Figure 7. Decay Curve of Y^{90}, $T_{1/2} = 65$ Hours.

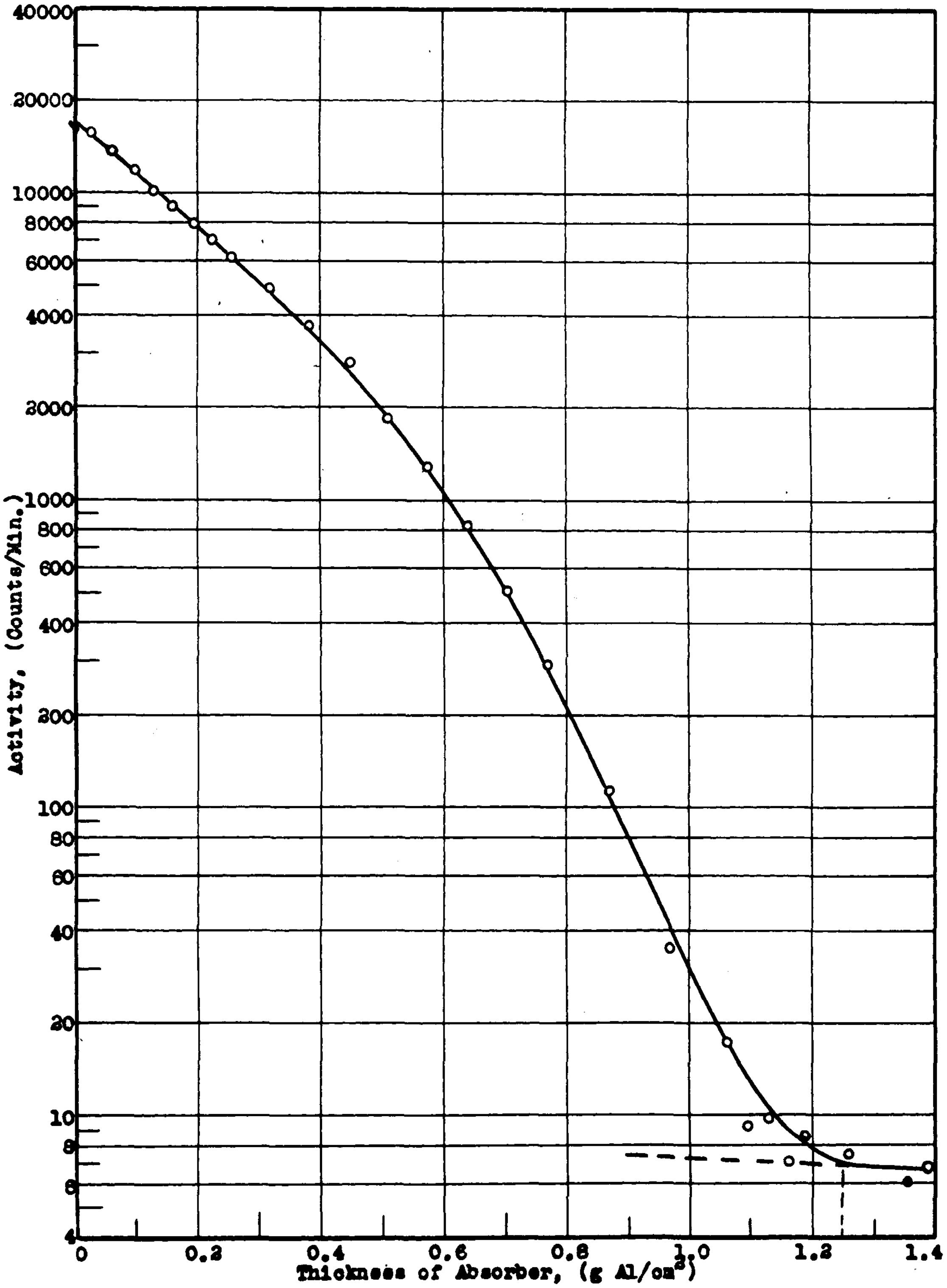

Figure 8. Absorption Curve of Y^{90}, Range = 1.25 g Al/cm^2.

R is the range of the beta particles (grams Al/cm^2),

E_m is the maximum energy of the radiation (Mev).

[Feather determined the equation experimentally by plotting the ranges (maximum penetration through aluminum) of monoenergetic beta particles as a function of their energy. The beams of monoenergetic beta particles were usually obtained from a mass spectrograph.] This activity is apparently identical with the previously reported Y^{90} (16), whose beta ray has this same energy and whose half-life has been reported to be 60 hours. The strontium fraction from which this yttrium was separated showed a growth of activity which was equal to the decay of the daughter yttrium. This gives additional proof of the parent-daughter relationship.

Visual comparison of the absorption curves identically determined on samples of fresh and eleven-month-old strontium activities indicated that Sr^{90} has a relatively weak radiation. Figure 9 shows an absorption curve determined on a nine-month-old strontium sample freshly separated from yttrium, and the curve for the Sr^{90} component estimated by subtracting the Sr^{89} background. The range of the beta ray was estimated to be about 130 mg Al/cm^2 (about 0.4 Mev) (49). Because the Sr^{89} contributes such a large part of the total activity of this sample, the absorption curve for Sr^{90} is only approximate. For a more exact determination a sample must be used whose age after bombardment makes the contribution of Sr^{89} activity smaller.

Direct determination of the half-life of Sr^{90} was not possible because its radiation is weak and it was available only in the presence of a high Sr^{89} background. However, if the ratio of the fission yields of Sr^{89} and Sr^{90} is a constant, for short bombardments the ratio of the Sr^{90} activity (or equilibrium Y^{90} activity) to Sr^{89} activity is a function only of the half-lives of Sr^{89} and Sr^{90} and the time after bombardment. With strontium samples of known ages after bombardment, in equilibrium with daughter yttrium, chemical separations can be made and Y^{90} activity determined as a function of Sr^{89} activity and time after bombardment. Assuming Sr^{89} to decay with a half-life of 55 days, a calculation of the actual decay of Sr^{90} can be made. In measuring the Sr^{89} activity, it is necessary to remove Y^{90} from the sample, and then measure the strontium activity through sufficient aluminum to absorb the beta ray of Sr^{90}. Samples of but a few different ages were available, and the effective age of one of these was uncertain because it had been given a non-uniform bombardment over a long period of time (about 6 weeks). The inability to fix the effective age after bombardment of the sample made it impossible to calculate the amount of decay which the 55-day Sr^{89} reference activity had undergone and thus reduced its value as a reference standard. The value of the standard is also dependent upon the accuracy of the determination of its half-life, and since this accuracy was not known for Sr^{89},

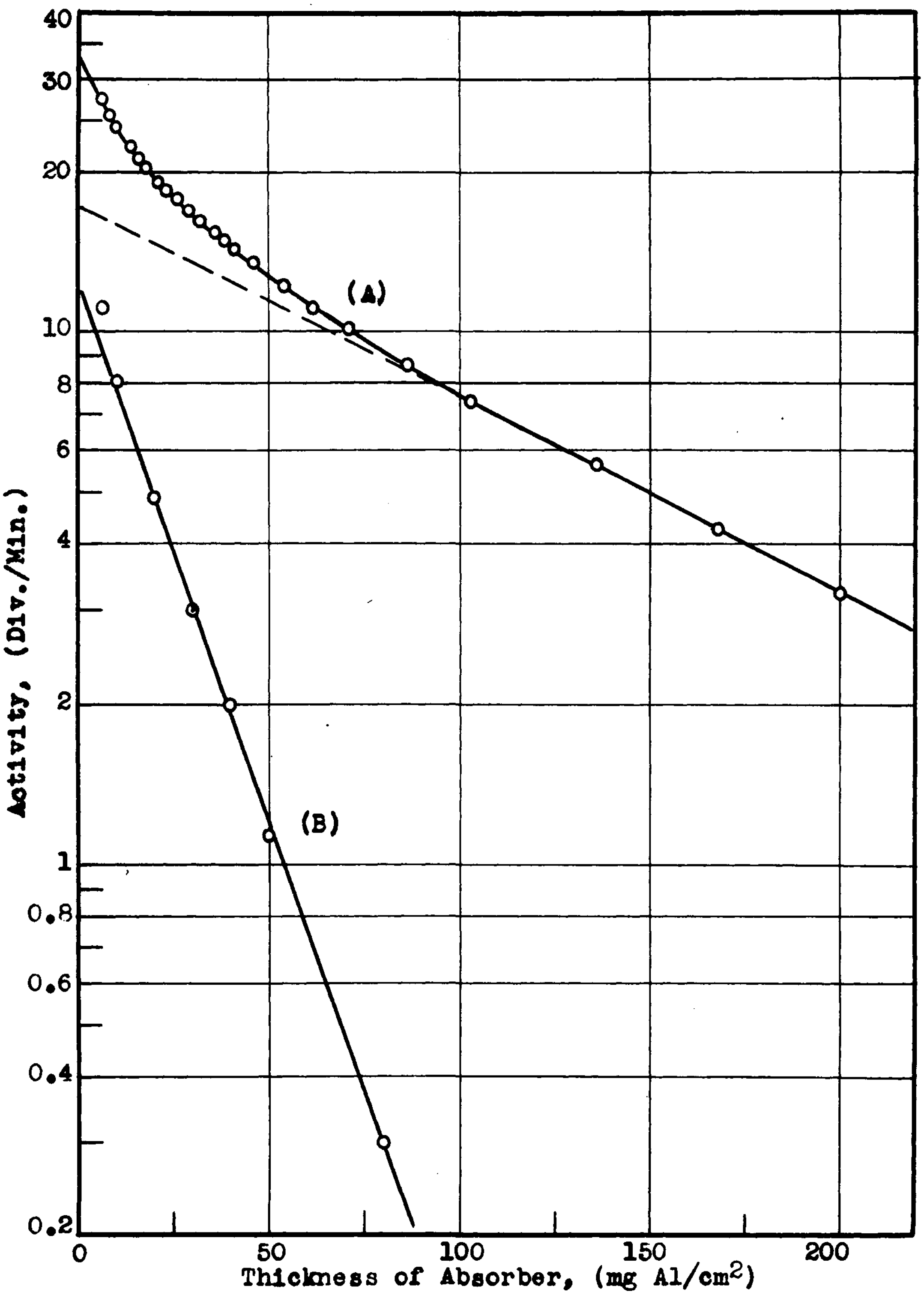

Figure 9. Absorption Curves of Radio-strontium from Uranium Fission. (A) Mixed Sr^{89} and Sr^{90} activities. (B) For Sr^{90}, by subtraction of Sr^{89} background.

the results based on the half-life were of uncertain meaning. It was concluded that when applied to the active samples which were available, this method was ineffective in the estimation of the half-life of Sr^{90}.

It is possible to make an indirect measure of the half-life of Sr^{90} by measuring the activity of Y^{90} decaying in equilibrium with its parent. Y^{90} has a hard beta ray which permits its measurement through 760 mg Al/cm^2, which is sufficient to absorb all of the strontium radiations except the slight bremstrahlung background. (The bremstrahlung background consists of continuous electromagnetic radiation produced by the interaction of high energy beta rays with the field of the nucleus of a heavy atom. Consequently, this radiation accompanies all beta radiation, and its counting rate is usually about 1/4000 of the counting rate of the beta ray.) A sample measured in this way over a period of 3 months (Figure 10) showed a probable decay of 1%, with individual readings deviating from the average by about 2%. Assuming 2% as the maximum error of the measurement, the decay could not have been more than 3% of the original activity. Under these conditions the minimum half-life can be calculated by the equation.

$$I/Io = e^{\frac{-0.693t}{T_{1/2}}}$$

If t is 90 days and I/Io is 0.97, $T_{1/2}$ is 2100 days or about 6 years. Using the observed value of $I/Io = 0.99 \pm 0.02$, the calculated half-life is 17 years. There is no way

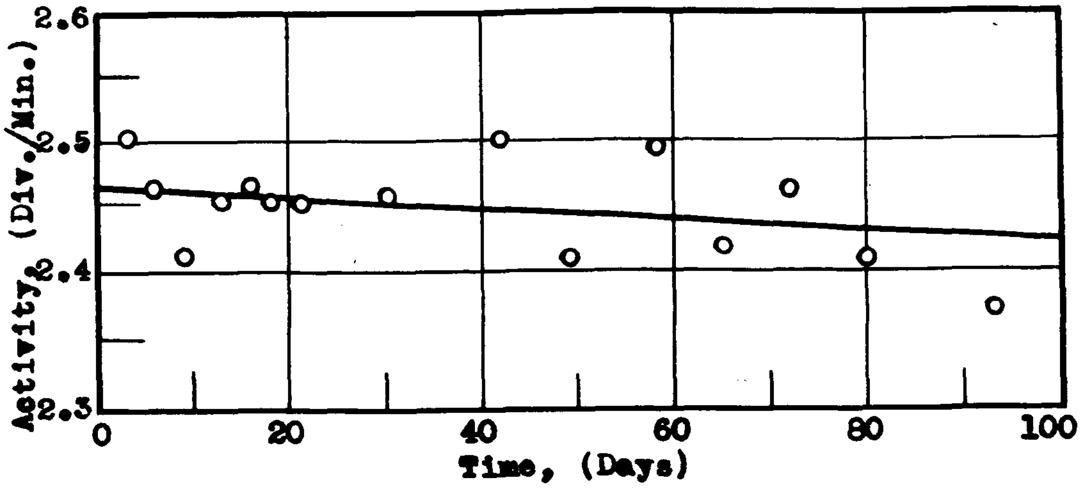

Figure 10. Decay Curve of Sr^{90}, Measured Via Y^{90} Daughter at Equilibrium.

to decide from the data how nearly correct this value may be. Until the decay is followed for a longer period of time the half-life may be given as greater than 6 years. This half-life, like the energy of the radiation, is approximate only, and is subject to revision when more accurate data become available. The value of the half-life is in agreement with Coryell's (17) theoretical prediction of 31-year half-life, based on expected fission yields and counting rates.

PART II

THE DETERMINATION OF THE VAPOR PRESSURE OF URANIUM TETRABROMIDE

2.1 Introduction

The slow neutron pile places rigid purity requirements on a number of components chief among which are the fissionable material and the moderating material. Many other components, e.g., the pile coolant, walls, coolant conduits, coatings of the slugs of fissionable material, also play parts of varying importance depending on the design of the particular pile. The fissionable material may sometimes be present as a compound, such as oxide or carbide, but it is usually desirable and sometimes necessary that it be present as the pure element. Factors which make the use of uranium metal desirable are the greater thermal conductivity of the metal, the greater ease of coating metal slugs to protect them when they are to be used in a water-cooled pile, and the elimination of the neutron reactions with the inert component when uranium is present as a compound. The extreme purity of metal required in some instances caused the initiation of a study on the production of very pure uranium.

Uranium metal can not be subjected to a sublimation to distill it *free* from its contaminants, nor can it be purified completely by the converse, heating the metal and letting the impurities boil out. If pure metal is desired, it must be produced directly from the reduction of a pure uranium compound by a pure reducing agent which does not itself remain in the uranium metal. The halides are about the only compounds of uranium which can be reduced readily to the metal, so the production of extremely pure metal must almost certainly go through the halide stage.

Uranium bromide was known to be reducible to metal, and after reduction the amount of bromine remaining in the metal as a contaminant was very small and within the tolerable maximum. Although UBr_3 is nonvolatile, UBr_4 was known to be volatile, and the possibility existed that a volatilization process could be worked out to yield a good separation of the uranium from both heavy and light elements and to produce pure UBr_4 in a form ready for reduction. The intelligent appraisal of such a process required a knowledge of the vapor pressure of uranium tetrabromide over a wide range of temperatures. The only vapor pressure data which were available for UBr_4 were those determined by Thompson and Scheldberg (18, 19) using the effusion method over the temperature range 300° to 450°C. The theoretical limitations of this method make it ineffective with vapor pressures above about 0.01 mm, when the mean free path of the molecules is nearly equal to the diameter of the effusion orfice. The data could only be used by extrapolating the plot of Log P versus 1/T to higher temperatures and, because the individual readings with the effusion method are accurate only to within 10 to 20 percent, this extrapolation was not reliable.

The transpiration method of determining vapor pressure is applicable over a higher range of pressures, it can be carried out to a greater degree of accuracy, and its operation is probably more reliable. Therefore this method was used to determine the vapor pressure of UBr_4 in the temperature range 450° to 650°C and the pressure range 0.3 mm to 107 mm Hg. The transpiration method depends in principle upon the saturation of an inert carrier gas with the vapors of the sample and then passing the saturated carrier gas through a collector, which removes the vapor and allows the carrier gas to pass on. Condensed sample and carrier gas are collected until the amounts of both can be measured. After measurement, the vapor pressure of the sample is calculated from the pressure in the saturation chamber and the mol fraction of its vapor in the gas.

2.2 Experimental Part

The uranium bromide used in the vapor pressure determination was prepared and sublimed in the apparatus pictured in Figure 11. This apparatus may be used in several ways. First, crude uranium tetrabromide may be prepared elsewhere and transferred to bulb (A) of the apparatus for sublimation. Second, uranium turnings may be placed in (A) and converted in place to UBr_4 through a series of intermediates.

$$U \xrightarrow[250^\circ]{H_2} UH_3 \xrightarrow[300^\circ]{HBr} UBr_3 \xrightarrow[300^\circ]{Br_2} UBr_4$$

Third, uranium turnings may be placed in the flask and converted to UBr_4 directly and with simultaneous sublimation, using purified helium at a flow rate of about 2 liters per minute to sweep bromine vapor into, and UBr_4 out of, the reaction chamber while it is held at 600-700°C.

Purified nitrogen may be used readily as an entrainer gas for the sublimation of preformed UBr_4, but it may be used only with much more care in the direct reaction-sublimation procedure. Nitrogen reacts with neither UBr_3 nor UBr_4, but it does react with hot uranium metal, and it is this reaction which causes difficulty. Bromine reacts with uranium nitride to displace nitrogen and form uranium bromide, and if this reaction can be maintained at a faster rate than the reaction of nitrogen with metal, the process works well. Otherwise, excess nitride is formed and it may either break up and clog the tubes to stop the process, or the reaction with nitrogen may be so rapid it draws air back through the exit trap.

Uranium bromide was prepared by all three methods, using both helium and nitrogen entrainer gas. The actual sublimation was always carried out at 600-700°C, and with rates of gas flow appropriate for each condition. Both with nitrogen and with helium entrainer gas the product was

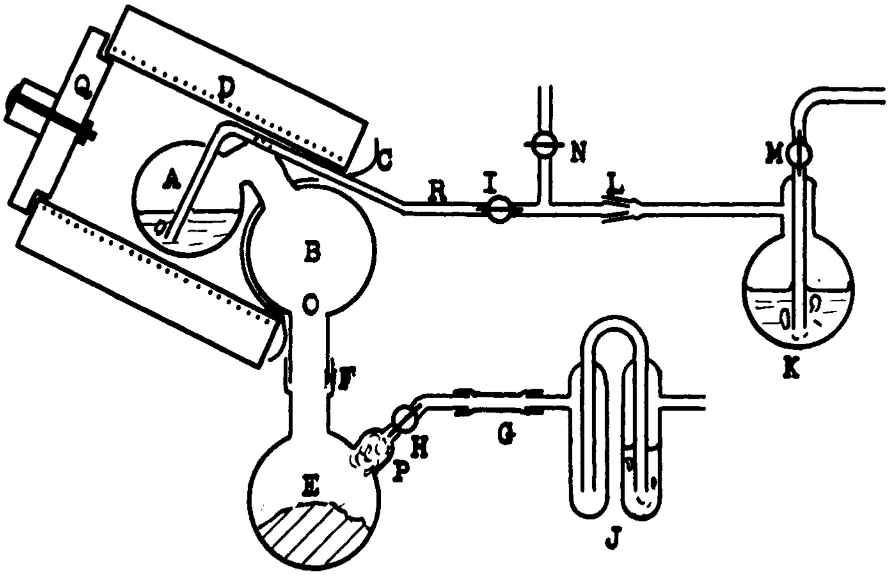

Figure 11. Apparatus for the Sublimation of Anhydrous UBr_4.

A.	Quartz reaction flask with inlet tube.
B.	Liter quartz flask used as condensing chamber.
C.	Aluminum foil reflector used for insulation.
D.	Electrical resistance furnace.
E.	Liter pyrex flask used as sublimate collector.
F.	Quartz to pyrex joint sealed with Apiezon W wax.
G.	Rubber tubing.
H.	Stopcock.
I.	Stopcock.
J.	Sulfuric acid bubbler and trap.
K.	Bromine reservoir.
L.	Standard taper ground glass joint.
M.	Gas inlet.
N.	Gas outlet to hood.
O.	Opening which occasionally plugs with sublimate.
P.	Glass wool plug to retain fine product.
Q.	Removable end of furnace for observation.
R.	Graded quartz to pyrex seal.

formed in flask (B) and dropped to flask (E) in the form of large brown plate-like crystals and a tan-colored, dense crystalline powder. No difference in appearance of the crystals was observed when nitrogen was substituted for helium as the carrier gas, and the analyses of all material used in the vapor pressure studies indicated a composition of UBr_4. The following is a typical analysis:

	Theoretical, UBr_4;	Found:
Percent Uranium	42.7 %	42.6 %
Percent Bromine	57.3 %	57.3 %

The apparatus and method used in the vapor pressure determinations were modified from those described by Jellinek and Rosner (20). The apparatus is shown in Figure 12. After preliminary experiments had indicated that uranium bromide was inert to pure nitrogen at the temperatures used in the experiments, nitrogen was chosen as the carrier gas. Since tank nitrogen contains small amounts of oxygen and perhaps other impurities, it is necessary to subject it to a rigorous purification before it can be used. The purification technique was that developed by Newton (21) and the purification unit is shown in the upper part of Figure 12 along with the pressure regulating and flow indicating devices.

Nitrogen was removed from a tank through a pressure regulator and admitted to the system through the stopcock

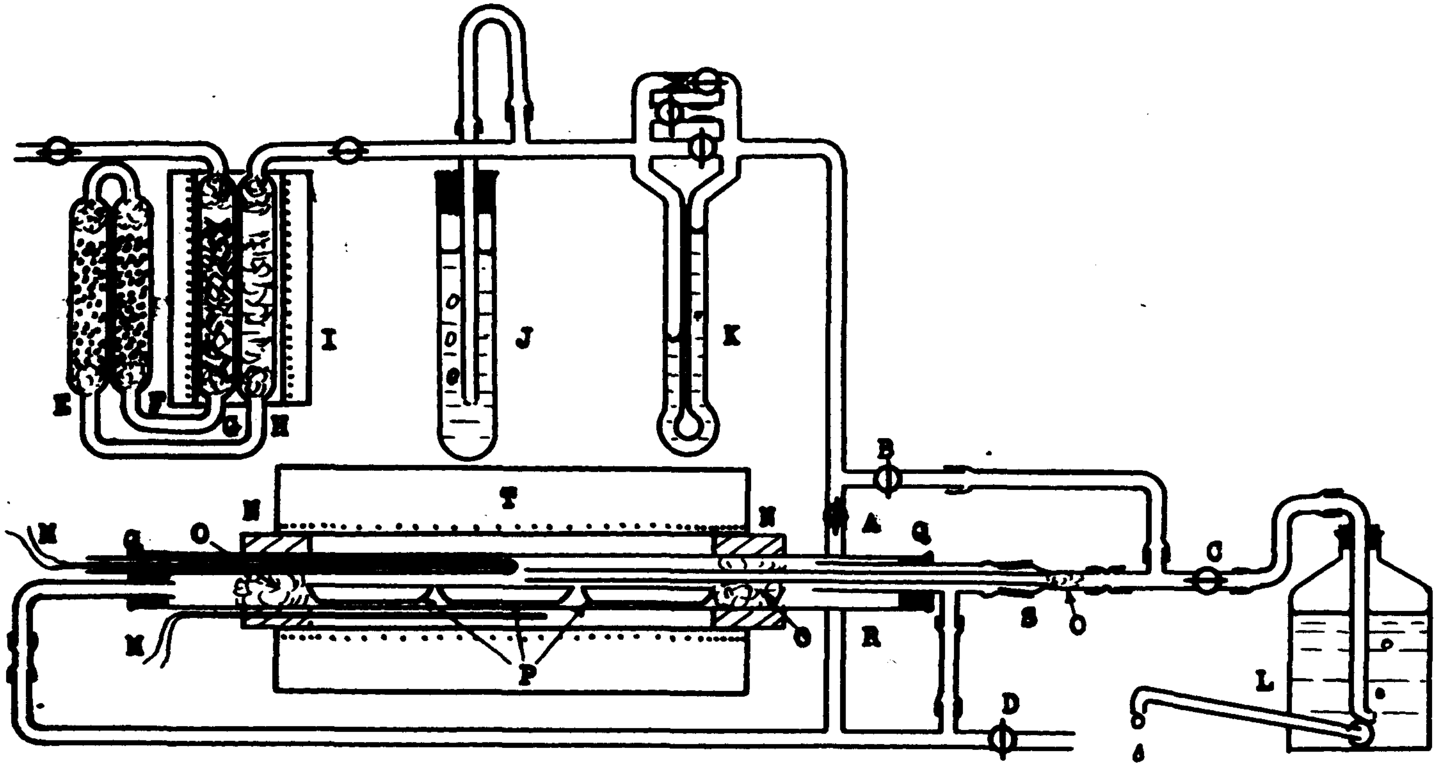

Figure 12. Apparatus for Determining the Vapor Pressure of UBr$_4$ by the Transpiration Method.

A) Stopcock--gas inlet for sample collection. B) Stopcock--gas inlet for flushing system. C) Stopcock--gas outlet for sample collection. D) Stopcock--gas outlet for flushing system. E) Anhydrone at room temperature. F) Ascarite at room temperature. G) Copper - copper oxide at 600°C. H) Uranium nitride loosely packed in glass wool at 600°C. I) Resistance furnace at 600°C. J) Pressure regulator. K) Capillary flowmeter with bypass. L) Mariotte flask. M) Chromel-Alumel thermocouples. N) Firebrick cylinders for insulation. O) Pyrex glass wool plugs. P) Gold sample boats. Q) Rubber stoppers. R) Quartz collection tube with graded quartz to pyrex seal. S) Glass standard taper joint. T) Resistance furnace.

at the upper left and passed through an all-glass purification chain consisting of a tube of Corning 172 glass containing mixed porous copper oxide and reduced copper (G) at 600°C, pyrex tubes containing Ascarite (F) and Anhydrone (E) at room temperature, and a tube of Corning 172 glass containing uranium nitride (H) loosely packed in glass wool, at 600°C. Much of the oxygen was removed by reaction with copper in the first tube, and any organic matter in the nitrogen was oxidized by the CuO. Carbon dioxide and other acidic impurities were absorbed in the Ascarite, and water was absorbed by the Anhydrone. This treatment gave nitrogen which contained only traces of reactive elements. The next tube containing uranium nitride, loosely packed in glass wool to lessen its resistance to the gas flow, removed the last trace of oxygen and possibly removed some other trace elements which might not have been caught in the previous tubes.

The two Corning 172 glass tubes which contained copper oxide and uranium nitride respectively, were kept heated to 600°C by placing them in a resistance furnace, or by insulating them with a few layers of asbestos paper and wrapping electrical resistance wire about the outside of the paper. In the latter case an inch or more of good insulating material was placed about the outside of the resistance wire to minimize heat losses.

The reaction of uranium nitride by which it absorbs oxygen and some other substances is one of displacement.

Uranium nitride, although a very stable substance, is much less stable than uranium oxide, and the following reaction takes place.

$$U_xN_2 + xO_2 \longrightarrow xUO_2 + N_2 \quad (x = 1.142 \text{ to } 1.333).$$

In air, uranium nitride burns vigorously when ignited, and some samples are pyrophoric. When used at 600°C in the purification apparatus, it removes the last trace of oxygen from the gas until it has been almost entirely converted to oxide. This method of nitrogen purification can be recommended very highly, for it not only yields a dry effluent gas in which oxygen is not detectable by alkaline pyrocatechol, but the method is very convenient to use. The apparatus can be built as a unit on a ringstand; the system can be closed by stopcocks to prevent the entry of air when it is not in use, and it can be set aside indefinitely without deterioration, ready for use simply by heating the furnace. The use of uranium metal and hydride in purifiers and "getters" for the removal of other gases suggests that the nitride may remove other contaminants than oxygen, but this has not been studied thoroughly.

The pressure of the nitrogen effluent from the purifier was controlled accurately by having an excess bubble slowly through the constant head escape (J). The depth of immersion of the bubbler exit could be varied by sliding the tube through the cork stopper at the top of the container. Dibutyl phthalate was used as the bubbler liquid, and a constant pressure head from 0 to 25 cm could be maintained.

The gas flow rate was measured on the flowmeter (K) by measuring the pressure drop of the gas as it flowed through a capillary constriction. Dibutyl phthalate was used in the manometer, and a bank of capillaries with a control stopcock for each capillary made it possible to select a capillary which was accurate for the flow rate desired, or to use an unconstricted by-pass to obtain large flow rates for sweeping out or evacuating the system. The gas flowmeters were carefully calibrated before use.

The furnace (T) in which the samples were heated was 16 inches in length, and had a temperature-equalizing core of Monel tubing 2 inches in outside diameter and with walls 1/8-inch thick. Outside this core was a layer of air-drying Sillimanite and then a wrapping of 32 feet of 18-gauge Chromel-A resistance wire. The wire was wrapped closely at the ends, so that in the four inches from each end the wrapping frequency doubled. This non-uniform wrapping was used in an attempt to make the temperature of the furnace uniform throughout. The high heat loss from the ends of the tube requires a much closer winding at the ends than is required in the center. Actually, even the increased frequency used in winding the ends of this furnace did not fully compensate for the extra loss, for a temperature traverse of the furnace showed the temperature four inches from the center to be about 5°C less than the temperature in the center. The core and electrical leads were anchored in 1/2-inch transite end-pieces and the outside of the furnace was an 8 inch diameter cylinder of galvanized iron sheet, also fastened into grooves in the transite end-pieces. The 3-inch cylindrical space between the core and the outside sheet was filled with Dicalite insulation. Fifty volts across the resistance wire of the furnace maintained the furnace temperature at about 600°C.

The temperature of the furnace was maintained constant to ±2°C by the photoelectric cell control circuit built by Gray (22). In this control apparatus a galvanometer was connected in a circuit actuated by a Rubicon potentiometer and a Chromel-Alumel thermocouple so that a drop in temperature caused the galvanometer needle to uncover a slit and allow passage of light to a photocell. The photocell actuated a switch which, when closed, shunted an external resistance in the furnace heating circuit. This external resistance was about one-fourth the resistance of the furnace. By a Variac transformer a voltage sufficient to heat the furnace slightly hotter than the desired temperature was applied across the furnace plus the external resistance. When the galvanometer needle uncovered the slit to the photocell, the external resistance was shunted out and the full voltage was applied to the furnace, causing a temperature rise. When the galvanometer needle covered the slit, the shunt circuit was broken and the external resistance reduced the voltage across the furnace to about 80% of its full value, causing a drop in furnace temperature.

Extending an inch inside and an inch outside the ends of the furnace tube were fire brick cylinders closing the ends of the furnace and supporting the sample tube, a Vycor tube 27 inches long and 1 inch in diameter. This Vycor tube was closed by two rubber stoppers. Through holes in the left stopper were a thermocouple sheath extending to the center of the furnace, and a gas inlet tube. The rubber stopper was not sufficiently rigid to hold the end of the thermocouple sheath inside the furnace against the top of the Vycor tube and, since this was essential to keep the sheath from dropping into and overturning the samples, an extra support was devised. A 3/4-inch length of glass tubing whose diameter permitted it to fit easily into the Vycor tube was heated on one side with a torch, and with the straight side of a carbon pencil a lateral indentation was made so that the tube was about one-fifth closed off. When viewed through the end this presented the appearance of a cylinder with a flat shelf across the inside. In use, this cylinder (not shown in figure) was slipped about 3 inches in the end of the Vycor tube and the thermocouple sheath was supported on the "shelf" it offered.

Through the stopper in the right end of the Vycor tube extended the female of a ground glass joint which had a side connection to the nitrogen supply. Through this joint the sample collection tube was inserted. The sample collection tube consisted of a 5-mm quartz tube extending to the center of the furnace and fastened to the male member of the ground glass joint through a graded quartz-to-pyrex seal just outside the furnace. There were three interchangeable sample collector tubes to facilitate rapid change from one collection to another. The uranium bromide whose vapor pressure was being determined was placed in three 4-inch sample boats made from heavy gold foil. To minimize convection currents in the tube, loose pyrex glass wool plugs were placed inside the tube even with the ends of the furnace. A glass wool plug was also placed near the exit end of the sample collection tube to trap fine solid particles of UBr_4 which condensed out in the carrier gas and were carried along in the gas stream. At the extreme exit of the collection tube was a Mariotte bottle which collected the total volume of carrier gas while maintaining the rest of the system at atmospheric pressure.

The charge of pure sublimed UBr_4 was placed in the vapor pressure furnace by the procedure described below. With the left-hand side of the apparatus completely assembled, the right stopper was removed from the furnace tube and a loose-fitting cork was placed in the end of the tube to prevent back diffusion of air into the apparatus. The gas passages at the right of the nitrogen inlet line were closed so that when stopcock (A) was opened a continuous sweep of nitrogen was maintained from left to right in the furnace tube, sweeping moist air out before it.

Because uranium tetrabromide is extremely hygroscopic, it must be handled only in a dry atmosphere. The technique used to get it inside the furnace tube was to fill the gold boats in a drybox and slide them in a pyrex tube of the same diameter as the furnace tube and slightly longer than the combined lengths of the gold boats. The ends of this tube were stoppered and the tube taken out of the drybox. The transfer to the furnace tube was made by removing the stoppers and, holding the tubes end-to-end, quickly pushing the boats into their positions in the furnace with a glass rod. A loose glass wool plug with a hole in its center was placed in the tube and the end stopper replaced, maintaining a steady sweep of pure nitrogen throughout this procedure.

When the apparatus had been swept free of air, the gas flow was diminished to a few cc per minute, the hole for the collection tube was stoppered, and the furnace was heated to temperature. When the correct temperature was reached and before the collecting tube was introduced into the furnace, it was flushed out with nitrogen from stopcock (B).

After closing stopcock (A) and removing the stopper from the collector tube entrance, the collector tube was inserted into position with stopcock (B) remaining open. While the tube was coming to furnace temperature a slight reverse flow of gas was maintained, from stopcock (B) through the collector tube into the furnace, escaping through stopcock (D). This prevented the back-diffusion of UBr_4 into the collector tube.

When the collector tube had attained furnace temperature (about 5 minutes after insertion) and with the Mariotte flask filled and attached properly, stopcock (A) was opened and stopcock (B) closed. The flow rate through the apparatus was adjusted, and after a minute or so to allow the gas at the collector tip to become saturated, stopcock (D) was closed. Stopcock (C) was then opened and the gas was collected in the Mariotte flask. The water displaced was collected in a graduated cylinder. When sufficient sample had been collected, stopcock (C) was closed and the collector tube carefully removed from the furnace. With a rubber policeman closing the tip of the tube, the outside was washed clean, and then the sample inside the tube was washed out and analyzed.

The sublimate samples were analyzed for both uranium and bromine. The sample solution obtained by washing out the collector tube was caught in a 60-ml centrifuge tube, diluted with water to fill the tube three-fourths full, and immediately treated with ammonium hydroxide to precipitate uranous hydroxide, $U(OH)_4$. This precipitate was centrifuged, and stirred up and washed twice by very dilute ammonium hydroxide. The combined decantates were acidified with nitric acid and treated with a known excess of standard silver nitrate solution to precipitate silver bromide. After the addition of ferric nitrate indicator, the excess silver was back-titrated with standard potassium thiocyanate solution to the first faint permanent pink (Volhard's method). The uranium hydroxide was dissolved in 60% perchloric acid, diluted, and reduced in a Jones reductor. After bubbling air through the solution to insure the absence of trivalent uranium, the uranium was titrated with ceric sulfate to the ferrous 1,10-phenanthroline end-point.

The mols of nitrogen carrier gas accompanying each sample were determined from the amount of water displaced from the Mariotte flask. Correction was made for the temperature of the gas collected, the vapor pressure of the water, the atmospheric pressure, and the difference between the pressure inside the flask and atmospheric pressure (measured by the height of the water level inside the flask above the water level at the tip of the exit tube). The vapor pressure of the uranium tetrabromide was calculated from the number of mols sublimed, the mols of carrier gas used, and the atmospheric pressure, by the equation

$$P_s = \frac{M_s}{M_s + M_c} \times P_{atm}$$

M_s = mols sublimate,

M_c = mols carrier gas,

P_{atm} = atmospheric pressure, mm.

P_s = Vapor pressure of the sample, mm.

To prevent errors due to incomplete saturation of the carrier gas its flow rate was varied up to as high as 15 ml per minute at each temperature and the observed vapor pressure was plotted as a function of flow rate. An extrapolation to zero flow rate gave a value which corresponded to the saturated gas. With flow rates of from 2 to 12 ml per minute, little reproducible decrease in apparent vapor pressure due to increased flow rate was observed. The observed data are given in Table 4, together with the vapor pressures obtained by extrapolation to zero rate of flow. Figure 13 shows the plot of the data and the extrapolation at each temperature and gives a plot of Log P vs. 1/T for the extrapolated values of vapor pressure.

A graphical-mathematical treatment of the vapor pressure data gives the following equations of state.

$$\text{For sublimation:} \quad \text{Log } P_{mm} = \frac{-10{,}900}{T} + 14.56$$

$$\text{For vaporization:} \quad \text{Log } P_{mm} = \frac{-7{,}060}{T} + 9.71$$

From these equations the following heats of change of state have been calculated.

$$\text{Sublimation:} \quad \Delta H = 10{,}900 \times 1.987 \times 2.303 = 50{,}000 \text{ cal/mol.}$$

$$\text{Vaporization:} \quad \Delta H = 7{,}060 \times 1.987 \times 2.303 = 32{,}000 \text{ cal/mol.}$$

Table 4

Data for the Determination of the Vapor Pressure of Uranium Tetrabromide

Temp. (°C)	N_2 Flow Rate (ml/min)	N_2 Collected (mols)	Pressure (mm Hg)	Millimols UBr_4 Calculated from		V.P. UBr_4 (mm Hg)
				U Anal.	Br Anal.	
450	10.0	0.329	740	0.110	0.109	0.247
"	6.1	0.297	742	0.110	1.110	0.275
"	1.9	0.290	735	---	0.124	0.314
"	00.0	---	---	---	---	0.300
475	10.1	0.139	738	0.179	0.184	0.96
"	5.4	0.265	735	0.376	0.356	1.02
"	1.8	0.132	742	0.167	0.171	0.95
"	0.0	---	---	---	---	1.00
490	9.9	0.1414	735	0.377	0.362	1.92
"	5.4	0.1284	738	0.316	0.319	1.82
"	2.7	0.1314	741	0.348	0.349	1.96
"	0.0	---	---	---	---	1.99
500	9.9	0.0938	733	0.390	---	3.04
"	9.8	0.1417	745	0.488	0.492	2.98
"	5.4	0.0894	735	0.354	0.355	2.91
"	0.0	---	---	---	---	3.00
525	9.7	0.0468	742	0.461	0.453	7.17
"	3.6	0.0604	742	0.648	0.648	7.87
"	2.8	0.0381	730	0.341	0.344	6.50
"	0.0	---	---	---	---	7.3
550	9.7	0.03132	740	0.563	0.568	13.2
"	5.2	0.02305	740	0.423	0.427	13.5
"	2.6	0.02495	740	0.468	0.472	13.4
"	0.0	---	---	---	---	13.6
575	10.1	0.01617	740	0.508	0.509	22.6
"	5.1	0.01550	740	0.492	0.494	23.4
"	2.9	0.01575	740	0.472	0.478	21.6
"	0.0	---	---	---	---	23.0
600	9.9	0.00795	745	0.464	0.467	41.2
"	9.8	0.00782	739	0.413	0.417	37.9
"	5.6	0.00854	739	0.395	0.401	32.3
"	4.6	0.00642	744	0.360	3.362	39.6
"	3.1	0.00736	739	0.383	0.385	36.7
"	0.0	---	---	---	---	39.0
625	8.4	0.00388	744	0.355	---	70.7
"	4.54	0.00366	744	0.384	.386	70.9
"	0.0	---	---	---	---	71.0
650	8.6	0.00206	744	0.346	---	107
"	4.4	0.00231	744	0.385	---	103
"	0.0	---	---	---	---	105

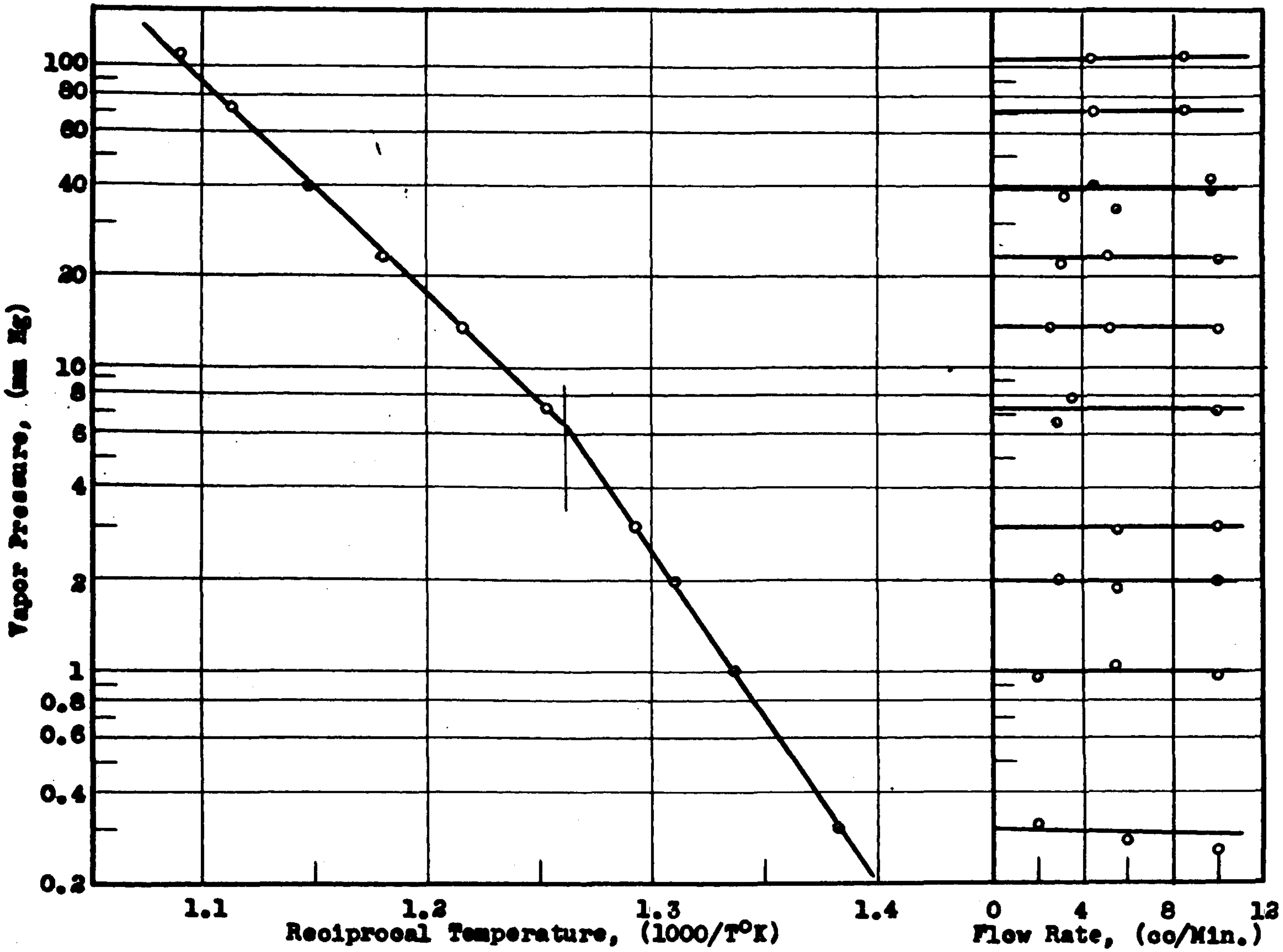

Figure 13. Vapor Pressure of UBr_4 Determined by Transpiration Method, Showing Extrapolations to Zero Flow Rate and Plot of $P_{(mm)}$ versus 1000/T°K.

Heat of fusion: ΔH = 18,000 cal/mol.

Boiling point (calc'd) = 761°C.

Trouton's constant, the entropy change on boiling, $\Delta H/T_{BP}$, is 31.0, and Hildebrand's constant is 32.8. Hildebrand's constant is similar to Trouton's constant, but the boiling temperature is replaced by the temperature at which the equilibrium vapor concentration is 0.05 mols per liter. Both Trouton's and Hildebrand's constants are higher than for normal substances, a characteristic usually associated with strongly polar liquids.

In these experiments it was discovered that below the melting point the measured vapor pressure gradually decreased with length of time the sample had been in the hot furnace. This decrease was not quantitatively measured, but was observed repeatedly. It may have been due to the accumulation of impurities at the solid surface. Scheldberg and Thompson (19) observed the same effect in the determination of the vapor pressure of uranium tetrabromide by the effusion method. In the present experiments data were discarded when the decrease in vapor pressure was observed, and the sample boats in the furnace refilled with fresh uranium tetrabromide. The effect of decreasing vapor pressure with time was much less noticeable above the melting point.

2.22 The Direct Determination of the Boiling Point of

Uranium Tetrabromide.

While the determination of the vapor pressure of uranium tetrabromide by the transpiration method gave values which were useful both above and below the melting point, it was desirable to check the accuracy of the vapor pressure data and to observe the thermal stability of uranium tetrabromide by a direct determination of its boiling point at atmospheric pressure.

No standard technique was found for the determination of a boiling point at such a high temperature, so a technique and apparatus were devised. It was felt that the simplest and possibly the most useful plan was to boil uranium tetrabromide and place a thermocouple in the saturated vapor to measure its temperature. While this method needs no special precautions at ordinary temperatures, at high temperatures secondary effects come into play which influence greatly the accuracy of the determination. First of these effects is that of radiation. Since the amount of radiation from a body is proportional to the fourth power of its absolute temperature, the thermal transfer by radiation at 761°C, the boiling point of uranium tetrabromide calculated from the vapor pressure data, is about 59 times as large as at 100°C. This indicates that great care must be taken to insure that as nearly as possible all radiating bodies which the tip of the thermocouple "sees" must be at the temperature of the saturated vapor. If this is not entirely possible the apparatus should be arranged so the errors approximately cancel each other.

A second cause of error which must be avoided is the superheating of the liquid uranium tetrabromide in the bottom of the container, and of the bromide vapors above the liquid. The temperature of the pure, saturated vapor is required. Since uranium tetrabromide undergoes some decomposition at its boiling point the liquid phase remaining in equilibrium with the uranium tetrabromide vapor constantly becomes more and more impure. As its impurities increase, its temperature rises to permit it to exhibit a uranium tetrabromide pressure of one atmosphere.

Several modifications of technique were tried before developing the one described below. An upright resistance furnace with a closed bottom and a chamber 4 inches in diameter and 7 inches in depth was used as the source of heat. A firebrick cap covered the mouth of the furnace and extended about 2 inches inside. Through a close-fitting hole in the center of the firebrick, a one-inch diameter Vycor tube with a closed end was extended slightly more than an inch below the brick, where the bottom received direct radiation from the inner walls of the furnace. This tube was charged with a 5-to 20-gram sample of pure distilled uranium tetrabromide, and a quartz thermocouple sheath and an evacuation tube were fitted through a rubber stopper at the end of the Vycor tube. The thermocouple sheath was placed so its bottom was level with the bottom of the firebrick.

It was observed in a previous experiment that some decomposition of uranium tetrabromide occurred at the boiling temperature, and that the observed boiling temperature thus increased with time. The above design was used, therefore, in order that the thermocouple would measure the temperature of the refluxing vapor rather than the temperature of the liquid itself. Radiation errors were minimized by the insulating layer of firebrick between the furnace and the portion of the Vycor tube which held the thermocouple. The position of the thermocouple in the refluxing vapor was chosen in an effort to equalize radiation losses to the colder region above by a small radiation gain from the hot furnace below. A balancing of these effects would make it possible to measure the temperature of the saturated vapor. The depth of immersion of the Vycor tube in the furnace was arbitrarily chosen to provide surface for sufficient heat transfer to reflux the vapor and to avoid superheating the vapor in the region immediately above the liquid level.

In the experiment from which the data in Figure 14 were obtained, a 10-gram charge of distilled uranium tetrabromide (analysis $UBr_{3.96}$) was placed in the Vycor tube and the tube evacuated and filled with dry nitrogen. A cotton plug was placed in the evacuation outlet and the apparatus was assembled as described above. The furnace was heated at a

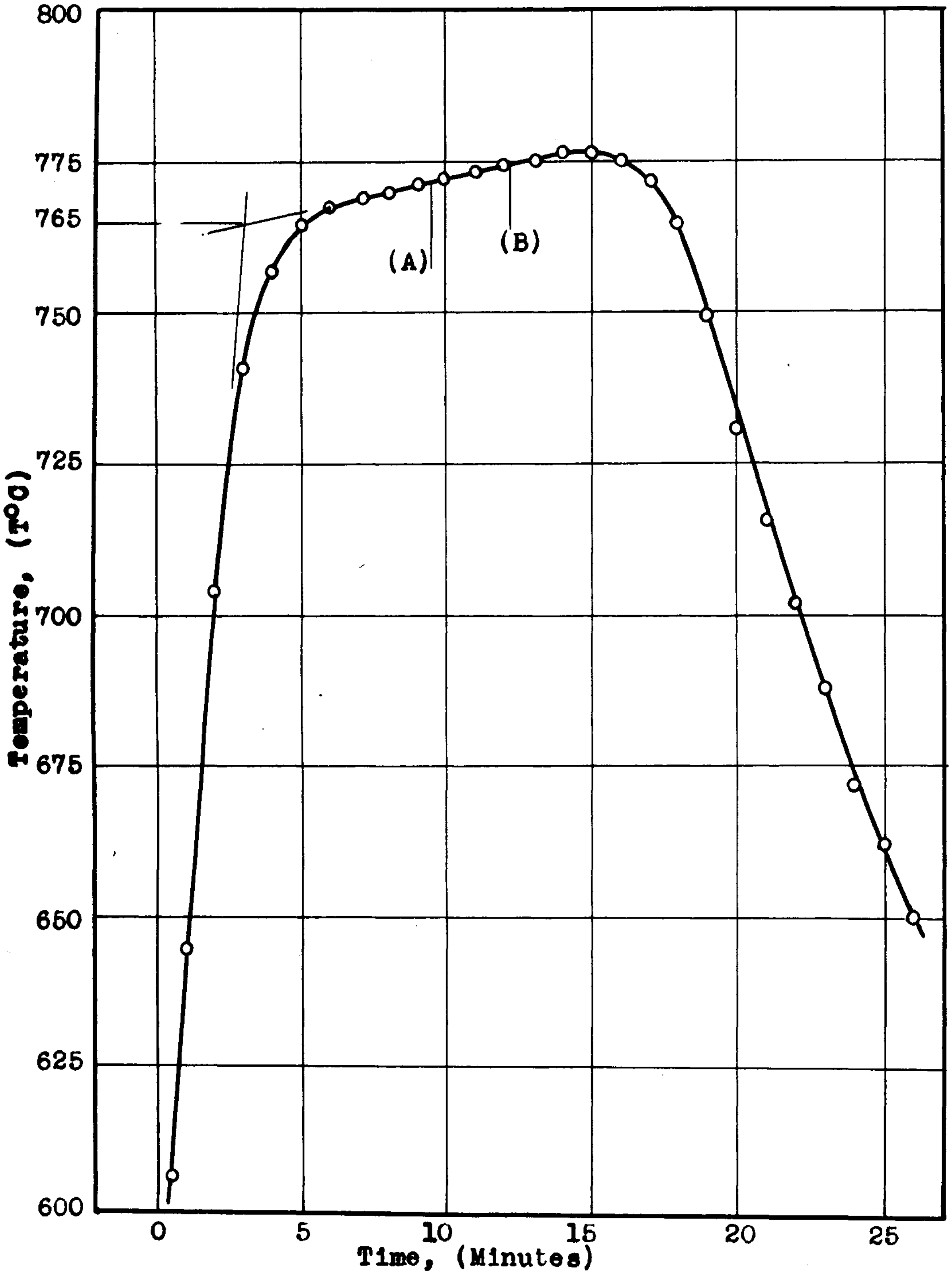

Figure 14. Time - Temperature Plot for the Boiling Point of UBr_4. (A) Reflux to top of firebrick. (B) Furnace power turned off.

fairly rapid rate, not measured, and the thermocouple temperature was recorded as the heating progressed. When the vapors reached 1/2 inch above the top of the firebrick the furnace was shut off and allowed to cool. Some bromine and hydrogen bromide were evolved during the heating and the fused residue at the end of the run had a composition of $UBr_{3.83}$ as shown by an analysis for uranium and bromine.

The initial steep portion on the curve (Figure 14) was interpreted to be the rapid rise in temperature as the uranium tetrabromide began to reflux up to the thermocouple sheath. Then there was a steady rise in temperature as the refluxing uranium tetrabromide decomposed and thus increased the boiling temperature of the mixture. There was vigorous boiling in the tube, and some superheated molten material may have splashed up on the thermocouple sheath and overheated it. Finally, soon after the furnace was turned off, the temperature began to drop.

Because of the decomposition of the uranium tetrabromide taking place during the heating, the initial boiling temperature more nearly represented the true boiling point than any other. Accordingly, straight lines were drawn through the points representing the periods before reflux and during reflux. The point of intersection of these lines was called the initial boiling point, 765°C at 740 mm pressure.

2.3 Discussion

The vapor pressure data determined by the transpiration method are plotted graphically in Figure 15 together with the data from the boiling point and the effusion data of Thompson and Scheldberg (18, 19). The data determined by the transpiration method check well with the observed boiling point, 765°C, and give a break at the observed melting point, 519°C. These data agree with one set of the data of Thompson and Scheldberg (18) but are considerably lower than others (19).

The most serious limitation of the effusion method is its tendency to give low results at higher vapor pressures, when the mean free path of the gas becomes comparable to the orfice diameter. Its other limitations rest chiefly in the fact that the orfice in the effusion capsule may not be calibrated correctly, and may thus give results which are consistently too high or too low. Thompson and Scheldberg used a 1-mm diameter orfice. At 450°C and 0.3 mm-pressure, their highest pressure reading, the mean free path of uranium tetrabromide vapor is 0.12 mm. Thus their orfice diameter is ten times as great as the mean free path of the vapor, and the reading was taken well beyond the reliable range of the method. The slopes of the log P versus 1/T plots of their data agree fairly well with that from the transpiration method in spite of this fact.

The data from the transpiration method are limited in accuracy by three main factors. First, the temperature in-

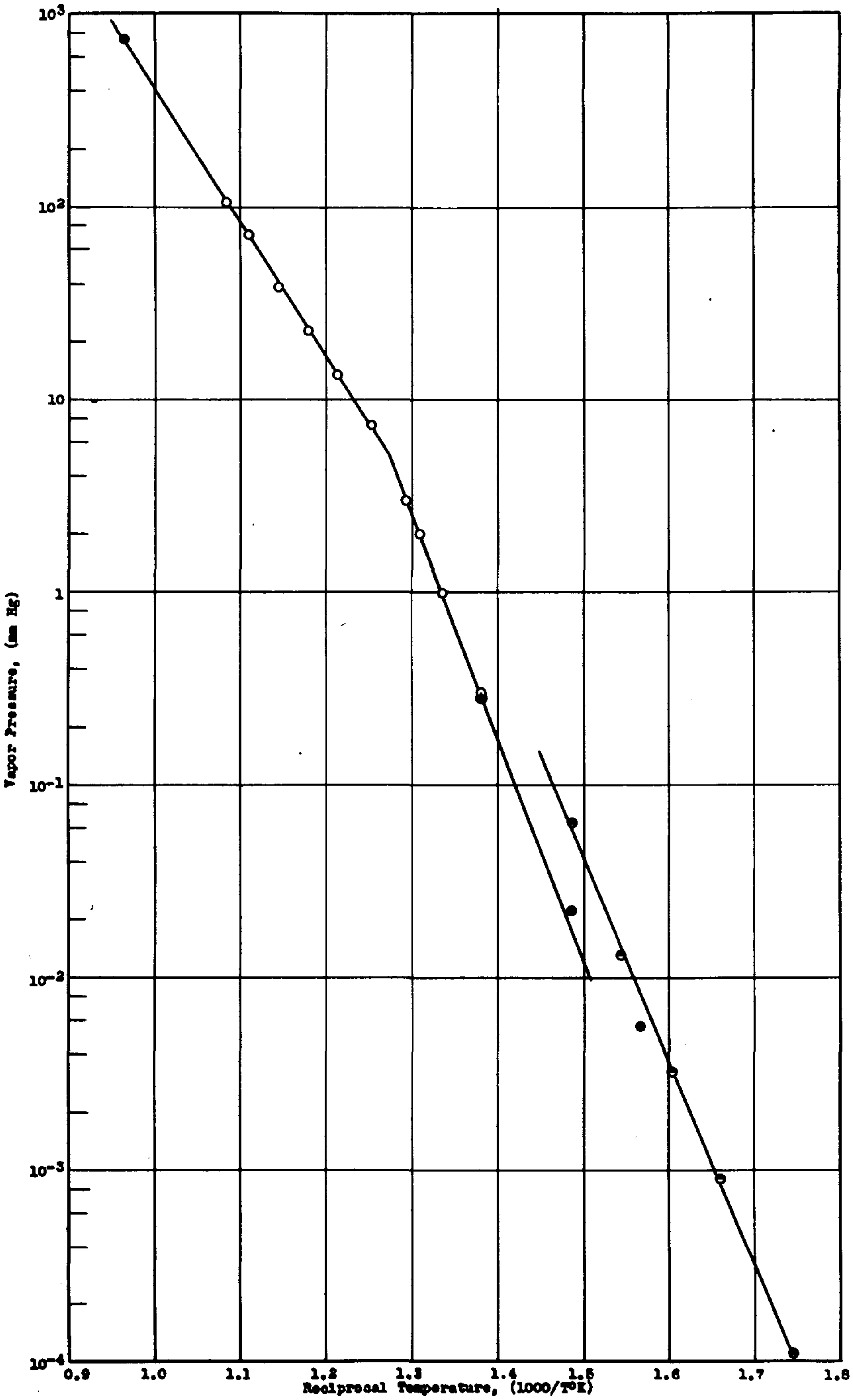

Figure 15. Vapor Pressure of Uranium Tetrabromide as a Function of Temperature(Collected Data). ● Boiling point of UBr_4. ○ Vapor pressure by transpiration method. ● Effusion data of Thompson and Scheldberg ([illegible]). ⊖ Effusion data of Scheldberg and Thompson (A-809).

side the furnace was not completely uniform throughout the length of the furnace, in spite of the fact that winding was modified to correct for "end effects" and a thick metal core was used to minimize small local hot spots caused by slightly irregular winding. However, the temperature was uniform to ±5°C in the center 7 inches of the furnace, and the attainment of equilibrium at the desired temperature should have been reached in that region. The temperature control apparatus was attached to a thermocouple whose junction was placed about an inch from the center of the furnace, between the furnace wall and the Vycor tube. Two inches away, opposite the center, another thermocouple measured the temperature inside the Vycor tube. Both thermocouples indicated exactly the same temperature, and the tip of the collector tube was placed between them at the center of the furnace, assuring the reliability of its temperature control. A gas inlet at each end of the furnace tube permitted a slower rate of gas flow across the sample, a modification from the apparatus of Jellinek and Rosner (20) who used only one inlet. Evidence that vapor equilibrium was reached lies in the fact that there was little change of observed vapor pressure with increased flow rate.

The second source of error lies in the limitation of the temperature control apparatus. The temperature was maintained constant to ±2°C, and it is probable that the error which this irregularity caused was small compared to unexplained variations from one determination to the next.

The third source of error arises from the fact that after samples have been in the hot furnace for some time, the observed vapor pressure decreases, either due to the formation of some surface oxide or the concentration of non-volatile impurities at the surface. When this "age effect" was observed, the data were discarded and the determination was repeated with a fresh charge. This effect is also observed with the effusion method, and is to be avoided by frequent recharging of the furnace.

No precise way of evaluating the magnitude of these errors is available, but the check determinations at any temperature did not usually differ by more than 5%. The correlation between transpiration data, direct boiling point data, and the sharp break at the melting point are indications of the accuracy of the determination. Probably the data are accurate to within 5%.

PART III

STUDIES ON THE HYDRIDES OF URANIUM AND THORIUM

3.1 Introduction

Uranium and thorium metals both combine readily with hydrogen to form stable hydrides. While it is true that uranium and thorium hydrides are pyrophoric and their reactions are typical of the metals themselves, the physical and chemical properties of uranium and thorium hydrides have made them the most useful intermediates in the study of the dry chemistry of these elements.

Hydrogen is comparable with metals in many respects, so that some of the products of the reactions between hydrogen and metals may be considered as alloys. According to Ephraim (23) there are, however, at least four different types of hydrogen-metal compounds, and only one of these has the character of an alloy. The four kinds of hydrogen-metal compounds are: 1) gaseous compounds, 2) alloy-like compounds, 3) field valency compounds, and 4) saline compounds.

Gaseous hydrides are formed by boron and all elements which occupy the four positions immediately preceeding an inert gas in the periodic system. Among them are elements which are quite metallic, such as germanium, tin, lead, arsenic, antimony, bismuth, and polonium.

Alloy-like compounds with hydrogen are given by many of the heavy metals. The compounds produced are mostly interstitial compounds. These metals are further divided into two subgroups: the first, in which the extent of hydrogen absorption at constant pressure increases with rise in temperature, includes iron, copper, nickel, and platinum; the second group, in which the hydrogen absorption decreases with rise in temperature, includes palladium and tantalum. The above elements absorb hydrogen when they are kept in the gas. On the other hand, Cd, Tl, An, Pb, Bi, Sn, Sb, Au, and Rh cannot absorb hydrogen gas, but seem to be able to form an alloy under certain conditions; thus a lead sheet becomes roughened when used as a cathode in electrolysis. These alloys all have a metallic appearance, and the hydrogen which they contain is in the monatomic condition, playing the part of a metal. The free hydrogen atoms alone are generally absorbed; when absorption of gaseous hydrogen occurs, it takes place by absorption of the small amount of monatomic gas always present in the gas phase (23).

Although a considerable amount of work has been done on the hydrides of this class, chiefly on palladium, the picture is not completely clear for any one element and it is even less consistent from one element to another. The palladium-hydrogen system has been considered a solid solution, a system of immiscible solid solutions, and a solid solution system also involving a true compound. Ephraim indicates that the number of elements which give hydrides which behave as solid solutions is much larger than formerly supposed, including the rare earths, Ti, Zr, Th, V, Cb, and Ta; in general, these are elements which occur in the long periods from three to five places after a rare gas element.

Field valency hydrides are probably the extreme members of the series of absorption products. They are formed only in special precipitations from solution, and are not formed by the direct reaction of hydrogen with a metal.

Saline metallic hydrides are true crystalline compounds of a metal with hydrogen. All of the alkali and alkaline earth metals form white crystalline compounds upon heating with hydrogen. The formulas of these compounds can be derived from the ordinary valence of the metals, *e.g.*, KH, CaH_2. These substances are true compounds and the hydrogen acts as a negative element, so that they deposit metal at the cathode and yield hydrogen at the anode when they are electrolyzed in the molten condition.

Saline metallic hydrides are formed by the reaction of metal with hydrogen. The alkaline earth metals react rapidly or even burn when heated to several hundred degrees in an atmosphere of hydrogen. The absorption of hydrogen by the alkali metals is exceptionally slow and cannot generally be brought to completion at atmospheric hydrogen pressure unless the hydride which is formed is sublimed off or the hydrogen is allowed to react on the vaporized or finely divided metal. These hydrides conduct electricity only at high temperatures, when they are molten. The alkali hydrides all decompose into the metal and hydrogen at 400°-500°C. The hydrides of the alkaline earths and of lithium behave quite differently upon dissociation. First, their dissociation temperatures are considerably higher than those of the alkali hydrides and second, they have no sharp dissociation point but the temperature of decomposition rises with the quantity of hydrogen evolved. The remaining hydride forms solid solutions with the metals set free. Probably as a result of the formation of solid solutions and mixtures, the pressure-temperature equilibrium in hydride systems is only very slowly attained.

Because of the usefulness of uranium and thorium hydrides it was imperative to know more about their physical and chemical properties in order to use them most efficiently and safely and possibly to extend their uses. The following sections consider each element in detail.

3.2 Uranium Hydride

3.2.1 Historical Survey

The first attempt to prepare uranium hydride was made in 1912 by Sieverts and Bergman (24) who found that 100 grams of impure uranium metal absorbed 1.6 milligrams of hydrogen. Driggs (25) of Canadian Westinghouse Co., Ltd. patented the formation of uranium hydride by the heating of uranium metal powder in hydrogen at a temperature greater than 225°C, and a pressure of hydrogen greater than the dissociation pressure of uranium hydride. He gave the dissociation pressure as 150 mm at 225°C, and 760 mm between 350° and 400°C.

Other workers have probably prepared uranium hydride inadvertently before 1943, *e.g.*, in an attempt to cast uranium metal in a hydrogen atmosphere (26). However, the systematic study of uranium hydride was begun in March, 1943. At this time Warf (27) prepared the hydride in an attempt to separate calcium from uranium metal via the hydrides. The finely divided character of the hydride immediately suggested its use in leaching processes for the removal of impurities from the uranium, in chemical reactions, and in the removal of inclusions in the metal for metallographic work.

The preparation of pure uranium hydride required cleaning of the uranium and purification of tank hydrogen. For the highest purity, uranium turnings or lumps of pure uranium metal were freed of oil by washing in trichloroethylene or carbon tetrachloride and then in acetone. They were then rinsed in water, and the surface oxide on the metal was removed by a treatment with 1:1 nitric acid. When the metal showed a bright surface it was washed carefully with distilled water, rinsed with acetone and, finally, dried. The smallest amount of oxidation occurred if the metal was dried by evacuation in the apparatus in which it was to be used. To obtain pure hydride, tank hydrogen was purified by passing it over a "getter" of uranium turnings at 700°C (21) to remove oxygen and nitrogen and probably nearly all other reactive gases.

Uranium hydride heated to 430°C, its decomposition temperature, is a source of very pure hydrogen, but its use is practical only for small scale preparations, or to meet an intermittent need for small amounts of very pure hydrogen. For this purpose it is convenient to have a pyrex bulb containing several hundred grams of uranium hydride sealed directly to a vacuum system.

To prepare uranium hydride, clean uranium metal is placed in a bulb large enough to accomodate the ten-fold volume expansion in hydride formation, and the system is filled with pure hydrogen, either after evacuation of the air, or by flushing it out with hydrogen. The metal is heated to 250°--300°C in hydrogen, and the first evidence of reaction is a blue coating which forms at about 200°C. This becomes dark as the temperature is increased to 250°C, and then uranium hydride begins to flake off. The time lag for the initiation of the reaction is greater when unpurified hydrogen is used. The uranium hydride powder continues to flake off in tiny particles, most of which pass through a

400 mesh sieve, until the entire metal piece has been converted to powder. The color of the powder ranges from brownish-gray to blue-gray and black, and there is some dispute concerning the color of pure hydride. It is probable that particle size has much to do with the observed color.

In the original report (27), the formula of uranium hydride determined by weight gain upon hydride formation was reported to be approximately UH_4, but subsequent work (28) showed the true formula to be UH_3. Apparently, oxygen impurity in the hydrogen caused an error in the original experiment.

The first reasonably accurate determination of the dissociation pressure of uranium hydride was made by Newton (27). A pyrex bulb containing 9.8 grams of uranium hydride and attached to a manometer system was heated in a resistance furnace. Vapor pressures were measured as a function of the temperature of the furnace as determined by a Chromel-Alumel thermocouple. Pressure readings were taken as the furnace was slowly heated from 253°C to 436°C, and again as the furnace was cooled. The pressure readings obtained as the uranium hydride cooled were from two to three times greater than those obtained during the heating.

The slow approach to equilibrium, the difference in pressures shown by heating and cooling samples, and the pressure-composition studies of other hydrides all indicated that a study of the dissociation pressure of uranium hydride would be desirable.

3.2.2 Pressure Isotherms of the Uranium-Uranium Hydride-Hydrogen System

Theoretical Approach: The pressure-composition isotherms of the uranium-hydrogen-uranium hydride system, when interpreted according to the concepts of the phase rule, should give a definite key to the nature of the system. The two extremes possible in the system are 1) a sharply defined three-phase system consisting of pure uranium, pure uranium hydride compound, and hydrogen, mutually insoluble, or 2) a solid solution system consisting of either hydrogen dissolved in uranium to form a perfect solution, or uranium hydride dissolved in uranium to form a perfect solution. Intermediate systems may also be interpreted even though they are more complicated.

If the system is one consisting of uranium and the compound UH_3, mutually insoluble, the dissociation pressure of the system will be a function of the temperature alone, providing all three phases are present and equilibrium exists. A pressure isotherm would then be a constant pressure line extending between the extremes of 0 to 100% uranium hydride in the solid phase.

When neither of these extremes is attained, the pressure would be a function of both temperature and composition.

Experimental Part: A satisfactory apparatus for determining a pressure isotherm must provide a constant temperature which produces a measurable dissociation pressure of hydrogen above uranium hydride, and it must provide for the measurement of the pressure. The temperature control unit used in this study is diagrammed in Figure 16. It is a modification of the familiar Abderhalden drier. Mercury was used as the refluxing liquid, and its vapors bathed the bulbs of uranium hydride and kept their temperature constant at 355.5 ±0.5°C, except in severe changes in atmospheric pressure, when the temperature varied as much as a degree. Three of these apparatus were mounted on a vacuum rack and attached to a pyrex manifold together with hydrogen storage bulbs, a hydrogen source (UH_3), and connections to a vacuum pump. The volume of each portion of the apparatus was determined by filling it with dry nitrogen at a known pressure and temperature, evacuating the gas by a Pressovac pump, and collecting the pump exhaust above water in a Mariotte flask. The calculation is similar to that used for the vapor pressure experiments, Part II. The volumes were accurate to about one percent.

The compositions of all uranium hydride-uranium samples were determined by weighing the amount of uranium involved, about 10 grams per sample, and measuring the pressure and volume of the hydrogen admitted to and removed from the system. These compositions were accurate to about the same degree as the volumes of the apparatus, *i.e.*, about one

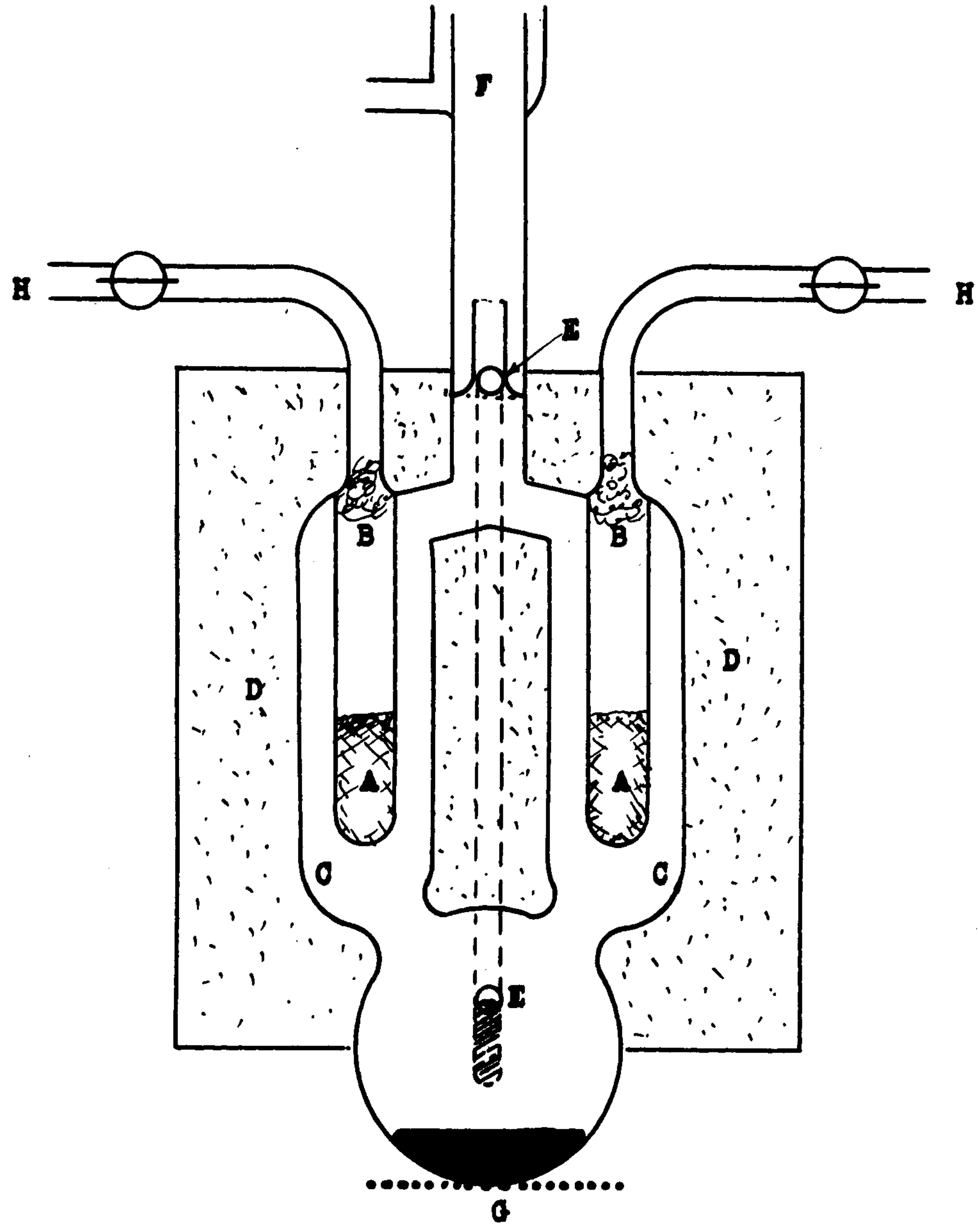

Figure 16. Constant Temperature Apparatus Used for the Study of the Dissociation Pressure of the U - UH_3 - H_2 System at 356°C. A. U - UH_3 samples. B. Glass wool plugs. C. Constant temperature chambers wrapped in aluminum foil. D. Insulating packing. E. Mercury return. F. Water-cooled condenser. G. Mercury boiled by gentle flame. H. Connection to individual manometer and main manifold.

percent.

Preliminary pressure measurements were completely erratic (28). Pressure readings taken when the pressure appeared to be reasonably constant varied by more than 5%. When hydrogen was introduced at a pressure greater than the equilibrium, *i.e.*, with formation of the hydride, the pressures obtained were 10% higher than the values obtained as equilibrium was approached by dissociating hydride into a vacuum. Experiments carried out for long periods of time showed that in cases where the pressure appeared to be constant there was still a rise after several days. Figure 17 shows the slow approach to constant pressure of a number of samples of varying compositions. The approach both from above and below equilibrium pressure indicates that for many samples constant pressure had not been reached at the end of 48 hours.

To eliminate the effects of variations in the treatment of the samples, it was decided to make a non-equilibrium study of the pressure-composition isotherm at 357°C by arbitrarily taking pressure readings 30 minutes after the hydrogen content of the system had been changed either by addition or removal (29). The data obtained in this way are given in Table 5 and plotted in Figure 18. The curves for formation and decomposition are different, but have reasonably flat portions in the composition range 10 to 80% UH_3. Naturally the curves do not represent true equilibrium

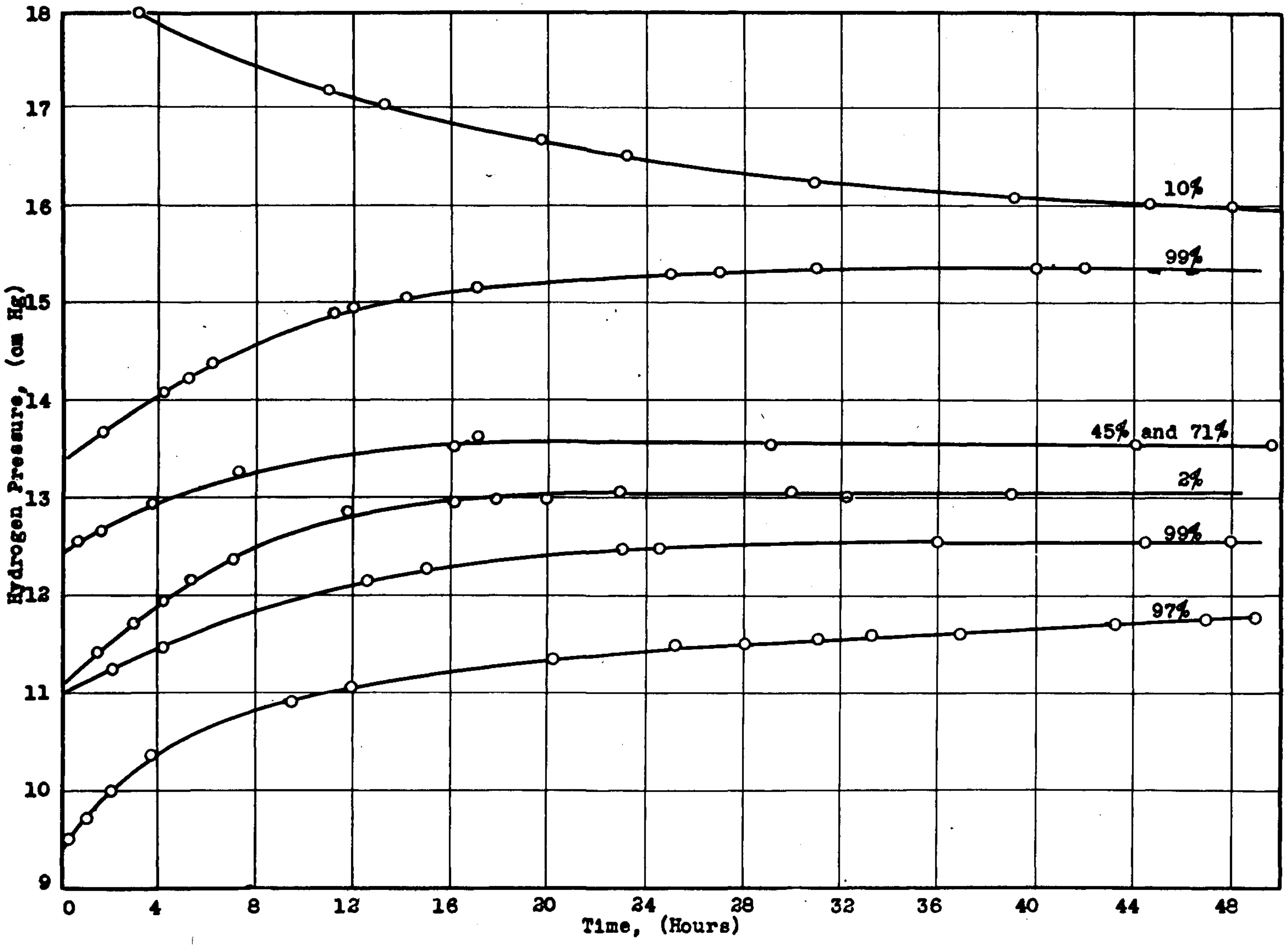

Figure 17. The Approach of Hydrogen Pressure to Equilibrium in the System U - UH_3 - H_2 at 356°C. The figures by the curves indicate the percent UH_3 in the solid phase of the system.

Table 5

Hydrogen Pressure of the Uranium-Hydrogen System at 356°C.

(Pressures reached 30 minutes after each change in contents of the system.)

A. Decomposition of UH_3		B. Formation of UH_3	
Composition (Mol % UH_3)	Pressure (cm Hg)	Composition (Mol % UH_3)	Pressure (cm Hg)
99.3	13.4	0.1	13.5
99.0	10.1	3.0	16.0
98.7	10.2	8.9	16.7
97.8	10.8	16.5	16.6
96.9	11.0	22.8	16.5
96.0	11.1	28.6	16.4
94.7	11.3	34.6	16.4
92.2	11.5	41.6	16.6
89.5	11.6	48.4	16.6
85.8	11.6	54.8	16.7
83.0	11.7	61.0	17.1
79.3	11.7	67.1	17.3
74.6	11.9	73.1	17.9
68.0	11.8	79.2	18.9
60.6	12.1	85.7	19.7
52.4	11.6	92.0	21.6
47.5	11.7	97.3	31.8
31.0	11.9	99.4	57.1
21.9	11.2	100.0	78.6
16.5	11.1		
11.9	10.8		
5.75	10.6		
1.73	9.1		
0.32	6.0		

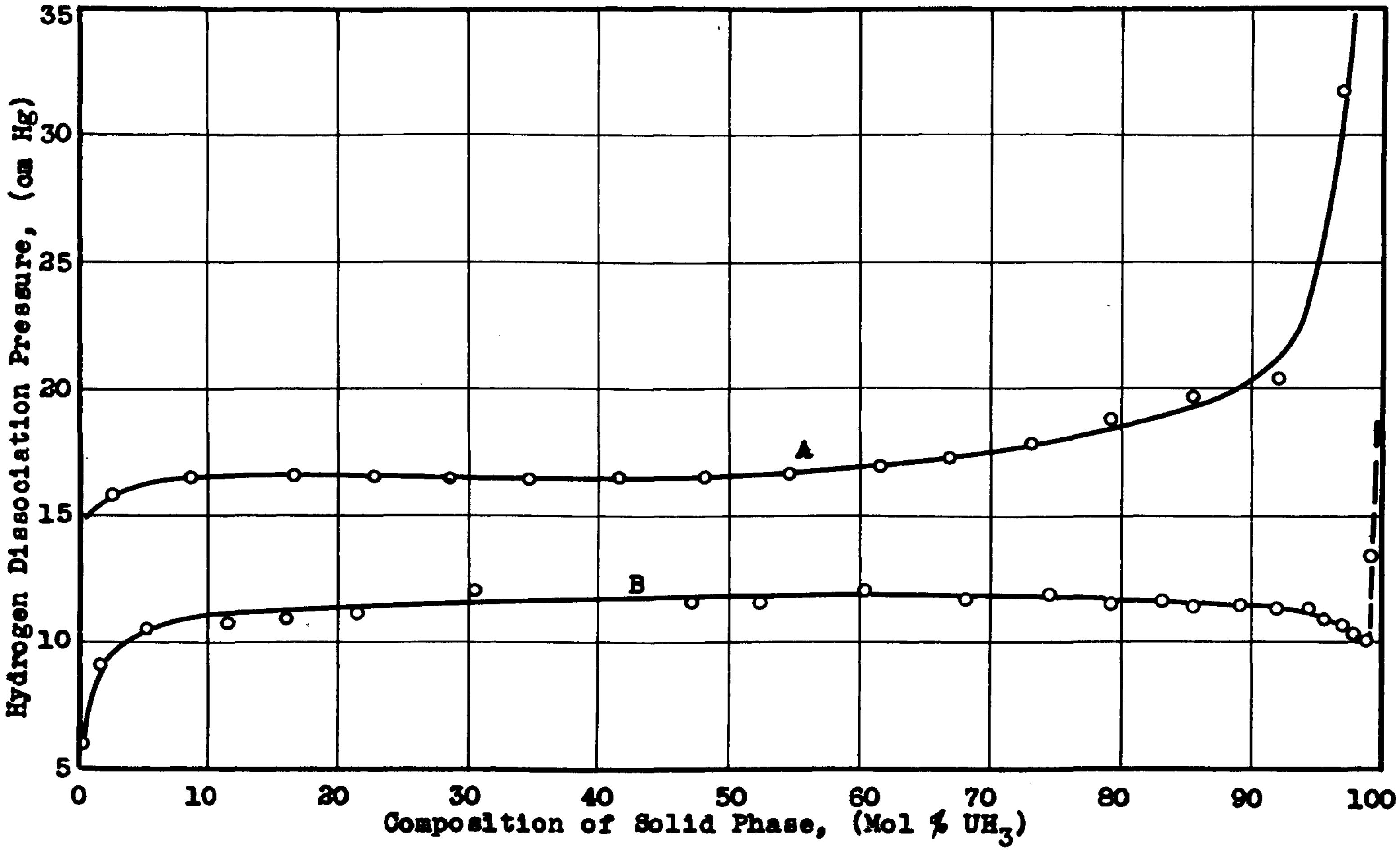

Figure 18. Non-equilibrium Pressure Isotherms of the System U - UH_3 - H_2. Pressures Measured 30 Minutes after Change in Hydrogen Content of the System. A. Increasing hydrogen content (formation). B. Decreasing hydrogen content (decomposition).

conditions, but they do give an idea of the behavior of the uranium-hydrogen system under practical conditions when it is impossible to wait for true equilibrium to be attained. Since these data are not equilibrium data, they will not apply exactly to other systems with different amounts of metal and hydride, different volumes, etc. An unexpected anomaly occurred in the system at a composition of about 97 to 98 mol percent uranium hydride. Solid of this composition showed a smaller dissociation pressure than solid whose composition was 50 mol percent hydride. This anomaly was surprising, but has been checked repeatedly, and is quite real.

True equilibrium pressures were determined by studying six samples simultaneously in the boiling mercury constant temperature systems, where each could be used for a particular composition range, and the sample allowed to stand until equilibrium was reached. A sample held at constant temperature was considered to be under its equilibrium dissociation pressure when the pressure did not change for 24 hours. Usually it was necessary to measure a sample for 48 hours before it was certain that equilibrium had been reached. In a number of cases, the sample was allowed to stand at constant temperature for as long as two weeks with no further change in pressure. The region of the dip in the decomposition isotherm was investigated particularly in this regard. The equilibrium pressure-composition data are presented in Table 6 and are shown graphically in Figure 19.

Table 6

Equilibrium Hydrogen Pressures of the
Uranium-Hydrogen System at 356°C

Decomposition of UH_3		Formation of UH_3	
Composition (Mol % UH_3)	Pressure (cm Hg)	Composition (Mol % UH_3)	Pressure (cm Hg)
99.8	20.4	98.6	23.7
99.5	19.5	98.1	17.3
99.3	15.2	96.8	14.8
99.0	14.7	96.0	14.5
98.1	11.7	94.5	14.4
98.0	11.8	91.6	14.4
97.5	12.1	89.0	13.9
97.4	12.1	40.8	14.3
96.6	12.2	3.2	14.9
96.4	12.2	0.15	13.2
93.3	13.1	0.10	12.7
92.8	13.1	0.10	14.4
89.8	13.0	0.02	11.4
89.5	13.0		
71.3	13.4		
44.5	13.4		
10.1	13.4		
4.1	13.3		
3.0	12.9		
1.0	12.7		
0.1	11.3		

In a constant temperature apparatus like that employing saturated mercury vapor as the heating bath, benzophenone was substituted for mercury as the refluxing liquid. At the

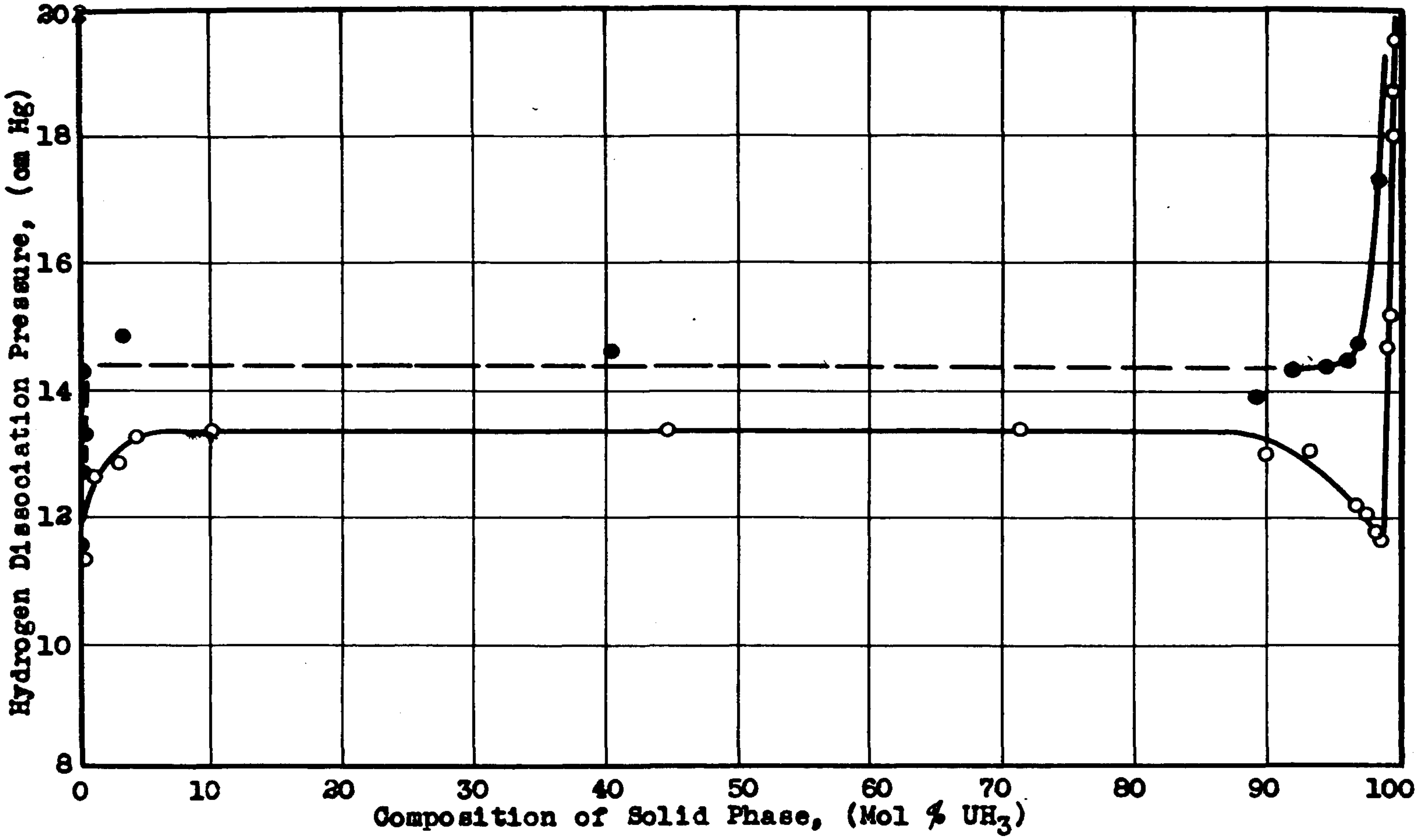

Figure 19. Equilibrium Pressure Isotherms of the System U - UH_3 - H_2. ● Increasing hydrogen content (formation). ○ Decreasing hydrogen content (decomposition).

boiling point of benzophenone, 307°C, the decomposition equilibrium pressure of 3.25 cm was obtained at a composition of 50 mol percent uranium hydride, 3.0 cm was obtained at 92.7 mol percent uranium hydride, and 2.9 cm at 97 mol percent uranium hydride. These meager data indicate that a dip occurs in the decomposition pressure isotherm at 307°C similar to the one at 356°C. No systematic study has been made of the equilibrium pressures of formation at 307°C.

It was suggested by Dr. F. H. Spedding that diffusion of mercury vapor from the mercury manometers into the hydride bulbs might affect the behavior of the hydride. According to Dr. Spedding's suggestion, the dip in the dissociation pressure-composition curve and the slow rate of attainment of pressure equilibrium might be caused by surface formation of amalgam on the metal and hydride particles.

An apparatus was constructed using the usual boiling mercury constant temperature control, but modified especially to prevent mercury contamination of the metal-hydride sample. The sample chambers were carefully freed of mercury by a nitric acid wash, the metal sample was introduced, and the apparatus was assembled. Double liquid air traps were placed between the sample chamber and the mercury manometer to protect the sample from the mercury vapors in the manometer. The metal samples were converted to hydride and dissociation pressures were obtained at compositions of 97%

uranium hydride and 51% uranium hydride. In each case the same slow rate of approach to equilibrium was observed and the same equilibrium pressures were attained as was the case without the protection from mercury vapor. It may be concluded that mercury does not cause the observed anomalies.

3.2.3 The Volume-Composition Relationships of the Uranium-Uranium Hydride and the Uranium-Uranium Deuteride Systems

Introduction: If uranium hydride is a compound and forms a separate phase from uranium metal, then the volume of a system of uranium hydride and uranium metal is the sum of the separate volumes of the two components. If a sample of uranium metal is converted to hydride in stages, the volume of the system, metal plus hydride, is a linear function of the mol percent conversion to hydride. On the other hand, if a solid solution is formed, the volume-percent conversion relationship may be, but need not necessarily be linear.

Irregularities in the dissociation pressure-composition isotherms of the uranium-hydrogen system, and particularly the unexplained dip in the 90-98 mol percent hydride composition range suggested that a volume-composition study might be enlightening. Furthermore, the absolute density of the hydride had previously been determined only under hexane (27) and a determination using a gas densitometer was expected to give better results.

Experimental Part: For these volume-compositions studies, a gas densitometer using helium as the pycnometer fluid was employed. It was a modified form of the instrument described by Schumb and Rittner (31). The modifications were in designing the apparatus so the useful sample volume was increased from 1 to 10 milliliters, and in attaching the sample chamber horizontally instead of vertically. In addition, the sample chamber had a capillary stopcock attached to the end opposite the ground glass joint, for greater ease in cleaning the chamber and to provide an additional support for it. A sample chamber was required which could be filled with a sample of uranium metal and which could then be subjected to the heating, evacuating, and cooling which are necessary in the stepwise conversion of uranium to uranium hydride and in the stepwise decomposition to metal. Because of the increased helium requirements of the large sample chamber, it was found more convenient to rely for pure helium on a helium tank attached to the apparatus through a purifying tube of uranium turnings heated to 700°C, rather than on a storage bulb.

The pycnometer volume was calibrated by the use of weighed mercury samples, according to the directions of Schumb and Rittner. The mercury sample was placed in the sample chamber, and the calculation procedure normally used for determining the volume of unknown samples was reversed for determining the volume of the apparatus. The calculation was made according to Boyle's Law, using the equations derived by Schumb and Rittner. The volume V_1 in a bulb between two marks on a capillary tube was used as a standard in the calculations, and the following determination of this volume indicates the likely accuracy of the subsequent measurements.

Sample	Wt. of Mercury taken (g)	Vol. of Mercury (ml)	V_1 (ml)
1	34.32	2.532	13.09
2	57.01	4.215	13.17
3	68.99	5.093	13.10
4	62.40	4.605	13.18
		Average	13.14

In the calibration of the volume of the apparatus, and in the determination of the volumes of samples, a minimum of five separate determinations were made on each sample. With the use of capillary manometers, as was the case with this apparatus, there was a tendency for the mercury level to stick in the capillary, causing a pressure reading to be in error by as much as several millimeters. The use of additional readings diminished the probable error of the average result.

In the experiments determining the sample volume of a uranium-uranium hydride sample as a function of the mol percent conversion to hydride, the apparatus was arranged so the sample-containing pycnometer bulb could be heated in a small resistance furnace which was hinged on one side to permit its being fitted over the bulb. Because the bulb was of pyrex and its volume was critical, great care had to be taken at all times to insure that it did not become hot enough to permit the glass to be deformed. The temperature in the furnace was measured by a 400°C thermometer. Hydride formation was carried out at 250°C, and decomposition was carried out under a vacuum at temperatures never exceeding 400°C. Because no glass wool or other plug could be used to hold the sample in the bulb, evacuations had to be made with great care to prevent blowing particles of the sample from the bulb into the other parts of the system.

The compositions of the systems were determined by weighing the sample of metal used and measuring the volume of gas added to or withdrawn from the system, following the technique used in the study of the pressure isotherms (Section 3.2.2). To prepare the system for a measurement, the desired composition was established by hydrogen additions or withdrawals, with the sample at the required temperature. Then the sample was cooled to room temperature and the apparatus completely evacuated. It was filled once with helium and re-evacuated to flush out the last traces of hydrogen gas, and then refilled with purified helium to the proper pressure. When the volume determination was completed the helium was completely evacuated and the proper change was made in hydrogen content of the sample.

A sample of 42.195 grams of uranium metal was converted stepwise to hydride and decomposed to metal to give the composition-volume relationships presented in Table 7 and drawn in Figure 20. In the same manner, the same metal sample was converted to uranium deuteride and decomposed to uranium metal to give the data shown in Table 8 and Figure 21.

The densities calculated from the volumes are 10.95 ±0.1g/cc for uranium hydride and 11.20 ±0.1g/cc for uranium deuteride. These are in agreement with X-ray densities of 10.90 ±0.01 (32) and 10.91 ±0.05 (33) reported for uranium hydride and 11.16 ±0.05 (33) for uranium deuteride. The density of uranium hydride determined by hexane displacement, 11.4g/cc, (27) seems to be too high.

3.2.4 The Separation of Hydrogen and Deuterium by the Use of the Uranium Hydride-Uranium Deuteride System

Introduction: It has been shown (34) that the equilibrium decomposition pressure of uranium deuteride is 1.4 times as great as that of uranium hydride. This fact, as well as the difference in reaction rate of formation expected due to the difference in zero point energies of hydrogen and deuterium, suggested the use of uranium hydride in the separation of deuterium from hydrogen.

The experiments reported here have been practical ones, rather than ones which can be given detailed theoretical

Table 7

Volume of Uranium-Uranium Hydride Mixtures Containing 42.195 grams Uranium

Formation of Hydride		Decomposition of Hydride	
Mol % UH_3	Volume (cc)	Mol % UH_3	Volume (cc)
0.0	2.21	89.8	3.67
7.1	2.32	65.2	3.23
30.5	2.68	35.2	2.78
66.6	3.27	11.5	2.43
90.5	3.72	0.0	2.20
100	3.88		

Table 8

Volume of Uranium-Uranium Deuteride Mixtures Containing 42.195 grams Uranium

Formation of Deuteride		Decomposition of Deuteride	
Mol % UD_3	Volume (cc)	Mol % UD_3	Volume (cc)
0.0	2.21	93.7	3.75
11.9	2.41	80.3	3.53
35.5	2.73	53.5	3.07
56.5	3.08	24.1	2.59
79.7	3.53	2.4	2.24
100	3.85	0.0	2.21

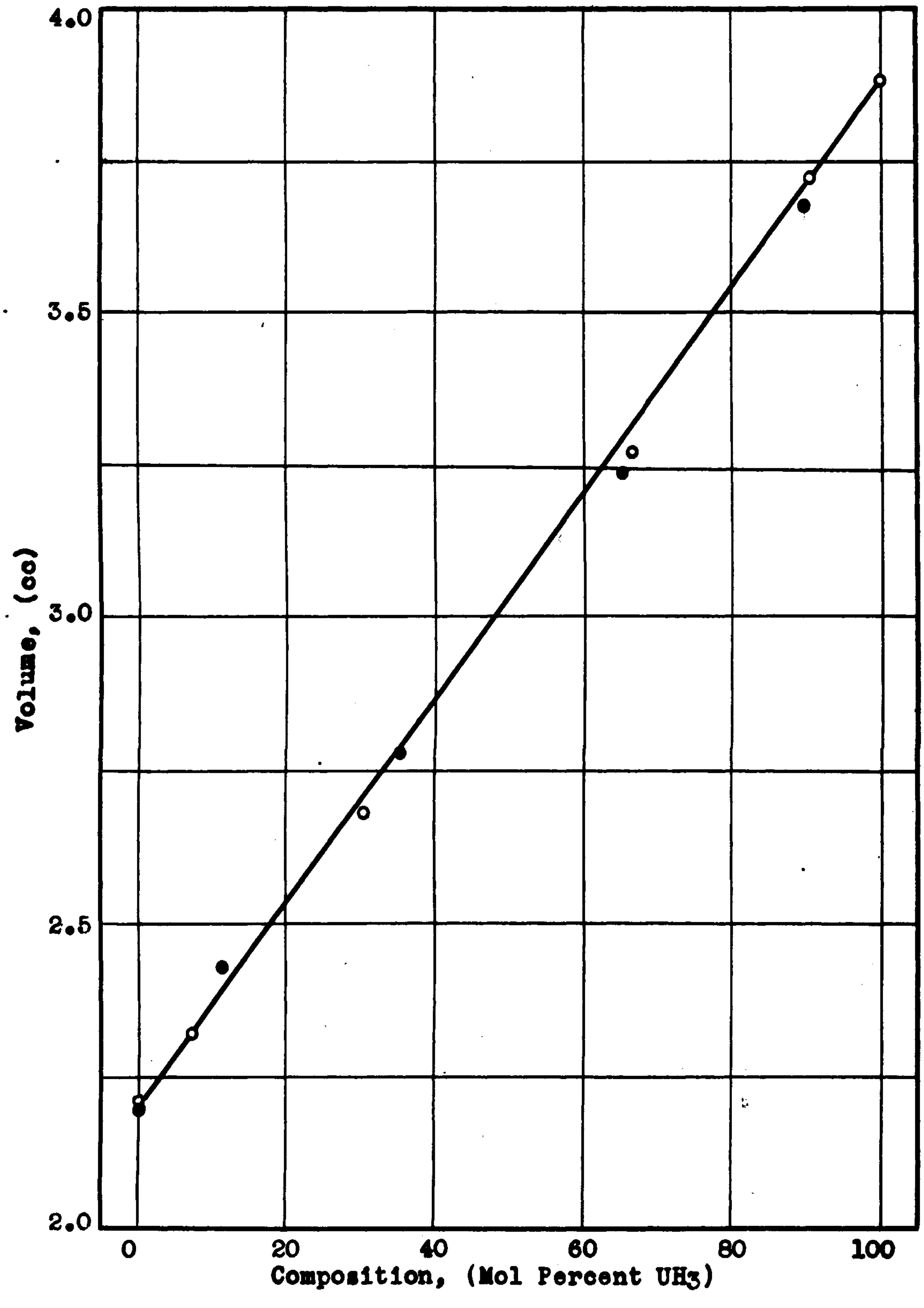

Figure 20. Volume of Uranium - Uranium Hydride Mixtures Containing 42.195 Grams Uranium. ○ Addition of hydrogen. ● Removal of hydrogen.

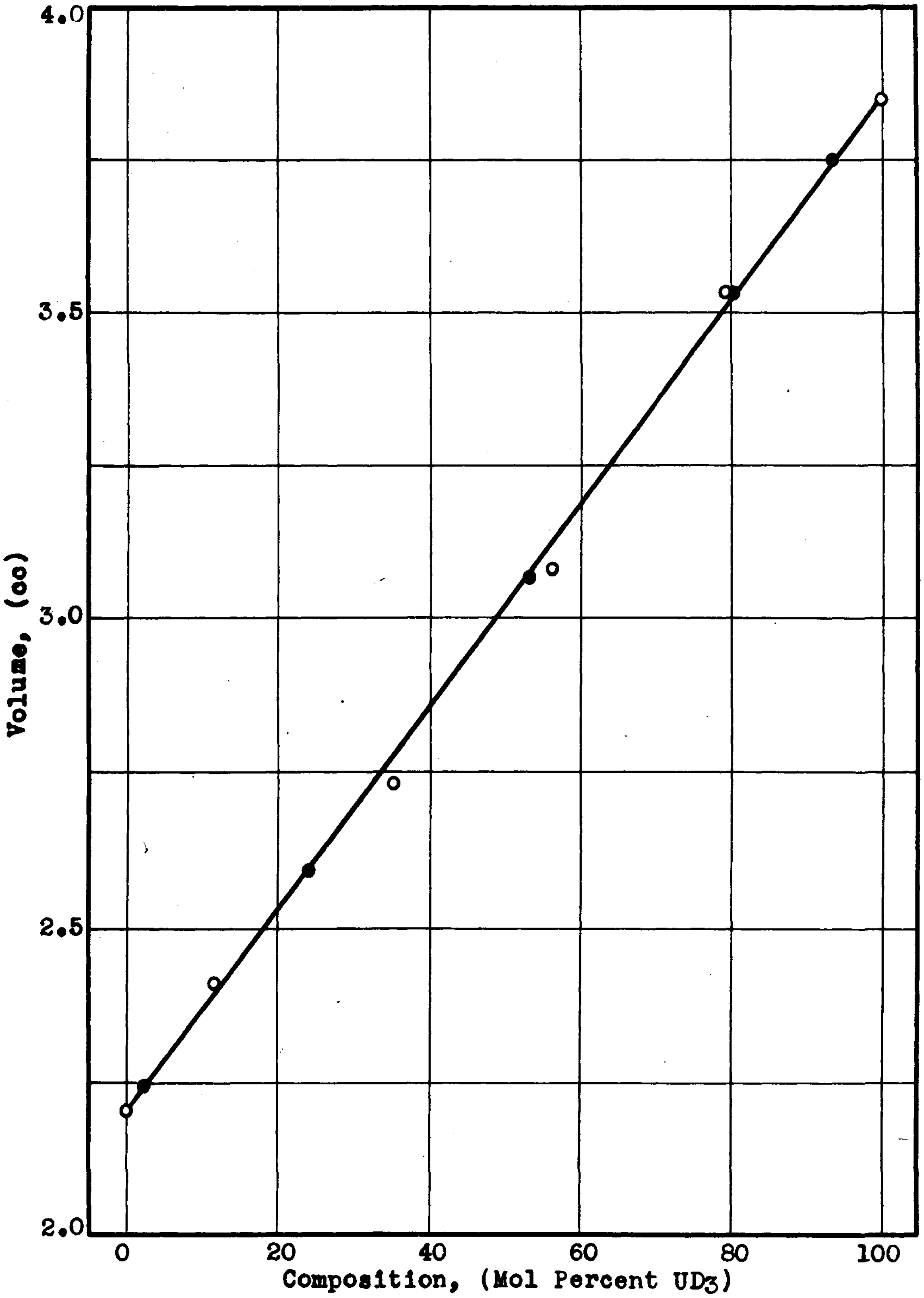

Figure 21. Volume of Uranium - Uranium Deuteride Mixtures Containing 42.195 Grams Uranium. ○ Addition of Deuterium. ● Removal of deuterium.

treatment, and the results are summarized and interpreted primarily from a practical point of view.

Experimental Part: Mixtures of uranium hydride and deuteride were made from mixtures of heavy water and ordinary water by the method developed by Newton (35). This method consists of releasing the hydrogen-deuterium gas from heavy water mixtures by passing the water vapor over uranium turnings heated to 700°C. The following reaction takes place.

$$D_2O + H_2O + U \longrightarrow UO_2 + H_2 + D_2$$

The hydrogen-deuterium gas mixture is then passed over uranium powder or uranium turnings at 250°C to form the uranium hydride-deuteride mixture.

A series of experiments was performed in which these mixtures of uranium hydride and deuteride were fractionally decomposed. The compositions of the gas fractions were measured with a quartz-fiber gas density balance built by Dr. I. B. Johns and similar to that described by Stock and Ritter (36). These gas density measurements were made at 0°C, and the instrument was calibrated with pure hydrogen and deuterium. It was sensitive enough to detect a few tenths of a percent deuterium in the gas phase, but its zero point drifted slightly, and its reliability was less when an experiment took a considerable length of time.

In a small pyrex bulb a sample of uranium hydride containing 3.01 mol percent deuteride was fractionally decomposed into ten fractions. The first gas fraction contained

4.8 mol percent deuterium and the final (tenth) fraction contained only 1.4 mol percent deuterium. Because the significance of the gas analysis was less with such low deuterium concentrations, further experiments were carried out with samples richer in deuterium.

It was believed that the greatest amount of fractionation of hydrogen and deuterium would be obtained when the gas withdrawn from a system was in complete equilibrium with the remaining solid phase. With hydride samples in small bulbs, the amount of gas in equilibrium with the sample was small compared to the total amount of gas required for an analysis by the gas density balance, i.e., about 250 cc. In this case the deuterium-hydrogen ratio in the gas phase was believed to be determined more by the dynamics of decomposition of uranium hydride and deuteride than by the ratios of their equilibrium vapor pressures. On the other hand, if a hydride-deuteride sample were heated in a bulb whose volume was large compared to the volume required for an analysis by the gas density balance, the observed separation factor would be more nearly a measure of the equilibrium conditions.

Accordingly, two experiments were carried out on a hydride sample containing 19.8 mol percent deuteride. In experiment A the bulb containing the hydride-deuteride mixture was of liter size and was kept heated at 410°C for two hours between withdrawals of gas samples for analysis.

In experiment B the gas bulb was about 50 cc in volume and samples were withdrawn at about 15-minute intervals. The hydride-deuteride samples were completely decomposed in each experiment to give the series of fractions of gas listed in Table 9. Each fraction contained approximately 10% of the gas in the original sample.

Table 9

Fractionation of Hydrogen and Deuterium by Decomposition of UH_3-UD_3 Mixtures.

Experiment A		**Experiment B**	
Gas Fraction	Mol % D_2	Gas Fraction	Mol % D_2
1	21.6	1	23.2
2	21.0	2	22.0
3	20.0	3	21.5
4	19.2	4	21.3
5	18.3	5	21.0
6	17.4	6	20.6
		7	17.6
		8	19.2
		9	18.1
		10	16.8

The hydrogen-deuterium ratios in the solid phases from which these samples were withdrawn were calculated from the original contents and the amounts of hydrogen and deuterium removed in the gas fractions. The separation factor, $\frac{N_{D_2}}{N_{H_2}} \text{ (gas)} \Big/ \frac{N_D}{N_H} \text{ (solid)}$, was calculated for successive withdrawals. It was found to be nearly 1.2 both for experiment A and for experiment B.

To determine the rate of interchange between the gas phase and the solid hydride, and see if lack of equilibrium were lowering the separation factor, the following experiment was performed. To a sample of uranium hydride in a large pyrex bulb at 300°C an amount of deuterium gas was admitted equal to the amount of hydrogen in the solid. Five minutes later a gas sample was withdrawn and was found to contain equal percents of hydrogen and deuterium. Apparently interchange between the gas and the solid was complete in five minutes.

3.3 Thorium Hydrides

3.3.1 Historical Survey

The reaction of thorium metal with hydrogen to form thorium hydride was first reported in 1891 by Winkler (37), who claimed to have produced ThH_2 from thorium metal containing ThO_2 and some magnesium. Matignon and Delepine (38) claimed the production of ThH_4 and $ThH_{3.8}$ from metal containing 26% ThO_2, while Sieverts and Roell (39) and Katz and Davidson (40) were unable to get hydrogen contents greater than approximately $ThH_{3.1}$, based on the weight of free thorium in the sample as determined by chemical analysis. The latter workers (39,40) made extensive dissociation pressure-composition-temperature studies of the thorium-hydrogen system, and plotted the hydrogen content of the solid under constant hydrogen pressure as a function of temperature. They found a rapidly decreasing hydrogen content with increasing temperature in the 100°-200°C range, then a slower decrease, and a sharp decrease in the hydrogen content between 800°C and 1000°C. They also plotted pressure isotherms and obtained widely varying results, depending on whether hydrogen was being added to or removed from the solid. These workers favored the concept that the thorium-hydrogen system was of the solid solution type and was similar to the palladium hydrogen system.

Klauber and von Mellenheim (41) claimed to have discovered a gaseous hydride of thorium, but this was disproved by Schwarz and Konrad (42) who showed that the material thought to be a hydride of thorium contained only H_2S, PH_3, and SiH_4.

The first positive evidence that the association of hydrogen with thorium metal involves compound formation rather than the formation of a solid solution was presented by Zachariasen (43). A sample of composition ThH_3 was subjected to X-ray analysis and proved to have a unique, cubic structure not related to that of thorium metal. The structure excludes the possibility that this hydride is an interstitial compound or a solid solution of hydrogen in metal.

3.3.2 Pressure Isotherms of the Thorium-Thorium Hydride-Hydrogen System

In a study similar to that carried out on uranium hydride, the equilibrium dissociation pressure of the thorium-hydrogen system was measured as a function of temperature and composition. The equilibrium was approached from both sides by studying the pressure developed when a) thorium-thorium hydride was partially decomposed into a vacuum, and when b) hydrogen at a higher pressure was added to the system and the pressure was reduced to the equilibrium pressure by the reaction of the lower hydride or metal with the excess hydrogen.

The dissociation pressures were determined in the apparatus shown in Figure 22. A quartz sample bulb was sealed through a quartz-to-pyrex seal to an all-pyrex system. This system contained a small-bore mercury manometer and a connection to a larger manifold to which were attached a large manometer, an Ace compact-type McLeod gauge, a 500-cc gas bulb, a vacuum connection, and a uranium hydride bulb for generating hydrogen. The small manometer system contained as small a volume as possible to permit a more rapid approach to equilibrium. The vacuum connection was to a mercury diffusion pump backed by a Cenco Pressovac pump. The volumes of the various parts of the system were carefully determined by evacuating through the Pressovac pump and collecting the gas as with the uranium hydride studies, section 3.2.2.

The sample of thorium hydride in the quartz bulb was

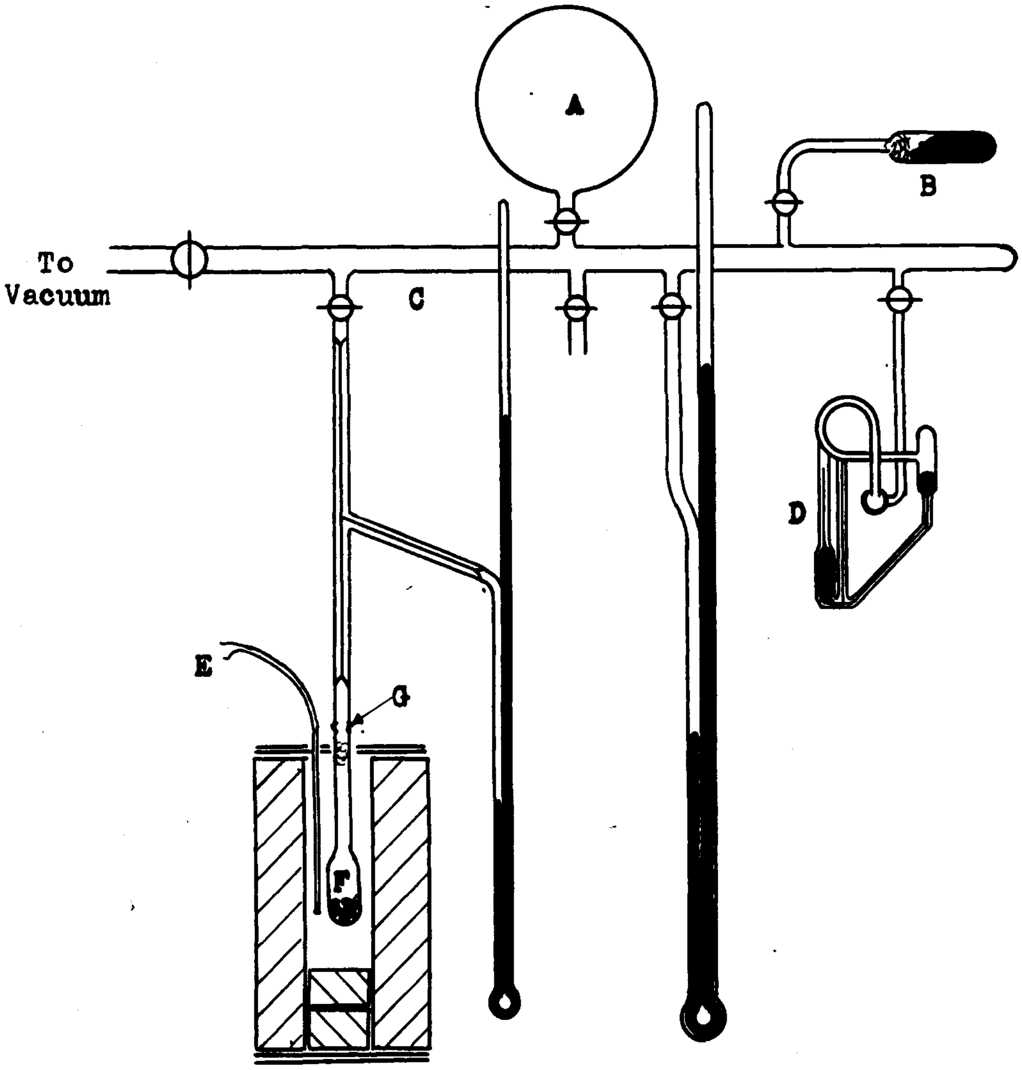

Figure 23. Apparatus for Determining Dissociation Pressures of the Thorium-Hydrogen System. A. Hydrogen storage bulb. B. Uranium hydride hydrogen source. C. Main vacuum manifold. D. Ace compact-type Mcleod gauge. E. Chromel-Alumel thermocouple with cold junction, to temperature control. F. Sample bulb. G. Quartz-to-pyrex graded seal.

heated by a resistance furnace whose temperature was measured by a Chromel-Alumel thermocouple with an ice-water cold junction. The temperature was controlled to an accuracy of ±2°C by the temperature control apparatus used in the study of the Vapor pressure of uranium tetrabromide (Part II).

A known weight of clean thorium metal, about 12 grams, was placed in the quartz bulb and the bulb sealed to the apparatus. The composition of the system was determined by the amount of hydrogen introduced or removed, so the system was filled with a known amount of hydrogen, calculated from the volume of the system, the pressure and temperature of the gas. The sample bulb was heated and the formation of hydride usually began at 300°-350°C. The samples were heated to 450°-500°C, and then allowed to cool slowly by shutting off the power to the furnace. If the hydrogen pressure in the system dropped very low (10 to 20 cm) in cooling, additional measured amounts of hydrogen were admitted to maintain the pressure at nearly one atmosphere. The hydrogen content of the solid phase was considered to be equal to the total hydrogen content of the system less the uncombined hydrogen in the gas phase. A thorium metal sample heated to 500°C, and then cooled slowly to room temperature under an atmosphere of hydrogen contained its maximum hydrogen content.

Two techniques were used to obtain the equilibrium pressure as a function of composition at various temperatures. The first, yielding the results plotted in Figure 23, was to isolate inside the small manometer system the solid of maximum hydrogen content by closing the connecting stopcock, and then to heat the sample to successively higher temperatures. The equilibrium pressures at this composition were measured after holding the temperature constant to ±2°C until a constant pressure was reached. The temperature of the sample was increased by regular intervals until the pressure was too large to measure on the manometer, and the composition of the system was then changed by withdrawing an appropriate amount of hydrogen from the system through the Pressovac pump and measuring it in the Mariotte bottle. The system was cooled to room temperature and a new series of readings was made at the new composition, again with progressively increasing temperatures. Thus, all pressure values in Figure 23 were obtained by the dissociation of preformed hydride. The composition values indicate the composition of the solid phase, and do not include the free hydrogen in the system.

When it was necessary to measure low pressures, 0 to 5 mm, a McLeod gauge was used. In this case the gas occupied the necessarily larger volume, but the connecting stopcock was closed as soon as the pressure reached a value which could be measured on the small manometer. When the dissociation pressure was large, the hydrogen in the gas phase was

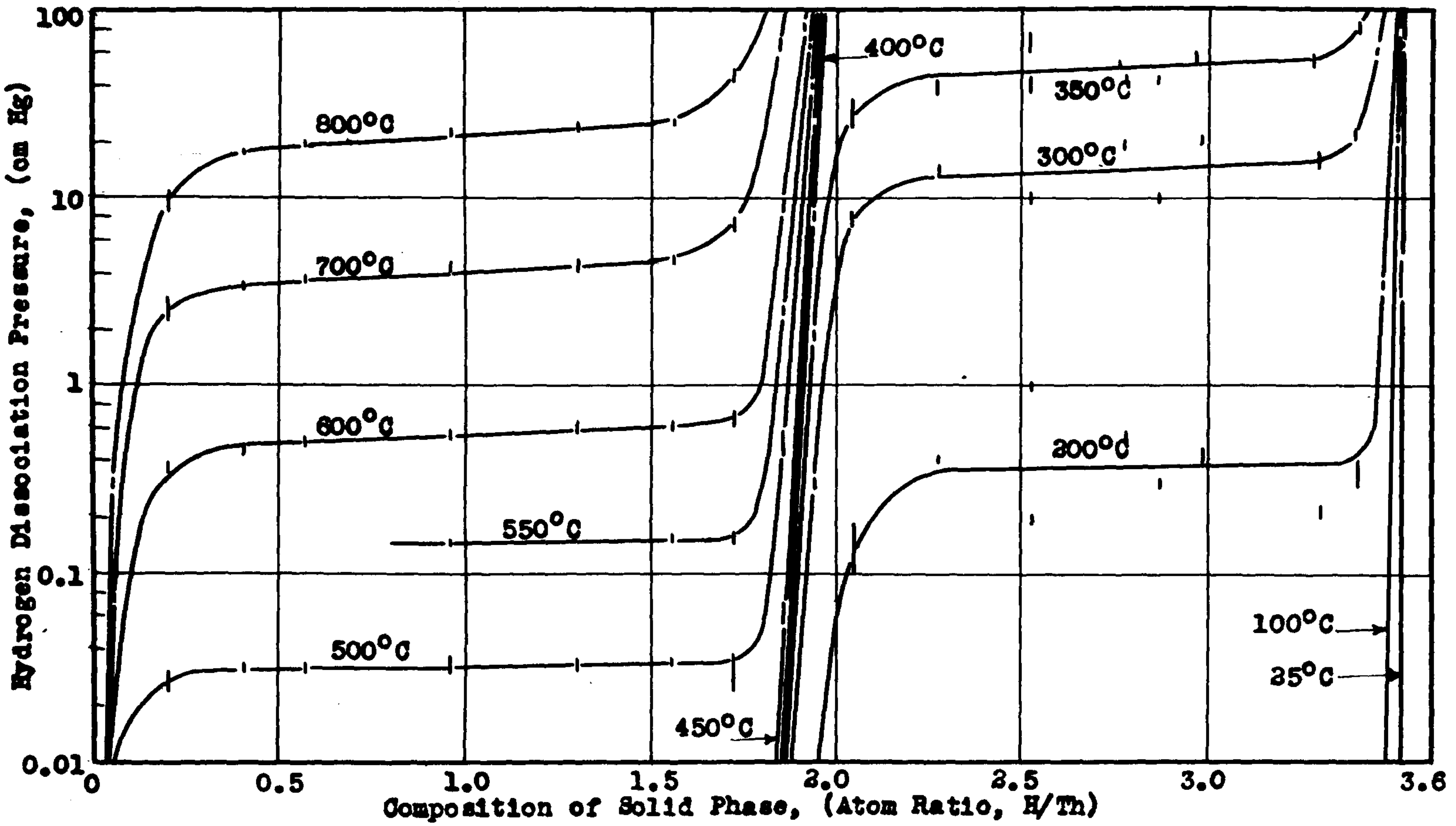

Figure 23. Equilibrium Pressure Isotherms of the Thorium-Hydrogen System (by Decomposition).

subtracted from the total content of the system to find the composition of the solid phase.

The pressure values in Figure 23 are either constant values reached by the system after standing at the given temperature, or are ranges through which the system fluctuated when the temperature was held constant. In most cases in the ThH_2-ThH_x-H_2 system ($x = 3.75$ or 4), nearly constant readings were obtained after 1 to 5 hours' heating at a constant temperature. In the Th-ThH_2-H_2 system, constant pressures were obtained in from 5 to 10 minutes at a constant temperature.

The isotherms in Figure 24 were obtained in a different manner. In this case the temperature was held constant throughout the experiment. Powdered thorium, obtained by pumping hydrogen from a thorium hydride sample at temperatures as high as 950°C, was used as the starting material. The desired temperature was established, and then hydrogen was admitted in appropriate amounts to establish a desired composition. After each addition of hydrogen the system was allowed to stand until the pressure became static. These additions were continued until hydride formation was complete. Then by a similar process of isothermal decomposition, the material was taken back to powdered metal. Of course, since the two different hydrides had to be studied at different temperatures, it was necessary to change the temperature when going from the Th-ThH_2 range to the ThH_2-ThH_x range.

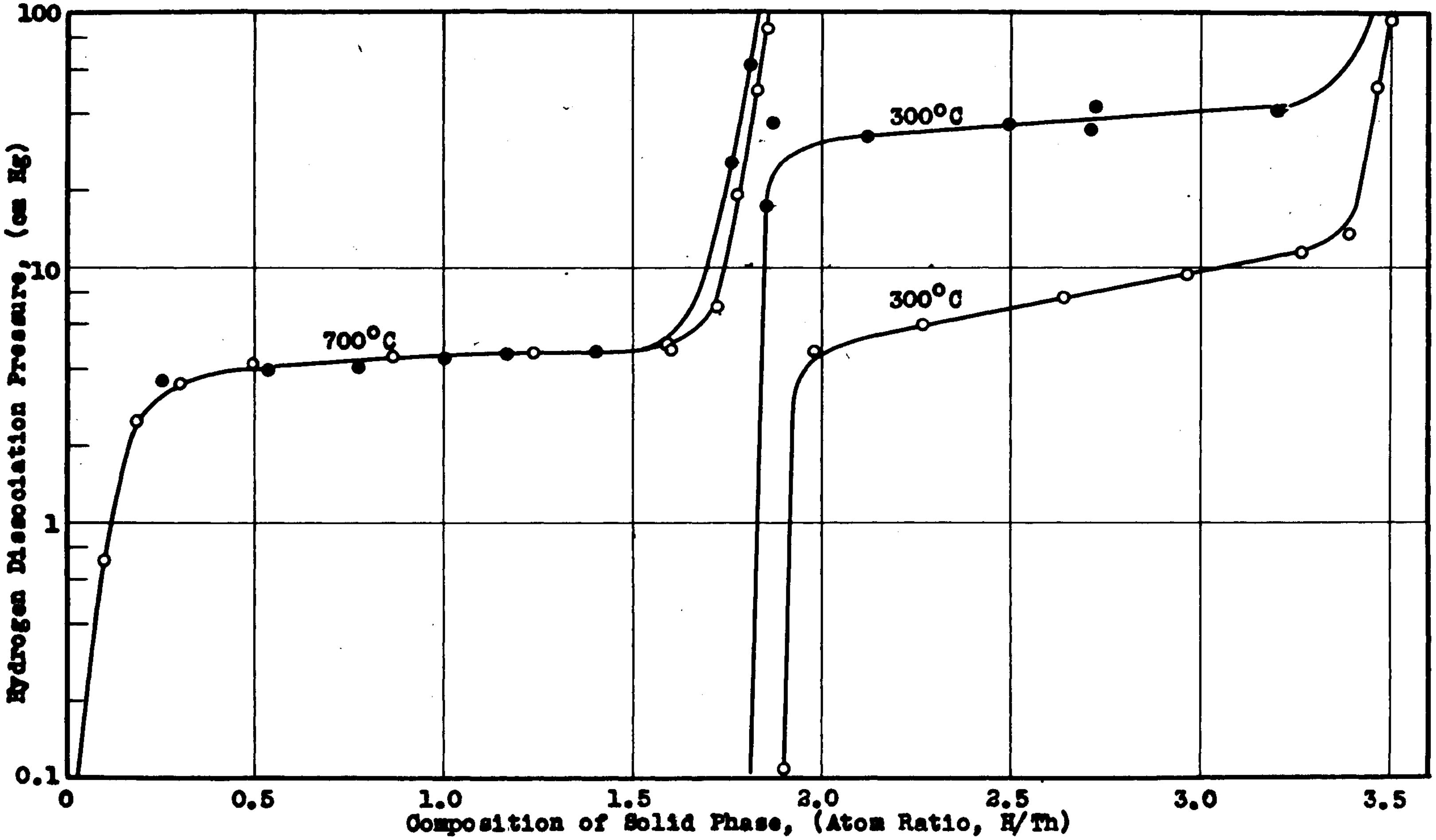

Figure 24. Pressure Isotherms of the Thorium-Hydrogen System. ● Pressures reached by absorption of hydrogen. ○ Pressures reached by dissociation of hydride.

Again with this procedure constant pressure values were reached in 5 to 10 minutes in the Th-ThH_2-H_2 system at 700°C, and pressures obtained on formation of the lower hydride equalled those on decomposition. With the ThH_2-ThH_x-H_2 system at 300°C, the approach to constant pressure was much slower; a nearly constant reading was reached only after the temperature had been held constant for 30 minutes to 24 hours. It can be seen from Figure 24 that even at the end of these times the formation pressures of the higher hydride were much greater than the decomposition pressures.

3.3.3 Thermodynamic Properties of the Thorium Hydrides.

The dissociation pressure curves of Figure 23 can be analyzed to give the heats of reaction for each of the steps in hydride formation. The plots of Log $P_{(cm)}$ vs. $1/T^{o}K$ are shown in Figure 25 for the composition ratios 0.5 H/Th and 1.5 H/Th, in Figure 26 for the composition ratios 2.4 H/Th and 3.2 H/Th. The slope $d(\log P)/d(1/T)$ gives $\Delta H/2.303R$, where ΔH is the heat of formation per mol of hydrogen added, and R is the molar gas constant, 1.987 cal/mol. In this manner the heats of reaction listed in Table 10 were calculated.

Table 10

Heat of Formation of Thorium Hydride

Reaction	Composition (Atoms H/Th)	ΔH (formation) (cal/mol H_2 Added) At Composition Stated	Average
$Th + H_2 = ThH_2$	0.5	-34,720	-35,200
	1.5	-35,670	
$ThH_2 + (\frac{x}{2}-1)H_2 = ThH_x$	2.4	-19,120	-19,300
(x = 3.75 or 4)	3.2	-19,490	

The dissociation pressures of the two compounds are given by the following equations, calculated for the center flat portion of the isotherms.

Th-ThH_2 system:

$$\text{Log } P_{(mm)} = \frac{-7700}{T} + 9.54$$

ThH_2-ThH_x system: (x = 3.75 or 4)

$$\text{Log } P_{(mm)} = \frac{-4220}{T} + 9.50$$

It is to be noted from the calculations of ΔH that the differential heat evolved upon hydrogen absorption is greater at an H/Th ratio of 1.5 than at 0.5, and greater at an H/Th ratio of 3.2 than at 2.4. Figures 25 and 26 illustrate this difference in ΔH graphically.

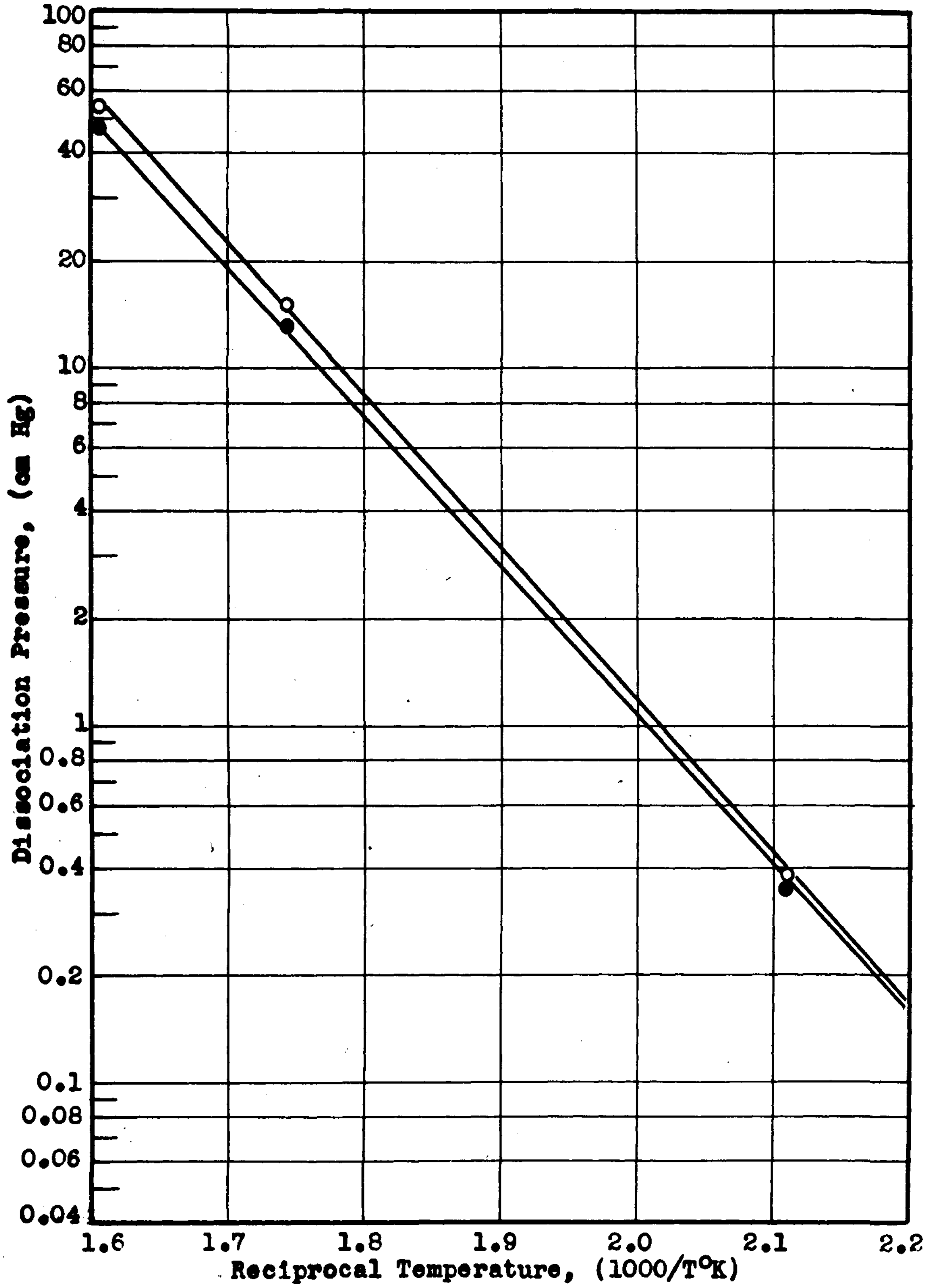

Figure 25. Decomposition Pressure of the Th-ThH$_2$-H$_2$ System as a Function of Temperature. ● Solid composition, atom ratio 0.5 H/Th. ○ Solid composition, atom ratio 1.5 H/Th.

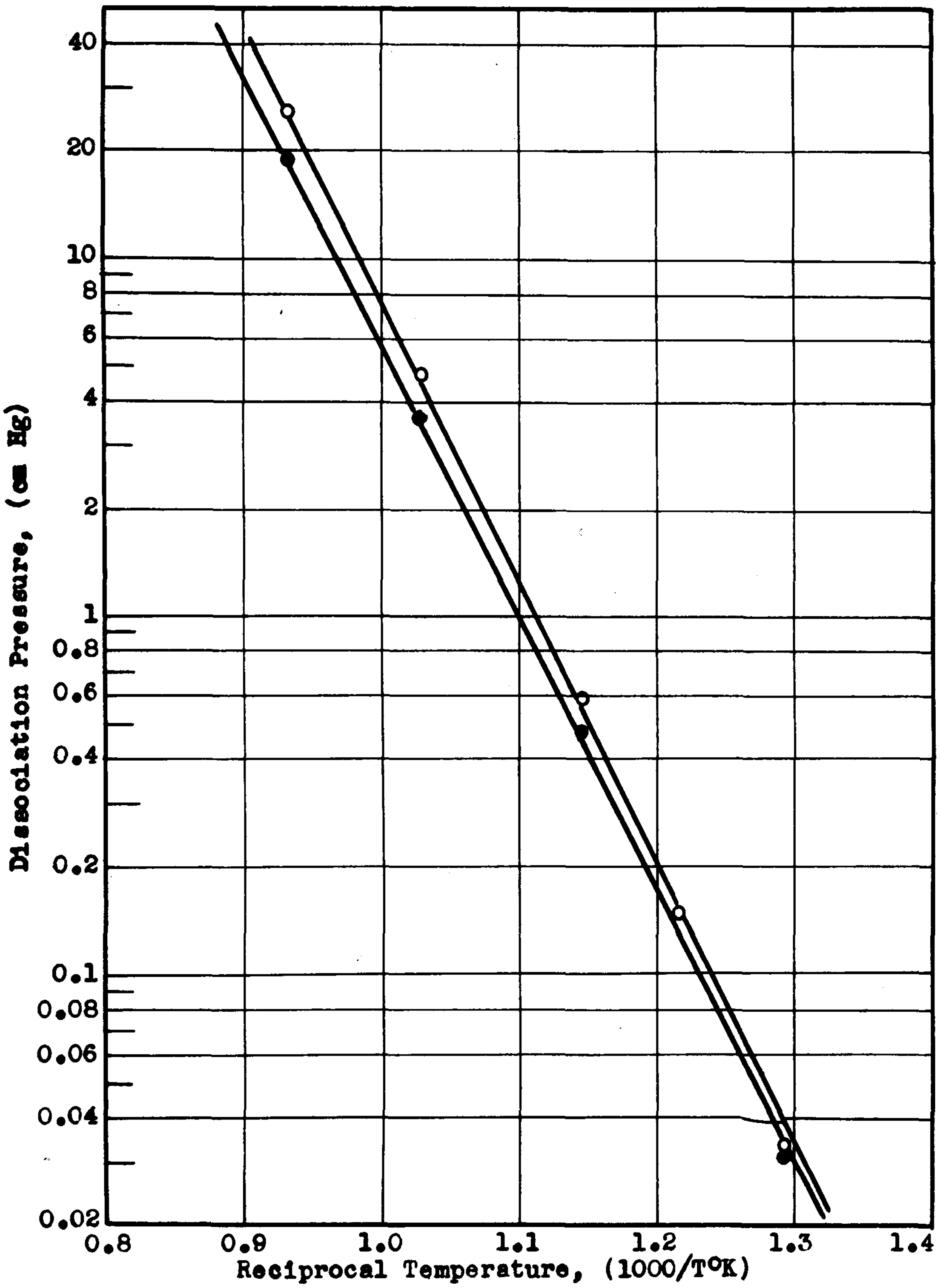

Figure 26. Decomposition Pressure of the ThH_2-ThH_x-H_2 System as a Function of Temperature. ● Atom ratio in solid, 2.4 H/Th. ○ Atom ratio in solid, 3.2 H/Th.

3.3.4 The Effect of Impurities on Thorium Hydride Formation

The maximum amount of hydrogen which a thorium sample will absorb varies with the sample and its method of preparation.

Recast thorium formed hydride whose maximum hydrogen content was $ThH_{3.19}$, the 1100°C biscuit formed $ThH_{3.52}$, and the 1600°C biscuit formed $ThH_{3.62}$, all based on the total weight of metal sample taken. The increased power of combination with hydrogen with increasing purity leaves little room for doubt that the higher hydride, with completely pure metal, has a formula of $ThH_{3.75}$ or ThH_4 (See discussion, section 3.4).

In a partially completed pressure isotherm using a cast thorium sample, the pressure values were much less sharp and the "flat" portions of the curves were narrower, more sloping, and in general much more poorly defined. It is probable that the previous investigators have worked with thorium of this type, and so did not detect the more subtle characteristics of the pure thorium-hydrogen system.

In this laboratory it was found that thorium samples could be converted to hydride, completely decomposed under a vacuum at 900°C, and completely converted to hydride again. This is contrary to the previous reports (39, 40) which indicated that heating to a high temperature lessens the amount of hydrogen which a sample can absorb. Explanation for the latter behavior might lie in the impurity of the samples these investigators used, or the possibility that previous investigators had decomposed their samples only to ThH_2. The total amount of hydrogen which a given thorium sample will absorb when cooled slowly to room temperature in hydrogen does not depend on previous heating to high temperatures, except when the temperatures are high enough to cause reaction with the walls of the vessel.

Powdered thorium reacts immediately with hydrogen at room temperature, becoming red hot. ThH_2 reacts very slowly with hydrogen at room temperature, but the rate gradually increases and after a few minutes the sample begins to get warm, which increases the rate rapidly.

3.4 Discussion

The rapid interchange of hydrogen and deuterium between the gas phase over uranium hydride samples and the solid phase of the samples gives a definite insight into the nature of the uranium-hydrogen system. At 300°C the system must be in dynamic equilibrium, with hydrogen from the gas phase constantly replacing that combined with the metal. The almost complete equilibrium reached between deuterium gas and uranium hydride in five minutes at 300°C indicates that the dynamic interchange must be rapid. Yet, a true equilibrium pressure is not attained, for the pressure required for formation of uranium hydride is consistently 1 cm greater than that reached upon decomposition of uranium hydride in systems where the hydrogen content of the solid is identical. This anomalous behavior remains without explanation.

The dip in the dissociation pressure isotherm at the uranium hydride end is of special interest because this behavior is theoretically impossible for a system of two solid phases, of low and high hydrogen content. A system in which a single solid phase is possible throughout the composition range from U to UH_3 could possibly exhibit a greater dissociation pressure at an intermediate composition than at either extreme of composition, but such a system would be in a metastable condition tending to disproportionate into two solid phases of lower and higher hydride content whose dissociation pressures equal that at the minimum. If the hydrogen transfer involved in this solid-phase rearrangement must be made through the gas phase, then the rearrangement would probably be prevented by the fact that the hydrogen pressure required for absorption in this region is greater than any developed by dissociation. This explanation, while tenable on the basis of dissociation pressure measurements alone, is not acceptable in the light of X-ray findings (33) which indicate only two phases, uranium metal and uranium hydride, throughout the entire composition range. The single-phase solid solution hypothecated by the explanation does not exist.

Rundle and Wilson (33) have shown that uranium hydride has a simple cubic structure with 8 uranium atoms per unit cell and a lattice constant of 6.650 Å. The uranium hydride structure is entirely unrelated to that of uranium (46), which is rhombic and has the lattice constants: a = 2.582 Å; b = 5.865 Å; c = 4.945 Å. Only slight solubility would be expected between substances with such different structures.

The slow approach to equilibrium was observed in both the U-UH_3-H_2 system and the ThH_2-ThH_x-H_2 system and is probably a characteristic of such hydride systems at moderate temperatures and pressures. Both of these moderate-temperature systems showed a slow attainment of "equilibrium" and different "equilibrium" values when approached from higher and lower pressures. On the other hand, at 700°C the Th-

ThH_2-H_2 system showed a rapid approach to equilibrium, and the same true equilibrium was reached from lower and higher pressures. The slow approach to equilibrium at moderate temperatures may be a general characteristic of systems involving solid-gas reactions. Gas diffusion in the solid phase is undoubtedly an important factor.

The pressure-composition relationship loses its linearity near pure uranium or pure uranium hydride, a behavior which is probably due to a slight interaction or solubility. This is of minor importance, however, because of the small portion of the system which it affects. The constancy of the equilibrium pressure over most of the composition range, the linear volume-composition relationship, and the X-ray data all point to the existence of a system consisting of two solid phases, uranium and the compound uranium hydride.

In the partial separation of deuterium from hydrogen by the fractional decomposition of uranium hydride-deuteride mixtures, the separation factor 1.2 which was obtained was less than that expected. The dissociation pressure of UD_3 is 1.4 times as great as that of UH_3. Johnson (51) has measured the total dissociation pressure of UH_3-UD_3 mixtures at 356°C. While the pressures which he observed above mixtures of UH_3 and UD_3 were slightly less than the values represented on a straight line drawn between the extremes, pure UH_3 and UD_3, he interpreted the difference to be within the limits of experimental error and considered the dissociation pressure to be a linear function of the solid composition. This would be expected from an ideal solid solution of UH_3 and UD_3. On this basis one would expect a separation factor of 1.4 from the partial decomposition of UH_3-UD_3 mixtures.

The uranium-hydrogen-deuterium system is complicated in that it involves such intermediate compounds as UH_2D, UHD_2, and HD as well as the substances UH_3, UD_3, H_2, D_2, and U. It is not known how these intermediate substances behave, and it is difficult to determine experimentally because their differences are subtle and they are almost certainly in heterogeneous equilibrium with each other at elevated temperatures. Since hydrogen and deuterium are isotopes of the same element, their compounds would be expected to form perfect solutions in each other and their mixtures would be expected to behave very nearly according to random distribution.

The separation factor 1.2 is not in agreement with Johnson's work. If, with low D/H ratios, the preponderance of HD over D_2 influences the separation factor, it also should have influenced the observed dissociation pressures of the UH_3-UD_3 mixtures.

The separation of hydrogen from deuterium by the use of the hydride system and the separation factor 1.2 requires a great many fractionations for a separation (more than 25 fractionations for a 100-fold concentration). It also has the disadvantage that since uranium deuteride has the higher dissociation pressure, if any pure deuterium is obtained from such a system, the hydrogen from which it was separated would have to be retained as uranium hydride. Either the fractionation would have to be obtained batchwise, which is a tedious procedure, or it would require a counter-current solid flow of uranium-uranium hydride. The separation would require very large amounts of uranium or a process whose details have not been devised.

The pressure-composition isotherms of the thorium-hydrogen system are much more sharply defined than those obtained previously by other investigators. They substantiate the fact that there are two thorium hydrides. The nature of these hydrides and of their pressure isotherms is clarified when they are considered in the light of their X-ray structures.

The lower hydride has the formula ThH_2, as evidenced both by the pressure isotherms and X-ray analysis. Wilson and Rundle (45) have shown the structure of ThH_2 to be very similar to, if not isomorphous with, the structure of ThC_2 and ZrC_2. The latter compounds are generally considered as interstitial compounds or interstitial solid solutions. They are derived from the cubic, closest-packed metal structure by introducing C_2 radicals into the octehedral interstices.

At the composition ThC_2 all the octehedral interstices are occupied by C_2 groups. Similarly at ThH_2 all the octehedral interstices should be occupied by H_2 groups, but the lower hydride phase should be stable over a considerable composition range of lower hydrogen content if ThH_2 is to be regarded as an interstitial solid solution. Actually the composition range of the lower hydride phase seems rather narrow both from the X-ray and dissociation pressure studies.

What variation there is in the composition of the lower hydride phase seems to increase with temperature. Thus, from Figure 25 it appears that as the temperature is increased, the lower hydride phase becomes stable at lower hydrogen contents. Because of this there is a greater ratio of pressures at two different temperatures at the higher hydrogen compositions, and consequently ΔH (formation) of ThH_2 appears to become more negative with composition as noted in Table 10.

Because of the similarity of ThC_2 and ThH_2, it has been assumed that H_2 groups are involved in the lower hydride structure (45). Actually the evidence for H_2 groups is slight, since even for the carbides having a ThC_2 structure the positions of the carbon atoms are mostly a matter of conjecture. It is difficult to understand the nature of the H_2 groups, if they exist. The lower hydride does not appear to be a solution of hydrogen molecules in thorium metal. If the H_2 group is an ion, it sould presumably possess a negative charge, yet $H^=$ is impossible and H_2^-

would require a relatively rare three electron bond.

Drs. Rundle and Newton have suggested that it should be possible to determine if the H_2 unit remains unseparated in ThH_2 by subjecting ThH_2 to an atmosphere of deuterium at a temperature high enough to obtain interchange between the gas and the solid. If the H_2 unit retains its identity in ThH_2, D_2 should interchange with H_2 to give a gas phase consisting of H_2 and D_2. If the H_2 unit is destroyed in hydride formation, the gas should consist of a mixture of H_2, HD, and D_2 in random proportions. Naturally the spontaneous interchange of H_2 with D_2 alone should also be measured at the same temperature. While this is a simple experiment, it requires the use of a mass spectrograph, which was not available in this laboratory.

Zachariasen (43) has determined the structure of the higher thorium hydride to be body-centered cubic, $a_o = 9.09 \pm 0.02$ Å, with 16 thorium atoms per unit. His calculations were based on the assumption of the formula ThH_3. Results presented in this paper show that hydrogen contents as high as $ThH_{3.62}$ can be attained, so the formula ThH_3 must be in error. Rundle (45) has shown that with the space group to which the higher hydride belongs, the compounds $ThH_{3.5}$, $ThH_{3.75}$, and ThH_4 are theoretically possible. The hydrogen content of hydride samples has exceeded $ThH_{3.5}$, and the amount of impurity in the metal could hardly account for a lowering of the hydrogen content from the theoretical ThH_4

to the observed $ThH_{3.62}$, so Rundle has concluded that the formula $ThH_{3.75}$ is the most likely. This higher hydride has a structure unrelated to that of the metal, and in this case there is no doubt that the hydride is a true compound. Nevertheless, the higher hydride may be stable over a moderate composition range.

X-ray diagrams above $ThH_{3.2}$ appear as to be one phase (45); decomposition pressures and formation pressures of the higher hydride diverge quite widely (Figure 24), and both decomposition and formation pressures at a given temperature increase with hydrogen content of the higher hydride. As in the case of the lower hydride, the composition range of stability of the higher hydride seems to increase with temperature, leading to an apparent increase of ΔH (formation) with composition (Table 10).

An unequivocal classification of the uranium-hydrogen and the thorium-hydrogen systems into one of the hydride groups of Ephraim (section 3.1) is not warranted by the experimental evidence. Actually, different properties of the systems under different conditions can justify their classification with either the saline compounds or the alloy-like compounds. Since the compounds UH_3, ThH_2, and ThH_x are all formed relatively pure, and have unique X-ray structures different from the metals (ThH_2 is probably derived by the introduction of H_2 radicals into the octehedral interstices of the cubic, closest-packed metal structure) the classification of the hydrides as saline compounds is fairly justified. The relatively flat dissociation pressure isotherms of the uranium-hydrogen system also lend support to its classification as a saline compound.

The derivation of the ThH_2 structure as an interstitial modification of the thorium metal structure indicates that the thorium-hydrogen system posesses some alloy-like or solid solution tendencies. The increasing dissociation pressures with increasing hydrogen content exhibited both by ThH_2 and ThH_x is typical of a solid solution or alloy. The tendency of the thorium hydrides at higher temperatures to become stable with lower hydrogen contents is also a characteristic of solid solutions. A reasonable conclusion is that the hydrides of uranium and thorium are borderline compounds between the two classes, saline compounds and alloy-like compounds.

SUMMARY and CONCLUSIONS

1. A procedure is given for the determination of barium and strontium activities in uranium fission product material which also provides for the recovery of the other fission products. After the addition of inactive carriers, barium and strontium are precipitated as nitrates from 80% HNO_3. This provides a nearly complete separation from all other fission product elements except antimony, tellurium, and sometimes, cerium. Barium and strontium can best be separated from the foreign activities which coprecipitate from 80% HNO_3 by using a scavenger precipitation to remove the contaminants. Precipitation of barium and strontium from a solution containing these foreign activities is less effective as a separation of the pure radioactivities than is the procedure involving preliminary removal of the impurities from the solution.

2. The precipitation of $BaCrO_4$ from solutions containing 1 gram per liter of barium and varying amounts of strontium may yield a precipitate which contains as much as 40% by weight of $SrCrO_4$, or which may carry down as much as 25% of the initial strontium in the solution, depending on the initial strontium concentration. When the initial strontium concentration is less than 100 mg/liter, the percent carried down is practically constant,

20 - 25%. For other strontium concentrations, the amount of coprecipitation is a continuous but non-linear function of the initial strontium concentration.

3. The isotope Sr^{90} has been discovered, and Sr^{90} and Y^{90} have been identified in uranium fission product material. Sr^{90} has a half-life of about 17 years, which is the longest half-life for any known strontium isotope. Sr^{90} emits a beta ray whose range has been determined to be approximately 130 mg Al/cm^2 (0.04 Mev).

4. The vapor pressure of UBr_4 has been determined by the transpiration method over the temperature range 450°C to 650°C. The vapor pressure of solid UBr_4 (M.P. 519°C) can be expressed by the equation:

$$\text{Log}_{10} P_{mm} = \frac{-10,900}{T} + 14.56 \qquad \text{(sublimation)}$$

The vapor pressure of liquid UBr_4 can be expressed by the equation:

$$\text{Log}_{10} P_{mm} = \frac{-7,060}{T} + 9.71 \qquad \text{(boiling)}$$

The following heats of change of state have been calculated:

ΔH (sublimation) = 50,000 cal/mol UBr_4

ΔH (boiling) = 32,000 cal/mol UBr_4

ΔH (fusion) = 18,000 cal/mol UBr_4

5. The boiling point of UBr_4 has been directly determined to be 765°C. This observed boiling point checks very closely that calculated from vapor pressure data (761°C).

6. The dissociation pressure of the uranium-uranium hydride-hydrogen system has been studied at 356°C, and the equilibrium dissociation pressure is essentially constant throughout the range of solid phase composition 10% - 90% UH_3. However, the equilibrium pressure reached by absorption of hydrogen from a higher pressure is about 14.5 cm Hg while that reached upon partial decomposition of solid into a system of lower hydrogen pressure is about 13.4 cm Hg. With UH_3 contents below 10% the dissociation pressure tends to decrease. With UH_3 contents above 90% the equilibrium pressure of formation is nearly constant to 97% UH_3, but the equilibrium pressure of decomposition shows a definite minimum at a composition of about 97 mol percent UH_3. No satisfactory explanation for this minimum has been found.

7. The volumes of the U-UH_3 and U-UD_3 systems have been measured by a gas densitometer and found to be linear functions of the hydrogen or deuterium content. The densities of UH_3 and UD_3 have been found to be 10.95 ± 0.1 g/cc and 11.25 ± 0.1 g/cc, respectively, at 25°C.

8. Hydrogen and deuterium have been fractionated by a partial decomposition of UD_3-UH_3 mixtures. A "separation factor", $\frac{N_{D_2}}{N_{H_2}}\,(\text{gas}) \Big/ \frac{N_D}{N_H}\,(\text{solid})$, of 1.2 has been obtained.

While this method may be used for the separation of D_2 from H_2, it has not yet been given practical application.

9. The thorium-hydrogen system has been subjected to a dissociation pressure-composition-temperature study and the existence of two thorium-hydrogen compounds has been proved.

The lower thorium hydride, ThH_2, is the more stable, and the dissociation pressure of a system whose solid phase contains equal amounts of ThH_2 and Th is given by the equation:

$$\text{Log } P_{(mm)} = \frac{-7700}{T} + 9.54.$$

The heat of formation of the hydride has been determined for the reaction:

$$Th + H_2 \longrightarrow ThH_2. \qquad \Delta H = -35{,}200 \text{ cal.}$$

The true equilibrium pressure of the system $Th\text{-}ThH_2\text{-}H_2$ is reached in 5 to 10 minutes at 700°C, either by decomposition or formation.

The higher thorium hydride, ThH_x (where x is probably 3.75), is much less stable than ThH_2. The dissociation pressure of a system whose solid phase consists of an equimolar mixture of ThH_2 and ThH_x is given by the equation:

$$\text{Log } P_{(mm)} = \frac{-4220}{T} + 9.50.$$

The heat of formation of the higher hydride has been determined for the reaction:

$$ThH_2 + (\frac{x}{2} - 1)\ H_2 \rightarrow ThH_x. \quad \Delta H = -19{,}300 \text{ cal/mol.}$$

At 300°C the "equilibrium" pressure on formation of ThH_x is much higher than that on decomposition, and the true equilibrium dissociation pressure is not reached.

10. The observed properties of uranium hydride indicate that in most regards this compound can be regarded as belonging to the saline-compound type proposed by Ephraim. The properties of the hydrides of thorium indicate that these compounds, too, have some saline-compound tendencies, but a consideration of all their properties leads to the conclusion that classification as an alloy-type compound is equally justified. It is likely that the hydrides of thorium and, to a lesser extent, the hydride of uranium are borderline compounds between the two classes.

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VITA

Robert William Nottorf was born in Dillon, Kansas on August 24, 1919. He was the second of three children born to Henry William and Minnie (Kohman) Nottorf. His first four years of elementary education were obtained at Dillon School. In 1928 his parents moved to near Abilene, Kansas, and he finished elementary education at Farmington School near that city. He attended Abilene High School and graduated in 1935.

His college education began in September, 1935 when he received part-time employment from the National Youth Administration and enrolled in Industrial Chemistry at Kansas State College, Manhattan, Kansas. In 1936 he gained employment as a laboratory assistant in the Chemistry Department and by this financial support was able to maintain himself in school. He received his B. S. degree in Industrial Chemistry in 1939.

He entered the Graduate School of Iowa State College in 1939 with a Research Fellowship in the Industrial Science Research Institute, and continued in that status until March, 1942. At that time he accepted employment with the Physical Chemistry Department at Iowa State to do work for the U. S. Government in connection with the development of atomic power. He completed the requirements for the PhD degree on August 10, 1945, and on August 20 he was drafted into the Army of the United States.