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NYO-3228

# NATURAL RADIOACTIVITY OF LANTHANUM AND NEODYMIUM (thesis)

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PHYSICS

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## ABSTRACT

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A search was made for natural activity of neodymium and lanthanum using a proportional counter of large surface area and 50% geometry. The background was reduced by means of massive shielding and guard counters connected in anti-coincidence. Normal analytical and radiochemical techniques and repeated ion exchange column separations were used to obtain pure samples.

Ten grams of lanthanum oxide gave a counting rate of 54.0 ± 0.6 counts per minute when spread over an area of 1650 $cm^2$. Analysis of an aluminum absorption curve yielded a specific activity for beta radiation of 0.07 disintegrations per second per gram of lanthanum and a partial half-life of $1.2 \times 10^{12}$ years for $La^{138}$. The maximum energy of the beta particles, believed to be negative, is estimated to be 1.0 ± 0.2 Mev. The x-radiation associated with electron-capture decay to $Ba^{138}$ was also measured. This gave a specific activity of 1.0 x-rays per second per gram of lanthanum, corresponding to an electron-capture specific activity of 1.2 disintegrations per second per gram of lanthanum and an electron-capture partial half-life of $7 \times 10^{10}$ years for $La^{138}$. The net half-life is essentially that of electron capture. The $\log_{10} \underline{ft}$ for the negatron transition is 21.3, which seems consistent with a fourth-forbidden transition from ${}_{57}La^{138}_{81}$ in a $g_{7/2}-d_{3/2}$ configuration with spin 5 and even parity.

At most 1 count per minute of soft or hard radiation

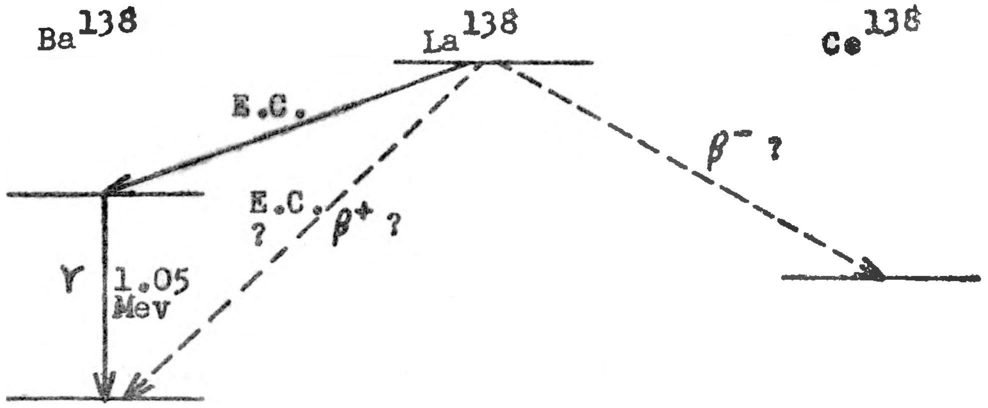
was observed from 15 grams of neodymium oxide spread over an area of 1650 $cm^2$, whereas from the results of Libby (1934) about 270 counts per minute would be expected. The maximum specific hard beta activity is 0.003 disintegrations per second per gram of neodymium, corresponding to a minimum half-life of $2 \times 10^{15}$ years for $Nd^{150}$. Reasons are given for supposing $Nd^{150}$ to be unstable but with a very long half-life. The maximum specific alpha activity is 0.02 disintegrations per second per gram of neodymium.

# CHAPTER I. INTRODUCTION

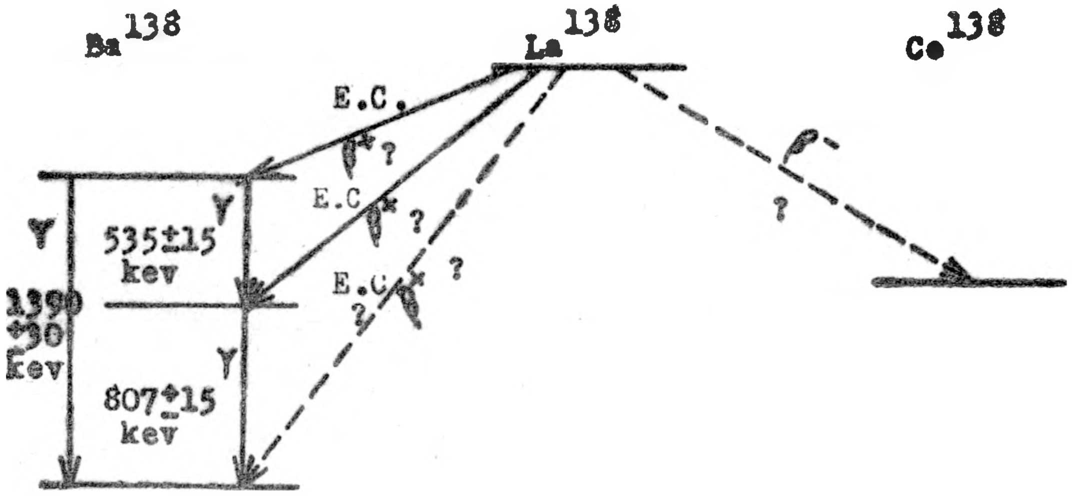
## 1. Lanthanum

In 1933 Libby and Latimer (1) reported a natural activity in lanthanum of about 8 times per mole that of potassium, or about 240 disintegrations per second per gram of lanthanum. This activity was not appreciably screened by 0.07 mm of aluminum, indicating that it was mainly of the hard beta type. They conceded that the possibility of actinium as an impurity had not been completely eliminated. No further attempt was made by these workers to characterize this radiation. Curie and Takvorian (2), Yeh (4), and much later Takvorian (9) could not find this activity reported by Libby and Latimer. Other workers (6,18,8) attributed the activity to radioactive impurities.

Pokrovskii (19) predicted that a radioactive element should exist in the neighborhood of atomic weight 137, and that the radioactivity found for lanthanum could be attributed to $La^{138}$. When Inghram, Hayden and Hess (20) reported a naturally occurring lanthanum isotope of mass 138 of abundance 0.089 ± 0.002%, the determination of the natural radioactivity of lanthanum took on an added significance since $La^{138}$, which is an odd-odd nuclide, occurs in the middle position of the triplet $Ce^{138}$-$La^{138}$-$Ba^{138}$. Analogous to the naturally occurring triplets $A^{40}$-$K^{40}$-$Ca^{40}$ and $Yb^{176}$-$Lu^{176}$-$Hf^{176}$, there was an excellent possibility that the middle member would be radioactive with a measurable half-life. Inghram, Hayden and Hess found no detectable activity when 200 mg of lanthanum oxide were spread over 5 cm$^2$ and counted at 40% geometry. On the basis of at most 1 count per minute and with a reasonable allowance for self-absorption, the maximum specific activity would be about one beta disintegration per second per gram of lanthanum. By the use of a scintillation counter (21) Pringle, Standil and Roulston (22) observed gamma radiation with a specific activity of 0.7 ± 0.1 photons per second per gram of lanthanum and an energy of 1.05 ± 0.05 Mev. The lanthanum was purified by hydrolysis and ion exchange separation. For a La$^{138}$ abundance of 0.089%, the half-life of the gamma radiation was $1.2 \times 10^{11}$ years. No beta radiation was found with a 1 mg/cm$^2$ window beta counter and a 100 mg/cm$^2$ thick lanthanum oxide sample. It was thus concluded that there were less than 0.4 beta particles of energy equal to or greater than 100 kev per second per gram of lanthanum. Hence they suggested the following disintegration scheme, with the gamma radiation attributed to an electron-capture transition to an excited state of Ba$^{138}$;



In a further study Pringle, Standil, Taylor and Fryer (23) using a scintillation spectrometer of improved resolution found evidence of gamma rays of energies 535 ± 15 kev, 807 ± 15 kev, and 1390 ± 30 kev of relative intensities 0.3:0.65:1, respectively. The activity of La$^{138}$ was estimated at approximately 0.45 disintegrations per second per gram of lanthanum, corresponding to 0.6 photons of all energies per second per gram of lanthanum. They also concluded that an x-radiation of energy 32 ± 1 kev was associated with the decay of La$^{138}$ and obtained a specific activity of 0.4 x-rays per second per gram of lanthanum. They thus gave a half-life of approximately 2 × 10$^{11}$ years to La$^{138}$. However, a search for electrons or positrons with a thin window Geiger counter indicated that the number of these particles with energy greater than 100 kev was less than 0.2 beta particles per second per gram of lanthanum. Their proposed decay scheme was as follows:



The work of Pringle, Standil, Taylor and Fryer set an upper limit for the specific beta activity of lanthanum without actually establishing the presence of beta radiation. In the work to be described, the use of a large proportional counter of large sample area and 50% geometry made possible the ascertainment that natural lanthanum does emit beta particles. Moreover, the x-rays that should be associated with electron capture were also observed.

## 2. Neodymium

A number of investigators have looked for natural radioactivity in neodymium (1-12). All agree that alpha activity is absent, and most either reported no beta activity or ascribed the observed activity to common radioactive impurities. However, Libby and Latimer (1) reported a beta activity in neodymium which was later characterized by Libby (7). Libby and Latimer found that the neodymium activity was not appreciably screened by 0.07 mm of aluminum, indicating that it was of the hard beta type, and that both neodymium sulphate and neodymium oxalate showed an activity which was approximately 2.5 times that of potassium per mole or about 75 disintegrations per second per gram of neodymium. The possibility of actinium as an impurity was not completely eliminated, however. Libby, who used a screen-wall counter, by far the most sensitive detection method, found that this beta radiation had a maximum energy of about 11 kev and a specific activity of about 60-120 disintegrations per second per gram of neodymium. This energy is much too low to correspond to the hard beta radiation found by Libby and Latimer, and it seems evident that the two radiations are not the same. From his work Libby concluded that the apparent half-life for the element cannot exceed $(1.46 \pm 0.20) \times 10^{12}$ years and is probably close to half this value. Since the rare earths cannot be readily freed from actinium, he purified one sample very thoroughly from impurities of other groups and allowed it to stand for seven months. After this time the activity was found to be unchanged within 50%, and since absorption experiments indicated that 5 mm of air completely absorbed the radiation, Libby felt that this showed the absence of actinium because the products of actinium should show an increased activity as well as a greater penetrability. However, that this activity is truly characteristic of neodymium has been in doubt because Libby did not repurify or fractionate his samples from all other elements to constant specific activity. Takvorian (9) reported an inability to detect activity in neodymium, but an inspection of his data shows that his sensitivity was grossly inadequate. He used an ionisation chamber with samples spread over an area of 0.5 $cm^2$ to a depth of 2 mm. He reported the activity of samarium as 23 and that of neodymium as 0, meaning presumably less than 0.1, or less than 1/230 of that of samarium. Using Libby's data and assuming an average beta energy of 5 kev, neodymium oxide would emit 13 kev per minute in his experimental apparatus. Now using a specific activity of 89 alpha rays per second per gram of samarium (13) and an average energy of 500 kev, it can be shown that samarium would give 101,000 kev per minute. This ratio of 101,000/13, or 7,800, is tremendously greater than his reported limit of 230. A reference by Broda (11) to unpublished work of Jha (1949) gave no data but implied confirmation of Libby's findings. In a private communication N. Feather gave some information on this work of Jha who was one of his students. The study was carried out with a Geiger counter containing layers of oxide of from 0.06 mg/cm$^2$ to 0.56 mg/cm$^2$ thickness and with a low gain proportional counter containing layers of oxide of between 1 and 5 mg/cm$^2$ thickness. An electron radiation of about one-half that calculated on the basis of Libby's results was obtained with the Geiger counter, and in addition the proportional counter indicated an alpha radiation of the order of 2% of that of a corresponding layer of samarium oxide. A recent report by Curran, Dixon and Wilson (12) stated that Libby's data were probably wrong and that the maximum beta energy may greatly exceed 11 kev, although a private communication from Wilson indicated that the possibility of beta particles of this maximum energy had not been completely eliminated. The implication was that radiation attributable to the element was observed, but no indication of the level of activity or degree of chemical purification was given.

On the basis of empirically determined beta-stability limits, Kohman (14) pointed out that Nd$^{150}$ appears to be outside the limits of beta stability for even-even nuclides, and he suggested the possible identification of the radiations found by Libby with those of $Nd^{150}$. This would imply the natural occurrence of $Pm^{150}$ in equilibrium with $Nd^{150}$ in rare earth minerals, a relatively long life-time for the daughter being required to explain the absence of hard radiations in Libby's samples. An alternate possibility suggested by Kohman, that $Nd^{140}$ is long-lived and occurs naturally, has been eliminated by the subsequent finding (15) that $Nd^{140}$ has a 3.3-day half-life with a 3.4-minute daughter emitting energetic radiations. The determination (16) that $Pm^{145}$ undergoes electron-capture decay to $Nd^{145}$ removes the possibility (17) that the latter is unstable.

It appears from the foregoing literature that the claims of Libby have been neither confirmed nor denied although reasonable doubt exists as to their validity. Hence an investigation of neodymium using modern purification and measurement techniques to dispel this uncertainty was undertaken. The present research on this problem utilizes a proportional counter of large sample area and 50% geometry as the detecting device. In addition to the inherent stability of the proportional counter, it has the advantage that energy measurements can be made by using an appropriate analyzer in conjuction with the counter. The background is lowered to a minimum by shielding with thick absorbing materials and with guard counters in anticoincidence to the proportional counter. By these means a very low specific activity can be detected, and the energy of soft radiations can be measured directly. By the use of ion exchange separation methods, a pure sample of neodymium was obtained for activity measurements.

## 3. Promethium

From the foregoing literature survey of the radioactivity of neodymium it is clear that if neodymium is beta active, then a search for a promethium daughter could be profitably undertaken. Since promethium has not been found in nature, although many reports of its discovery were made, it might be of interest to review the large amount of literature bearing on the existence of element 61 (2,5,9,14, 17,24-108). This list of references is reasonably complete, but only the most important will be mentioned. In 1917 Eder (24) found evidence from the lines of the arc spectrum of a samarium preparation for the existence of a new element. A few years later Brinton and James (25) postulated that the rates of hydrolysis of some rare earth carbonates seemed to indicate that an element existed between neodymium and samarium. From the x-ray spectrum of fluocerite Hadding (26) supposed the existence of a new element was indicated. Kiess (27) advanced the thought that 125 lines common to the arc spectra of neodymium and samarium may be characteristic of element 61. Yntema (28) asserted that the arc spectra of neodymium and samarium showed five lines common to both which indicated a new element. However, x-ray absorption and emission spectra gave no evidence of a new element. Prandtl and Grimm (29) also found no indication of element 61 upon the examination of the x-ray spectra of about fifty preparations resulting from the exhaustive fractionation of the cerium earths. They did suggest, however, that this element might be a homolog of manganese rather than a rare earth. Following this suggestion Druce and Loring (30) examined the x-ray spectrum of a concentrate from a manganese preparation, but they found nothing new. In a series of papers Harris, Yntema and Hopkins (33-36) claimed to have discovered element 61, for which they proposed the name illinium, and they gave the arc spectrum lines, absorption bands and x-ray emission lines for the element. However, Prandtl (47) and Prandtl and Grimm (48) criticized this work and stated that the x-ray spectral lines were probably due to impurities. K series lines of element 61 were reported by Cork, James and Fogg (41), Meyer, Schumacher and Kotowski (45), and Dehlinger, Glocker and Kaupp (46). Rolla and Fernandes (37-40) asserted that they had first undertaken the search for element 61 in 1922. The x-ray emission spectrum gave negative results, but the absorption spectrum gave characteristic lines of element 61. They proposed the name florenzium for element 61, and based their title as discoverers of the element on the claim that Rolla had sealed the results of their work in a vault of the Academy of Lincei in 1924. Marsh (66) and Noddack (71,75) among others could find no evidence of element 61.

Different groups of workers (79,83,84,85,89) attempted to synthesize element 61 by the cyclotron bombardment of neodymium and praseodymium targets. However, no separations of the products of the bombardment were made, nor was the purity of the targets determined. Consequently, the activities assigned to the various products were very much in doubt. It was found on the Plutonium Project that many rare earths were formed in the slow-neutron-induced fission of uranium. Marinsky, Glendenin and Coryell (102) using first qualitative separations and second ion exchange separation techniques on these rare earths led to the first positive identification of two isotopes of element 61, isotope 147 of half-life 3.7 years and isotope 149 of half-life 47 hours. Slow neutron irradiation of neodymium also gave $61^{149}$ which was similarly separated using ion exchange methods. Subsequently, Marinsky and Glendenin (104) proposed the name promethium for the element, and their claim was accepted.

There are two possibilities for the natural existence of promethium: as a natural radionuclide of long half-life, or as the daughter of a beta-active neodymium nuclide or an electron-capture-active samarium nuclide. Considering the known stable isotopes of neodymium and samarium, and applying the rule that no stable pairs of isobars exist whose atomic numbers differ by only unity, it can be seen that the only near-stable isotopes of promethium would be those of mass numbers 145, 147 and 149. Ballou (17) has calculated from the Bohr-Wheeler theory that the energy content of $Nd^{145}$ and $Pm^{145}$ should be nearly equal as should be the case of $Nd^{147}$ and $Pm^{147}$. He thus felt that $Nd^{145}$ could be a long-lived beta emitter forming $Pm^{145}$. However, this has been negated by the finding (16) that $Pm^{145}$ undergoes electron-capture decay to $Nd^{145}$, thus removing the possibility that $Nd^{145}$ is unstable. As has already been mentioned (102), $Pm^{147}$ is beta-unstable with a half-life of 3.7 years. Ballou, however, felt that a long-lived isomer of this isotope might exist. Isotope 149 has also been shown to be unstable (102). Kohman (14) has postulated that $Nd^{150}$ appears outside the limits of beta stability, in which case $Pm^{150}$ would be formed in very small amounts. Recently, Long and Pool (109) assigned a 2.7-hour beta activity to $Pm^{150}$. Fischer (110) obtained a half-life of 161 minutes for the beta decay of $Pm^{150}$. Moreover, she characterized this beta decay as composed of a 2 Mev negatron and a 3 Mev negatron along with gamma radiation. The alternate possibility mentioned by Kohman that $Nd^{140}$ is a long-lived beta emitter has been eliminated by the finding (15) that $Nd^{140}$ has a 3.3-day half-life with a 3.4-minute daughter emitting energetic radiations.

Thus the possibility of finding promethium existing in nature is very small. However, if natural activity for neodymium can be confirmed, a search for an unstable promethium daughter should be undertaken.

## CHAPTER II. EXPERIMENTAL APPARATUS AND PROCEDURES

### 1. Materials

a. Reagents, raw materials, and radioactive materials. - All chemicals used in the purification of the rare earth samples were of analytical reagent grade.

Neodymium oxide (99% pure) and lanthanum oxide (98% pure) were obtained from the Lindsay Light and Chemical Company, West Chicago, Illinois.

The Dowex 50 cation exchange resin, 150-250 mesh, was obtained from the Dow Chemical Company, Midland, Michigan.

The radioactive nuclides $Fe^{55}$, $Co^{60}$, and $Tl^{204}$ were obtained from the Isotopes Division of the Atomic Energy Commission, Oak Ridge, Tennessee.

b. Purification of the rare earth oxides. - Before the advent of ion exchange resins the preparation of pure rare earth compounds was notoriously difficult (111, 112). The great similarity in chemical properties of the rare earth elements results from the filling of the inner 4f subshell by electrons which do not enter into the formation of chemical bonds. However, because of the so-called lanthanide contraction, there is a slight gradation in chemical properties among the rare earth elements. Three conventional methods of separation are based upon these slight differences in chemical properties: (1) differences of basicity, the weaker bases precipitating first when ammonium hydroxide is slowly added; (2) differences in the solubilities of various salts; and (3) differences in valence, where a valence other than the normal one of three can be utilized. With the exception of method (3), which is quite limited in application, the separations were long and tedious.

During World War II the Plutonium Project began using ion exchange processes for the separation and purification of fission products. This technique was adapted successfully to the separation of the rare earths to give spectrographically pure rare earths (100,101,102, 113,114,115,116). The procedure used is to adsorb the rare earth mixture at the top of a cation exchange resin bed contained in a column and to elute the rare earths down the column by the use of a complexing agent, such as citric acid. Since the affinity of each cation for the exchanger differs, the various cations will move down the column at varying speeds with the result that each cation will tend to be concentrated in a separate band. The organic complexing agent increases the differences in adsorbability of the rare earth cations and gives more clear-cut separations. If the variable conditions, such as length of column, rate of flow, concentration of rare earths, resin particles size, complexing agent concentration, pH of eluting solution, and temperature, are chosen favorably, an appreciable amount of a particular rare earth can be obtained completely free from other rare earths. Consequently, for the separation of the rare earths from one another and from actinium (117), ion exchange methods are extremely useful. The separation from thorium and the decay products of thorium and actinium, however, may be done in another manner because of differences in valence, and normal analytical techniques can be adopted to accomplish this.

In general the procedure followed in the purification of neodymium and lanthanum by ion exchange methods was that recommended by Lilly and Stewart (118). The ion exchange columns were built from pyrex glass, 90 cm long and 6 cm in diameter. A coarse sintered glass funnel was attached to the bottom of each, and below this was affixed a pressure stopcock. The Dowex 50 cation exchange resin was washed well with 4 N hydrochloric acid, and the smallest particles were decanted off. After washing 10-15 times with distilled water, the resin was treated 5 times with a hot 4 N solution of ammonium chloride in order to convert the resin to the ammonium form. The resin was again washed 10-15 times with distilled water and finally slurried into the columns to a height of 80 cm.

Two five-gallon jugs, each with a hole bored through the wall near the base, were set on a high shelf. In each hole was placed a one-hole rubber stopper through which was passed a small piece of glass tubing bent at right angles. To the other end of this glass tubing was affixed a large one-hole stopper which was placed in the top of the column. In this manner the column was joined to the reservoir of eluting solution. This system is illustrated in Figure 1.

The eluting solution used was 5% citric acid.

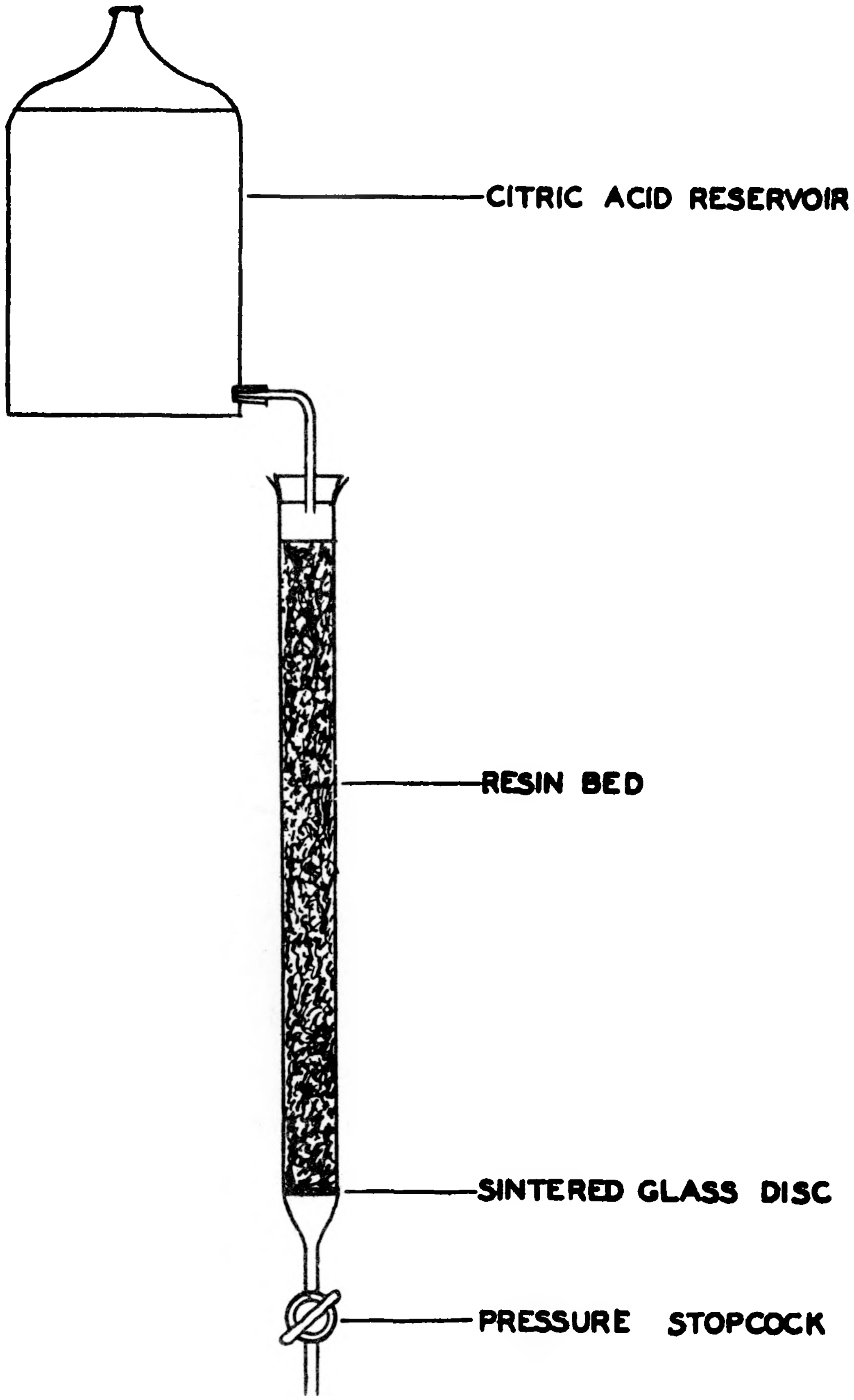


Fig. 1—Ion Exchange Column System.

This was prepared by dissolving 600 grams of citric acid and 20 grams of phenol, which served the purpose of eliminating the growth of mold in the citrate solution (116), in distilled water, adding 133 ml of concentrated ammonia and diluting to 12 liters with distilled water. A solution of pH 3.1 was obtained, the proper pH for the neodymium purification. The lanthanum elution was carried out at a pH of 3.6, so sufficient ammonia was added to the solution prepared above in order to obtain the proper pH for the lanthanum purification. After these first main elutions were carried out, later elutions were speeded up by increasing the pH of the neodymium eluting solution to 3.4 and the lanthanum eluting solution to 3.8 by adding sufficient ammonia to the solution of pH 3.1. The pH of all the solutions used in the elutions was checked with a pH meter.

The neodymium oxide and lanthanum oxide were found to contain a radioactive impurity when counted by a small proportional counter. This activity could be removed by precipitating it as the iodate using zirconium carrier, indicating that it was probably due to thorium. In order to remove most of this activity prior to the ion exchange treatment, a preliminary zirconium iodate precipitation was carried out by the method described below. After the iodate treatment the oxides were dissolved in a minimum amount of concentrated hydrochloric acid and diluted to 100 ml with distilled water. The solution was evaporated to dryness, diluted to 50 ml with distilled water and again evaporated to dryness. Finally, the residue was dissolved is distilled water, and several drops of concentrated hydrochloric acid were added to dissolve small amounts of oxide formed on the evaporation to dryness. The samples were then ready to be adsorbed on the resin.

The rare earth solution was added to the top of the column, and one column volume of distilled water was passed through the column before the elution was started. In order to eliminate air bubbles, the following procedure was used to connect the column to the citric acid reservoir. The space above the resin in the column was completely filled with water. The large rubber stopper was then pressed down into the column forcing the air contained in the glass tubing back through the citric acid solution. After the reservoir was connected to the column, the elution was started by opening the stopcock. The rate of flow was adjusted at 4-5 seconds per drop, and samples were collected at the bottom.

In order to obtain some idea of the efficiency of the separation, an elution curve was drawn. This is a plot of the concentration of the rare earth in the eluant versus the eluate volume. Consequently, during the entire elution it was necessary to measure the volume of each sample and to obtain the amount of rare earth in each sample. The volume of each sample was determined by the use of a large graduated cylinder. To determine the concentration of rare earth, each sample was first evaporated under an infrared lamp for several hours to concentrate the rare earth. A large excess of a hot, saturated solution of oxalic acid was added, and the precipitate was allowed to settle overnight. It was then filtered, washed well with distilled water and ignited at 800°C for two hours. After cooling, the resulting oxide was weighed, and the concentration was obtained in milligrams per milliliter. A typical elution curve is that shown for the lanthanum elution in Figure 2.

To complete the purification it was necessary to remove thorium and the decay products of thorium and actinium in order to free the rare earth from all possible extraneous sources of activity. This can be accomplished by normal procedures for the removal of +2 and +4 cations of naturally radioactive elements. The rare earth oxide was dissolved in a minimum of concentrated hydrochloric acid, diluted to 100 ml with distilled water and evaporated to dryness. About 50 ml of distilled water were added, and the solution was again evaporated to dryness. Finally, the residue was dissolved in 100 ml of distilled water, and several drops of concentrated hydrochloric acid were added to dissolve the oxide.

Radium and lead can be removed by precipitating as sulphates using barium as a carrier. One ml of concentrated hydrochloric acid was added to the solution of the rare earth chloride. The solution was heated to boiling, and 0.2 gram of barium chloride was added. To this boiling solution was added an excess of hot, dilute sulphuric acid (5 ml of concentrated sulphuric acid per 100 ml of solution).

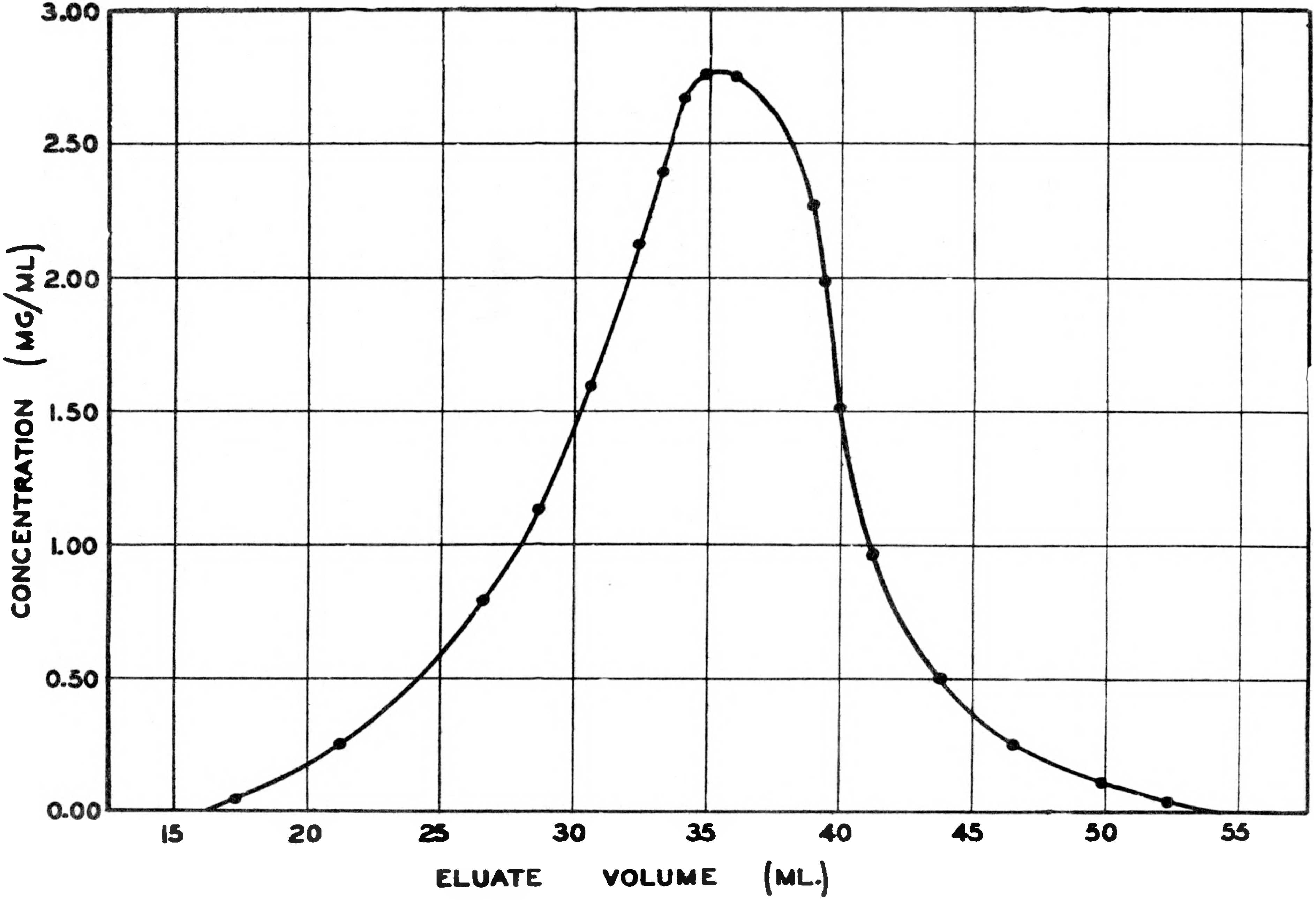


Fig. 2—Elution Curve for Lanthanum.

After digestion on a hot plate for several hours, the precipitate was filtered and discarded without washing.

Any bismuth present can be precipitated as the sulfide using copper as a carrier. Consequently, the solution was made 0.2 N with respect to the hydrochloric acid, and 0.2 gram of cupric nitrate was added. The solution was heated to boiling and saturated with hydrogen sulfide. Upon cooling, the precipitate was filtered and discarded without washing.

If thorium is present, it can be removed as the iodate using zirconium as the carrier. The filtrate from the sulfide treatment was evaporated to 50 ml, and 25 ml of concentrated nitric acid was added. To this solution was added 0.2 gram of zirconium nitrate. A very large excess of a solution containing 100 grams of sodium iodate in 333 ml of concentrated nitric acid per liter of solution was added slowly with stirring, and the precipitate was allowed to settle. It was then filtered, washed once with a small amount of distilled water and discarded. Concentrated ammonia was added to the filtrate until it was basic. The rare earth hydroxide formed was filtered with the aid of suction and washed well with cold, distilled water. To the precipitate on the filter paper was added a sufficient amount of a hot solution containing 5 ml of concentrated hydrochloric acid per 100 ml of solution to dissolve the hydroxide. This solution was heated to boiling, and an excess of a hot, saturated solution of oxalic acid was added. After allowing the precipitate to settle overnight, the rare earth oxalate was filtered, washed well with cold, distilled water and ignited to the oxide at 800°C.

## 2. Apparatus

a. Counter arrangement. - A cross-section of the counter arrangement and external shielding is shown in Figure 3. The external shield consisted of an iron box made of 2 inch thick pieces of iron in which the counters were placed. The inside chamber of the box was 36 inches long, 16 inches wide and 16 inches high. Around the iron box was placed a layer of lead bricks 4 inches thick at the top, 3 inches thick along the sides and ends, and 2 inches thick at the bottom. Swinging doors at each end of the iron box gave easy access to the counters. Friction tape was used to hold the thirteen Geiger counters together. A long, insulated wire running from the binding post of one Geiger counter to another served to connect all the Geiger counters together. A resistor and by-pass condenser served to filter the high voltage introduced on the bank of Geiger counters, and a blocking condenser was used to take the pulse from the counters. The Geiger pulse was led into a two-stage amplifier and finally into the mixing tube of the anticoincidence circuit. The proportional counter was located in the center of the bank of Geiger counters and was provided with a similar filter and blocking condenser. The pulse taken from the proportional counter was put into a four-stage amplifier, finally ending up in the mixing tube of the anticoincidence circuit.

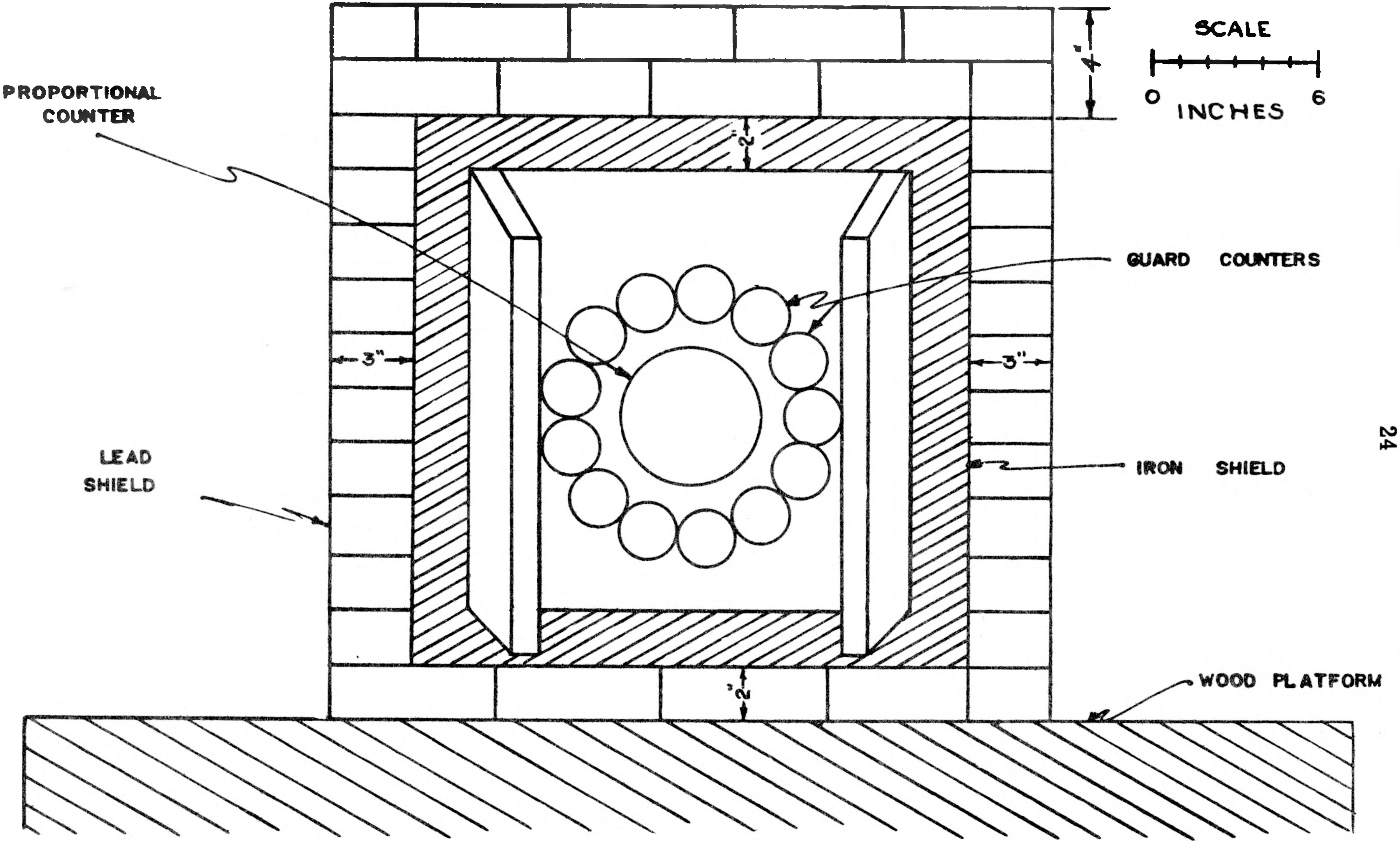


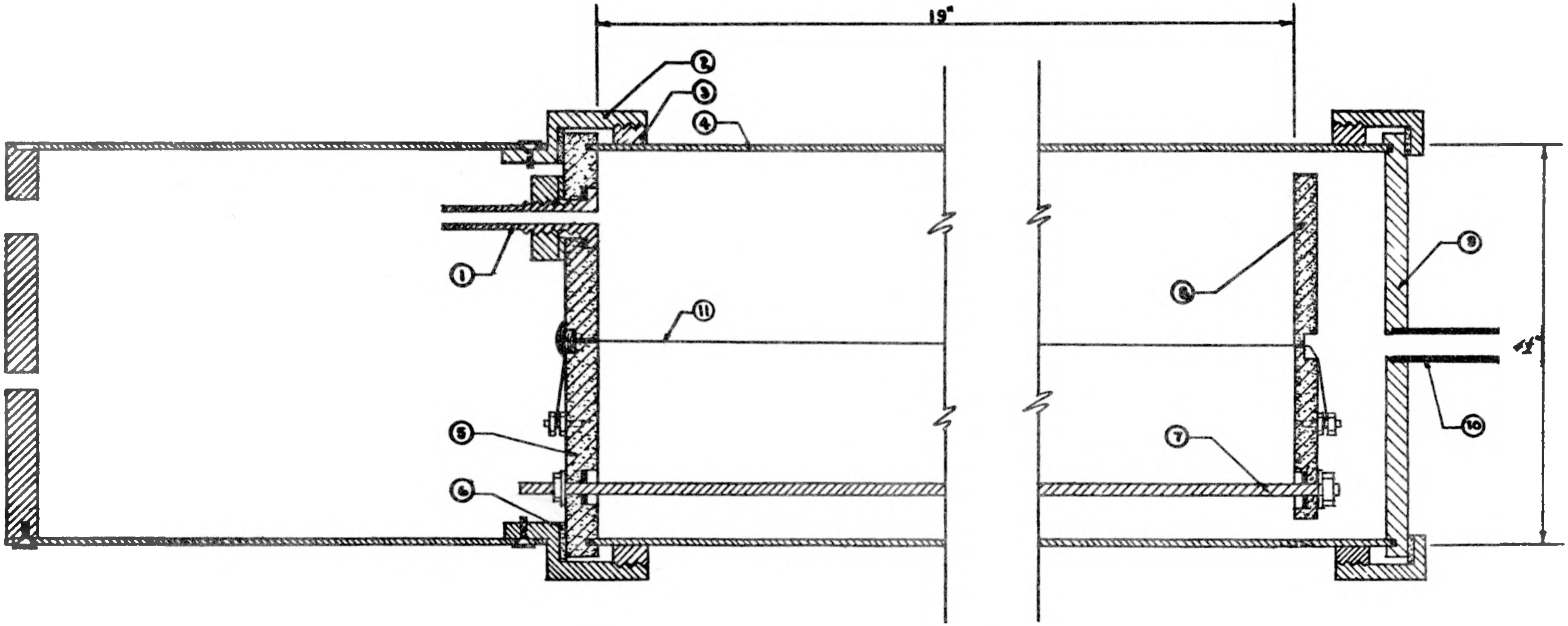
Fig. 3—Counter Arrangement.

It was of interest to notice the effect of the various forms of shielding on the background. With no shielding whatsoever the background of the proportional counter was 1150 counts per minute; with 2 inches of lead shielding the background was reduced to 500 counts per minute; increasing the shielding to 4 inches of lead only lowered the background to 480 counts per minute; however, using the iron box surrounded by 3 inches of lead reduced the background to 350 counts per minute; the use of the guard counters with an external shielding of 4 inches of lead gave a background of 55 counts per minute; with the iron box surrounded by 3 inches of lead the use of the guard counters lowered the background to 32 counts per minute. Martell and Libby (118) found that for a Geiger counter with an area of 400 $cm^2$ the background with no shielding was 450 counts per minute; with an external shield of 8 to 10 inches of hot rolled steel the background was lowered to 104 counts per minute; when a bank of Geiger counters was used in conjunction with the external shield, the background was decreased to 6 counts per minute.

It was noticed that the background was dependent on the sample mount. This had been noted by Martell and Libby who attributed it to the effect described by Crane (120,121) as characteristic of certain metals. However, this effect is due to chemical or mechanical changes on the surface and shows up only in Geiger counters. Radioactive contamination, which seems especially bad in aluminum, affects all counters alike. A bare aluminum sheet 0.012 inch thick gave a counting rate 16% higher than that for the empty counter. A copper sheet of the same thickness did not increase the counting rate. For this reason copper sheets were used to mount the samples.

b. Proportional counter. - For the investigation of weak radioactivities a proportional counter was selected. Sufficient work has been done to indicate that a proportional counter is capable of detecting low energy beta radiation (121-128). This is exemplified by the fact that Curran, Angus and Cockroft (123) were able to detect completely the beta rays of tritium where the energy ranged from a few electron volts to 18 kev by using a proportional counter with a high gain amplifier of low noise level. A proportional counter avoids the problems of surface effects and multiple discharges which cause difficulties in Geiger counter operation (129). Moreover, since the pulse size is proportional to the particle energy, it is possible to obtain an energy spectrum of low energy radiation with a proportional counter by the use of an appropriate analyzer.

The proportional counter used in these experiments can best be described by referring to Figure 4. The main body of the counter was 4 3/8 inches in inside diameter and 19 inches in length and was made of 1/16 inch thick brass tubing. Removable ends, one of brass and one of lucite, both grooved to fit snugly over the ends of the tubing, were sealed tight by means of brass end clamps. To the lucite end plate were affixed three brass rods which ran



① OUTLET TUBE - BRASS
② END CLAMPS BRASS
③ THREAD RINGS - BRASS
④ MAIN BODY - BRASS
⑤ END PLATE - LUCITE
⑥ BEARING WASHERS - BRASS
⑦ WIRE SPACER RODS - BRASS
⑧ WIRE SUPPORT - LUCITE
⑨ END PLATE - BRASS
⑩ INLET TUBE - BRASS
⑪ WIRE — 0.003" TUNGSTEN

Fig. 4—Proportional Counter.

the length of the counter and terminated in a smaller lucite disk, which served as a support for the center wire of tungsten, 0.003 inch in diameter. Since this disk was only 3 7/8 inches in diameter, compared to 4 3/8 inches for the inside diameter of the counter, and concentric with the latter, the sample, painted on a circular copper sheet, could easily be slid into the chamber between the brass tubing and the lucite disk. Rubber tubing was used to connect the inlet tube to the vacuum system, and the counter was evacuated and filled through this tube. A gas mixture of 90% argon and 10% ethylene at atmospheric pressure was used as the counter filling. At this particular filling for $Fe^{55}$ a plateau of slope 1% per 100 volts was obtained between 3100 volts and 3400 volts, and the pulses from the counter observed on an oscilloscope varied continuously in height from very small ones to large ones, which would be expected for a proportional counter. When the ethylene was increased to 20%, the very small pulses disappeared, and some very large ones appeared. A rough calculation indicated that the amplification factor was $10^6$ which is very large for proportional operation. At 5% ethylene the voltage plateau was short and steep. The argon gas (99.9% pure) and the ethylene gas (99.5% pure) were obtained from The Matheson Company, East Rutherford, New Jersey. The tungsten center wire was operated at a positive potential of 3300 volts; the counter wall acted as the cathode and was at ground potential. The brass shell attached to one end of the brass tubing contained the resistor (1 megohm) and by-pass condenser (0.05 microfarad, 7500 volts D.C., glassmike) used to filter the high voltage to the center wire, and a blocking condenser (600 micromicrofarads, 20 kilovolts, ceramic) to transmit the pulse from the center wire to the counting apparatus.

c. Geiger counters. - The Geiger counters are illustrated in Figure 5. They consisted of pieces of brass tubing 30 inches in length, 2 inches in outside diameter, and 1/16 inch in thickness. The interior of each was cut inward 1/2 inch to a thickness of 1/32 inch, and the ends were closed by lucite disks, 1/4 inch thick, which rested on the ledges formed. Small holes were drilled through each disk, and the center wire of tungsten, 0.003 inch in diameter, was passed through these holes and attached to a binding post on the outside of the lucite disk. The binding post was merely a screw threaded into the lucite disk. Pyseal cement, obtained from the Fisher Scientific Company, Pittsburgh, Pennsylvania, was used to seal the lucite disks to the brass ends. At the center of the brass tubing was drilled a hole 1/4 inch in diameter, and a short piece of copper tubing was soldered into this hole. Through this tubing the counter was evacuated and filled. A gas mixture of 95% argon and 5% ethylene at atmospheric pressure was used as the counter filling (131). A positive voltage of 2300 volts was placed on the center wire anode, while the cathode brass tubing was kept at ground potential.

d. Circuits. - The anticoincidence circuit is

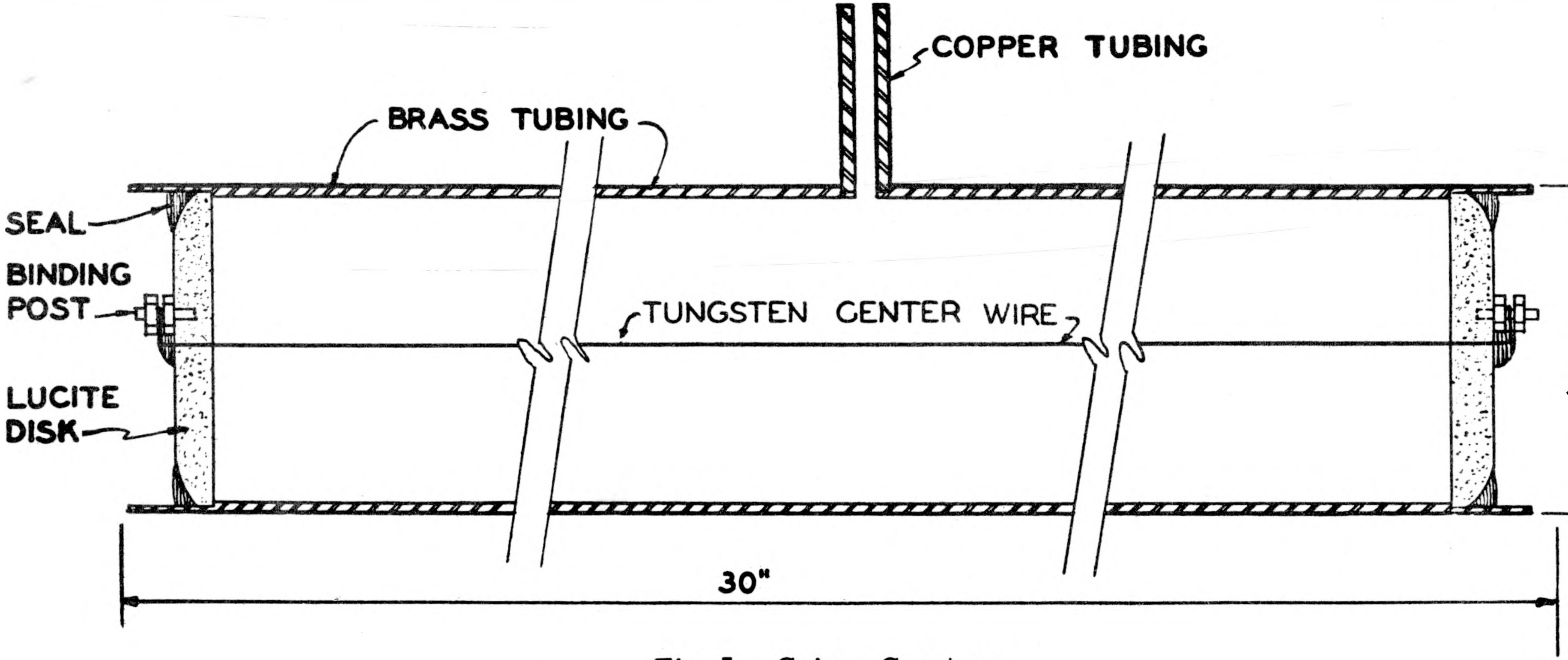
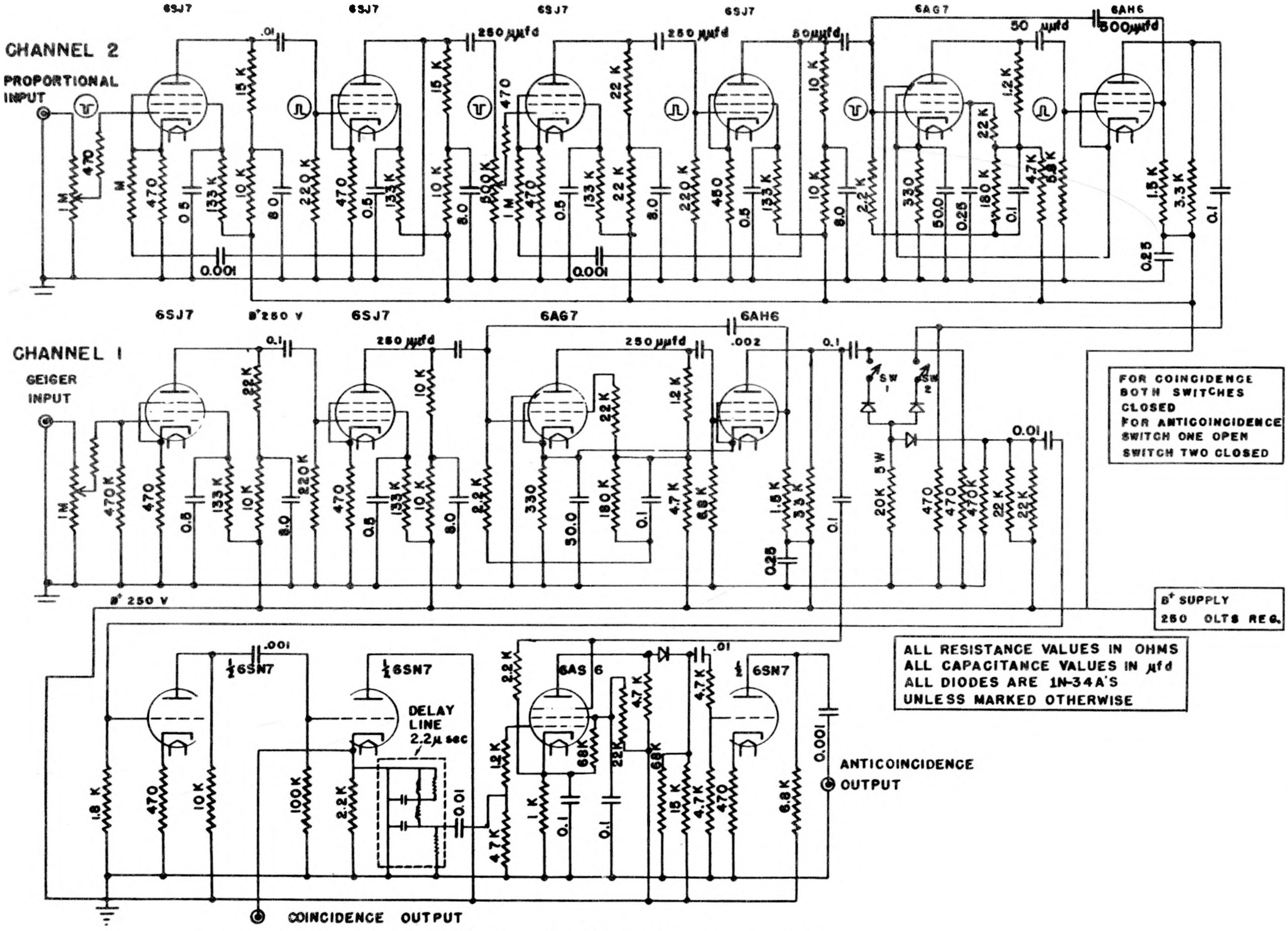


Fig. 5—Geiger Counters.

shown in Figure 6. It was composed of two channels, one for the proportional counter and one for the bank of Geiger counters. The proportional channel, denoted as Channel 1 on the diagram, consisted of a four-stage amplifier and a triggered univibrator. A gain of 5000 was obtained through the proportional counter amplifier. The gain was stabilized by the use of negative feedback from the plate of the second tube back to the cathode of the first tube and from the plate of the fourth to the cathode of the third. Gain control was provided by the incorporation in the circuit of two attenuators, one before the first stage and the other before the third stage. These two gain controls provided adequate gain adjustment. After amplification, the pulse was led into a triggered univibrator. This gave a square wave output pulse which was 4 microseconds long. The pulse was then inverted, led through a delay line of 2.2 microseconds, and finally as a positive pulse was placed on the control grid of a mixing tube. The Geiger channel, denoted as Channel 2 on the diagram, consisted of a two-stage amplifier and a triggered univibrator. Since the Geiger pulses were considerably greater in amplitude than those from the proportional counter, a two-stage amplifier was found to be sufficient. Gain control was provided for by the use of an input attenuator in front of the first stage. The amplified pulse was led into a triggered univibrator which gave a uniform negative square wave output pulse, 12 microseconds long. This pulse was led as a negative pulse onto the cathode of the mixing tube. When



FOR COINCIDENCE BOTH SWITCHES CLOSED
FOR ANTICOINCIDENCE SWITCH ONE OPEN SWITCH TWO CLOSED

ALL RESISTANCE VALUES IN OHMS
ALL CAPACITANCE VALUES IN μfd
ALL DIODES ARE 1N-34A'S UNLESS MARKED OTHERWISE

Fig. 6—Anticoincidence Circuit.

the two pulses occurred simultaneously, the pulse from Channel 2 overlapped and cancelled that from Channel 1, and no output pulse was obtained; when there was no pulse from the Geiger counters occurring at the same time as a pulse from the proportional counter, the tube conducted, and an output pulse was obtained which could be detected by a scaling unit. The pulses from the Geiger counters alone gave no output. The scaling unit was one of the conventional type manufactured by the Nuclear Instrument and Chemical Company, Chicago, Illinois (Model 165). Two independent voltage supplies were utilized, one for the proportional counter and one for the Geiger counters. They were 5000 volt regulated power supplies manufactured by the Nuclear Instrument and Chemical Company (Model 1090). A block diagram of the entire counter system is shown in Figure 7.

### 3. Counting techniques

a. Sample preparation. - After the final purification step and ignition of the oxalate, the rare earth oxide was painted on a 0.012 inch thick copper sheet which had been bent into a cylindrical shape. It was necessary to take care in the ignition of the oxide that the temperature did not rise above 800°C. Below this temperature the resulting oxide was powdery and quite easy to paint on the copper backing; above this temperature it was refractory and difficult to crush into a powdered form. The normal procedure of preparing samples of this type is to suspend the material in a smooth layer on the backing material. Both ethyl alcohol and agar-agar solutions were tried, but it

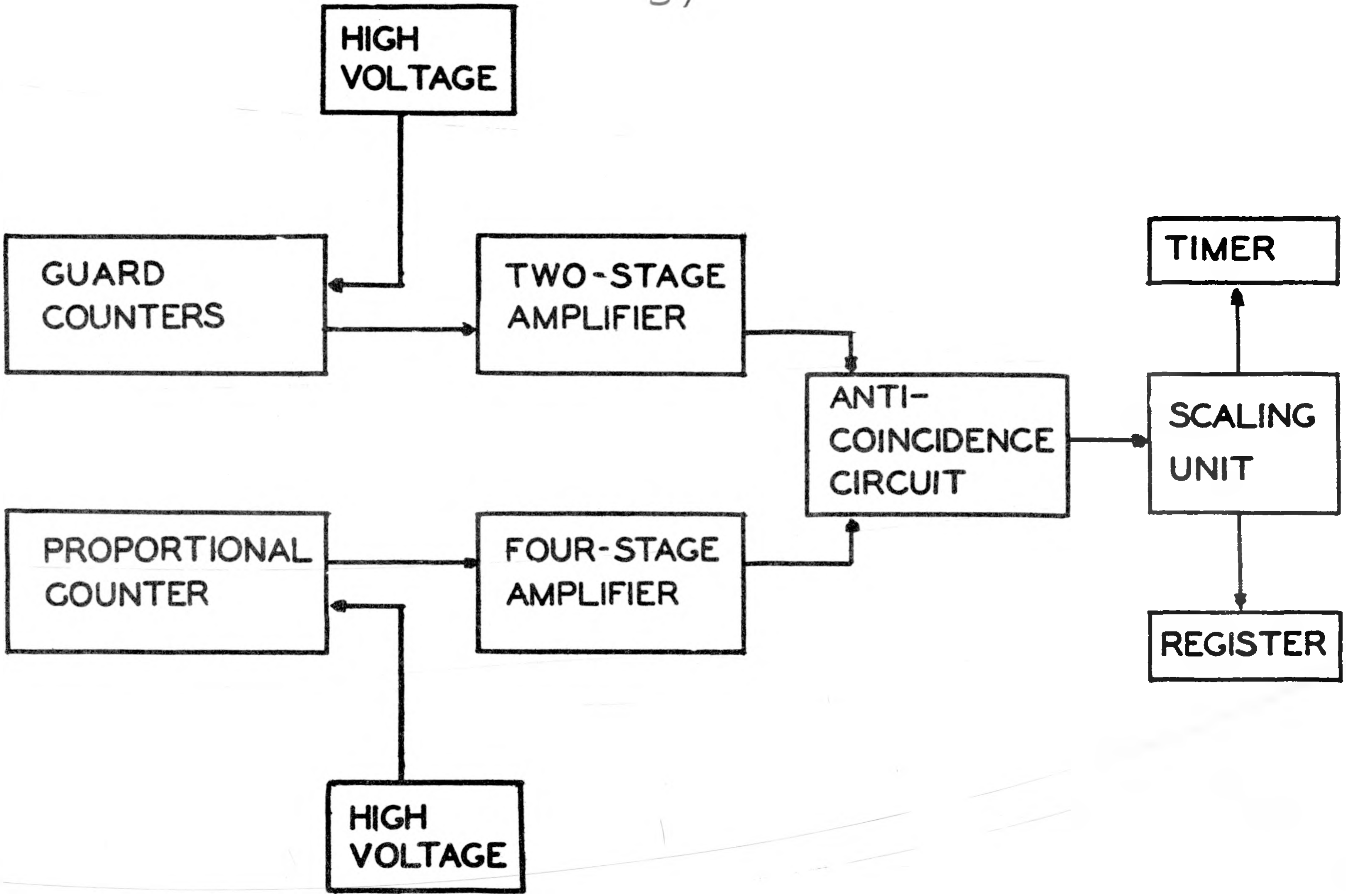


Fig. 7—Block Diagram of The Counter System.

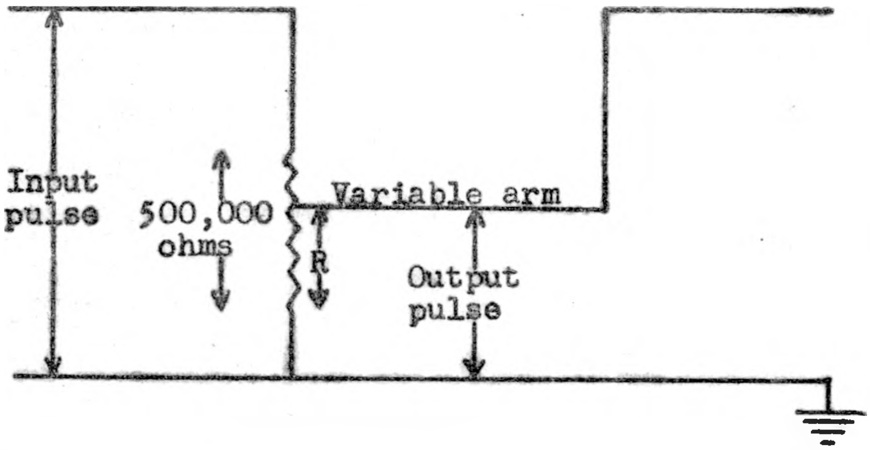
was found that the oxide coating would not adhere to the copper on drying. Consequently, a 2% solution of collodion in butyl acetate was used to paint the oxides on the copper surface. Enough of the solution was added to the oxide to give a thick slurry which was painted on the copper backing with a 1/4 inch brush. Butyl acetate was selected as the solvent for the collodion because the entire surface could be painted before the material had dried, thus making it possible to obtain a smoother coating. The collodion had no effect on the background since a copper sheet with and without a layer of collodion gave the same background counting rate. After the rare earth oxide had been painted on the copper backing, the sample was allowed to dry for three days. It was then placed in the proportional counter and pumped under a vacuum for 12-24 hours. Finally, the counter was filled with the argon-ethylene gas mixture, and the counting was started.

b. Sample counting. - After the sample had been prepared and placed in the proportional counter, the counter was pumped for one-half hour, filled with a mixture of 90% argon and 10% ethylene at atmospheric pressure and allowed to stand for one-half hour at 3300 volts before the counting was started. This was done to give the voltage supply an opportunity to warm up at the operating voltage and to give the gases a short time to mix. In every case this same procedure was followed so that any inherent errors in the filling technique would cancel. When counting measurements were made, the sample was counted first, and then the appropriate background was taken. A bare copper backing was used for the background sample, and this was covered with exactly the same absorber that had been used for the sample. It was important to take the sample and background counting rates as close together as possible in order to eliminate the effect of any outside influences. For all backgrounds taken without aluminum the variation about a mean of 32 counts per minute was ± 2 counts per minute.

c. Energy measurements

i. Bias curves. - Qualitatively, some indication of the energy of low-energy radiation can be obtained by means of bias curves. If neodymium is naturally beta-active, and if the energy of the beta radiation is as low as was reported by Libby (7), it should be possible to confirm this since the bias curve will have a large negative slope at the beginning; if the radiation is hard, the slope will be much less. The bias curve technique is valid for energies less than about 30 kev. Above this energy the electrons have too long ranges at atmospheric pressure, and it would be quite difficult to obtain an indication of the energy. Bias curves can furthermore be of assistance in determining the degree of purification of the rare earth samples. A bias curve run on portions of lanthanum or neodymium taken from different regions of the elution curve should give an indication of any contamination since the curves will differ if a radioactive impurity is present.

The bias curves were obtained by varying the gain on the proportional counter amplifier and plotting the counting rate obtained against the reciprocal of the resistance at that particular gain setting. The gain control was a 500,000 ohm potentiometer, and the resistance was measured for various settings of the control knob. Since the resistance measured was that between the variable arm and ground, a large resistance would correspond to a large output pulse. In other words, for this case small pulses would not be decreased greatly and would be of sufficient size to be amplified and counted. Conversely, for a small resistance reading, the output pulse would be considerably decreased in size, and only the large pulses would still be of sufficient amplitude to be amplified and counted. Thus the amplitude of the input pulse, which is directly proportional to the energy lost by the particle in the counter gas, can be considered to be inversely proportional to the resistance at which it will just barely be biased out, and a measure of the resistance will yield a measure of the



minimum energy of the radiation counted provided a calibration of the reciprocal of the resistance as a function of the particle energy is made.

This was done using the sharp cut-off of the manganese K x-rays of $Fe^{55}$ (6 kev). A solution containing $Fe^{55}$ in the form of the chloride was appropriately diluted and placed upon a small stainless steel disk. After evaporation, the sample was very briefly dipped in concentrated hydrochloric acid to remove any excess sample, and dried. The sample was put into the center of the proportional counter, and the counting rate was taken at various gains. Figure 8, Curve I, shows the bias curve obtained for one run. It will be noted that the large negative slope of the curve is not as steep as should be expected. In the various runs taken several of the curves showed this more gradual slope, and it was difficult to explain this variance between runs. A series of bias curves were taken on one sample at various counter voltages, and it was found that the gain varied by a factor of approximately 1.4 for a change of 50 volts in the counter supply. Since the amplification is sharply dependent on the applied voltage, a change in voltage shifted the energy scale markedly. For any work of this type in which reasonably quantitative results are desired, it would be better to use a battery pack to eliminate any possibility of voltage changes. If the proper equipment is available, the technique of bias curves should be replaced by that of pulse analysis.

Curve I as shown gave a rough indication of the energy for photons absorbed in the interior of the counter, but it gave no information as to the efficiency of the counter for electrons absorbed near the walls. In order to determine this, it was necessary to make tests with electrons of known energy. The Auger electrons associated with the manganese K x-rays from $Fe^{55}$ should have energies of about 5 kev and thus can easily be absorbed using very thin absorbers. The effect on the bias curve should be a lowering of the counting rate by a factor corresponding to the fluorescence yield and a general flattening of the curve in the low energy region due to the fact that only the nearly monoenergetic x-rays are unabsorbed. Bias curves were run using plastic absorbers 0.1 $mg/cm^2$, 0.2 $mg/cm^2$, and 0.3 $mg/cm^2$ thick and cellophane absorbers 3.0 $mg/cm^2$ and 6.0 $mg/cm^2$ thick. As expected, a flatter plateau was obtained, and with the thinnest absorber the counting rate decreased by about 70%. This corresponds well with the estimated fluorescence yield of 0.26 (132). The bias curve for the 0.3 $mg/cm^2$ thick plastic absorber is shown in Figure 8, Curve II, and that for the 6.0 $mg/cm^2$ thick cellophane absorber in Figure 8, Curve III. Curve II, which shows the bias curve for the x-rays only, would make a good curve for estimating the energy. The change in slope is sharp, and assuming that the mid-point of the negative slope, $1/R = 70 \times 10^{-6}$ $ohm^{-1}$, corresponds to 6 kev, a linear energy scale can be obtained which is given on the top scale of Figure 8. At $1/R = 3.0 \times 10^{-6}$ $ohm^{-1}$ the energy

40

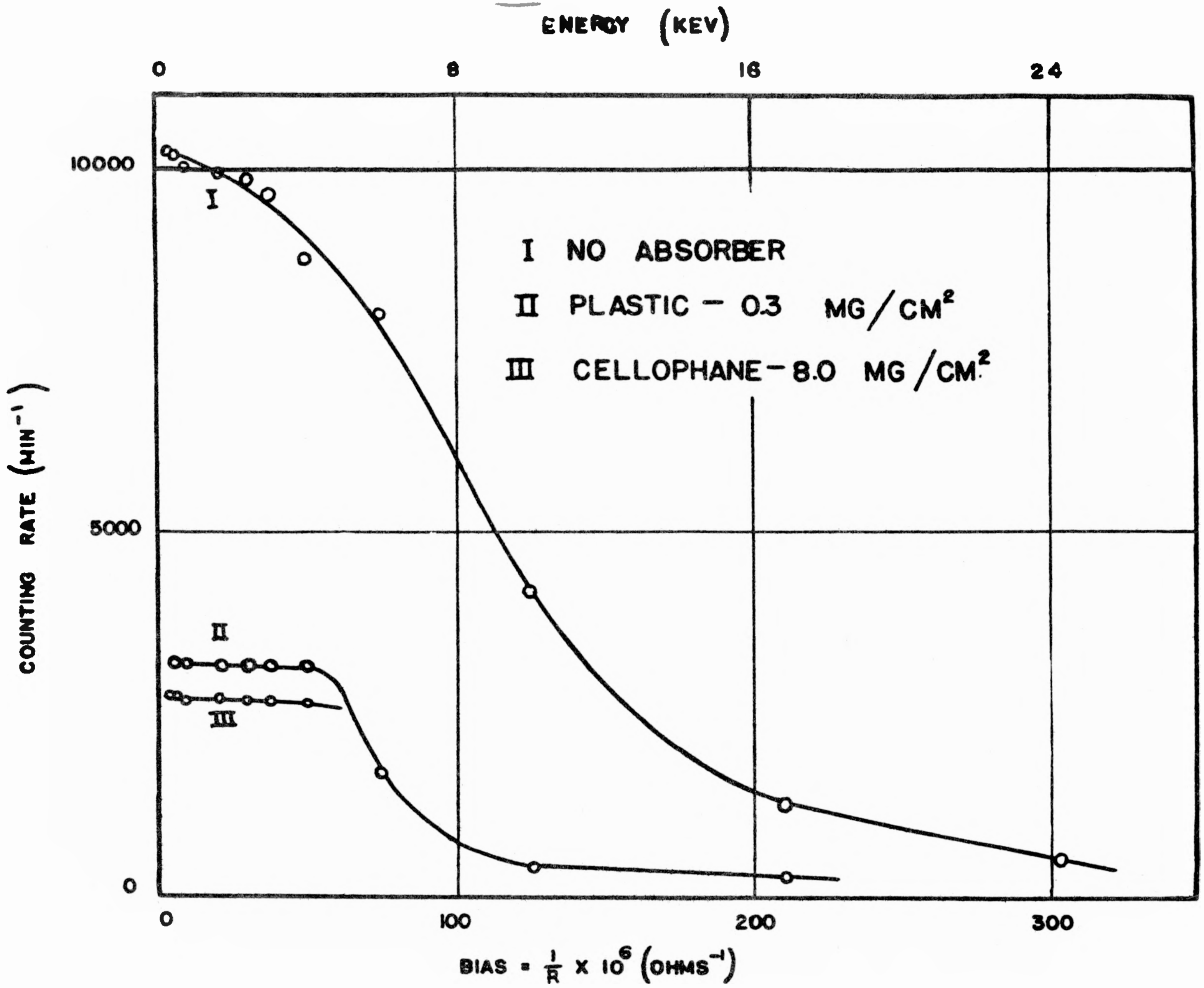


Fig. 8—Bias Curve for $Fe^{55}$ with and without Absorbers.

is 0.3 kev. The low energy portion of Curve III was reproduced to show that the absorption of x-rays by the cellophane absorber was very close to that expected. A rough calculation shows that 18% of the x-rays should be absorbed. The agreement is quite satisfactory. Thus it appears that the counter is capable of detecting electrons of very low energy with apparent high efficiency and no appreciable reduction in energy.

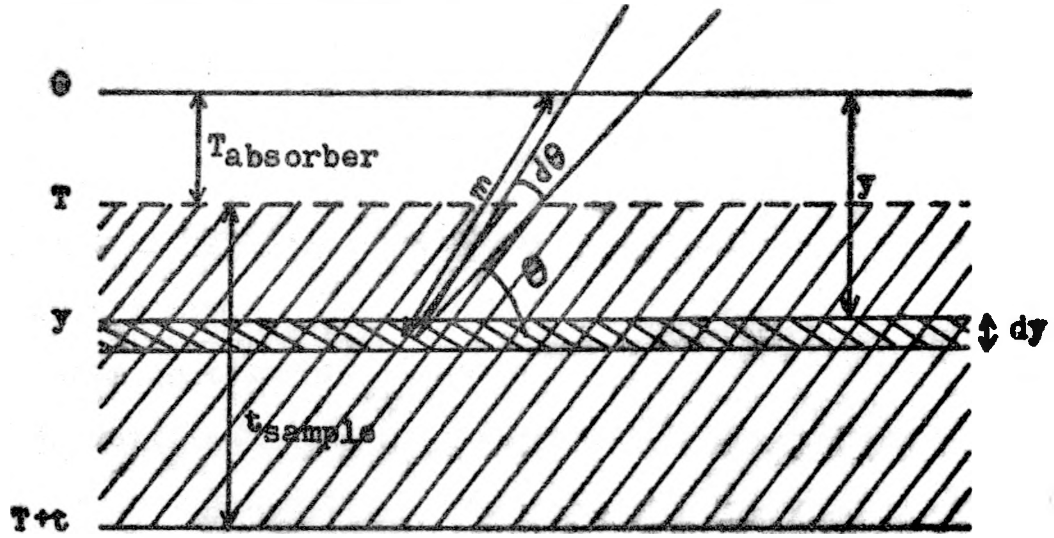
In all bias curve measurements the count was taken over a period of ten minutes for each gain. This was a sufficient length of time for high counting rates, but was probably not long enough for low counting rates. However, since it was the shape of the bias curve that was of primary importance, not the actual counting rate at any particular gain, the method served its purpose. The application of the bias curve technique to lanthanum and neodymium will be mentioned in Chapter III.

ii. Absorption measurements of beta radiation. - A comparison analysis was carried out to obtain the energy of the beta radiation from lanthanum. The standard sample used for comparison was $Tl^{204}$. In order to count both the lanthanum and thallium under the same sample conditions, the thallium was deposited on a copper backing that was spread with inactive neodymium and slurried into the neodymium. To obtain the data for this analysis, absorption measurements were taken on both samples using aluminum absorbers of varying thicknesses.

The aluminum absorbers were placed directly over the sample and introduced into the counter with the sample. The very thin absorbers were held in place against the sample by Scotch tape around the edges; the thick absorbers of the same area as the sample backing were bent into a cylindrical shape and allowed to rest on the sample. Since the background was found to increase from about 4 counts per minute for the thinnest absorber to about 80 counts per minute for the thickest, it was determined using the appropriate absorber immediately after the sample counting rate had been taken. For lanthanum the period of counting was two hours in duration for each absorber; for $Tl^{204}$ the period of counting was two hours in duration below 1000 counts per minute; above this counting rate a counting time was chosen to give a minimum of 20,000 counts as the total count. The data and results will be given in Chapter III.

iii. *Absorption measurements of x-radiation.* - In most experimental arrangements for the absorption measurements of x-radiation, a well-collimated beam of radiation is used. In this case there is no degradation of energy, but rather the complete removal of a photon. Thus the expression $I/I_0 = e^{-\mu x}$ gives a good representation of the absorption of a parallel beam of x-rays normal to the absorber. However, when the case of 50% geometry is considered, this simple picture no longer applies. The x-radiation cannot be represented as a well-collimated beam since most of the photons have to pass through greater distances of absorber than its thickness. Thus the reduction in intensity will be a function of the angle at which the radiation is emitted as well as the thicknesses of sample and absorber.

Consider a material of thickness t and assume that the material is covered by some external absorber of thickness T. Now consider an infinitesimal layer of active material of thickness dy at a depth y.



For simplicity the measure of thickness is chosen in units of mean free path, that is,

$$\left(\begin{array}{c}\text{sample thickness in units}\\ \text{of mean free path}\end{array}\right) = t = \mu_{\text{sample}}d_{\text{sample}}$$

$$\left(\begin{array}{c}\text{absorber thickness in units}\\ \text{of mean free path}\end{array}\right) = T = \mu_{\text{absorber}}d_{\text{absorber}}$$

where $\mu$ is the mass absorption coefficient and d is the thickness in mass per unit area. Let i be the intensity of radiation emitted per unit solid angle per unit sample thickness. The radiation emitted by a layer of thickness dy into the solid angle $d\Omega$ between $\theta$ and $\theta + d\theta$ is

$$I_0'' = i\,dy\,d\Omega = 2\pi i \cos\theta\,dy\,d\theta \qquad (1)$$

The total radiation emitted in an upwards direction from the layer is

$$I_0' = \int_0^{\frac{\pi}{2}} I_0'' = 2\pi i\,dy \int_0^{\frac{\pi}{2}} \cos\theta\,d\theta = 2\pi i\,dy \qquad (2)$$

The total radiation emitted in an upwards direction by the whole sample is

$$I_0 = \int_T^{T+t} I_0' = 2\pi i \int_T^{T+t} dy = 2\pi i t \qquad (3)$$

On the other hand, radiation emitted at an angle $\theta$ is attenuated by absorption by a factor $e^{-m}$, where $m = y\csc\theta$ is the distance traversed in the sample in units of mean free path. Thus the radiation emerging from the layer of thickness dy in the solid angle $d\Omega$ between $\theta$ and $\theta + d\theta$ is

$$I'' = i e^{-y\csc\theta}\,dy\,d\Omega = 2\pi i \cos\theta\, e^{-y\csc\theta}\,dy\,d\theta \qquad (4)$$

The total emergent radiation from the layer is then

$$I' = \int_0^{\frac{\pi}{2}} I'' = 2\pi i\,dy \int_0^{\frac{\pi}{2}} \cos\theta\, e^{-y\csc\theta}\,d\theta \qquad (5)$$

The total emergent radiation from the whole sample is

$$I = \int_T^{T+t} I' = 2\pi i \int_T^{T+t} \int_0^{\frac{\pi}{2}} \cos\theta\, e^{-y\csc\theta}\,d\theta\,dy \qquad (6)$$

The quantity of interest is the fraction f of the radiation emitted in an upward direction which emerges.

$$f = \frac{I}{I_0} = \frac{2\pi i}{2\pi i t} \int_T^{T+t} \int_0^{\frac{\pi}{2}} \cos\theta \, e^{-y\csc\theta} \, d\theta \, dy \qquad (7)$$

$$f = \frac{1}{t} \int_0^{\frac{\pi}{2}} \cos\theta \left[ \int_T^{T+t} e^{-y\csc\theta} \, dy \right] d\theta \qquad (8)$$

This is the general expression for the self-absorption and external absorption of x-rays. Equation (8) can be integrated in the following manner. First integrate the expression with respect to y.

$$f = \frac{1}{t} \int_0^{\frac{\pi}{2}} \cos\theta \left[ - \frac{e^{-y\csc\theta}}{\csc\theta} \right]_T^{T+t} d\theta \qquad (9)$$

$$f = \frac{1}{t} \int_0^{\frac{\pi}{2}} \cos\theta \left[ \frac{e^{-T\csc\theta}}{\csc\theta} - \frac{e^{-(T+t)\csc\theta}}{\csc\theta} \right] d\theta \qquad (10)$$

$$f = \frac{1}{t} \int_0^{\frac{\pi}{2}} e^{-T\csc\theta} \sin\theta\cos\theta \, d\theta - \frac{1}{t} \int_0^{\frac{\pi}{2}} e^{-(T+t)\csc\theta} \sin\theta\cos\theta \, d\theta \qquad (11)$$

Let

$$z = T\csc\theta = \frac{T}{\sin\theta}$$

$$dz = -\frac{T}{\sin^2\theta} \cos\theta \, d\theta$$

$$\sin\theta\cos\theta \, d\theta = -\frac{\sin^3\theta}{T} dz = -\frac{T^2}{z^3} dz \qquad (12)$$

$$w = (T+t)\csc\theta = \frac{(T+t)}{\sin\theta}$$

$$dw = -\frac{(T+t)}{\sin^2\theta}\cos\theta\, d\theta$$

$$\sin\theta\cos\theta\, d\theta = -\frac{\sin^3\theta}{(T+t)}\,dw = -\frac{(T+t)^2}{w^3}\,dw$$

Substitute equation (12) into equation (11). The new limits will be determined by substituting the limits of $\theta$ into equation (12).

$$f = \frac{1}{t}\int_{\infty}^{T} e^{-z}\left[-\frac{T^2}{z^3}\,dz\right] - \frac{1}{t}\int_{\infty}^{T+t} e^{-w}\left[-\frac{(T+t)^2}{w^3}\,dw\right] \qquad (13)$$

$$f = \frac{T^2}{t}\int_{T}^{\infty}\frac{e^{-z}}{z^3}\,dz - \frac{(T+t)^2}{t}\int_{T+t}^{\infty}\frac{e^{-w}}{w^3}\,dw \qquad (14)$$

Integrate by parts.

$$f = \frac{T^2}{t}\left\{\left[-\frac{e^{-z}}{2z^2}\right]_T^{\infty} - \frac{1}{2}\int_T^{\infty}\frac{e^{-z}}{z^2}\,dz\right\} - \frac{(T+t)^2}{t}\left\{\left[-\frac{e^{-w}}{2w^2}\right]_{T+t}^{\infty} - \frac{1}{2}\int_{T+t}^{\infty}\frac{e^{-w}}{w^2}\,dw\right\} \qquad (15)$$

Integrate again by parts.

$$f = \frac{T^2}{t}\left\{\left[-\frac{e^{-z}}{2z^2}\right]_T^{\infty} - \frac{1}{2}\left(\left[-\frac{e^{-z}}{z}\right]_T^{\infty} - \int_T^{\infty}\frac{e^{-z}}{z}\,dz\right)\right\} - \frac{(T+t)^2}{t}\left\{\left[-\frac{e^{-w}}{2w^2}\right]_{T+t}^{\infty} - \frac{1}{2}\left(\left[-\frac{e^{-w}}{w}\right]_{T+t}^{\infty} - \int_{T+t}^{\infty}\frac{e^{-w}}{w}\,dw\right)\right\} \qquad (16)$$

$$f = \frac{T^2}{t}\left\{\frac{e^{-T}}{2T^2} - \frac{e^{-T}}{2T} + \frac{1}{2}\int_T^{\infty}\frac{e^{-z}}{z}\,dz\right\} - \frac{(T+t)^2}{t}\left\{\frac{e^{-(T+t)}}{2(T+t)^2} - \frac{e^{-(T+t)}}{2(T+t)} + \frac{1}{2}\int_{T+t}^{\infty}\frac{e^{-w}}{w}\,dw\right\} \qquad (17)$$

$$f = \frac{1}{2t}\left\{e^{-T}(1-T) + T^2\left[-E_i(-T)\right] - e^{-(T+t)}(1-T-t) - (T+t)^2\left[-E_i(-T-t)\right]\right\} \tag{18}$$

where

$$\left[-E_i(-T)\right] = \int_T^{\infty} \frac{e^{-z}}{z}\,dz$$

and

$$\left[-E_i(-T-t)\right] = \int_{T+t}^{\infty} \frac{e^{-w}}{w}\,dw$$

This function is tabulated in <u>Tables of Sine, Cosine and Exponential Integrals</u>, Volume II, Federal Works Agency, Works Projects Administration for the City of New York as a Report of Official Project No. 765-97-3-10, New York, 1940. Equation (18) is the final integrated form of the general case.

Two special cases must be considered individually.

Case I: T = 0. For this case equation (8) becomes

$$f = \frac{1}{t}\int_0^{\frac{\pi}{2}} \cos\theta \left[\int_0^t e^{-y\csc\theta}\,dy\right] d\theta \tag{19}$$

This can be integrated as follows. As before, first integrate with respect to y.

$$f = \frac{1}{t}\int_0^{\frac{\pi}{2}} \cos\theta \left[-\frac{e^{-y\csc\theta}}{\csc\theta}\right]_0^t d\theta \tag{20}$$

$$f = \frac{1}{t}\int_{0}^{\frac{\pi}{2}} \cos\theta \left[\frac{1}{\csc\theta} - \frac{e^{-t\csc\theta}}{\csc\theta}\right] d\theta \tag{21}$$

$$f = \frac{1}{t}\int_{0}^{\frac{\pi}{2}} \cos\theta \sin\theta \, d\theta - \frac{1}{t}\int_{0}^{\frac{\pi}{2}} e^{-t\csc\theta} \cos\theta \sin\theta \, d\theta \tag{22}$$

The first integral can be integrated directly; the second integral is treated in the same manner as those in the general case. Let

$$r = t\csc\theta = \frac{t}{\sin\theta}$$

$$dr = -\frac{t}{\sin^{2}\theta}\cos\theta \, d\theta \tag{23}$$

$$\cos\theta\sin\theta\, d\theta = -\frac{\sin^{3}\theta}{t}\, dr = -\frac{t^{2}}{r^{3}}\, dr$$

After substitution and integration twice by parts, equation (22) becomes

$$f = \frac{1}{t}\left[\frac{1}{2}\sin^{2}\theta\right]_{0}^{\frac{\pi}{2}} - \frac{t^{2}}{t}\left\{\left[-\frac{e^{-r}}{2r^{2}}\right]_{t}^{\infty} - \frac{1}{2}\left(\left[-\frac{e^{-r}}{r}\right]_{t}^{\infty} - \int_{t}^{\infty}\frac{e^{-r}}{r}\, dr\right)\right\} \tag{24}$$

$$f = \frac{1}{2t} - \frac{t^{2}}{2t}\left\{\frac{e^{-t}}{t^{2}} - \frac{e^{-t}}{t} + \int_{t}^{\infty}\frac{e^{-r}}{r}\, dr\right\} \tag{25}$$

$$f = \frac{1}{2t}\left\{1 - e^{-t}(1-t) - t^{2}\left[-E_{i}(-t)\right]\right\} \tag{26}$$

Thus the case for T = 0 results in equation (26).

Case II: t = 0. This case assumes an infinitely thin sample. The radiation emitted by an infinitely thin layer into the solid angle $d\Omega$ between $\theta$ and $\theta + d\theta$ is

$$I_0' = i\, d\Omega = 2\pi i \cos\theta \, d\theta \tag{27}$$

The total radiation emitted in an upwards direction by the layer is

$$I_0 = \int_0^{\frac{\pi}{2}} I_0' = 2\pi i \int_0^{\frac{\pi}{2}} \cos\theta \, d\theta = 2\pi i \tag{28}$$

On the other hand, radiation emitted at an angle $\theta$ will be attenuated by absorption by a factor $e^{-p}$, where $p = T\csc\theta$ is the distance traversed in units of mean free path. In this case the distance traversed will depend on the absorber thickness only since the sample thickness is considered infinitely thin. Thus the radiation emerging from the layer of infinite thinness in the solid angle $d\Omega$ between $\theta$ and $\theta + d\theta$ is

$$I' = i e^{-T\csc\theta} d\Omega = 2\pi i \cos\theta \, e^{-T\csc\theta} d\theta \tag{29}$$

The total emergent radiation is

$$I = \int_0^{\frac{\pi}{2}} I' = 2\pi i \int_0^{\frac{\pi}{2}} \cos\theta \, e^{-T\csc\theta} d\theta \tag{30}$$

Thus the fraction of radiation emitted in an upward direction which emerges is

$$f = \frac{I}{I_0} = \frac{2\pi i}{2\pi i} \int_0^{\frac{\pi}{2}} \cos\theta \, e^{-T\csc\theta} d\theta \tag{31}$$

$$f = \int_0^{\frac{\pi}{2}} \cos\theta \, e^{-T\csc\theta} d\theta \tag{32}$$

This is integrated in the same manner as the previous cases. Let

$$z = T\csc\theta = \frac{T}{\sin\theta}$$

$$dz = -\frac{T}{\sin^2\theta}\cos\theta\, d\theta \qquad (33)$$

$$\cos\theta\, d\theta = -\frac{\sin^2\theta}{T}\, dz = -\frac{T}{z^2}\, dz$$

Substitute equation (33) inte equation (32) and change the limits.

$$f = T\int_T^\infty \frac{e^{-z}}{z^2}\, dz \qquad (34)$$

Integrate by parts.

$$f = T\left\{\left[-\frac{e^{-z}}{z}\right]_T^\infty - \int_T^\infty \frac{e^{-z}}{z}dz\right\} \qquad (35)$$

$$f = T\left(\frac{e^{-T}}{T}\right) - T\int_T^\infty \frac{e^{-z}}{z}dz \qquad (36)$$

$$f = e^{-T} - T\left[-E_i(-T)\right] \qquad (37)$$

This gives the final result for t = 0.

The three cases are summarized as follows:

(1) General case.

$$f(t,T) = \frac{1}{2t}\left\{e^{-T}(1-T) + T^2\left[-E_i(-T)\right] - e^{-(T+t)}(1-T-t) - (T+t)^2\left[-E_i(-T-t)\right]\right\}$$

(2) T = 0.

$$f(t,0) = \frac{1}{2t}\left\{1 - e^{-t}(1-t) - t^2\left[-E_i(-t)\right]\right\}$$

(3) $t = 0.$

$$f(0,T) = e^{-T} - T\left[-E_i(-T)\right]$$

Calculated values of $f(t,T)$ for several values of $t$ and $T$ are given in Table 1 and plotted in Figures 9 and 10. A comparison with the "normal" absorption and self-absorption curves, which apply when all of the radiation is essentially normal to the sample and absorbers, shows that the absorption is considerably greater for 50% geometry, especially at the beginning. This is due to the fact mentioned in the introduction to this section that most of the photons have to pass through greater distances of absorber than its thickness.

## TABLE 1

Absorption and Self-absorption of Photons in $2\pi$ Geometry

| T<br>t | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | 1.0000 | 0.1485 | 0.0375 | 0.0106 | 0.0032 | 0.0010 |
| 1 | 0.3903 | 0.0796 | 0.0212 | 0.0062 | 0.0019 | 0.0006 |
| 2 | 0.2349 | 0.0504 | 0.0137 | 0.0040 | 0.0012 | 0.0004 |
| 3 | 0.1637 | 0.0356 | 0.0098 | 0.0029 | 0.0009 | 0.0003 |
| 4 | 0.1243 | 0.0272 | 0.0075 | 0.0022 | 0.0007 | 0.0002 |
| 5 | 0.0998 | 0.0219 | 0.0060 | 0.0018 | 0.0006 | 0.0002 |

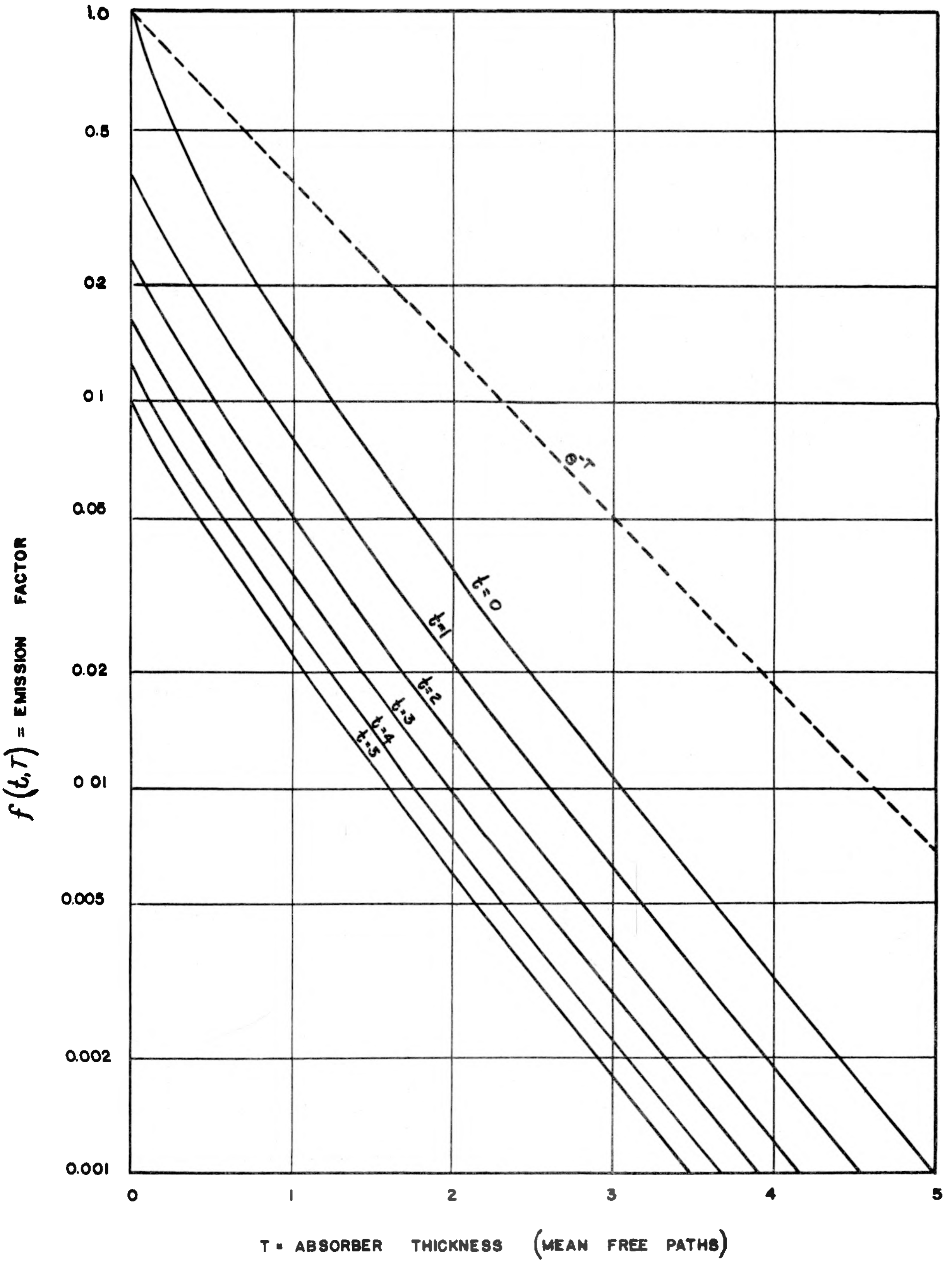


Fig. 9—Absorption of Photons in $2\pi$ Geometry.

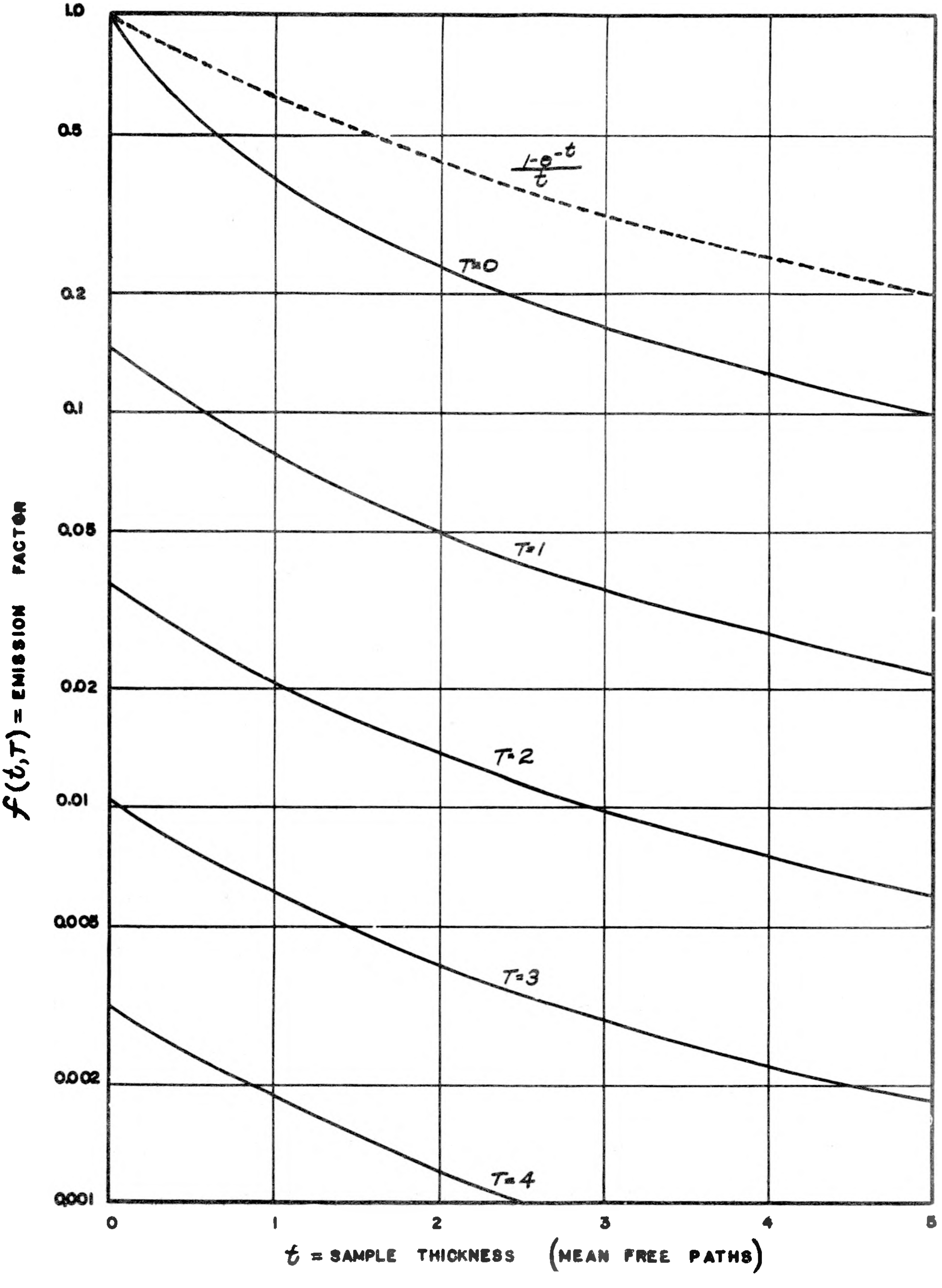


Fig. 10—Self-absorption of Photons in $2\pi$ Geometry.

# CHAPTER III. RESULTS

## 1. Lanthanum

Bias curves on successively eluted portions of lanthanum from the first column run were dissimilar, indicating that the lanthanum was contaminated. The three portions were mixed together, scavenged well, and a bias curve was run on the one sample of 13 grams, shown with the background subtracted in Figure 11. A counting rate of 82 counts per minute was obtained at a gain corresponding to 0.3 kev. A complete repurification of the lanthanum was carried out using ion exchange and scavenging processes. At a gain corresponding to 0.3 kev this sample of 11.0 grams gave a counting rate of 54.0 ± 0.7 counts per minute. The error in this and succeeding counting rates is the probable error. Another complete repurification was undertaken, and the counting rate for a 10.0 gram sample was found to be 54.0 ± 0.6 counts per minute. Thus the lanthanum activity has been reduced to a constant specific activity. The last 0.67 grams eluted was counted separately and gave 3.2 ± 0.5 counts per minute, essentially the same specific activity as the main sample, which verified the absence of actinium after the second purification.

Absorption experiments were run on this sample using aluminum absorbers of varying thicknesses. The data are reproduced in Table 2, and the curve is shown in Figure 12, Curve I. At an absorber thickness of about 200 mg/cm$^2$ the curve started to flatten out, indicating the presence

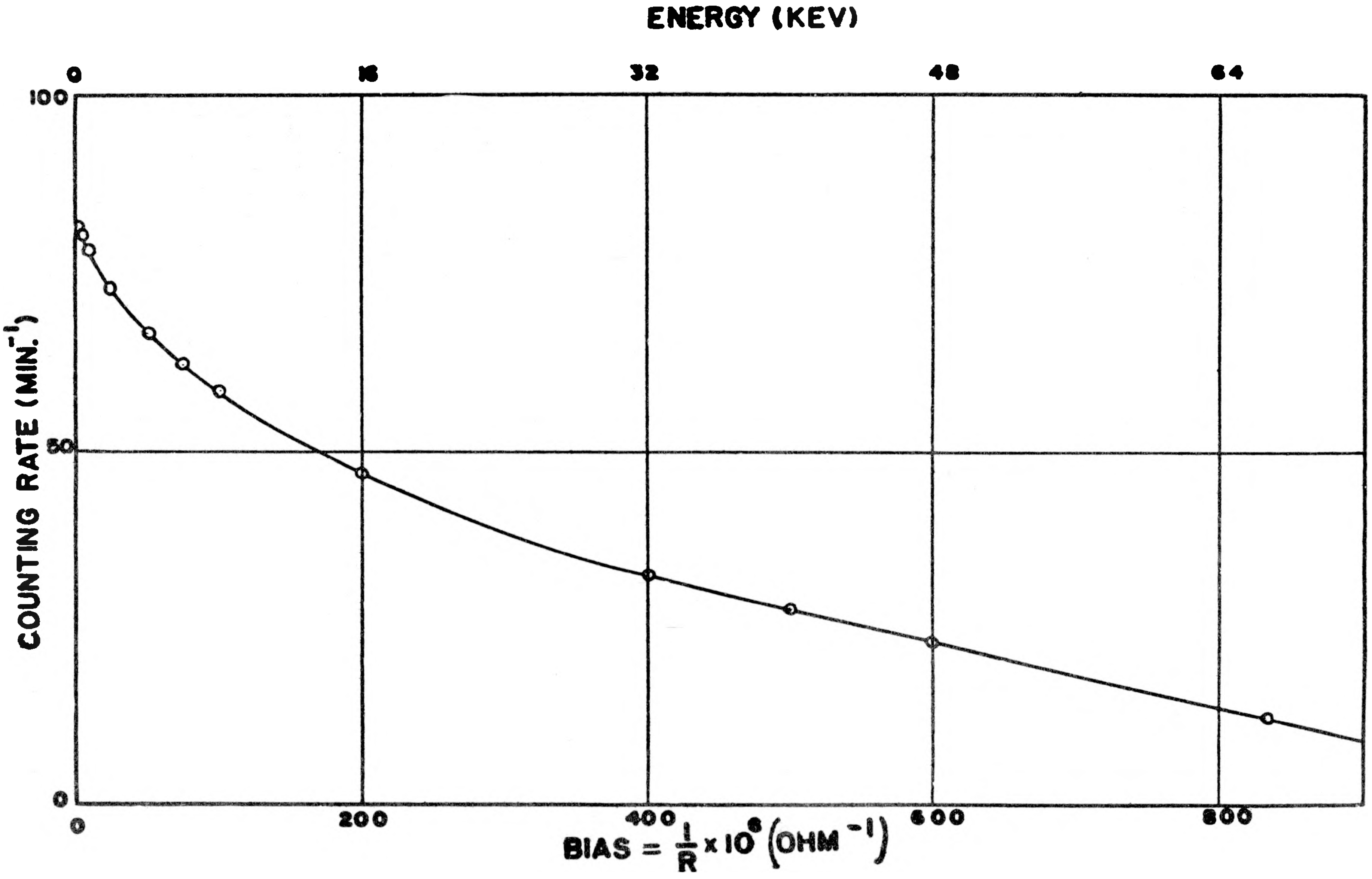


Fig. 11—Bias Curve for One-purified Lanthanum.

## TABLE 2

### Absorption of Lanthanum Activity

| Absorber thickness (mg/cm$^2$) | Counts per minute |
|---|---|
| 0 | 54.0 ± 0.6 |
| 2.06 | 45.1 ± 0.7 |
| 4.80 | 34.0 ± 0.7 |
| 17.1 | 20.1 ± 0.6 |
| 34.3 | 15.1 ± 0.7 |
| 81.0 | 10.3 ± 0.8 |
| 174 | 6.6 ± 0.9 |
| 301 | 4.9 ± 0.9 |
| 440 | 4.0 ± 0.9 |

of a hard component. The intensity of the gamma radiation is known (23). This cannot account for most of the hard component, so the hard component must be something else. It appears logical to conclude that it is due to barium K x-rays which are expected to be present. It might be of interest to see if the slope of the hard component will give an energy corresponding to that of barium x-rays. This cannot be obtained to any great degree of accuracy since the errors in the last three points are quite large. The average value of the wave length for the K series line of barium is taken as 0.38 Å. This is obtained from the values for $K_{\alpha_1}$, $K_{\alpha_2}$, $K_{\beta_1}$, and $K_{\beta_2}$ (134) utilizing the intensity ratios of Williams (135). This wave length corresponds to an energy of 33 kev. An extrapolation of the flat line back to zero absorber thickness results in a half-thickness of 500 mg/cm$^2$. From a plot of half-thickness versus energy for low-energy photons by Glendenin (136), the energy corresponding to this half-thickness was found to be 28 kev. Since the slope will be greater and the apparent energy smaller at 50% geometry, it appears that the hard component is compatible with barium x-rays. By the use of equations (18) and (26) the shape of the absorption curve for the x-radiation of known energy can be calculated. In order to carry out this calculation it is necessary to know the absorption coefficients and thicknesses of lanthanum oxide and aluminum. Using 0.38 Å as the wave length for the K radiation of barium, the mass absorption coefficient for aluminum corresponding to this wave length is 1.00 cm$^2$/gm (137). Thus

$$T = 1.00\, x_{Al} \tag{38}$$

where $x_{Al}$ is the thickness of aluminum absorber in gm/cm$^2$. The absorption coefficient of the lanthanum oxide can be represented by the sum of the contributions of lanthanum and oxygen.

$$\mu_{La_2O_3} = \frac{\mu_{La} n_{La} A_{La} + \mu_O n_O A_O}{n_{La} A_{La} + n_O A_O} = \frac{\mu_{La} A_{La} + \frac{n_O}{n_{La}} \mu_O A_O}{A_{La} + \frac{n_O}{n_{La}} A_O} \tag{39}$$

where $\mu$ is the mass absorption coefficient in cm$^2$/gm, n is the number of atoms, and A is the atomic weight. At $\lambda$ = 0.38 Å, $\mu_{La}$(estimated) = 8.0 cm$^2$/gm (138) and $\mu_O$ = 0.33 cm$^2$/gm (137). Therefore from equation (39)

$$\mu_{La_2O_3} = \frac{(8.0)(139) + \frac{3}{2}(0.33)(16)}{139 + \frac{3}{2}(16)} \tag{40}$$

$$\mu_{La_2O_3} = 6.9\ cm^2/gm \qquad (41)$$

Since the sample weight is 10.0 grams, and the sample area is 1650 $cm^2$, the sample thickness is

$$x_{La_2O_3} = \frac{10.0\ grams}{1650\ cm^2} = 0.0061\ gm/cm^2 \qquad (42)$$

Thus

$$t = \mu_{La_2O_3}\, x_{La_2O_3} = (6.9)(0.0061) = 0.042 \qquad (43)$$

The fraction of x-radiation transmitted was calculated as a function of absorber thickness, the sample thickness being constant, by the method of Chapter II.3.c.iii. Table III indicates the results of this calculation, and a plot of this data is shown in Figure 12, Curve II.

### TABLE 3

Fraction of X-radiation Transmitted

| $x_{Al}$ ($gm/cm^2$) | t = 0.042 | |
|---|---|---|
| | T | $f_{T,t}$ |
| 0 | 0 | 0.914 |
| 0.005 | 0.005 | 0.897 |
| 0.010 | 0.010 | 0.881 |
| 0.030 | 0.030 | 0.827 |
| 0.060 | 0.060 | 0.760 |
| 0.120 | 0.120 | 0.655 |
| 0.180 | 0.180 | 0.573 |
| 0.240 | 0.240 | 0.507 |
| 0.330 | 0.330 | 0.426 |
| 0.440 | 0.440 | 0.350 |

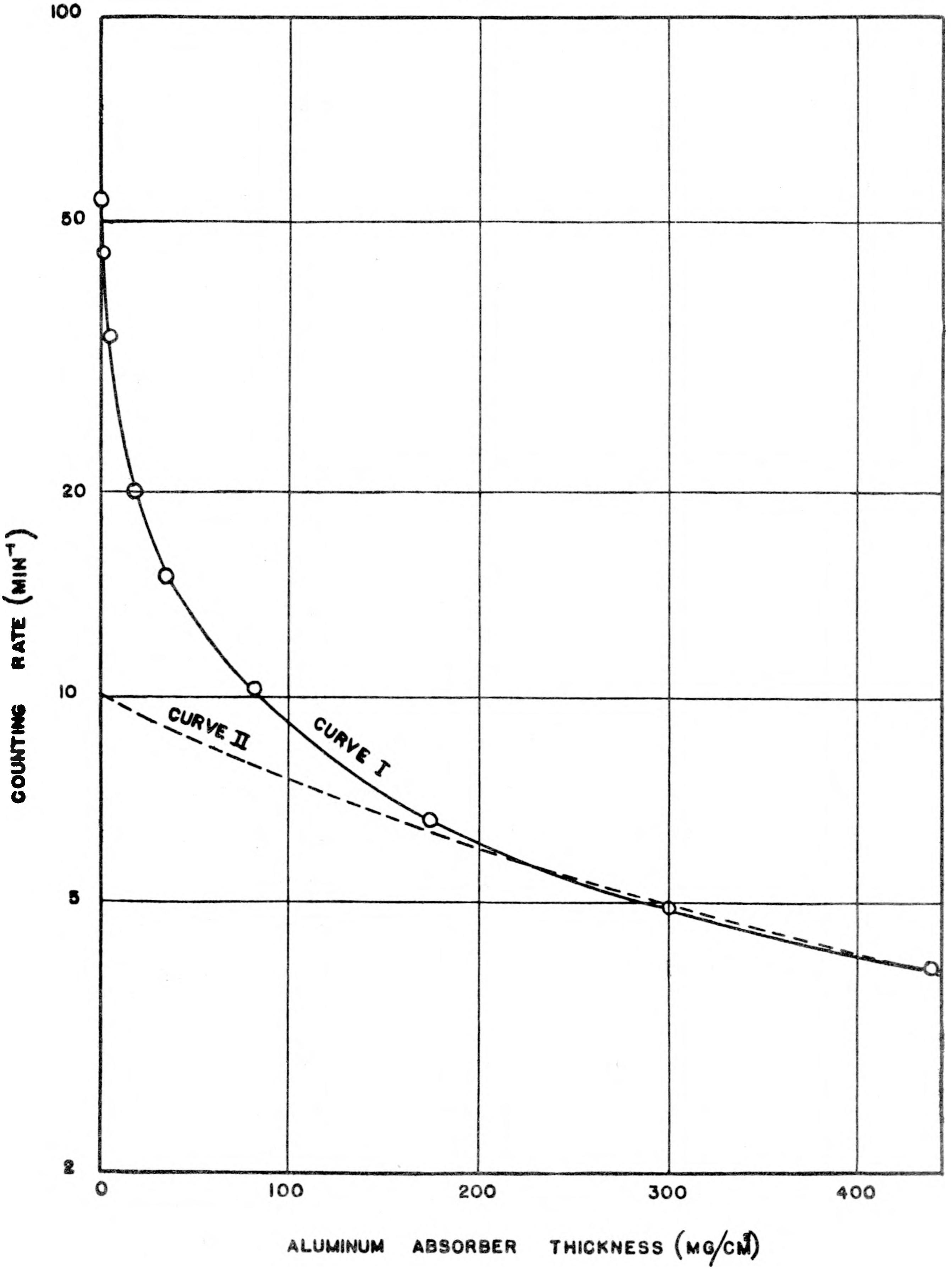


Fig. 12—Absorption Curve for Lanthanum.

When this x-radiation was subtracted from the complete curve for the lanthanum radiation, the resultant curve gave the absorption curve for the beta radiation of lanthanum. This curve is illustrated in Figure 14, Curve I.

Since the visual method of obtaining a range is uncertain, especially for such weak activities, a Feather plot was attempted, using the $Tl^{204}$ for comparison. This method assumes that for two beta emitters the same fractional reduction in the activity by absorbers corresponds to the same fraction of the range. Thus the absorber thickness for this fraction of the range can be determined by the comparison of a beta emitter of unknown range with a beta emitter of known range. The beta emitter chosen as the standard was $Tl^{204}$ which has a maximum beta energy of 0.78 Mev (139). The $Tl^{204}$ was slurried into neodymium oxide as mentioned previously, and absorption measurements were taken. Table 4 gives the data for this run, and Figure 13 represents a plot of this data. It was noted that the curve tailed off at the high absorber thicknesses indicating the possible presence of a photon component. This was extrapolated as a straight line back to zero absorber thickness, and the straight line was subtracted from the thallium curve. The resultant curve is that due to the beta radiation from $Tl^{204}$ and is illustrated in Figure 14, Curve II. Unfortunately, the Feather plot was unsuccessful because the initial intensity (zero absorber) of the component being analyzed was not known, as it must

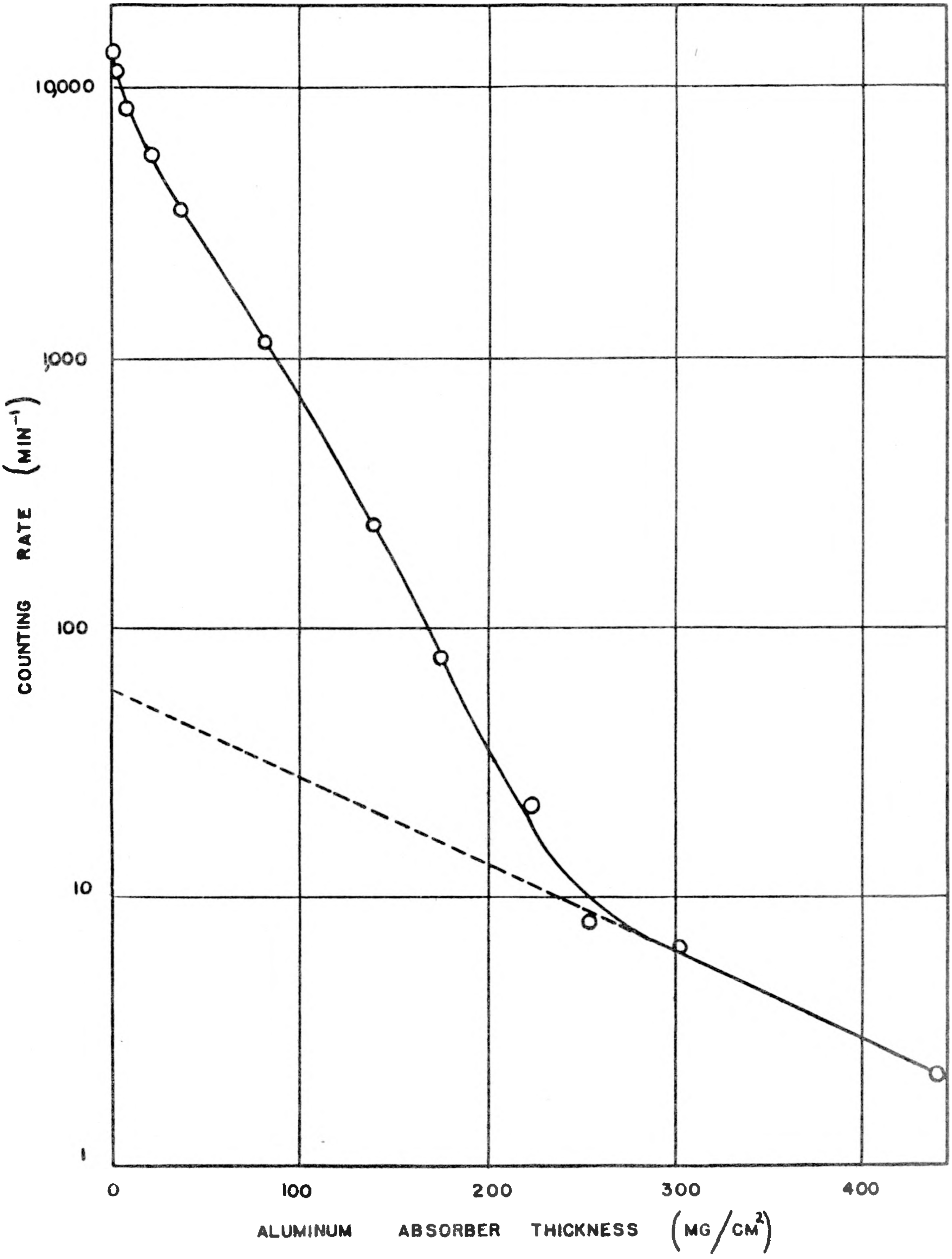


Fig. 13—Absorption Curve for $Tl^{204}$

TABLE 4

Absorption of $Tl^{204}$ Activity

| Absorber thickness (mg/cm$^2$) | Counts per minute |
|---|---|
| 0 | 13,551 |
| 2.06 | 11,474 |
| 6.86 | 8,412 |
| 19.2 | 5,702 |
| 36.4 | 3,566 |
| 81.0 | 1,155 |
| 139 | 241 |
| 174 | 77.1 ± 2.0 |
| 222 | 21.9 ± 1.8 |
| 253 | 8.1 ± 1.3 |
| 301 | 6.5 ± 1.3 |
| 440 | 2.2 ± 0.9 |

be for a Feather analysis, and because the data near the end-point were inadequate. It was found, however, that a better comparison could be made by fitting the $Tl^{204}$ curve to the $La^{138}$ curve. If the absorber thickness is multiplied by 1.3 and the counting rate by 0.0014, a reasonably good fit can be obtained, especially in the middle range. This transposed $Tl^{204}$ curve is shown in Figure 14, Curve III. Since the range of $Tl^{204}$ beta radiation is 300 mg/cm$^2$, the end-point for $La^{138}$ should be 1.3 × 300 mg/cm$^2$, or 390 mg/cm$^2$. Using the Coryell

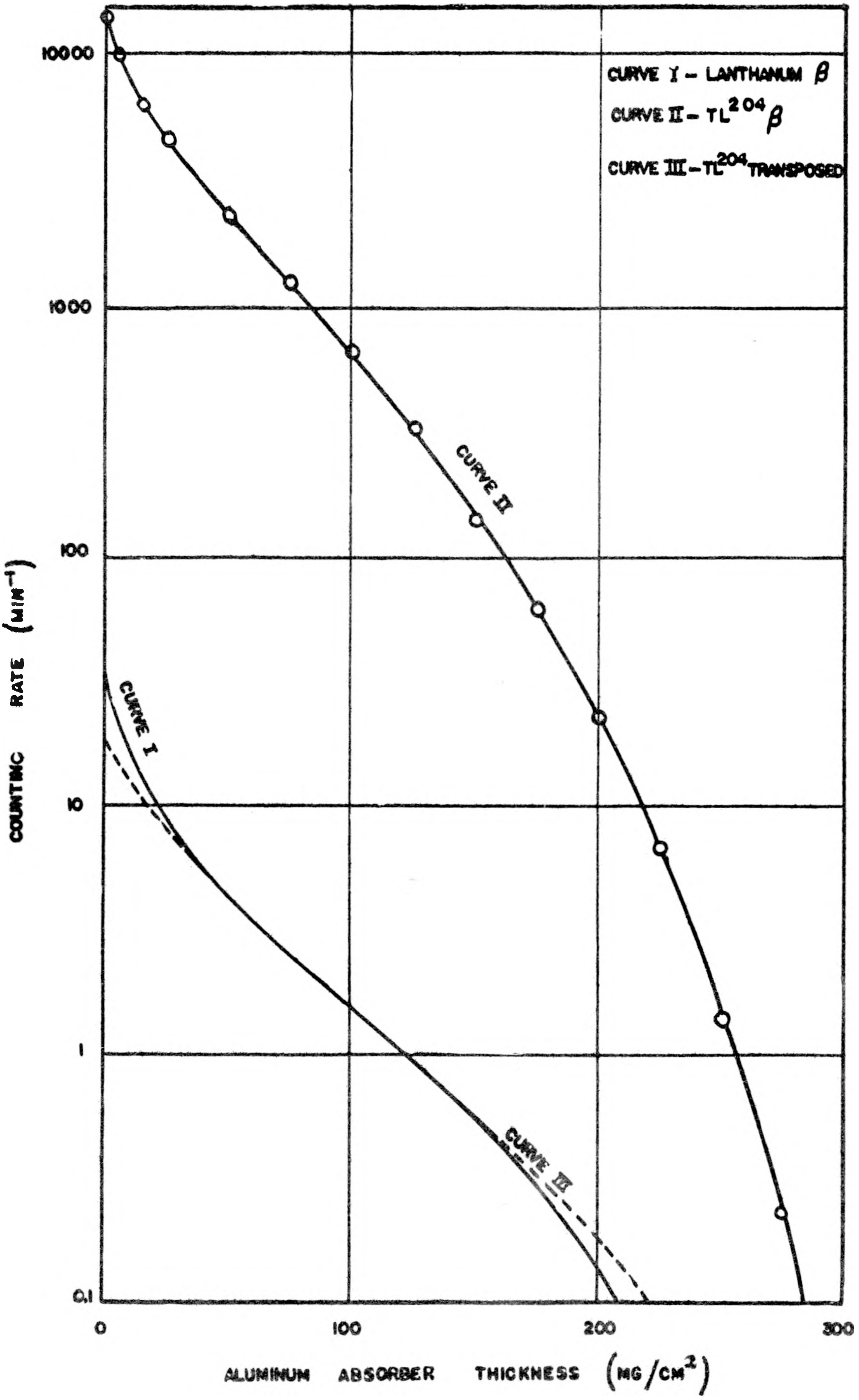


Fig. 14—Absorption Curves for Beta Radiation of Lanthanum and $Tl^{204}$.

and Glendenin range-energy relationship that

$$R = 0.542E - 0.133,$$

where R is the range in aluminum in gm/cm$^2$ and E is the maximum beta energy in Mev, the maximum energy for the beta particles from La$^{138}$ is 1.0 ± 0.2 Mev.

For a calculation of the specific activity certain assumptions and approximations will have to be made in order to obtain the counting yield. Let us assume that backscattering due to the sample itself may be neglected, that is, the amount backscattered by the sample in a forward direction is equal to the amount backscattered by the sample in a backward direction. For copper a saturation backscattering factor for thin samples has been determined for 50% geometry (140). This factor is 1.44 which means that 44% of the downward radiation is backscattered by the copper backing. A consideration of self-absorption of both the original radiation and the backscattered radiation gives a self-absorption factor of approximately 0.82. If it is assumed that the geometry is less than 50% only by the amount of sample that is obscured by the three longitudinal rods supporting the center wire, which is estimated to be 10%, the overall counting yield is

$$Y = (1.44)(0.82)(0.45) = 0.53$$

The specific activity can be calculated from

$$C = YWS \qquad (44)$$

where C is the counting rate, Y is the counting yield, W is the weight of element, and S is the specific activity. From the transposed $Tl^{204}$ curve of Figure 14, which is assumed to be the best curve for the main beta component of $La^{138}$, the counting rate at zero absorber was 19 counts per minute. Knowing the counting rate, the counting yield, and the fact that 10.0 grams of lanthanum oxide was the weight of the sample, substitution of these values in equation (44) gives

$$S = \frac{\left(19\ \frac{\text{counts}}{\text{minute}}\right) \times \left(\frac{1\ \text{minute}}{60\ \text{seconds}}\right)}{\left(0.53\ \frac{\text{counts}}{\text{disintegration}}\right) \times \left(10.0\ \text{grams}\ La_2O_3\right) \times \left(\frac{138.9\ \text{grams}\ La}{162.9\ \text{grams}\ La_2O_3}\right)} \tag{45}$$

$$S = 0.07\ \text{disintegration/second/gram}\ La \tag{46}$$

The minimum half-life for beta emission can be calculated from the following relationships:

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \tag{47}$$

$$\lambda = -\frac{1}{N}\frac{dN}{dt} = +\frac{1}{N} S W \tag{48}$$

$$N = f \frac{W}{A} N_0 \tag{49}$$

where $\lambda$ is the decay constant, N is the number of unchanged atoms at time t, S is the specific activity, W is the weight of sample, f is the fractional isotopic abundance, A is the atomic weight, and $N_0$ is Avogadro's Number which is $6.02 \times 10^{23}$ atoms/mole. Substituting equations (48) and

(49) into equation (47) gives

$$t_{\frac{1}{2}} = \frac{(\ln 2)(f)(N_o)}{(S)(A)} \qquad (50)$$

For $La^{138}$, which is 0.089% abundant (20), the partial half-life from equation (50) is

$$t_{\frac{1}{2}} = \frac{(0.693)\left(0.00089\,\frac{\text{atom } La^{138}}{\text{atom } La}\right)\left(6.02\times10^{23}\,\frac{\text{atoms } La}{\text{mole } La}\right)}{\left(0.07\,\frac{\text{disintegrations } La^{138}}{\text{grams } La \text{ second}}\right)\left(138.9\,\frac{\text{grams } La}{\text{mole } La}\right)\left(3.15\times10^{7}\,\frac{\text{seconds}}{\text{year}}\right)} \qquad (51)$$

$$t_{\frac{1}{2}} = 1.2\times10^{12} \text{ years} \qquad (52)$$

Before attaching too much significance to this result, it is necessary to eliminate the possibility that these beta rays are not conversion electrons or positrons. First let us consider the case of positrons. According to the Feenberg-Trigg curves (142), the ratio of positron decay to K-capture for an energy of 1 Mev ($W_o=3m_oc^2$) and $Z=56$ is about 0.08. If the positron activity were 0.07 disintegrations per second per gram of lanthanum, the K-capture activity to the same state would be about 0.9 disintegrations per second per gram of lanthanum, somewhat larger than that observed by Pringle, Standil, Taylor and Fryer (23), but close to our value discussed in the following paragraph. However, they report a gamma of 535 kev energy, while Bell and Cassidy (141) give the energy as 0.545 Mev which is significantly higher than 0.511 Mev annihilation radiation. It would moreover be difficult to reconcile the observed intensity of this component, 0.09 photons per second per gram, with annihilation radiation of the requisite intensity, 0.14 photons per second per gram. Let us look at this problem from another viewpoint. Because of the repulsion of positrons by the nucleus, fewer low energy positrons would be found than would be the case for electrons of the same maximum energy. This would tend to reduce the range and consequently the energy as determined by a comparison method. Thus the positron to K-capture ratio would be less than the 0.08 given above. Moreover, Pringle, Standil, Taylor and Fryer mention the possibility (which certainly appears justified) of transitions to two or more levels of $Ba^{138}$. This would further raise the total electron capture (including L captures) to positron ratio, and it appears improbable that the intensity observed could be accounted for completely by positrons. Thus if it is concluded that some of the 1 Mev beta particles are electrons, then there is no reason to suppose that there are any positrons of this energy. For ground state transitions for both negatron decay and positron decay the ratio of positron to negatron for a 1 Mev particle would be about 0.04 (142), which is quite small. Positrons of a lower energy than 1 Mev can be excluded because they would have a small intensity relative to electron capture. Now let us consider the possibility of conversion electrons. Pringle, Standil, Taylor and Fryer reported gamma radiation of about 0.3 gamma per second per gram of lanthanum of less than 1 Mev in energy. However, Rose, Goertzel, Spinrad, Harr and Strong (143) in a paper on conversion coefficients indicated that for an energy of 1 Mev for Z = 54 the electric dipole conversion coefficient is about $2\times10^{-4}$ and the quadrupole coefficient $3\times10^{-4}$. These will be larger for energies in the region of 0.5 Mev , but the increase for an energy of this order will only be about a factor of 100. The coefficient will also be higher for higher multipole orders, and for very high multipole orders the conversion coefficient would be large enough. However, this would also involve long lifetimes, and isomerism is never observed in even-even nuclei, so this would seem to rule out high multipole order transitions in $Ba^{138}$. Since the conversion coefficient is defined as the ratio of the number of electrons emitted to the number of photons emitted, it would appear that the specific activity of 0.07 particles per second per gram of lanthanum is too high for conversion electrons.

For the calculation of the specific activity of the x-radiation, the fraction of x-rays stopped by the argon must be obtained. Let us assume that the mean range of the x-rays in the counter is the counter inside diameter, which is 10.8 cm. Using a density of 1.47 mg/cm$^2$ for argon at a pressure of 0.90 atmosphere and a temperature of 298°K, the thickness of argon becomes 0.016 gm/cm$^2$. The mass absorption coefficient of argon is 2.20 cm$^2$/gm. For small absorptions $1 - e^{-\mu x} = \mu x$, so substituting our values into $\Delta I/I_0 = \mu x$, it is found that only 3.5% of the x-rays are stopped. Assuming a self-absorption factor of 0.91 previously calculated, the counting yield for the 45% geometry is

$$Y = (0.035)(0.91)(0.45) = 0.014$$

A consideration of the effect of ethylene and the walls will slightly increase Y to 0.015. From a consideration of the data of Pringle, Standil, Taylor and Fryer (23) for specific gamma activity and assuming that the efficiency of the brass counter is 1.0% for these gamma rays of average energy 1 Mev, it can be calculated that the proportional counter would count about 2.4 gammas per minute. The counting rate at zero absorber was 10.1 counts per minute, so the counting rate for x-rays is 10.1 - 2.4, or 7.7 counts per minute. Substituting this into equation (44) gives

$$S_K = \frac{\left(7.7\ \frac{\text{counts}}{\text{minute}}\right) \times \left(\frac{1\ \text{minute}}{60\ \text{seconds}}\right)}{\left(0.015\ \frac{\text{counts}}{\text{disintegration}}\right) \times \left(10.0\ \text{grams}\ La_2O_3\right) \times \left(\frac{138.9\ \text{grams}\ La}{162.9\ \text{grams}\ La_2O_3}\right)} \qquad (53)$$

$$S_K = 1.0\ K\ \text{x-rays/second/gram}\ La. \qquad (54)$$

If the value for $S_k$ is divided by the fluorescence yield, the specific K-shell electron-capture activity will be obtained. Steffen, Huber and Humbel (144) have given an empirical formula for the calculation of fluorescence yield of the form

$$W_K = \frac{Z^{3.5}}{Z^{3.5} + 220{,}000} \qquad (55)$$

For barium this gives $W_k = 86\%$ so that

$$S_{E.C.} = \frac{S_K}{W_K} = \frac{1.0}{0.86} = 1.2 \qquad (56)$$

The true electron-capture activity would be even higher because of L capture. Pringle, Standil, Taylor and Fryer obtained about 0.45 disintegrations per second per gram of lanthanum as the specific activity for gamma emitting transitions. The fact that our value of 1.2 is considerably larger might indicate considerable electron capture to the ground state of $Ba^{138}$.

For $La^{138}$ the partial half-life for electron capture is obtained from equation (50) using $S_{E.C.}$ above.

$$t_{\frac{1}{2}} = \frac{(0.693)\left(0.00089\,\frac{\text{atom La}^{138}}{\text{atom La}}\right)\left(6.02\times10^{23}\,\frac{\text{atoms La}}{\text{mole La}}\right)}{\left(1.2\,\frac{\text{disintegrations La}^{138}}{\text{gram La second}}\right)\left(138.9\,\frac{\text{grams La}}{\text{mole La}}\right)\left(3.15\times10^{7}\,\frac{\text{seconds}}{\text{year}}\right)} \qquad (57)$$

$$t_{\frac{1}{2}} = 7\times10^{10}\text{ years} \qquad (58)$$

The net half-life is essentially that of electron capture.

At zero absorber it has been found that the lanthanum oxide gave a counting rate of 54 counts per minute. This was composed of 2.4 counts per minute from gamma radiation, 7.7 counts per minute from x-radiation, and 19 counts per minute from beta radiation, leaving 25 counts per minute unaccounted for. The excess radiations are probably compounded of L x-rays, K Auger electrons, and background enhancement (discussed in the following section on neodymium), although a weak soft beta component may also be present.

Some speculation can be made as to the nuclear properties of $La^{138}$. From graphs given by Feenberg and Trigg (142) an energy of 1.0 Mev for the beta decay, corresponding to a total energy, including the rest mass, of 3.13 in units of $m_0c^2$, gives a $\log_{10}$f value of 1.73 for Z=58. Using the experimental half-life for the beta decay of $1.2\times10^{12}$ years, or $3.8\times10^{19}$ seconds, a value of 21.3 is obtained for $\log_{10}$ft. Nordheim (145) presents a comparison of $\log_{10}$ft and spin for various even A nuclei, and it would appear that the spin should be about 5 for $La^{138}$. Nordheim makes three hypotheses for even A nuclei:

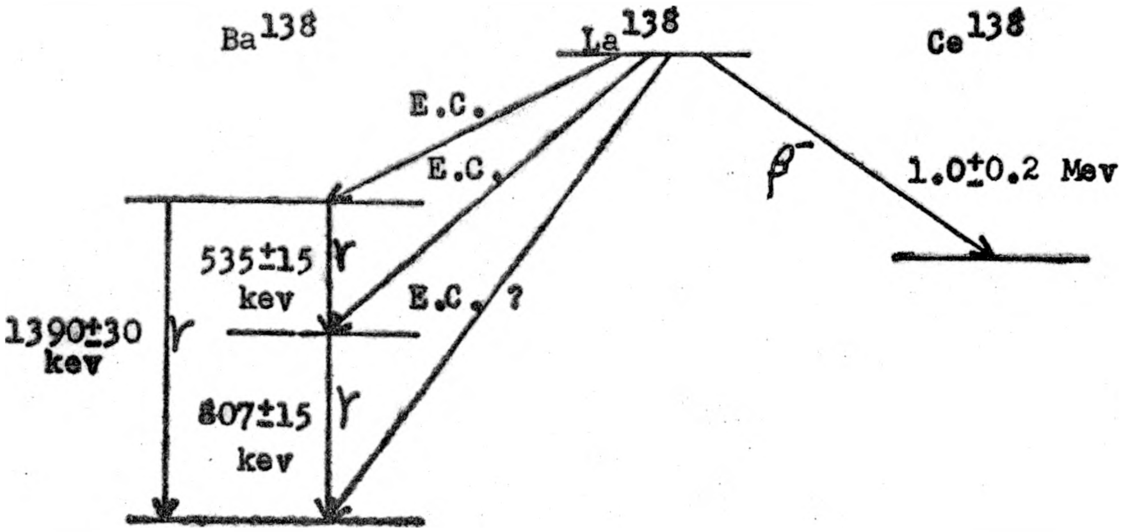
(1) The individual configurations of neutrons and protons in odd-odd nuclei are the same as in odd nuclei with the same number of nucleons in the odd particle group.

(2) If the odd neutron and proton groups belong to different Schmidt groups, then their resultant spins will subtract.

(3) If the odd neutron and proton groups belong to the same Schmidt group, their spins will couple to a larger than minimum resultant and will most likely have a resultant equal to or close to the maximum possible, their sum. Consider first postulate (1). It is known that the configuration for 57 protons in ${}_{57}La^{139}_{82}$ is $g_{7/2}$ and that the configuration for 81 neutrons in ${}_{56}Ba^{137}_{81}$ is $d_{3/2}$. Combining these it would appear that the configuration for ${}_{57}La^{138}_{81}$ could be represented by $g_{7/2}-d_{3/2}$. Since these belong to the same Schmidt group, postulate (3) says that the spin for $La^{138}$ will be 3, 4 or 5, with 5 being the most likely. A spin of 5 would agree well with a $\log_{10}$ft value of 21.3, so it can be stated that the spin of $La^{138}$ is probably 5

with the possibility of spin 4 not excluded. Moreover, the proton and neutron groups are both of even parity, and coupling will result in even parity. Gamow-Teller parity selection rules then will restrict the transition to allowed, second forbidden, fourth forbidden, etc., but not first forbidden, third forbidden, etc. On this basis the transition of $La^{138}$ to $Ce^{138}$ can be considered fourth forbidden with $\Delta I=5$ and no parity change.

A disintegration scheme may be postulated for the decay of $La^{138}$ as follows:



## 2. Neodymium

After the first ion exchange purification a bias curve was taken on each of the three neodymium samples from different parts of the elution curve. From these curves several conclusions could be drawn. In the first place, the neodymium gave very little indication of activity, producing only about 7 counts per minute at a gain corresponding to an energy of 0.3 kev. Since Libby (7) observed 10 counts per minute from an area of 193 $cm^2$ at 14% geometry, we would expect 270 counts per minute from our 1650 $cm^2$ at 45% geometry if his data were correct, the sample thickness being immaterial for such low energy radiation. The bias curves gave no indication of very weak radiation. Secondly, the three curves were quite close together, indicating that the purification was reasonably efficient. It must be emphasized that these results can be considered only in a qualitative manner since the counting rate at each gain was much too short to be treated otherwise. The three samples were mixed together, scavenged with barium sulphate, cupric sulfide, and zirconium iodate, and another bias curve was run. Figure 15 shows the curve obtained with the background subtracted. There seems to be very little indication of any weak activity, the counting rate at the highest gain being 7 counts per minute. The general shape of the curve is similar to that obtained for a gamma source. Figure 16 shows the bias curve for $Co^{60}$.

The neodymium was again carried through the complete purification process of ion exchange treatment and scavenging. Fifteen grams of neodymium oxide were painted on the copper backing, and after drying, the counting rate was obtained. In order to attach significance to the counting rate, the next measurement was made at a fixed gain setting corresponding to 0.3 kev on the energy

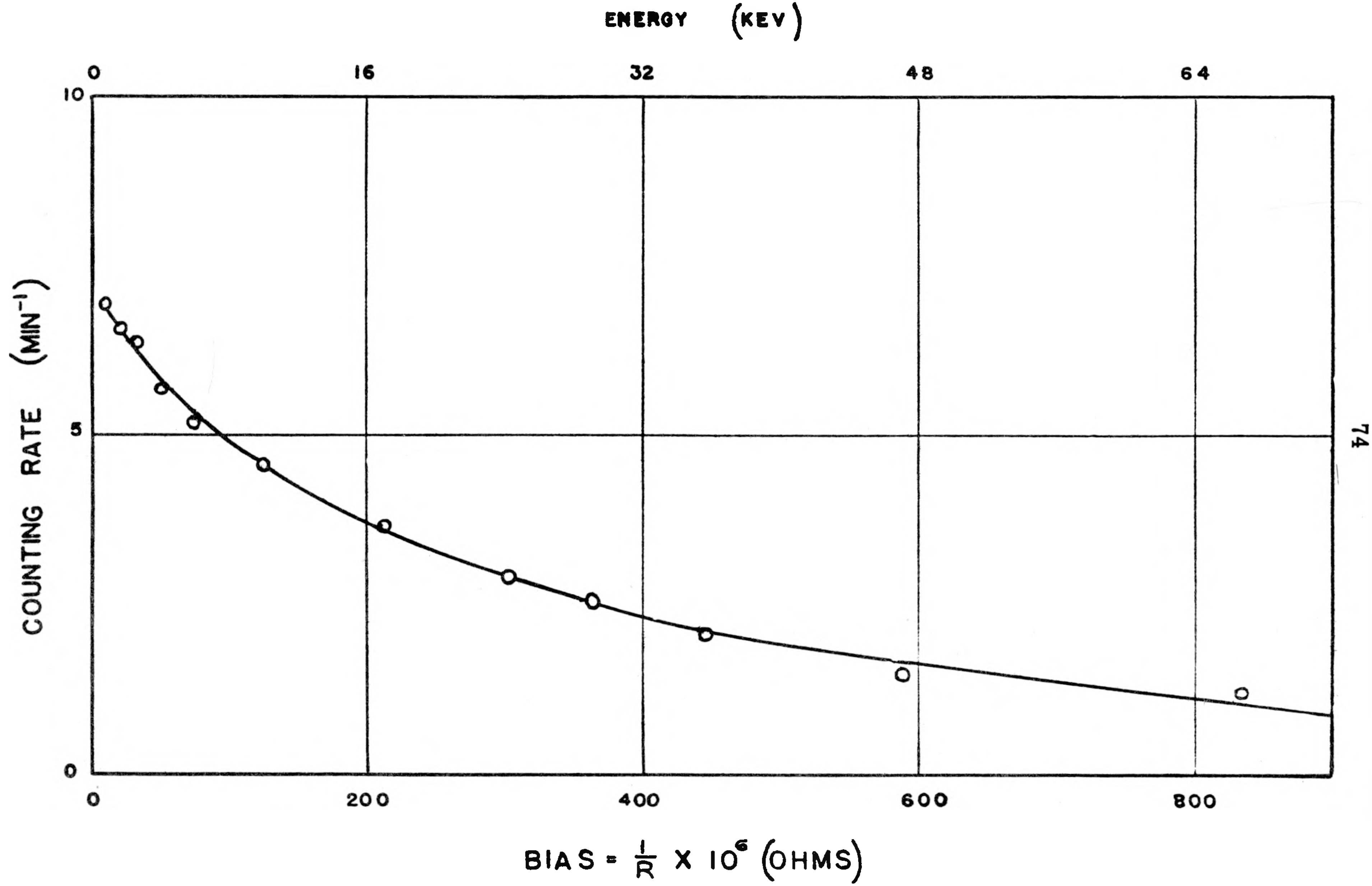


Fig. 15—Bias Curve for Once-purified Neodymium.

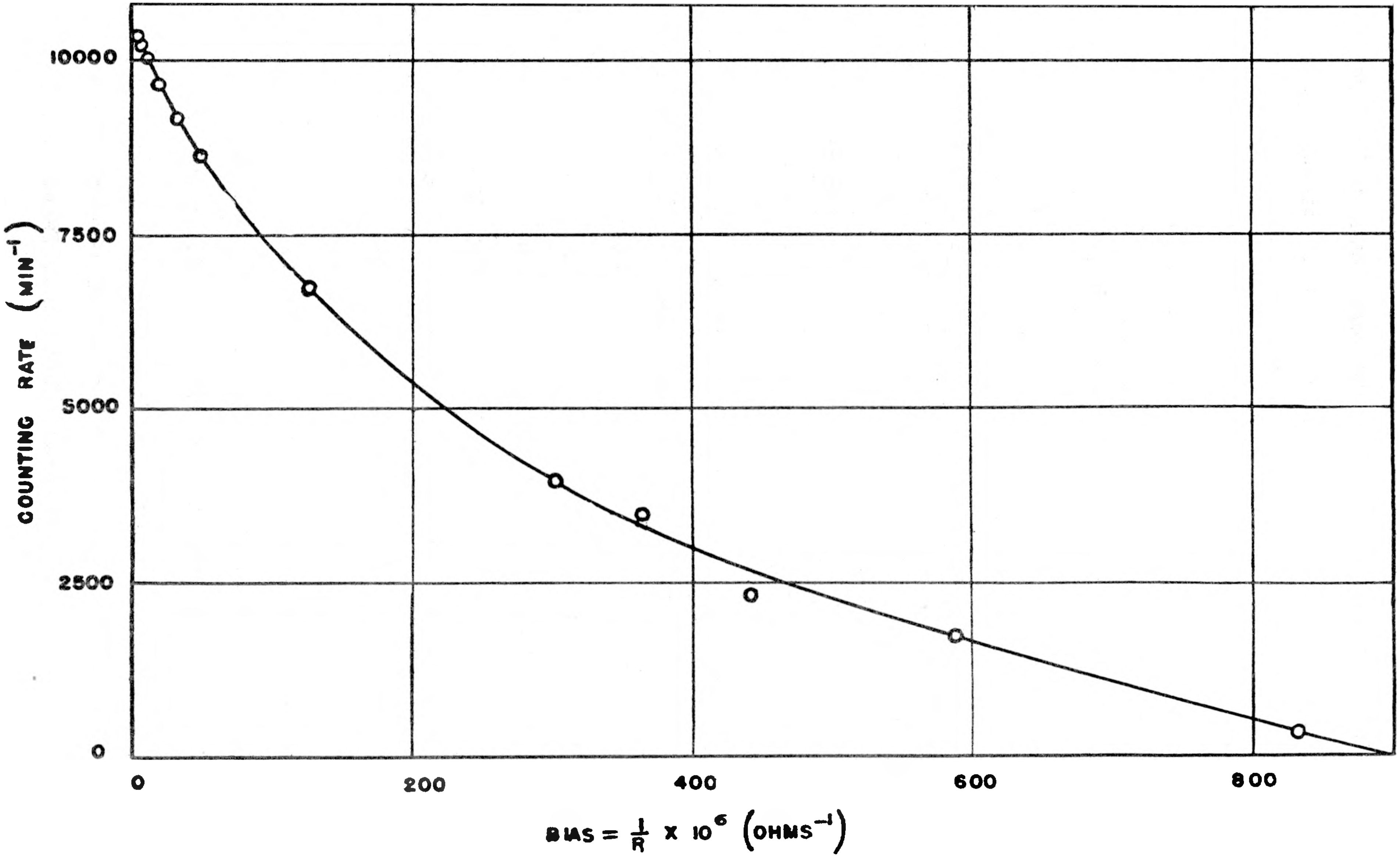


Fig. 16—Bias Curve for $Co^{60}$.

scale, and the sample and background were counted for two hours each. Table 5 gives the data for three measurements.

TABLE 5

Activity Measurement of Neodymium Oxide

| Days after scavenging | Counts per minute | | |
|---|---|---|---|
| | Sample with background | Background | Sample |
| 6 | 37.0 ± 0.4 | 32.5 ± 0.3 | 4.5 ± 0.5 |
| 25 | 34.2 ± 0.3 | 30.5 ± 0.3 | 3.7 ± 0.4 |
| 47 | 39.3 ± 0.4 | 34.9 ± 0.3 | 4.4 ± 0.5 |
| Average | 36.8 ± 0.4 | 32.6 ± 0.3 | 4.2 ± 0.5 |

Thus the 15 grams of neodymium oxide gave an average counting rate of 4.2 ± 0.5 counts per minute. The uncertainty is the probable error calculated according to counting statistics.

By taking the counting rate of a $Co^{60}$ gamma source in the presence of both the bare copper backing and the copper backing coated with neodymium oxide, it was found that the counting rate with the neodymium backing increased by 11%. It appeared that the presence of the rare earth oxide coating increased the counter sensitivity to external gamma radiation, which presumably was the cause of most of the residual background. The constancy of this excess of 4.2 counts per minute is in line with this interpretation, since contamination by natural radioelements would have shown growth. When this factor was taken into account, the counting rate attributable to the neodymium oxide was 0.6 ± 0.5 counts per minute. Thus it was concluded that not more than 1 count per minute of either soft or hard radiation was contributed by the neodymium. From the recent work of Long and Peel (109) and Fischer (110) on $Pm^{150}$, any decay of $Nd^{150}$ would be accompanied by hard betas. Assuming that self-absorption and backscattering roughly compensate for each other for hard betas, the counting yield will be 0.45, since it was estimated that 10% of the sample was obscured by the three longitudinal rods supporting the center wire. On this basis the maximum specific hard beta activity can be calculated from equation (44).

$$S = \frac{\left(\leq 1\,\frac{\text{count}}{\text{minute}}\right)\left(\frac{1\text{ minute}}{60\text{ seconds}}\right)}{\left(0.45\,\frac{\text{count}}{\text{disintegration}}\right)\left(15\text{ grams }Nd_2O_3\right)\left(\frac{144.3\text{ grams }Nd}{168.3\text{ grams }Nd_2O_3}\right)} \tag{59}$$

$$S \leq 0.003\text{ disintegration/second/gram }Nd \tag{60}$$

Assuming that the most likely beta active isotope is $Nd^{150}$ according to the suggestion by Kohman (14), the minimum half-life for beta emission by this nuclide can be calculated from equation (50).

$$t_{\frac{1}{2}} = \frac{(0.693)\left(0.0565\,\frac{\text{atom }Nd^{150}}{\text{atom }Nd}\right)\left(6.02\times10^{23}\,\frac{\text{atoms }Nd}{\text{mole }Nd}\right)}{\left(\leq 0.003\,\frac{\text{disintegration }Nd^{150}}{\text{gram }Nd\text{ second}}\right)\left(144.3\,\frac{\text{grams }Nd}{\text{mole }Nd}\right)\left(3.15\times10^{7}\,\frac{\text{seconds}}{\text{year}}\right)} \tag{61}$$

$$t_{\frac{1}{2}} \geq 2\times10^{15}\text{ years} \tag{62}$$

The low maximum beta specific activity and long minimum half-life in conjunction with little evidence of soft beta radiation conflicts with the results of other workers (1,7,11,12). This conflict can be reconciled only by assuming that the neodymium used by these investigators was not completely purified from radioactive impurities. Libby and Latimer (1) and Libby (7) did not repurify their samples to constant specific activity. Certainly, as mentioned in Chapter I, there seems to be quite a large difference in the energies of the radiations reported in these two papers. In neither the work of Jha (11) as briefly described by Feather in a private communication, nor the work of Curran, Dixon and Wilson (12) was mention made of the degree of chemical purification. Since a critical factor such as the purification was not mentioned, it must be assumed that the samples were not repurified to constant specific activity. Thus it is felt that the results given in this paper more nearly represent the true natural radioactivity of neodymium than those reported by the other investigators because of the repurification of the samples to a constant or zero specific activity, in this case the latter.

In spite of the negative results of this experiment, it is felt that $Nd^{150}$ may be unstable but with a highly forbidden decay and very long lifetime. In the discussion of the limits of beta stability (14), $Nd^{150}$ and $Ca^{48}$ were given similar special mention as being apparently outside of the stability zone, and work done by Jones and Kohman (147) cites evidence that $Ca^{48}$ is indeed unstable but with an extremely long lifetime. Nordheim (145,146) has pointed out that odd-odd nuclides frequently have large nuclear spins, and this may well be the case for $Pm^{150}$. It has recently been found that the spin of the odd-even nuclide $_{89}Ac^{227}$ is 3/2 (149). According to present ideas, this spin can be attributed to one proton only. Now in the 83-126 shell (148) the only possible orbital with total spin of 3/2 is $3p_{3/2}$. Thus the total spin of $_{89}Ac^{227}$ is probably from a $p_{3/2}$ 89th proton. Let us postulate that the 89th neutron is in the same orbital as the 89th proton, that is, $p_{3/2}$. The 61st proton is almost certainly $d_{5/2}$, since $_{59}Pr^{141}$, $_{63}Eu^{151}$, and $_{63}Eu^{153}$ have spin 5/2. Thus $_{61}Pm^{150}_{89}$ could probably be represented by $d_{5/2}$-$p_{3/2}$. Since the two odd nucleons belong to the same Schmidt groups, the spins should add, giving a total spin of 4. According to Gamow-Teller selection rules the forbiddenness would then be 3. Since $Nd^{150}$ could probably decay only to the ground state of $Pm^{150}$, the large spin change would make this transition highly forbidden as must be the case for $Ca^{48}$. Fischer's work on $Pm^{150}$ (110) shows that it does not decay to the ground state of $Sm^{150}$, so that this transition must be highly forbidden. The $Nd^{150}$-$Pm^{150}$ transition would be equally forbidden.

Although no specific search was made for alpha activity, the measurements made will allow an upper limit to be calculated. The ratio of the ranges of an alpha ray in neodymium oxide and air can be expressed by

$$\frac{R_{Nd_2O_3}}{R_{air}} = \frac{\text{no. atoms air per cm}^3}{\text{no. molecules } Nd_2O_3 \text{ per cm}^3} \times \frac{1}{\text{molecular stopping power of } Nd_2O_3} \tag{63}$$

An empirical rule (Friedlander and Kennedy) states that the atomic stopping power relative to air, where s=1, can be expressed by

$$S = 0.563 \frac{Z}{\sqrt{Z+10}} \tag{64}$$

By this rule the molecular stopping power of neodymium oxide is given by

$$S_{Nd_2O_3} = 0.563\left[\frac{2Z_{Nd}}{\sqrt{Z_{Nd}+10}} + \frac{3Z_O}{\sqrt{Z_O+10}}\right] \tag{65}$$

$$S_{Nd_2O_3} = 0.563\left[\frac{2\times 60}{\sqrt{60+10}} + \frac{3\times 8}{\sqrt{8+10}}\right] \tag{66}$$

$$S_{Nd_2O_3} = 11.26 \tag{67}$$

The number of atoms of air per $cm^3$ can be given by

$$n = \frac{\text{density}}{\text{"atomic weight"}} N_0 \tag{68}$$

A similar expression is obtained for the number of molecules of neodymium oxide per $cm^3$ except that the molecular weight is used.

$$\frac{R_{Nd_2O_3}}{R_{air}} = \frac{\dfrac{\text{density of air}}{\text{"atomic weight" of air}} N_0}{\dfrac{\text{density of } Nd_2O_3}{\text{molecular weight of } Nd_2O_3} N_0} \times \frac{1}{S_{Nd_2O_3}} \tag{69}$$

Substituting numerical values in equation (69) gives

$$\frac{R_{Nd_2O_3}}{R_{air}} = \frac{\frac{0.001226}{14.4}}{\frac{7.24}{336.6}} \times \frac{1}{11.26} \qquad (70)$$

$$R_{Nd_2O_3} = 0.000351\ R_{air} \qquad (71)$$

If it is assumed that the energy of detectable alpha radiation would be 2 Mev, then the range in air would be 1.1 cm. By using equation (71) the range in neodymium oxide can be found. Thus

$$R_{Nd_2O_3} = (0.000351)(1.1) = 0.000386 \text{ cm.} \qquad (72)$$

Knowing the density of the oxide, the range in gm/cm$^2$ can be obtained.

$$R_{Nd_2O_3} = (0.000386)(7.24) = 0.00279 \text{ gm/cm}^2 \qquad (73)$$

The surface area of the sample is 1650 cm$^2$, so

$$\text{effective sample weight} = (0.00279)(1650) = 4.6 \text{ gm} \qquad (74)$$

It can be calculated for a sample of thickness equal to the range that one of every two alpha rays will be counted from a 50% geometry, so that the counting yield will be 0.25. Now the data have been obtained for substitution in equation (44).

$$S = \frac{\left(\le 1\ \frac{\text{count}}{\text{minute}}\right)\left(\frac{1\text{ minute}}{60\text{ seconds}}\right)}{\left(0.25\ \frac{\text{count}}{\text{disintegration}}\right)\left(4.6\text{ grams }Nd_2O_3\right)\left(\frac{144.3\text{ grams }Nd}{168.3\text{ grams }Nd_2O_3}\right)} \qquad (75)$$

$$S \le 0.02\ \text{disintegration/second/gram La} \qquad (76)$$

The minimum half-life for the alpha decay of neodymium can be calculated as follows using equation (59).

$$t_{\frac{1}{2}} = \frac{(0.693)\left(1\,\frac{\text{gram Nd}}{\text{gram Nd}}\right)\left(6.02\times10^{23}\,\frac{\text{atoms Nd}}{\text{mole Nd}}\right)}{\left(\leq 0.02\,\frac{\text{disintegration Nd}}{\text{gram Nd second}}\right)\left(144.3\,\frac{\text{grams Nd}}{\text{mole Nd}}\right)\left(3.15\times10^{7}\,\frac{\text{seconds}}{\text{year}}\right)} \qquad (77)$$

$$t_{\frac{1}{2}} \geq 5\times10^{15} \text{ years} \qquad (78)$$

This is approximately twenty times as great as the previous lower limit set by Bestenreiner and Broda (10) of $2.6\times10^{14}$ years by the nuclear emulsion method.

It might be of interest to speculate whether alpha activity might be expected in neodymium. Utilizing the calculated atomic masses given by Metropolis and Reitwiesner (150) and a mass of 4.00390 for $He^4$, the Q for the following decays can be calculated:

$Nd^{142} = Ce^{138} + He^4$; $Q = -0.29$ Mev

$Nd^{143} = Ce^{139} + He^4$; $Q = -0.49$ Mev

$Nd^{144} = Ce^{140} + He^4$; $Q = -0.68$ Mev

$Nd^{145} = Ce^{141} + He^4$; $Q = -0.88$ Mev

$Nd^{146} = Ce^{142} + He^4$; $Q = -1.07$ Mev

$Nd^{148} = Ce^{144} + He^4$; $Q = -1.48$ Mev

$Nd^{150} = Ce^{146} + He^4$; $Q = -1.90$ Mev

From the Q values obtained it would appear that neodymium should not be alpha active. However, in spite of the negative Q values, there is one possibility, and this is the decay of $Nd^{144}$ to $Ce^{140}$. The Q of the decay calculated above is probably much too small since $Ce^{140}$ should be particularly stable by virtue of the 82 neutrons in the nucleus. This added stability would make the mass of $Ce^{140}$ lower than that calculated with the result that Q would be more positive. According to Suess and Jensen (151) the energy for the N=82 shell jump is about 1.8 Mev. This would put the Q for the decay in the region of +1.1 Mev, for which the lifetime would be of the order of $10^{30}$ years. This would be much too long for measurement. Thus if the above approximations were reasonably accurate, it would appear that neodymium should not be detectably alpha active. However, the above values must be treated as approximations. If the energy is as high as 1.6 Mev, then the lifetime will be of the order of $10^{18}$ years, and thus would be observable. Consequently, although it appears that neodymium is not alpha active, the possibility cannot be ruled out, and a more intensive search should be made. This can be done with the present apparatus by reducing the voltage so as to count alphas only, thus greatly reducing the background.

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