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NATURAL TRITIUM ASSAY, ROUTINE METHOD FOR ABSOLUTE ASSAY OF
BETA RADIOACTIVITY, AND THE REACTIONS OF NEGATIVE
PI MESONS WITH ELEMENTARY BROMINE

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ABSTRACT

The measurement of the abundance of tritium in natural waters using the electrolytic concentration plant and the tritium counting technique developed during the previous contract has been the principal business during this year. It develops that the abundance of natural tritium considerably exceeds the earlier expectations, and that its possible usefulness to meteorology and the dating of organic materials on a 12.5 year half life basis becomes much more practical than we had originally supposed it would be. Some 200 grams of tritium appear to be present in the atmosphere at any given time, and some 15 kilograms to be the total world assay. These quantities are small enough so that care must be taken with respect to atomic bomb production of tritium. It is observed, however, that the time for flushing the atmosphere probably does not exceed a few months, so the contamination is likely to be temporary. The assay is being continued; samples of old water are being measured to determine whether the tritium content correlates with the expected exponential decay law. A series of vintage wines are being purchased to give further check on this point. The wines have been selected with considerable care to come from the same vineyard and to be of definitely known vintages.

A routine method of absolute assay for beta radioactivities which are pure beta emitters and do not emit gamma radiations or have complicated decay spectra has been developed. This technique involves very little more work than the ordinary counting methods which give relative assays only. It is estimated that the error in the absolute assay will not exceed 5 or 10%. Since it is obtained with essentially no extra effort but solely by the consideration of the geometry and type of counter instrument used, it appears that a considerable advance in radiochemical technique has been made.

The mysterious reactions of pi mesons with the materials in the photographic plate as observed by the exposure of plates to cosmic ray and artificial pi meson beams can hardly be fully elucidated until those reactions which involve the emission of neutrons can be discovered and measured. Neutrons do not activate the emulsion. For this reason the elements bromine and silver are being studied by radiochemical techniques. During the past year bromine was irradiated and radioactivities produced, which necessarily belong to the elements selenium, arsenic, germanium, gallium, and zinc, were separated and measured and the absolute yields determined by the use of our absolute beta assay techniques, together with an absolute measurement of the number of mesons entering the elementary bromine target. In general one observes that neutron emission is more probable than charged particle emission. In fact, for bromine the most probable process is emission of about three neutrons and one proton. This corresponds to a mountain peak on the yield map, the height of the peak being about 8%, i.e., 8% of all negative pi mesons absorbed will yield the 26-hour As^{76} . The slope of the yield peak is quite steep in all directions from the peak, the lowest slope corresponding to about 3 neutrons for every proton. For example, at 2 protons and 6 neutrons the yield has dropped to 1.5%.

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I. INTRODUCTION

The earlier report¹ on the detection of natural tritium and other

¹"Sensitive Radiation Detection Techniques for Tritium, Natural Radioactivities, and Gamma Radiation," Air Force Contract #AF 33(038)-18013, Final Report 1951, W. F. Libby.

radiochemical studies was devoted in its natural tritium section primarily to the development of the equipment and technique for the assay. During this present year of 1952 the construction of equipment has been completed and the first assays made. The completion of a world wide assay for natural tritium will require a very considerable number of measurements in addition to those we have made already. A part of the present report will be devoted to the discussion of the principles to be used in this measurement and to planning for the collection of the samples.

A method for the routine absolute intensity and energy measurement of beta radioactivities has been developed based on the empirical observation that beta radioactive solids display exponential absorption curves when the source, absorber, and detector are in close contact. The absorption coefficient is correlated with the energy, and the self absorption by the sample itself is immediately calculable from the absorption coefficient also. Evidence has been obtained for a general relation between the energy and the absorption coefficient which apparently is applicable to pure beta emitters and will allow the routine absolute assay of such radioactivities as C^{14} , S^{35} , T , P^{32} , etc. - a very considerable fraction of the most important tracers ordinarily used. The effort required to accomplish the assay is very little greater than that for the usual measurement of radioactivity and afford the additional advantage that an accounting of the total radioactivity can be made. The method has been applied to a redetermination of the half lives and energies of the naturally radioactive alkali elements potassium and rubidium and to the rare earth lutecium. The results were in close agreement with those in the literature for both the energy and half life. These confirmatory conclusions are not given in this report but are reported in detail in Dr. A. D. Suttle's thesis, from which a section of this report is abstracted.

The interaction of pi mesons with photographic plates ordinarily studied by direct observation of the tracks on plates has been further elucidated by radiochemical investigation of the interaction with the

element bromine, which together with silver constitutes the only heavy elements present in a photographic plate. This work has demonstrated the importance of neutron expulsion following the assimilation of the negative pi meson. The neutrons of course are not observable in a photographic plate so the radiochemical evidence should eventually enable a clearer picture of the nature of the over-all reaction to be drawn. The investigation itself presented some considerable difficulties in that a large amount (6 pounds) of liquid elementary bromine was the target material. This rather large quantity of this rather noxious and dangerous chemical was processed and the resultant extracted radioactivities measured with the low level techniques² developed in this laboratory.

²"Sensitive Radiation Detection Techniques," Air Force Contract #AF 33(038)-6492, Final Report 1950, W. F. Libby.

II. MEASUREMENT TECHNIQUES

A. ENRICHMENT PROCESS

The water sample to be assayed for tritium content first is distilled in a standard 2 gallon per hour gas fired still, mixed with sodium hydroxide to produce a 3% by weight solution, electrolyzed in an iron cathode nickel anode plant to a final volume of 1 cubic centimeter or less, and the deuterium and tritium content of the final product determined. In addition it has been our custom to remove samples during the course of the enrichment to obtain confirmatory evidence of the correctness of the assay and assurance of freedom from tritium contamination. The plant consists of 38 water-cooled steel cells of 3 liter capacity each, operated in series at 100 amperes and arranged in 3 stages, and a series of smaller cells which constitutes the final stages. The gases generated in each stage are collected by iron header pipes and conducted out of doors or simply allowed to escape into the lightly constructed drafty shed in which the plant is housed. The cells are constructed of Shelby seamless steel tubing 4 inches in diameter and 18 inches in length. A bottom plate and a central tie rod which secures the head are attached by arc welding. The head carries a gas outlet tube and a tube through which the cell is filled and drained. The cell itself, insulated from the cooling water by paint, serves as the cathode. The anode consists of a perforated cylinder of sheet nickel 3.5 inches in diameter and 5 inches high, attached by nickel rivets to the flattened end of a half inch nickel rod which passes through an inverted rubber stopper in the lead of the cell. The nickel cylinder is insulated from the cell wall by small pieces of hard rubber. The small cell which constitutes the fourth stage is constructed on the same design, but the material is 2.5 inch iron pipe.

The water cooling is achieved by placing the cells in a trough through which water is circulated, the insulation between ground potential water and the cell wall being achieved (with some difficulty) by

painting the cells with 3 coats of Tygon paint series TP, then wrapping with Scotch Electrical Tape (No. 33).

The source of electric power is a 10 kw DC generator capable of delivering up to 100 amperes at 100 volts. The plant is located in a lightly constructed wooden shack in a moat-like excavation surrounding the basement level rooms in the Jones Chemical Laboratory at the University of Chicago. In order to avoid freezing of the solutions and cooling water, a steam radiator has been installed, and the assembly has withstood one 10° F cold spell so far. The possibility of explosion is such that the closure of the shack has purposely been made poor so a considerable air circulation takes place. It is also supposed that in case all the hydrogen-oxygen gas in the plant should explode at once it would do little damage. Such an explosion should damage the cells relatively little. The connections to the header pipe have purposely been made of gum rubber so that expansion will prevent ignition of the gas stored in the main cell. Recently, however, the gas has been allowed to escape directly from the cells into the shed.

The 30 cells of the first stage are charged with 3 liters each of the 3% sodium hydroxide solution made up of the water sample. The sodium hydroxide is a C.P. electrolytic grade, and the water is distilled once or twice before use. The charges are measured out and placed in the cells with the aid of a portable apparatus built for the purpose.

When the electrolysis has proceeded for about 72 hours the initial charge, totaling 90 liters, is reduced to about one-sixth of its original volume. It is then removed, part of it distilled and transferred to the second stage. Similarly the residue from the second is transferred to the third stage, etc. Brown and Daggett³ claim to have observed average fractionation factors of 8.6 for protium relative to

³"A Plant for the Production of Heavy Water," W. G. Brown and A. F. Daggett, J. Chem. Phys., 3, 216 (1935).

deuterium, which is appreciably higher than the generally accepted values. This agrees with our own experience as shown in Table 1.

The final stages of the enrichment are accomplished on laboratory bench cells made by the use of iron and nickel strips in glass containers. The current supply found to be most satisfactory for the laboratory bench cells has been commercial battery chargers (we have used Mallory 6RS25 bench power supply, costing \$70.00).

The most important factor in the attainment of large fractionation has proved to be the cooling of the cells. The extreme importance of this moderately elementary point escaped us at first. Since we realized its significance our fractionations have risen to the very high values shown in Table 1. One notes that in the method of separation used in this work, in which the hydrogen and oxygen gases are discarded without recirculation and no attempt is made to remove the water vapor from them, the volume of electrolyzed vapor is so large that a moderate vapor pressure of the liquid water makes the removal of water by straight volatilization equal to that by electrolysis.

For example, electrolysis of 1 mole of water produces 36 liters of gas NTP, the volume of water vapor corresponding to 1 mole at only $2/3$ of an atmosphere. Therefore at some temperature well below the boiling point the effective separation factor will have been reduced by exactly a factor of 2. Even at low temperatures where the vapor pressure of water is of the order of $1/30$ of an atmosphere the vaporization removal corresponds to a 2.5% reduction in separation factor. The heat dissipated in the cells is quite considerable. The base stage of our plant consumes about 10 kw and the normal temperature drop is 4° between the electrolyte and the cooling water.

The deuterium assays have been used to measure the tritium separation actually attained, it being assumed that alterations in conditions which would change the deuterium enrichment would alter the tritium enrichment proportionately. The deuterium assays were made by the falling drop technique.⁴ It was found feasible to determine deuterium

⁴"Physical Properties and Analysis of Heavy Water," I. Kirshenbaum, National Nuclear Energy Series III-4A, pp. 324-343.

contents as low as as 0.1% with an accuracy of 0.01%. The concentration range normally encountered was between 1 and 4% where the accuracy is .01%. The more highly enriched samples are diluted down to this concentration with ordinary water. This dilution tends to reduce the error due to O^{18} accumulation to less than 1% in the deuterium content.

Since the plant was purposely constructed to allow the hydrogen and oxygen gases to mix and the explosive mixture to be vented to the roof, some possibility of explosion naturally exists. Provision was made for this by the use of gum rubber tubing to connect the cells to the manifold leading to the roof, the thought being that in case of explosion the gum rubber tubing would expand and blow off the connections, thereby saving the cells from rupture.

During several months of nearly continuous operation we have experienced only two explosions, both of which occurred during the early morning hours when no one was present so far as we know, and one of which resulted in the complete disconnection of all 36 rubber connectors and the dislocation of a considerable fraction of the rubber gaskets between the anode electrode and the cathode case of the cells. After this experience the header manifold was disconnected and the individual cells allowed to discharge their gas directly into the electrolytic room, which is a lightly constructed shack in a moat adjoining our basement laboratory. The second explosion occurred in just one cell and we think it possible that the rubber tubing and header manifold caused the damage to spread from the explosion site. Of course it is not unlikely that future operations will be less fortunate, but we believe that we should continue to fare well in this regard and recommend that the use of explosion proof traps and even the header manifold is not necessary.

It is anticipated that in the future a considerable number of assays of solutions of as little as 1 or 2 liters initial volume will be made for various purposes, particularly in meteorological studies, since we have found that rain water is sometimes sufficiently radioactive in tritium to require no greater concentration than 1000 or

2000 fold. If this should be a correct prediction, the development of a laboratory bench cell which has a low explosion hazard and is relatively simple to operate might be a task of considerable importance.

B. COUNTING

The measurement of the tritium content of the enriched water samples consists in the conversion of the water to hydrogen gas in a low level Geiger counter. The procedure has been described previously.¹ Routine utilization of it has revealed no essential weaknesses and our experience reinforces our earlier belief that a satisfactory tritium assay method was in hand. The technique for the conversion of water to gaseous hydrogen consists of the use of finely divided zinc dust at about 500°C to form hydrogen and zinc oxide.⁵

⁵"Tritium in Nature." A. V. Grosse, W. H. Johnston, R. L. Wolfgang, and W. F. Libby, Science 113, 1 (1951).

The zinc dust is mixed with freshly dehydrated calcium oxide into which the water sample is distilled at room temperature. When this step is complete the mixture is gently heated in a pyrex tube to about 500°C to cause the evolution of hydrogen gas. It has been found that the conversion is essentially quantitative by this technique, so that isotopic separation is of no consequence. The gaseous hydrogen is stored in a bulb and transferred to the manifold used for filling the counters.

The counting technique was described in detail earlier.^{1,2} It is a pleasure to report that an additional year's experience has verified the expectation that this technique is eminently satisfactory. To review, it consists of the use of an ordinary Geiger counter with flat ends in order that a correction may be made for the end loss,⁶

⁶"End and Wall Corrections for Absolute Beta Counting in Gas Counters." A. G. Engelkemeir and W. F. Libby, Rev. Sci. Inst., 21, 550 (1950).

and a gaseous mixture of about 2.0 cm of mercury pressure of ethylene gas, 3.0 cm of argon gas, and 0 to 20 or 30 cm pressure of hydrogen or deuterium gas in which the tritium is contained. The counters used in our research were 2 inches inside diameter and 18 inches in length. They were made of brass tubing with lucite ends waxed in place. The wire was #28 copper. The counter voltages depended a great deal on the pressure of hydrogen, but ranged from 1500 to 3000 volts. The anticoincidence shield¹ was customarily used, the shield consisting of 8 inches of iron with a protective ring of 11 counters in anticoincidence. The background for the brass counters in the iron shield with the anticoincidence counters disconnected is 160 counts per minute, and is 8 counts per minute with them connected. We normally did not measure a sample with less radioactivity than 1 count per minute above the background. In general the activities were at least 5 or 10 counts above the background. In several instances 2 or

3 different pressures were taken for a given filling to observe whether the specific activity was found to be the same for the different pressures, thus checking on the constancy of the counter efficiency and the general reliability of the method. A further check is shown in Table 1, where the assay data are given. Samples at various stages of enrichment were measured. This not only involves a check on the enrichment theory but also on the correctness of the counting technique. The satisfactory checks observed thus can be taken as evidence for the counter technique's being correct. The ease with which samples are measured - a normal measurement can be completed in a half hour from the time the counter and sample are placed on the manifold of the vacuum line used to fill the counter - is of very considerable importance, for it guarantees that tritium assay will not be a serious barrier to the widespread use of tritium as a tracer isotope.

III. TRITIUM ASSAY IN NATURAL WATERS

A. DATA OBTAINED

The earlier data on the occurrence of tritium in nature^{5,7} cor-

⁷"Tritium Content of Atmospheric Hydrogen." V. Faltings and P. Harteck, Zeits f. Naturf., 5A, 438 (1950); P. Harteck and V. Faltings, Nature, 166, 1109 (1950).

responded to 0.8×10^{-18} tritium atoms per average hydrogen atom in lake Mösavann, Norway, and 1500×10^{-18} for atmospheric hydrogen collected from the air over Hamburg, Germany. Lake Mösavann collects the water from the mountain plateau Hardangervidda in southern Norway. The plateau is at a height of 900 meters or more above sea level. The Lake Mösavann water was taken into the plant at the end of January 1948, and it is likely that it originated from snow fallen during the winter of 1946-47. As we shall see later, if this statement is true, we have cause to worry about a conflict with our later assays of Lake Michigan given in this report, in that the Lake Michigan assay is only slightly higher than the Lake Mösavann, and we know that the Lake Michigan assay is appreciably lower than fresh rain and snow. The Norwegian assay was made, however, on heavy water prepared by the Norsk Hydro-Elektrisk Kvoelstofaktievelskab, and though the workers of this corporation cooperated most heartily in the research there remains reasonable doubt that the accuracy of our knowledge of the fractionation factors actually attained was comparable with that which we have customarily operated with in the recent research. In other words, the fact that the heavy water was produced in Norway causes considerable doubt that the calculation of the absolute assay from the observed tritium content of the concentrate is as correct as the assays obtained during the past year.

The Harteck and Faltings value for atmospheric hydrogen is remarkably higher than any other assays obtained on water. As Harteck and Faltings state in their article, this may not be too surprising

in view of the difficulty with which atomic hydrogen can react with oxygen at the very highest layers of the atmosphere, where its chances of combining with atmospheric hydrogen to form molecular hydrogen are comparable with its chances of combustion. These statements rest on the knowledge of kinetics which Dr. Harteck possesses and are not to be taken as completely definitive except insofar as the postulates he makes are correct. It is worthy of note that the specific activities observed by Harteck and Faltings were somewhat low and there may have been considerable error in their measurement. It is of importance that the tritium content of atmospheric hydrogen be redetermined.

Measurements of commercial heavy water samples always revealed a certain tritium content. It is difficult to calculate the corresponding absolute assay of the feed water for the reason that the fractionation factors applicable are not known, though one can attempt to estimate them from the observed deuterium assay, and the possibility that a given sample of heavy water may have been exposed to the extreme neutron intensity of the atomic piles, giving it a tritium content far above any natural assay.

The data obtained during the past year are shown in Table 1. Columns 1 and 2 designate the test samples removed during the electrolysis of a particular sample, column 2 giving the volume enrichment. Column 3 gives the calculated tritium enrichment based on the observed deuterium enrichment and the assumption that the ratio of the tritium to deuterium enrichment is constant at 2.0. Column 4 gives the deuterium content of the test sample. Column 5 is the observed enrichment factor for deuterium relative to protium. Column 6 is the specific activity of the hydrogen gas obtained from the test sample in counts per minute per cm of mercury pressure as measured in the 2" x 18" counters used in this research. These entail a 3 or 4% end loss and have a volume of about 800 cc. Column 7 is the absolute assay calculated from the specific activity and the tritium enrichment factor, that is, the number of counts per minute per cm of mercury pressure in the counter is converted to number of tritium atoms per hydrogen atom in the gas as measured and then this is divided by the tritium enrichment factor to obtain the original assay. The errors quoted are the errors in measurement of the radioactivity and do not include any other errors in the complicated processing involved in the assay. Therefore in striking the average we have written an error for the average which is commensurate with the mean deviation of the various values obtained during the enrichment process from the mean.

The first sample was a sample of rain water collected from the roof of the old power house building on the University of Chicago campus on May 11, 1951. The water was bottled and measured during the past year. As the data show, this water was about 30 times more radioactive than the Lake Mös vann Norwegian water and about 15 times more radioactive than Lake Michigan. The two Lake Michigan samples were obtained on May 12, 1952, and July 7, 1952, from the tap in the Jones Laboratory, it having been ascertained that the city water in the southern section of Chicago was being supplied at that time from the Dunne Crib, which is located about 3 miles offshore at 79th Street South. The water intake at the crib is 35 feet below the surface of the lake. The two values obtained, 2.0 ± 0.1 and 1.4 ± 0.2 , probably

TABLE 1
Tritium Assays

Sample	Volume Enrichment	Tritium Enrichment (calc. $\frac{\beta}{\alpha} = 2$)	% D ₂ O	α	Sp. Act. (cpm/cm)	Abs. Assay ([atom T/atom H] x 10 ¹⁸)
Chicago Rain Water May 11, 1951						
A	35.4	29.0	0.35	9.1 ± 0.6		
B	241	167	1.75	6.3 ± 0.3	0 ± 0.1	
C	1.56 x 10 ³	920	8.10	5.7 ± 0.3	1.51 ± 0.2	29 ± 4
D	6.25 x 10 ³	3.44 x 10 ³	28.1	11.3 ± 2.0	6.15 ± 0.2	36 ± 2
E	1.85 x 10 ⁴	9.0 x 10 ³	64.5	7.1 ± 1.3	15.3 ± 0.2	30 ± 2
Av.						32 ± 2
Lake Michigan, Dunne Crib May 12, 1952						
A	27.6	22	0.31	12.3 ± 1.7		
B	236	160	1.59	4.2 ± 0.3	0.11 ± 0.08	
C	1.80 x 10 ³	1.00 x 10 ³	8.34	5.7 ± 0.3	0.13 ± 0.05	
D	5.5 x 10 ³	2.85 x 10 ³	21.9	8.9 ± 1.3	0.37 ± 0.37	2.1 ± 2.1
E	4.6 x 10 ⁴	1.5 x 10 ⁴	74.0	3.6 ± 0.6	1.70 ± 0.10	2.0 ± 0.1
Av.						2.0 ± 0.1
Lake Michigan, Dunne Crib July 7, 1952						
A	25.7	24.5	0.35	11.6		
B	254	174	1.76	3.4 ± 0.1		
C	1.38 x 10 ³	820	7.14	6.1 ± 0.3	0 ± 0.1	
D	6.1 x 10 ³	3.2 x 10 ³	24.3	6.6 ± 0.4	0.24 ± 0.094	1.31 ± 0.47
E	2.45 x 10 ⁴	1.1 x 10 ⁴	70.0	7.0 ± 0.4	0.67 ± 0.11	1.15 ± 0.15
F	5.8 x 10 ⁴	1.9 x 10 ⁴	96.5	5.6 ± 0.7	1.86 ± 0.17	1.70 ± 0.2
Av.						1.4 ± 0.2

TABLE 1--Continued

Sample	Volume Enrichment	Tritium Enrichment (calc. $\frac{Q}{\alpha} = 2$)	% D ₂ O	α	Sp. Act. (cpm/cm)	Abs. Assay ([atom-T/atom H] $\times 10^{18}$)
Lake Michigan, closed-off water main March 19, 1942						
A	223	157	1.64	7.8 $\pm$ 0.3		
B	4.24 $\times 10^3$	2.25 $\times 10^3$	17.6	5.5 $\pm$ 0.4	0.32 $\pm$ 0.07	2.44 $\pm$ 0.57
C	4.5 $\times 10^4$	1.56 $\times 10^4$	79.6	4.4 $\pm$ 0.1	1.77 $\pm$ 0.09	2.07 $\pm$ 0.1
D	8.4 $\times 10^4$	2.37 $\times 10^4$	98.5	7.9 $\pm$ 1.1	2.95 $\pm$ 0.12	2.27 $\pm$ 0.09
						Av. 2.2 $\pm$ 0.1
Columbia University distilled water 1944						
A	147	105	1.10	7.2 $\pm$ 0.2		
B	1.51 $\times 10^3$	880	7.53	5.9 $\pm$ 0.4	0.12 $\pm$ 0.06	2.4 $\pm$ 1.2
C	5.77 $\times 10^3$	3.10 $\times 10^3$	24.5	9.7 $\pm$ 0.8	0.39 $\pm$ 0.03	2.23 $\pm$ 0.19
D	5.50 $\times 10^4$	1.85 $\times 10^4$	91.8	4.8 $\pm$ 0.1	2.37 $\pm$ 0.12	2.23 $\pm$ 0.1
E	1.15 $\times 10^5$	2.72 $\times 10^4$	95	2.1 $\pm$ 0.6	4.03 $\pm$ 0.55	2.72 $\pm$ 0.37
						Av. 2.4 $\pm$ 0.1
Cistern closed up ca. 29 years ago, Decatur, Ill.						
A	236	160	1.60	7.0 $\pm$ 0.2		
B	1.24 $\times 10^3$	730	6.38	6.2 $\pm$ 0.3	0.246 $\pm$ 0.036	5.85 $\pm$ 0.65
C	4.64 $\times 10^3$	2.48 $\times 10^3$	19.4	7.0 $\pm$ 0.5	0.59 $\pm$ 0.077	4.13 $\pm$ 0.58
D	3.78 $\times 10^4$	1.53 $\times 10^4$	91.0	7.9 $\pm$ 0.9	4.74 $\pm$ 0.16	5.03 $\pm$ 0.19
E	1.09 $\times 10^5$	4.03 $\times 10^4$	98.5	2.9 $\pm$ 0.6	9.92 $\pm$ 0.15	4.51 $\pm$ 0.068
						Av. 4.7 $\pm$ 0.1
Cistern closed up 14 years ago, Sullivan, Ill.						
A	2.29 $\times 10^3$	1.40 $\times 10^3$	12.7	8.0 $\pm$ 0.2	0.311 $\pm$ 0.062	4.1 $\pm$ 0.8
B	9.7 $\times 10^3$	5.25 $\times 10^3$	42.0	7.6 $\pm$ 0.6	0.89 $\pm$ 0.09	2.9 $\pm$ 0.3
C	3.88 $\times 10^4$	1.58 $\times 10^4$	95.5	7.0 $\pm$ 0.4		
						Av. 3.5 $\pm$ 0.3

are not significantly different, and we shall take the average, 1.7 ± 0.2 , as our present best value for Lake Michigan. The other samples were samples of old water obtained from various sources. The first was a city water main at 130th Street South in Chicago, which was opened for us by the city Water Department. It was not certain that the main had been tightly closed for the whole time, but it did seem likely that it had been. It had been removed from the water system on March 19, 1942. We see from the assay, however, that it probably is modern lake water. The next sample was distilled water taken at Columbia University in 1944. It was a standard sample for deuterium assay and possessed normal deuterium content. Again one sees that the assay is lower than one might expect from other data given in the table, it being about the same as Lake Michigan or somewhat higher. Of course, being distilled water there may have been some fractionation of tritium. The next sample was obtained from an old cistern which was sealed up about 30 years ago at Decatur, Illinois. The farm house to which the cistern was attached was purchased by its present owners at that time, and they proceeded to seal the cistern, since they had small children. If, therefore, one can assume that the seal was perfect, this water should be 29 years old. The last sample was from a similar cistern 14 years old at Sullivan, Illinois.

It is gratifying to observe that in most instances the absolute assays deduced from the test samples obtained at various stages of enrichment agree with one another. This shows that the method of calculation of the tritium enrichment, as well as the counting techniques, probably are not seriously in error. The values for alpha, the deuterium enrichment factor, fluctuate rather widely from run to run, demonstrating that the process is not under perfect control as yet. It appears, however, that deuterium analyses on the test samples do allow proper corrections to be made for the fluctuating enrichment factor. Table 2 shows the data obtained on the tritium to deuterium separation factor ratio. It is on the basis of these data that the value of 2.0 is used. It is perfectly clear from this table that a more accurate determination of this number is in order.

B. THEORETICAL IMPLICATIONS OF THE TOTAL PRODUCTION RATE FOR NATURAL TRITIUM AND ITS DISTRIBUTION IN NATURE

The basic postulate in this research, that tritium is produced by the action of the cosmic rays,⁸ appears to be confirmed by the data

⁸"Atmospheric Helium-3 and Radiocarbon from Cosmic Radiation." W. F. Libby, Phys. Rev., 69, 671 (1946).

available at present, though there is still further evidence to be obtained for the deep ocean samples. One sees, for example, that the rain waters can be much more radioactive with tritium than any surface water, and finds a rough correlation between the radioactivities of the surface waters and the rains, as seen below. If we make the following

definitions:

(a) Q = tritium production rate in T atoms per second per cm^2 at the particular location

TABLE 2

DATA ON TRITIUM TO DEUTERIUM SEPARATION FACTOR RATIOS

Sample	β/α Values	
	Observed	Average
Rain Water May 11, 1951		
D	> 2.4	2.5 ± 1.2
E	1.4 ± 0.7	
Lake Michigan July 7, 1952		
E	0.9 ± 0.8	4.3 ± 2.7
F	large	
Lake Michigan March 19, 1942		
C	1.3 ± 0.4	1.7 ± 0.2
D	3.6 ± 2.0	
Columbia University 1944		
D	2.1 ± 0.4	2.5 ± 1.1
E	3.5 ± 2.4	
Cistern, Decatur, Ill. 29 years old		
C	0.5	1.7 ± 0.5
D	> 5	
E	3.0 ± 0.3	
Standard Tritium Water #2		
A	1.9 ± 0.8	1.7 ± 0.4
B	1.5 ± 0.4	
Cistern, Sullivan, Ill. 14 years old		
B	1.4 ± 0.2	

- (b) $\bar{Q}$ = the world wide average tritium production rate per cm^2 per second
- (c) r = annual rain fall in meters at the particular locality
- (d) $\bar{r}$ = average annual rain fall in meters
- (e) (T_r) = the tritium concentration in rain (T atoms/H atom $\times 10^{18}$)
- (f) $(\bar{T}_r)$ = world wide average tritium concentration in rain

then we may set up an equation expressing the fact that essentially all the tritium produced by the cosmic rays must be precipitated as rain. This assumes that the tritium that goes into the hydrogen, as shown by Harteck and Faltings,⁷ is not an appreciable fraction of the total produced. This equation would be

$$\bar{Q} (3.16 \times 10^7) = \bar{r} (\bar{T}_r) \frac{100}{18} (1.2 \times 10^6), \quad (1)$$

or

$$\bar{Q} = \frac{\bar{r} (\bar{T}_r)}{4.7}. \quad (1')$$

In other words, if the mean annual rain fall all over the world be of an order of 1 meter and the tritium production rate should be of the order of 1 tritium atom per cm^2 of the earth's surface per second, then the average tritium content of the world's rain water should be 4.7×10^{-18} tritium atoms per average hydrogen atom.

It is certain that tritium is produced as a secondary product by the cosmic radiation, and being a secondary product probably parallels the neutron intensity curves. It has been shown that neutron production by cosmic radiation varies strongly with both latitude and altitude, the maximum production occurring at an altitude of about 45,000 feet and the latitudinal variation being such that it is a minimum at the equator and reaches maxima at the north and south poles in a symmetrical manner.⁹ These considerations have been developed and applied in the case of natural radiocarbon.¹⁰ Whereas in the case of the long

⁹"The Latitude Dependence of Neutron Densities in the Atmosphere as a Function of Altitude." J. A. Simpson, Jr., Phys. Rev., 73, 1389 (1948).

¹⁰"Radiocarbon Dating." W. F. Libby, University of Chicago Press, 1951; particularly Chapter 2.

lived radiocarbon no reflection of the latitudinal variation of the cosmic ray intensity was expected or found, it is expected that in the case of tritium a very strong variation with latitude, probably closely approximating the 3.5 or 4 fold neutron intensity variation between the equator and northern latitudes in the vicinity of Chicago, will be found.

Various theoretical problems connected with the distribution of tritium in nature present themselves immediately after we realize the general principles set forth above.

1. RAIN THEORY

The generation of tritium at the considerable altitudes where the cosmic rays are most active (we estimate the maximum to occur at something like 45,000 or 50,000 feet if the phenomenon of tritium production parallels that of neutron production) constitutes a continual contamination mechanism for atmospheric water. If we assume that vertical mixing is adequate, and this of course is a very considerable assumption, we may develop a theory for tritium rain fall which might be expected to be approximately true. As we saw above in Equation (1'), the average tritium content of rain will vary inversely as the average rain fall. As we shall see later, $\bar{Q}$ appears to lie between 0.5 and 1 T atom/cm²/sec, as deduced from the data in Table 1. Taking the world wide average rain fall to be 0.37 meters, we calculate that the average tritium content of rain should be 12.7 $\bar{Q}$, measured in units of tritium atoms per 10¹⁸ average hydrogen atoms, or between 6 and 13 x 10⁻¹⁸ tritium atoms per hydrogen atom.

The average moisture content of air appears to be about 9 grams of water per cm² of the earth's surface. From this it follows that the average residence time for water in the air is the ratio of the average content to the average annual rain fall, 0.09/0.373, or 0.24 years, or 3 months. In other words, the average water molecule which falls as rain has been out of the sea for 3 months. The mechanism for washing the tritium out of the atmosphere then consists in the evaporation of water followed by its reprecipitation about 3 months later as rain. Of course it may be that the figures used for this calculation are not the most authoritative, in which case the correct number should be substituted.* From this model it follows that the periods

*The authority for the rain fall figures and the atmospheric moisture content figure was "Water," C. S. Fox, Philosophical Library, Inc., 1952.

of drouth, in which the residence time rises inordinately, will be followed by very radioactive rain, and conversely, periods of heavy rain will result in low tritium assays. In fact, if T be the residence time for the moisture in a particular air mass, which for simplicity is assumed to move longitudinally at a constant latitude, one can write

$$QT = \frac{r(T_r)}{4.7} \quad (2)$$

In this equation T must be measured in years. If we imagine that the air mass follows a trajectory which crosses various latitudes, we then make a plot of the cosmic ray intensity Q to which it has been subjected as a function of time, this being done by converting its trajectory with the curve relating cosmic ray intensity to latitude. Then we write

$$\int_0^T Q(t) dt = \frac{r(T_r)}{4.7} \quad (3)$$

In other words, knowing the trajectory of an air mass, we should be able to predict the tritium concentration in rain fall occurring from it.

For a given type of air mass, the tritium content ought to be a nearly linear function of its residence time, T , and one can imagine that the measurement of the tritium concentration might be of general meteorological interest.

2. LAKE THEORY

As the rain falls it accumulates in lakes and rivers and either re-evaporates or returns to the sea. We consider first the lake problem. Making the following definitions:

- (a) ℓ = mean depth of the lake in meters
- (b) (T_ℓ) = tritium content of the lake water in T atoms/
 10^{18} H atoms.
- (c) A = effective drainage area in units of lake area.

we can write the conservation equation

$$4.7 Q = r(T_r) = \frac{r(T_\ell)}{1+A} + \frac{\ell(T_\ell)}{18(1+A)} \quad (4)$$

The first term in Equation (4) expresses the evaporative and out-flow loss of tritium. We assume that the lake level is steady and that the mixing is complete. This latter assumption means that the depth ℓ must not exceed a few hundred meters. All of the temporal phenomena involved in this theory are on the scale of the mean life of tritium, which is 18 years. The second term of Equation (4) expresses the radio-active decay law of tritium, 18 years being the mean life. The factor $1 + A$ corrects for the fact that tritium is collected from a wider area than the lake surface. The number A is not just the drainage area but is the drainage area divided by the area of the lake and further reduced by the ratio of the water actually delivered to the lake in streams to the total rain fall on the drainage area. In other words, it is corrected for evaporation from the water shed. For a lake such as Michigan, for which ℓ is 95 meters and r is 0.8 meters, we deduce

$$\frac{(T_r)}{(T_\ell)} = \frac{1}{1+A} \left(1 + \frac{\ell}{18r} \right) \quad (4')$$

The ratio of the tritium contents of the average rain water and the tritium content of the lake water should be $7.6/(1+A)$. It seems not unlikely that A may be of the order of 1, in which case we would

predict a 3.9 fold ratio for rain in the Lake Michigan area relative to the radioactivity of the lake. We note from Table 1 that Lake Michigan seems to average about 1.7×10^{-18} T atoms/H atom. From Equation (4') therefore we expect that the average rain fall over the area would average about 6.7, with a possibility that if A be negligible it might rise to 13. The question of the exact size of A requires further investigation. It is by no means certain that we shall be able to determine A accurately enough to use our Michigan assays for the determination of Q. This danger leads us to consider using waters from lakes with no water sheds, or relying essentially on rain or snow fall. The type of lake with a minimum value of A would be a volcanic crater.

3. OCEAN THEORY

In the case of the great open seas an additional mechanism for loss from the surface waters exists, in that the tritium may escape into the Great Depths. We define the Great Depths as all of the sea except for a thin surface layer of depth ℓ in meters in which mixing is rapid due to wave action. It appears that ℓ is likely to be in the vicinity of 800 meters.* If we introduce a new time constant τ (in

*Thanks are due to Prof. Fermi for considering this point and deriving a formula from which this estimate is made.

years), which measures the average time for a tritium atom to escape from the Surface Layer to the Great Depths, and the concentration of tritium in the Surface Layer be (T_S) , then our conservation relation becomes

$$4.7 Q = r(T_r) = r(T_S) + \frac{\ell(T_S)}{18} + \frac{\ell(T_S)}{\tau} \quad (5)$$

From this we predict that ocean water will be found to have a very low tritium assay. In fact, taking Q to be unity and the depth of the Surface Layer to be 800 meters, we find that (T_S) should be

$$\frac{4.7}{800} \left(\frac{1}{\frac{1}{18} + \frac{1}{\tau}} \right)$$

Even if we assume τ to be infinite, i.e., no escape to the Great Depths, we have a lake 800 meters deep, and its assay will be 0.11. If τ should be of the order of 1 year, which seems not unlikely, the tritium content will drop by about a factor of 10. In other words, the measurement of the tritium content of the open ocean may well reveal something about the rates of mixing in the surface waters and their rates of communication with the Great Depths. The simple theory presented here has taken no account of the surface currents. We probably should have written $\bar{Q}$ instead of Q. Obviously one must take care to determine for a given ocean current at what latitude the rain fall occurs on that part of the ocean feeding the current.

C. PROBABLE FUTURE USES OF NATURAL TRITIUM

Turning now to Table 1, if we take the Michigan assay to be 1.7 ± 0.2 on the basis of the two data contained there, and if we assume for simplicity that $A = 1$, i.e., the effective drainage area is just equal to the lake area, then we find $Q = 1.1$. As mentioned earlier in this report the observed latitudinal variation of the cosmic rays is so strong that the intensity at Chicago is reduced by a factor of 3.5 or 4 at the equator. If one makes a world wide average compensating for the fact that more land area lies in equatorial regions of lower latitude, one deduces that a measurement made at the latitude of Chicago should be multiplied by the factor 0.58 to convert it to a world wide average. Therefore we find $\bar{Q} = 0.65$ T atoms/cm²/sec from the Lake Michigan assay. If the number A be zero, then the assay becomes 1.3. It seems likely that the true production rate will lie between these limits, and it is interesting to make certain calculations on $\bar{Q}$'s being 1.0 as a sort of average possible value.

If $\bar{Q}$ be 1.0 T atoms/cm²/sec, then 5.1×10^{18} T atoms are formed each second on the earth, and the tritium assay required to maintain a steady state balance will be equal to $5.1 \times 10^{18} \times 18 \times 3.16 \times 10^7$, or 14.6 kilograms of tritium in the entire world. This quantity of course appears to be large, but one must remember that the rain water washes the tritium out of the air every 3 months, carrying with it only 200 grams of tritium. In other words, the steady state tritium content of the atmosphere is of the order of 200 grams.

It is a little early to predict possible future uses of natural tritium, but we begin to see the following possibilities:

- (1) The movement of air masses in meteorology and measurement of their ages, age being relative to the time the water evaporated from the sea or deep lakes which is contained in the air masses.
- (2) The movement of the surface waters of the ocean, particularly in the problem of mixing of the Great Depths and also the movement of the surface currents.
- (3) The determination of the age of agricultural products by assay of the tritium content of their tissue fluid, it having been established that the rain water - ground water - tritium content for a given region has a certain value. Then the tritium assay for the products should decrease exponentially with the lapse of time since harvesting.
- (4) The rate of escape of helium from the earth: When our world wide assay is completed we should know the total rate of production of tritium in the world. Since tritium produces He³ when it decays we would then have a lower limit for the rate of production of He³. The He³ content of the atmosphere is now known with some accuracy, and since this isotope is chemically non-reactive and radioactively stable, the only way in which it can escape from the earth is by leaving the earth to fly into interstellar space. Our assay, therefore, should yield for the first time a rigorous lower bound for the rate of escape of helium from the earth. The

reason that it is only a lower bound is that there may be other possible mechanisms for the production of He^3 by the cosmic rays as suggested by Morrison and Beard^{10a}. It seems unlikely, however, that these mechanisms would be more important than the tritium one, and

^{10a}" He^3 and the Origin of Terrestrial Helium." P. Morrison and D. B. Beard, Phys. Rev., 75, 1332 (1949).

so it is likely that the lower bound would not be less than the true value by more than a factor of two. The geophysical and geochemical usefulness of such a number is probably considerable. One sees possibilities of more quantitative considerations on the great geological processes which we observe to have occurred than have previously been possible.

D. MEASUREMENT PROGRAM PLANNED FOR THE FUTURE

Several cases of vintage wines have been ordered, an attempt being planned to determine conclusively whether the tritium content of natural waters is sufficiently constant in a vineyard fed solely by rain fall to afford a good correlation between age and the tritium concentrations in the product. These wines come from Spain and Southern France, and have been selected from very carefully chosen vineyards, the vintages ranging in one instance over a period of 20 years.

A collection program of sea waters has been instituted in which water from both the Atlantic and Pacific is being collected. We are taking samples from both the surface and the Great Depths. We expect, of course, that the ocean water assays will be very low and that for the deep ocean water will be essentially zero.

We are contemplating a rather extensive rain sampling program, utilizing the rivers in flood stage as a method of averaging over a considerable area. It appears to be necessary to take them in flood stage to avoid the incorporation of spring water which may have some antiquity. Another possibility we are considering is the utilization of a complete section of a full snow pack such as in the high Sierras, where each winter the snow melts completely and it seems probable that relatively little evaporation occurs during the winter. However, this latter point is still worrying us. We probably will need assistance in the procuring of samples from the great rivers of the world. We hope particularly to investigate a wide range of latitude.

Probably one of the most practical parts of our measurement program is the assay of a group of lakes with small water shed areas, but which are nevertheless deep enough to store water over a considerable period and yet shallow enough to insure thorough mixing. At the moment we are planning a sampling program from a series of such lakes spread over the northern and southern hemispheres.

IV. METHOD FOR THE ROUTINE ABSOLUTE INTENSITY AND ENERGY MEASUREMENT OF BETA RADIOACTIVITIES

(Abstracted from Doctoral Thesis of A. D. Suttle, Jr.)

A. INTRODUCTION

It has been noted in the past that the absorption of beta radiation is quite accurately exponential under certain geometrical conditions. Later work has fairly well established that with few exceptions the absorption curves are exponential in character if the source, absorber and detector lie in intimate contact, as for example in the arrangement in which the source constitutes the wall of a Geiger counter and the absorber is placed directly over it.¹¹ There is some

¹¹W. F. Libby, Anal. Chem., 19, 2 (1947).

evidence that the cylindrical geometry is important in itself, but it is quite probable that the essential condition is close proximity so that scattering effects by the absorber have no importance. Johnston and Willard¹² have recently demonstrated in a most conclusive fashion how serious scattering effects by the absorber can become. For example,

¹²F. Johnston and J. E. Willard, Science, 109, 11 (1949).

with an end window counter and a P³² beta source at shelf 4 of the standard arrangement, which places the beta source 5.4 cm from the counter window, and with a lead absorber 109 mg/cm² thick, placed directly on the sample, 3712 cpm was the observed rate, whereas placing the absorber 0.9 cm from the tube window and 4.5 cm from the sample gave 1856 cpm as the rate. Similar but somewhat smaller effects were observed with aluminum absorbers, indicating, as is well known, that the scattering effect increases rapidly with atomic number. Furthermore, the absorption curves taken with the standard end window counter arrangement usually are far from exponential, showing a strong tendency to curve with the thinner absorber thicknesses. For all of these reasons we adopt the practice of using close cylindrical geometry in the method of absolute assay developed in this research.

If it be assumed that the absorption of beta rays is strictly exponential, one immediately has at hand a method of absolute assay of beta radioactive solids. It is a principal purpose of this research to develop this technique. The methods will appear to be satisfactory if an accuracy no greater than 5 or 10 per cent is desired. These methods have been applied in this research to the measurement of the half lives of several of the naturally radioactive elements.

It has been observed often in the past that the absorption coefficient of a beta radiation is dependent upon the upper energy limit of the spectrum. With the increase in the number of accurately known beta ray energies it has been possible to formulate a range energy relation of some considerable accuracy, adopting aluminum as the standard absorption medium. This relation¹³ is represented analytically

¹³L. Katz and A. S. Penfold, Rev. Mod. Phys., 24, 28 (1952).

and graphically later in this paper (Figure 2). It appears to be remarkably accurate over the wide range of energies from 10 Kev to 2.5 Mev. One observes a very satisfying agreement between the recently accurately determined energies of the Rb^{87} natural beta spectrum with that obtained in this research by measurement of the absorption coefficient in aluminum and using the Katz and Penfold range energy relation. Similarly satisfying checks occur in the cases of K^{40} , the naturally radioactive potassium isotope, and P^{32} .

The instrument used in this research is the screen wall counter, which consists essentially of the usual center wire around which the sample being measured is placed on the inner wall of a cylinder. Between the sample and the wire is mounted a screen cathode which in the case of the present instrument consisted of a set of wires running parallel to the cylinder axis, the purpose of the screen cathode being to ensure smoothness of the electric field in the all important region near the counter wire and to minimize and obviate any effects of poor conductivity on the part of the sample itself. Figure 1 represents this instrument. Two conditions of operation are available for this instrument, the one in which the sample is at a negative potential with respect to the screen cathode, known as the "drag in" condition, and the other in which it is at a positive potential, known as the "drag out" condition. In the drag in condition it is easily proven experimentally that the sensitive volume of the counter extends clear to the sample, so one is assured of very nearly complete counting of any radiation which enters the cylindrical volume defined by the sample and the cylinder on which it is mounted. In the drag out condition the volume defined by the screen cathode itself is the sensitive volume and the solid angle subtended by this body at the sample is of course less than the 2π figure which obtains under drag in conditions. The drag out condition is useful in a number of ways. The principal use made in this research has been to use the gas between the sample and the screen cathode as an absorber so that absorption curves of beta emitters as weak as tritium (18.9 Kev) and Zr^{97} (60 Kev) could be determined. The absorption coefficients obtained (cf. Table 4) are in very satisfactory agreement with the spectroscopically determined energies. It seems therefore safe to conclude that we are able to measure the energy of a pure beta spectrum by measuring the absorption coefficient of the radiation emitted from the solid sample in aluminum. This technique, developed largely in this research, though used previously on various occasions in somewhat more elementary form, is used to determine the energies of the various naturally radioactive elements.

With the procedures developed in this research, it should be possible to complete absolute intensity and energy measurements for isotopes emitting pure beta radiation in essentially a routine manner providing errors of 5 or 10 per cent are tolerable. It has been the principal purpose of this research to develop these methods for the routine assays of beta radiation and to apply them to naturally radioactive elements.

B. DEVELOPMENT OF THE METHOD

The screen wall counter was used throughout this research for

1 - DISTANCE FROM SAMPLE TO
SCREEN.

2 - DISTANCE FROM ABSORBER TO
SCREEN.

θ - DIHEDRAL ANGLE IN WHICH
ELECTRONS WILL COUNT UNDER
DRAG OUT CONDITIONS.

A - COUNTER WALL

B - SAMPLE CYLINDER WALL

C - SAMPLE

D - ABSORBER

E - SCREEN

F - CENTER WIRE

Fig 1

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the measurement of all solid samples.^{14,15,16} The biasing voltage for

¹⁴W. F. Libby, Phys. Rev., 46, 196 (1934).

¹⁵W. F. Libby and D. D. Lee, Phys. Rev., 55, 245 (1937).

¹⁶E. A. Martell, "The Natural Radioactivity of Indium 115," Ph. D. thesis, University of Chicago, 1950.

the sample cylinder relative to the screen cathode ranged between 50 and 300 volts. The counter filling employed was 1.5 cm of ethylene and 15 cm of argon unless gas absorption curves were being measured for soft beta emitters under the drag out condition. This standard filling gave an operating potential of about 1800 volts with a 10 mil center wire. "O-ring" seals were used for the end caps. Lead free brass was the material of construction.

The gaseous samples used in this research were measured in flat ended Geiger counters constructed by the use of lucite plugs in the ends of a brass or copper cylinder, these plugs being waxed in position.

The electronics were standard in all respects. Data were usually taken to 1 per cent statistical error, i.e., at least 10,000 counts were recorded. The chemical apparatus is standard in type and the procedures usually orthodox in nature.

The enormous effects of absorption scattering, demonstrated by many workers and more recently by Johnston and Willard,¹² some of whose results are presented in Table 3, require the most elaborate conclusive demonstration that the exponential absorption law holds under the conditions of our measurements. Figures 2 through 16 inclusive, which present both drag in and drag out absorption curves in copper, in aluminum, and in some cases the gases argon and helium, for K^{40} , P^{32} , Co^{60} , T , Zr^{97} , and Rb^{87} , clearly demonstrate the validity of the exponential law in our apparatus. From these data one obtains absorption half thicknesses, and from the range energy relation of Katz and Penfold¹³

$$R = 412 E[1.265 - 0.0954 \ln E]$$

(R in mg of Al/cm² and E in Mev), (6)

one obtains range values corresponding to the spectroscopically determined energies of many of these radioactivities. Table 4 presents these results. Column 6 of this table gives the ratio of the range to the observed half thickness. It has been noted several times that the range and absorption coefficient are related.^{11, 17, 18}

¹⁷J. A. Chalmers, Proc. Camb. Phil. Soc., 28, 319 (1932).

¹⁸B. W. Sargent, Can. J. Res., 17, 82 (1939).

It is clear from Table 4 that for beta spectra of energies less

TABLE 3

Observed Count Rate as a Function of Position
for End Window Counters*

Energy of Beta Radiation (Mev)	Absorber and Thickness (mg/cm ²)	Distance (cm) of Bottom of Absorber from		Observed Count Rate
		Sample	Counter Center	
1.69	109 of Pb	0	5.4	3712
		1.5	3.9	3200
		3.0	2.4	2528
		4.5	0.9	1856
1.69	102.7 of Al	0	5.4	6368
		1.5	3.9	5568
		3.0	2.4	4512
		4.5	0.9	4288
(For the data below a collimated source of 12° angular spread was used.)				
1.69	50.7 of Pb	1.5	5.8	312
		3.0	4.3	425
		4.3	2.8	661
		6.0	1.3	1045
1.69	120 of Al	1.5	5.8	369
		3.0	4.3	491
		4.5	2.8	737
		6.0	1.3	1185

*Source: Johnston and Willard, op. cit., p. 11.

than .76 Mev the range is about 13.5 times the half thickness. ⁶¹⁴C appears to be a slight exception in presenting the ratio of 15.5, and it seems that the higher energy beta radiations of ³²P and ⁴⁰K, 1.71 and 1.36 Mev respectively, have a lower ratio of about 9.5. If for the moment we can consider that the range, l_0 , is proportional to the half thickness, $l_{1/2}$; and assuming that the absorption is strictly exponential, as the data presented show to be nearly true for our equipment and procedures using close geometry, one can set down the following general relations:

(1) Absolute activity of an infinitely thick beta radioactive solid: Consider a layer of the solid 1 mg/cm² from the top surface and of thickness dl mgm/cm², then the radiation (dI) escaping from this layer to the counter at the top surface will be

$$dI = \frac{\sigma A e^{-.693 \frac{1}{l_{1/2}} dl}}{S} \quad (7)$$

if σ is the absolute disintegration rate per mg of solid, A is the

Fig. 2

Fig 3

Fig. 4

3/34-29

Fig 5

26

3/34-30

Fig. 1

82

3/34-32

Fig 7

Fig 8

3/13/4-34

Fig 9

15

5/13/43

COUNTING RATE (cpm)

100
80
70
60
50
40
30
20
10

0.2

0.4

0.6

0.8

1.0

1.2

1.4

ABSORBER THICKNESS (mg A/cm²)

Fig 10

Fig 11

32

3134-36

AN-243-9

FIG. 12

Fig 13

32

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FIG. 14

Fig 12

36

3134-40

Fig 16

57

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TABLE 4

Value in Aluminum of Absorption Coefficient, Half Thickness, Range and Ratio of Range to Half Thickness for Various Beta Emitters

Isotope	E_{β} Max. (Mev)	Half Thickness (mg/cm ²)	Absorption Coefficient (cm ² /mg)	Range (mg/cm ²)	Ratio of Range to Half Thickness	References
T	0.0189	0.050	13.9	0.7	14.0	Fig. 14
Zr ⁹⁷	0.060	0.35	1.98	5.0	14.3	Fig. 15, a
Sm ¹⁵¹	0.0755	0.63	1.10	8.7	13.8	b
Cl ³⁴	0.155	1.93	0.359	30.0	15.5	Fig. 22
Rb ⁸⁷	0.270	4.85	0.141	63.6	13.1	Figs. 16 - 19 incl.
Tc ⁹⁹	0.296	6.09	0.114	76.5	12.6	c
Co ⁶⁰	0.319	6.30	0.110	83.5	13.3	d, c
In ¹¹⁵	0.63	16.0	0.043	212.0	13.2	d
Tl ²⁰⁴	0.762	20.6	0.0337	283.0	13.7	f
K ⁴⁰	1.36	67.0	0.0139	605.0	9.1	Figs. 7 - 11 incl.
P ³²	1.708	84.3	0.0120	801.0	9.5	g

^aE. P. Steinberg and L. E. Glendenin, Phys. Rev., 78, 624 (1950).

^bH. M. Agnew, Phys. Rev., 77, 655 (1950).

^cM. S. Freedman, Abstracts New York Meeting American Phys. Soc., January, 1952.

^dMartell, op. cit., Table 4.

^eM. A. Waggoner, M. L. Moon, and A. Roberts, Phys. Rev., 78, 295 (1950).

^fNuclear Data, NBS Circular 499, Supp. 2 (value of L. G. Elliott and R. E. Bell is quoted).

^gS. D. Warshaw, J. J. L. Chen, and G. L. Appleton, Phys. Rev., 80, 288 (1950).

area of the solid in cm^2 , and $1/g$ is the geometry factor, usually one-half. Integrating, we obtain

$$I_{\infty} = \frac{\sigma A l_{1/2}}{g \cdot 0.693} \quad (8)$$

as the expression for the total intensity expected from an infinitely thick layer. If for example the half thickness is taken to be $1/13.5$ of the range l_0 , we can write

$$I_{\infty} = \frac{\sigma A l_0}{g \cdot 13.5 \cdot 0.693} \quad (8')$$

or

$$I_{\infty} = 0.054 A l_0 \sigma \quad (8'')$$

when g is taken as 2.

In other words, 5.4 per cent of the total radiation emitted by a layer of thickness equal to the range will be recorded. Direct experimental test of this has been accomplished in the case of Cl^{40} , in which the measured efficiency of 5.46 per cent is found.

(2) Activities expected from samples of finite thickness: If the samples be of finite thickness integration of Equation (7) gives

$$I = \frac{A \sigma l_{1/2}}{0.693 g} (1 - e^{-0.693 \frac{l}{l_{1/2}}}) \quad (9)$$

or, using the 13.5 ratio of l_0 to $l_{1/2}$, we have

$$I = 0.054 A \sigma l_0 (1 - e^{-9.45 \frac{l}{l_0}}) \quad (9')$$

(3) Absorption curve: If $l_0/l_{1/2}$ be assumed to be a constant ratio the absorption curves are all superimposable by a scale change such that the unit thickness of absorber is l_0 . In other words, analytically

$$I = I_0 e^{-9.45 \frac{l}{l_0}} \quad (10)$$

in which I_0 is the intensity with zero absorber.

(4) Self absorption curve: Consider a given number of milluries of beta radioactivity which is successively diluted with inert material making a thicker layer always of the same area, A . What will be the count rate for each of the various dilutions? Stating all thicknesses in terms of l_0 as a unit, then a thickness l will be given as x , the dimensionless quantity l/l_0 . In these terms the initial thickness x_0 contained $A l_0 x_0 \sigma_0$ disintegrations per minute or disintegrations per second, depending on the definition of σ_0 , of

beta radioactivity. For any other thickness x we have

$$\sigma_0^A l_0 x_0 = \sigma^A l_0 x . \quad (11)$$

In this equation x/x_0 is the dilution ratio. Returning to Equation 9 we have

$$I = \frac{\sigma_0 x_0 l_0^A (1 - e^{-9.45 x})}{x g 9.45} \quad (12)$$

writing the intensity for the very thin layer x_0 as I_0 , we have

$$\frac{I}{I_0} = \frac{1 - e^{-9.45 x}}{9.45 x} \quad (12')$$

This is a self absorption curve of general applicability.

(5) Backscattering effects for samples of finite thickness:

As a practical consideration beta emitting solids of thickness less than l_0 and mounted on other solids of thickness not negligible with respect to l_0 display a radioactivity in excess of that which would be calculated from the above equations, due to the scattering of radiation by the underlying supporting solid matter. Glendenin and Solomon¹⁹ have shown that the backscattering effect for a series of solids of widely varying atomic number is identical for P^{32} of 1.7 Mev and S^{35} of 0.167 Mev. The magnitude (Y) of the backscattering effect was found to depend on the atomic number of the backscattering material, and is given approximately by

$$Y (\%) = 130 (1 - e^{-0.693 \frac{Z}{30}}) , \quad (13)$$

in which Z is the atomic number of the backscatterer. It has been demonstrated further by Glendenin and Solomon¹⁹ and others that the

¹⁹L. E. Glendenin and A. K. Solomon, Science, 112, 623 (1950).

backscattering radiation is less penetrating, its half thickness for absorption being approximately half that of the radiation incident on the backscatterer. In other words, if the half thickness of the primary beta radiation be x mg/cm², that of the backscattered radiation will be $0.5 x$ mg/cm².

With these generalities at hand it is possible to calculate the absolute specific activity from the observed radioactivity of a beta radioactive solid of known chemical composition or of known average atomic number, and deposited on a sample support of known atomic number over a known area and with a known thickness, which must be smooth unless the sample be thicker than the range.

For example, a weakly radioactive BaCO₃ sample weighing 294 mg and spread over 3.16 cm² of area was observed to give 6.6 cpm with a

counter having a wall thickness 2.62 mg/cm^2 and with a geometry factor g of 2.5, i.e., 0.40 as $1/g$. The mean atomic number of BaCO_3 is 13.5, which is close to that of aluminum, so self scattering effects would be at a minimum. The half thickness of radiocarbon is 1.94 mg/cm^2 , and since the deposit was thick as compared with the radiocarbon range, no backscattering from the underlying lucite support need be considered. Therefore the absolute specific activity (dpm/mg) will be

$$\frac{6.6 \times 10^6 \times \frac{2.62}{1.94} \times 0.693 \times 2.5}{3.16 \times 1.94}$$

or 4.8 dpm/mg for a total activity of 1405 dpm or, 0.00063 μc in the 294 mg sample. This type of employment of the method outlined in this paper gives a result of considerable importance to the radiochemistry in that it makes possible many determinations not otherwise made and allows a complete check on the radioactivity because it converts to an absolute basis. For instance the partial combustion of a radioactive organic material might form carbon dioxide and a solid residue the radiochemical assay of which would present some difficulties. By the use of the methods described here it is possible to correlate a gas counter determination of carbon dioxide activity with a count made on the solid organic residue. A check on this is of course readily possible in this instance by completing the combustion and assaying the residual carbon dioxide gas. In other cases, however, such conversion to a common chemical state is not possible. For example, if a noble gas be in radioactive equilibrium with a solid parent there is little possibility of checking the absolute assays of the two radioactivities by placing in the same chemical state, so even the simplest determination of the relative activities is a matter of some difficulty. With the present procedure one would measure the noble gas in a gas counter, measure the freshly milked solid parent under conditions of close cylindrical geometry and by the methods outlined here calculate absolute activities for both.

V. NEGATIVE PI MESON ACTIVATION OF BROMINE

(From the doctoral thesis of T. T. Sugihara)

A. INTRODUCTION

General

The existence of mesons, particles of mass about 300 times the electron mass, was postulated by Yukawa²⁰ in 1935 to account for nuclear

²⁰H. Yukawa, Proc. Math. Phys. Soc., Japan, 17, 48 (1935).

forces. Subsequently such particles, later identified as π mesons, were found as secondary particles in cosmic radiation. The two types of mesons best known currently are the π and μ mesons although other

types, of much higher mass, have been reported.²¹ The π (for primary)

²¹For example, Brown, Camerini, Fowler, Muirhead, Powell, and Hitson, Nature, 163, 47 (1949); 163, 82 (1949).

meson has been found in cosmic rays and is produced artificially in high-energy accelerators. The μ is a decay product of the π . The identity of π mesons detected in cosmic rays and those created artificially has been shown: Their masses are the same, the same "prong distributions" (see the next section of this chapter) are obtained, and the number of star-producing mesons (i.e., those that produce nuclear disintegrations) in cosmic rays which are not π mesons is either zero or small.²²

²²C. Franzinetti, Phil. Mag., 41, 86 (1950).

There is evidence, however, that π mesons in about 9 per cent of cases of capture also lead to stars.²³ In general no separation of data will be made as to the origin of π mesons. The constants applicable

²³E. P. George and J. Evans, Proc. Phys. Soc. (London), A64, 193 (1951); Sherman, Heckman, and Barkas, Phys. Rev., 85, 771 (1952); W. F. Fry, Phys. Rev., 85, 676 (1952).

to π and μ mesons are listed in Table 5.

TABLE 5
Properties of Mesons

Property	$\pi^{\pm}$	π^0	$\mu^{\pm}$
Rest mass (m_0)	275	265	208
Spin	0	0	1/2
Half-life at rest, in vacuo (sec.)	1.84×10^{-8}	$<10^{-13}$	2.15×10^{-6}
Decay products	$\mu^{\pm} + \nu$	2 γ	$e^{\pm} + 2\nu$

Fast π mesons--that is, those with kinetic energy--interact with bulk matter in a manner intermediate between that of protons and electrons. Ionization is the chief interaction in the slowing down process. Negative π mesons have a strong interaction with nuclei both in flight and at rest while positive ones at rest are repelled by the coulomb barrier. The total cross-section of $\pi^{\pm}$ has been found to be approximately geometrical for all nuclei that have been studied. 24, 25, 26

²⁴Bernardini, Booth, Lederman, and Tinlot, Phys. Rev., 82, 105 (1951); 80, 925 (1950).

²⁵Camac, Corson, Littauer, Shapiro, Silvernian, Wilson, and Woodward, Phys. Rev. 82, 745 (1951).

²⁶Martin, Anderson, and Yodh, Phys. Rev., 85, 486 (1952).

Geometrical is defined as

$$\pi A^{2/3} \left(\frac{\hbar}{\mu_{\pi} c} \right)^2$$

for these purposes

The theoretical process of capture of π mesons has been considered in the case of liquid hydrogen²⁷ and in the general case.^{28,29}

²⁷A. S. Wightman, Phys. Rev., 77, 521 (1950).

²⁸E. Fermi and E. Teller, Phys. Rev., 72, 399 (1947).

²⁹J. A. Wheeler, Phys. Rev., 71, 320 (1947).

The π^- , when its energy has been reduced sufficiently, moves into the outer electronic orbit of an atom and successively cascades from shell to shell until absorbed in the nucleus. The lifetimes of all these transitions are short compared to the half-life toward decay. Consequently no π^- at rest is expected to decay under ordinary conditions. This is especially true for heavier elements since the probability of capture increases with Z .²⁹

When a π^- meson at rest is absorbed by a nucleus, the entire rest mass, about 140 Mev, is available for excitation. With protons and deuterons the following reactions have been observed:³⁰

³⁰Panofsky, Aamodt, and Hadley, Phys. Rev., 81, 565 (1951).

$$\pi^- + p = \begin{matrix} p + \pi^0 \\ n + \pi^+ \\ n + \gamma \end{matrix} \text{ (scattering)}$$

$$\pi^- + d = \begin{matrix} 2n + \gamma \\ 2n + \pi^0 \\ 2n \end{matrix}$$

It is assumed that within nuclei the exchange reaction.

$$\pi^- + p = n$$

occurs constantly. Such a reaction is not possible between individual nucleons since momentum cannot be conserved. The exchange reaction is postulated to explain nuclear forces.

The interaction of π mesons with nucleons in a nucleus is with at least two particles at a time. Tamor³¹ has calculated what might

³¹S. Tamor, Phys. Rev., 77, 412 (1950).

be expected experimentally for two models. In model I the π^- is absorbed by a proton or a proton-proton or proton-neutron pair, and the recoil momentum is taken by a single nucleon, either a neutron or proton. In Model II the recoiling particle is a triton, the residual part of an alpha particle of which the absorbing proton is taken to be a member. The neutron in this case carries away 95 Mev while the recoil triton has 31 Mev, which goes into excitation of the nucleus.

Photographic Plate Meson Studies

The result of the capture of a π^- by a nucleus in a photographic plate is a star, in which the tracks of ionizing particles leaving the excited nucleus can be distinguished. In general the stars are classified according to the number of emitted tracks or prongs that appear. In the case where only neutrons are emitted after capture, no tracks are seen except for a very short one due to the recoil of the resultant nucleus. These are called zero-prong stars. Some ambiguity exists in this classification since it is sometimes difficult to distinguish between a recoil prong and the track of a low energy proton or alpha particle. The standard practice seems to be to classify all tracks less than 5 or 6 microns long as recoil prongs.

In the capture of artificially created π^- mesons in photographic plates the following prong distributions have been found. In cosmic-ray plate studies it has been found that slow π^- mesons give rise to zero-prong stars 27 per cent of the time and one-prong stars 26 ± 6 per cent of the time.³²

³²W. F. Fry, Phys. Rev., 83, 594 (1951); 82, 747 (1951).

TABLE 6

π^- Prong Distributions

Number of Prongs (1)	Percentages			
	(2) ^a	(3) ^b	(4) ^c	(5) ^d
0	26.8	35.2	28.0	9.5
1	21.5	13.3	24.0	29.9
2	27.0	21.9	24.0	21.2
3	15.2	18.9	16.1	21.2
4	7.8	8.8	6.7	16.5
5	1.8	1.9	1.2	1.6

^aSlow mesons, F. L. Adelman and S. B. Jones, Science 111, 226 (1950).

^bSlow mesons, W. B. Cheston and L. J. B. Goldfarb, Phys. Rev., 78, 683 (1950).

^cSlow mesons, Menon, Muirhead, and Roohat, Phil. Mag., 41, 583 (1950).

^dFast mesons, G. Bernardini, quoted in Proceedings of the International Conference, Nuclear Physics and the Physics of Fundamental Particles, Chicago, 1951.

In this research we study the π^- capture in bromine by radio-chemical techniques. The correlation of data obtained from photographic plates and those from this research, then, will be somewhat uncertain since the stars observed in emulsion can result from π^- capture in silver, bromine, carbon, oxygen, or nitrogen nuclei. Menon and associates³³ have attempted to classify the stars they have observed in

³³Menon, Muirhead, and Rochat, Phil. Mag., 41, 583 (1950).

plate studies on the basis of light and heavy nuclei absorption. The prong distribution they obtained is given in Table 7.

TABLE 7
Prong Distribution Classified According
to Light or Heavy Nuclei Capture

Number of Prongs	Percentages			Observed
	Light	Heavy	Light + Heavy	
1	11	27	37	33.9 ± 1.4
2	13	18	31	31.3 ± 1.3
3	15	4	20	21.8 ± 1.1
4	6	4	10	10.9 ± 0.8
5	1	1	2	1.9 ± 0.3
Totals	46	54	100	

Their classification of heavy nuclei includes silver and bromine (mean mass number = 100) and of light nuclei, carbon, oxygen, and nitrogen. These distributions are averages based on three different methods of distinguishing between heavy-nuclei and light-nuclei capture. The premises on which these methods are based are the following: (1) Three-prong stars are of much higher frequency in the gelatin than in the silver bromide of the emulsion, (2) alpha tracks occur five times as often in light nuclei stars as in heavy, and (3) heavy nuclei are more likely to emit Auger electrons in capture. Their experimental results indicate for heavy nuclei on the average 1.1 ± 0.15 prongs per star, average nuclear-excitation energy of 109 Mev and an alpha to proton distribution of 0.30 ± 0.04 .

A further difficulty in analysis exists in that the charge is not directly related to the prong distribution since not all prongs are due to protons but some to alpha particles. Only very rarely are identifiable heavier nuclei, such as Li^6 "hammer tracks," observed. If Menon's data are extended to include zero-prong stars on the basis of his results that 28 per cent of all prongs are zero-prong stars and 80 per cent of these are due to heavy-nuclei capture, then the resulting distribution is as shown in Table 8.

In column (3) the percentage is based on capture in all nuclei, light and heavy. The percentages in column (4) are calculated from

TABLE 8

Prong Distribution Including Zero-Prong Stars

Number of Prongs (1)	Percentages		
	Light (2)	Heavy (3)	Heavy (4)
0	7	21	34
1	8	19.5	33
2	9.5	13	22
3	11	3	5
4	4	3	5
5	0.5	0.5	1
Totals	40	60	100

column (3), considering only heavy-nuclei captures. For example, 21 per cent of captures in all nuclei result in zero-prong stars in heavy nuclei while 34 per cent of heavy-nuclei stars are zero-prong.

The Purpose of This Research

It is clear from the inspection of photographic-plate studies that the residual nucleus after star formation has a high probability of being radioactive. For example, let us consider a one-prong star in a nuclear emulsion and assume that the capturing nucleus is a bromine nucleus. The one prong indicates that a proton, deuteron, alpha particle or perhaps some other ionizing particle has been ejected from the capturing nucleus. An unknown number of neutrons has also been ejected. The bromine nucleus after capture is an excited selenium nucleus. If the prong is the track of a single-charged particle, the resultant nucleus is an arsenic isotope. Since only one of the nine arsenic isotopes is stable, the resultant nucleus is quite likely to be radioactive. Similar considerations apply if the prong is the track of a double-charged particle and the resultant nucleus is a germanium isotope.

In this research liquid bromine was irradiated with π^- mesons. If to the irradiated bromine, carriers of elements near bromine in atomic number are added and separated according to radio-chemical techniques, one would expect to be able to separate out the resultant nuclei of π^- capture according to their chemical nature. If these chemically different samples are counted on a Geiger counter calibrated for efficiency and geometry and activities are identified on the basis of half-life and/or energy, it should be possible to calculate what per cent of meson capture led to the formation of each of the identifiable activities. The radiochemical approach to π^- capture studies should then give more information than plate studies of prong distributions as to particles emitted and resultant nuclei since the exact change in nuclear charge and the number of neutrons ejected can be determined. The choice of bromine as a target is obvious since prongs in photographic plates are due in large measure to π^- capture in

silver and bromine. This same sort of research is also under way with silver as the target.³⁴ Turkevich and Niday³⁵ have found the Cl^{11} yield

³⁴W. Goishi and W. F. Libby, private communication.

³⁵A. Turkevich and J. B. Niday, Phys. Rev., 84, 1253 (1951).

from water as a target to be about 2 per cent and the Cl^{11} yield from an 11M solution of NH_4NO_3 to be 3.6 per cent. It is hoped that π^- capture in all the elements in a photographic emulsion will be studied eventually.

A new type of difficulty in experimental technique arises in radiochemical research by meson activation. All samples to be irradiated must be large if the full benefit of the meson beam is to be utilized. This arises from the following considerations: The meson intensity locally available (about 6×10^5 per minute) is several orders of magnitude lower than that obtainable for neutrons, protons, gammas, etc., so that one must use the full range of the mesons in a target to ensure that all mesons are stopped in the sample irradiated. Otherwise count rates may be so low that resolution of decay curves will not be possible. The range of π^- mesons in matter can be calculated from known proton ranges in the same matter.³⁶ The π^- ranges in copper and silver are shown graphically in Appendix I. From these curves the range in bromine can be estimated by interpolation. For 122 Mev π^- mesons--the energy at which the highest intensity is obtained on the Chicago synchrocyclotron--the range is about 55 gms/cm². If the capture cross-section is geometrical, i.e.,

$$\pi A^{2/3} \left(\frac{h}{\mu \pi c} \right)^2$$

or 1.13 barns, about 37 per cent interact in flight and 62 per cent at

³⁶W. A. Aron, Ph.D. Thesis, Univ. of Calif., 1951.

rest at the end of the range. The remaining 1 per cent undergo $\pi^- \mu$ decay in flight. Since the density of bromine is about 3.1 gms/cm³, the range corresponds to 18 cm. The meson beam has a diameter of about 8 cm.³⁷ Volumes of sample must then be about $\pi(4)^2(18)$ or 905 ml. It

³⁷N. Sugarman and A. Turkevich, private communication.

has been necessary to devise an experimental chemical separation procedure in which tracer amounts of selenium, arsenic, germanium, gallium, and zinc could be separated rapidly and quantitatively from a liter of bromine. Radiochemical studies of π^- activation may be limited because of the difficulties of the chemical treatment of large samples, especially solid samples. Fortunately, in the case of liquid bromine an aqueous acid extraction procedure could be used to effect the necessary separations.

In other meson-activation studies now in progress, Sugarman³⁸

³⁸N. Sugarman, Bull. Am. Phys. Soc., 27, No. 2 (1952). 3.34 51

reports that the irradiation of mercury with fast mesons causes fission to occur about 2 per cent of the time.

About 10 per cent of slow π^- capture leads to protons of energy greater than 30 Mev. Similarly, high-energy neutrons are expected to be produced. Consequently, it is not unreasonable to expect secondary reactions to be induced, although Turkevich and Niday³⁵ have found secondary neutron-induced reactions to be negligible in the formation of Cl^{11} from water or NH_4NO_3 solution. Besides the straightforward irradiation of a sample with mesons it is usually necessary to make a series of auxiliary experiments to determine the effect of secondary reactions. In this research this determination will be made by looking for activation beyond the range of π^- in bromine.

The general plan of this research is as follows:

(1) Irradiate liquid bromine; look for radioactivity in chemically separated samples of selenium, arsenic, germanium, gallium and zinc. Repeat irradiations enough times to check the reproducibility of numbers. Check for absence of activity when the meson-beam magnet is off. As a preliminary experiment irradiate bromine and perform carrier separations of a scavenging type to determine what general chemical group contains the most activity.

(2) Irradiate solid bromine in disks, each about one-fourth of the range in thickness, using more disks than the range. Look for activity beyond the range. At the same time determine the yield versus energy relationship, i.e., the relationship of capture in flight to capture at rest. Confirm the solid-bromine experiment by irradiating bromine behind absorbers that are sufficiently thick to be the range in that material. Look for the same activities in bromine as found when absorbers are not present.

B. EXPERIMENTAL PROCEDURE: IRRADIATION

The Meson Beam and Irradiation Geometry

The meson beams from the 170-inch synchrocyclotron of the University of Chicago are obtained from the proton beam impinging on a beryllium target. The π^- mesons formed in a forward direction are thrown out of the cyclotron by the fringing magnetic field. Ports, 6 inches by 6 inches, of proper angle in the median plane of the cyclotron have been placed in the 6 feet of steel shielding (12 feet in run 7 and subsequently) between the cyclotron pit and the adjoining experimental room so that beams of π^- mesons of known energy are available in the experimental room. A schematic cross-sectional view of the median plane of the cyclotron and surroundings is shown in Figure 17. Since the highest intensity is obtained in the 122-Mev channel, it has been used throughout this research except for the first run in which the 145-Mev channel was used.

The 122-Mev π^- beam contains neutrons, protons, electrons, and μ^- mesons as contaminants in coming through the port. In order to remove most of these, the beam is bent through 45 degrees by a deflecting

6/7

3/34-53

Fig 17

magnet. The composition of the beam after deflection²⁶ is 95 ± 4 per cent π^- , the remainder being negatively charged particles of lighter mass but of same momentum as the π^- mesons. The beam focuses at a point 54 inches from the front vertical-pole-face of the deflecting magnet. An additional iron shield, a 30-inch cube, with a 6-inch by 6-inch channel down the middle, is placed in front of the deflecting magnet to eliminate stray radiation. After the addition of six extra feet of steel shielding between the cyclotron pit and the experimental room, it was found in run 7 that the cubical iron shield was not necessary from a background point of view. Hence it was not used in run 8.

Because of the dangers associated with the leakage of bromine during an irradiation, a special container was built to contain the sample. A commercial one-liter bromine bottle was placed in a wooden box lined on the outside with 1/32-inch copper sheet. The bottle rested in a reproducible position between two sets of half-moon supports above and below. The flat end of the bottle faced the beam. The outside dimensions of the box were such that it fit closely in the channel of the iron shield. The space between bottle and box was packed with the commercial absorbent in which bromine bottles are shipped. This was the irradiation geometry for the liquid-bromine bombardments. The inside dimensions of a one-liter bromine bottle are as follows: overall length 22.5 cm, length of neck about 4 cm, and diameter 10 cm. The bromine depth was about 8 cm when the bottle lay on its side during an irradiation. The solid-bromine disks, encased in open-ended pyrex cylinders, were placed on a 1/32-inch copper sheet shaped into a half-cylinder which was held in place by three half-moon supports on the bottom of a wooden box. All the space around the disks was packed with dry ice. The method of preparation of solid bromine is given in Appendix II.

Before a sample was put in place to be irradiated, the location of the beam was checked with a pair of scintillation counters in coincidence. Up to and including run 5 a scintillation counter of 4-inch effective diameter was placed 44 inches from the front vertical-pole-face of the deflecting magnet, and one of 3-inch effective diameter was placed 13 inches from the 4-inch one. The position of the two counters relative to each other was only moderately reproducible, but the coincidence rate was not sensitive to small displacements. In runs 7 and 8, two 4-inch scintillation counters of higher efficiency than the previous two were used, and the distances were 8 inches between counters and 48 inches from the deflecting magnet to the first counter. The distance from the magnet to the bottle was about 24 inches. In run 8 the front solid-bromine disk was about 10 inches from the magnet.

Meson Intensity

The cyclotron current is monitored by the heat dissipated in the beryllium target struck by the proton beam. A thermocouple output is fed into a Brown recorder so that the beam is continuously monitored. The coincidence counting rate is determined per watt of cyclotron intensity per minute. The deflecting magnet current is set at the maximum count rate for a fixed-target wattage and left at this setting throughout the bombardment.

The box containing the sample is then placed in the proper position, and the irradiation is begun. On several occasions the coinci-

dence rate when the sample was in place was checked. This was on the order of 3 per cent of the impinging π^- beam. The 3 per cent probably consists of μ^- mesons. However, since the background of the scintillation counters was not clearly known, this figure is not meant to imply the μ^- content of the beam. It was quite clear in any case that virtually all the π^- mesons had been absorbed in the sample and box.

Lengths of runs 1 to 7 varied from 1 hour to 6 hours. The meson intensity in these runs was about 35,000 per watt-minute. The operating level of the cyclotron ranged from 8 watts to as high as 20 watts, the average being about 14 watts. Control runs were made in order to determine the background, that is, activities induced by incident radiation other than mesons. These were done by turning off the deflecting magnet and leaving all other conditions the same. In general, control runs were made immediately before or after a meson run (in which the deflecting magnet is on) in order to minimize the systematic errors. A comparison of results (see section V-E) for the two types of runs indicates that not more than 5 per cent of the activities observed could have been induced by non-meson activation although secondary neutrons produced by mesons might contribute. The cyclotron intensity was quite low in run 8, about 3 watts being the average, so that the run was continued for 11 hours. The meson intensity for this run was raised to about 71,000 per watt-minute by using a 4-inch by 5-inch magnet pole-opening instead of the 2-inch by 3-inch opening used in all previous runs and by deflecting the beam through an angle of about 40 degrees instead of the 45 degrees used previously. The higher intensity may have been observed because of the greater sensitivity and larger effective area of the second pair of scintillation counters.

Calculation of Expected Disintegration Rates

Since the operating level of the cyclotron varied over wide limits during a run, there is no simple scheme to determine the disintegration rate expected for an isotope. The following method was found to be satisfactory for this calculation:

Let $\lambda \text{ min}^{-1}$ be the decay constant of the isotope in question. The cyclotron watt-meter is read every 2 minutes and then the readings totaled over a 20-minute interval. There are i_f such 20-minute intervals in the run. This totaled watt-minute reading (I_1) is multiplied by the number of mesons per watt-minute (N). The product NI_1 is corrected for decay to the end of the run by multiplying by $\exp [-\lambda(i_f - 1) 20]$ and for saturation by multiplying by $1 - \exp (-20\lambda)$. The corrected product is summed over all i_f intervals in the run, and the result is the disintegration rate (A_0) expected for the isotope of decay constant $\lambda \text{ min}^{-1}$ if every meson leads to the formation of that isotope. The equation used in these calculations has the form

$$A_0 = N \sum_{i_f=1}^{i_f} \frac{I_1}{20} (1 - e^{-20\lambda}) e^{-\lambda(i_f - 1)20}$$

The function A_0/N has been calculated for several values of λ in each run, and then the function has been plotted against the half-life. The expected A_0 value for an isotope of given half-life is found by reading off the A_0/N value corresponding to the half-life and then

multiplying by the number of mesons per watt-minute. The counting results are intended to give an absolute disintegration rate so that the ratio of the latter to A_0 is a direct measure of the yield of that isotope. The graphs for each run are presented in Appendix III.

In order to determine whether summing over 20-minute intervals introduced appreciable error as compared to using 2-minute intervals, the worst case possible was chosen. Run 4 showed the greatest fluctuation in cyclotron intensity in the last few minutes of the irradiation, but the difference in expected disintegration rates for a 20-min. half-life isotope was on the order of 2 per cent for the two methods, much less than the error in measuring N . It would be expected then that the A_0/N graphs are suitable for all half-lives of the order of 20 minutes or longer.

Since the yields of only long-lived isotopes were under consideration in runs 7 and 8, the watt readings were summed over 60-minute intervals instead of 20-minute intervals. This is not believed to have introduced appreciable error in the calculated values of A_0 for reasons mentioned above.

C. EXPERIMENTAL PROCEDURE: CHEMICAL SEPARATIONS

General

The chemical separation procedures that we have used are based on those found in Noyes and Bray³⁹ or Coryell and Sugarman⁴⁰. Some revisions

³⁹A. A. Noyes and W. C. Bray, Qualitative Analysis for the Rare Elements, The Macmillan Company, New York, 1927.

⁴⁰C. D. Coryell and N. Sugarman, Radiochemical Studies: The Fission Products, McGraw-Hill Book Co., Inc., New York, 1951, National Nuclear Energy Series, Vol. IX, Book III.

sions in technique were made in adjusting the procedures to our experimental conditions.

A summary of the complete procedure is given in abbreviated form in Figure 18. Before the procedure was decided upon in its present form, a series of preliminary tests were made. A description of these tests and a few general comments on the procedure follow in this section.

The separation of arsenic, germanium, and selenium from liquid bromine is based on the premise that 6N HCl will quantitatively extract these substances from the bromine. As a check on this, $AsBr_3$ and $GeBr_4$ were dissolved in CCl_4 , which was expected to behave like bromine in solvent characteristics. Water was then added. At the interphase a cloudy film formed due to hydrolysis and precipitation of slightly soluble products. When the aqueous layer was made slightly acidic with HCl, the cloudiness disappeared. Quantitative

Irradiated Bromine

Add GeBr_4 , AsBr_3 and Se carriers.

Extract with 6N HCl containin GaCl_3 and ZnCl_2 .

Bromine layer
Return to container.

Aqueous layer
Wash with CCl_4 .

Aqueous layer
Add $\text{NH}_2\text{OH}\cdot\text{HCl}$. Filter.

CCl_4 Layer
Discard.

Filtrate
Divide into $1\frac{1}{5}$ & $4\frac{1}{5}$ aliquots.

$1\frac{1}{5}$ aliquot
Add H_2S . Filter.

Ppt.
Mixed Sulfides

Filtrate
Combine with
Filtrate from $4\frac{1}{5}$
aliquot.

$4\frac{1}{5}$ aliquot
Add H_2S . Filter.

Ppt. (Se)
Dissolve in HNO_3 . Add As_2O_3
in HNO_3 . Neutralize with
 NH_4OH . Add $\text{NH}_2\text{OH}\cdot\text{HCl}$. Filter.

Filtrate
Discard

Ppt.
Selenium

Filtrate

Add As_2O_3 in HCl.
Add H_2S . Filter.

Ppt.
Discard

Filtrate
Extract with ether.

Ether layer

Extract with H_2O .

Ether layer
Discard

H_2O layer

Add ZnCl_2 and
 NH_4HSO_3 . Boil.
Filter.

Ppt. $[\text{Ga}(\text{OH})_3]$

Dissolve in HCl. Neut.
with NH_4OH . Add 30H
quinoline. Filter.

Filtrate
Discard.

Filtrate
Discard.

Ppt.

$\text{Ga}(\text{30Hquin})_3$

Aqueous layer

Neut. with NH_4OH . Add
 NH_4Ac and 30H-quinoline.
Filter.

Filtrate
Discard.

Ppt.
 $\text{Zn}(\text{30Hquin})_2$

Ppt. (mixed sulfides)

Dissolve in NH_4OH . Place in
still. Saturate with HCl gas.
Bubble in Cl_2 and distill.

Distillate

Add H_2S and filter.

Filtrate
Discard.

Ppt.
 GeS_2

Residue in still

Add CuCl in conc. HCl.
Bubble in air and distill.

Distillate

Add H_2S and filter.

Filtrate
Discard.

Ppt.
 As_2S_3

Residue
Discard.

Fig 18

separations of arsenic and germanium were possible. Selenium could also be removed quantitatively by this extraction technique. In trial runs made with bromine, the separations by extraction were also quantitative.

The separation of selenium from arsenic and germanium was attempted by the precipitation of BaSeO_4 . It was believed possible that bromine would oxidize selenium to the $+6$ oxidation state and that SeO_4^{2-} would exist in the aqueous HCl phase. Barium ion as BaCl_2 was added in excess but no precipitate could be obtained within 30 minutes or so.

It is reasonably certain that the sulfide of arsenic precipitated in the mixed sulfides was the arsenous sulfide, As_2S_3 . The rate at which the sulfide formed was much faster than that for arsenic pentasulfide, As_2S_5 . In addition, washing freshly formed precipitates with CS_2 caused no change in weight, indicating little, if any, sulfur formation, as might be expected from H_2S reduction of As (V). Furthermore, Hevesy⁴¹ states that As (V) is reduced to As (III) by HBr in 6N HCl. Since our extraction solutions always contained dissolved bromine which is reduced by hydroxylamine to Br^- , there is more evidence that the sulfide of arsenic precipitated is the arsenous one.

⁴¹G. Hevesy, Radioactive Indicators, Interscience Publishers, Inc., New York, 1948, p. 6.

Carrier-free solvent extractions have been reported in the literature many times.⁴² The Berthelot-Nernst distribution law indicates

⁴²For example, A. C. Wahl and N. A. Bonner, Radioactivity Applied to Chemistry, John Wiley and Sons, Inc., New York, 1951, p. 149.

that the ratio of equilibrium concentrations (more exactly activities) of a substance in two phases is a constant at a given temperature. Consequently, one would expect the distribution of a substance at tracer concentrations to be the same as at macro concentrations unless, of course, the activity coefficient of the substance changes with dilution at extreme dilutions--an unlikely occurrence. It is expected that Ga^{+++} and Zn^{++} activities would be extracted by HCl. In order to prevent adsorption and/or coprecipitation, however, carriers of these substances were present during the extraction process in the HCl phase. That is, neither gallium nor zinc compounds were placed directly in the bromine.

The bottle in which the bromine was irradiated was washed with 6N HCl containing carriers in all runs but the first. All run 1 yields were quite low, about 1 per cent being the maximum, but the results cannot be compared directly with subsequent ones since a different π -energy, a short irradiation time, and a low intensity beam were used. It is also suspected that a sizeable amount of activity may have been left on the walls of the bottle.

In runs 1 and 2, 1 liter of chemically pure bromine was irradiated. In all subsequent runs the same bromine samples, suitably purified, were used. After a run had been completed and the chemical

separation was over, the bromine was washed with 6N HCl, and the aqueous layer was removed. In Section V-E the errors that may arise from impurities present are discussed at some length. Since some bromine was lost each time chemistry was done on it, the volumes varied from about 925 ml to 1 liter for various runs. The total amount of solid bromine used in run 8 corresponded to about 2 liters of liquid bromine.

Extraction of Bromine

The procedure that follows was used in runs 3 through 8. A few departures from this procedure, which are noted below, were made in those cases in which a complete separation was not necessary.

Carriers in the form of AsBr_3 and GeBr_4 were added directly to the bromine in the bottle after irradiation. Appropriate amounts of selenium metal were placed in a separatory funnel and about 100 ml of irradiated bromine were added. The separatory funnel was shaken to allow all the selenium to react, and this solution of SeBr_4 and Br_2 was returned to the bottle. The bottle was shaken for a few minutes to effect complete solution of the AsBr_3 and GeBr_4 . The Br_2 volume was divided approximately equally between two 1-liter separatory funnels.

One hundred ml of 6N HCl containing carrier amounts of Ga^{+++} as GaCl_3 and Zn^{++} as ZnCl_2 were added to the bromine bottle and the bottle was extracted for a few minutes. The volume was divided approximately equally between the two separatory funnels. An additional 100 ml of 6N HCl containing no carriers were added to the bottle and the bottle was washed again. This volume was divided between the two separatory funnels as before.

The bromine in each separatory funnel was extracted by shaking vigorously for at least 2 minutes. The layers were separated, and the separatory funnels were each rinsed with about 10 ml of 6N HCl. The aqueous-HCl layers were combined and washed twice with 25-ml portions of CCl_4 to remove Br_2 dissolved in the aqueous solution. The dissolved Br_2 left after this extraction was reduced with SO_2 (as $\text{Na}_2\text{S}_2\text{O}_5$) or hydroxylamine hydrochloride. Care was taken not to use excess SO_2 since this interferes later in H_2S precipitations.

Separation of Selenium

Elementary selenium begins to form as a red colloidal phase on further addition of hydroxylamine hydrochloride when the bromine has been completely reduced. In order to hasten the formation and coagulation of the selenium, the solution was warmed gently to about 40°C . The solution was filtered periodically through a fine sintered-glass funnel, continuing the heating of the filtrate between filtrations. This process required about 2 hours to effect a 90-per cent yield of selenium. The last filtrate was carried on to subsequent separations.

The selenium collected on the sintered-glass funnel was cautiously dissolved in 25 ml of hot concentrated HNO_3 . Then As^{+++} carrier as As_2O_3 in 6N HNO_3 and Ga^{+++} carrier as GaCl_3 were added. While the solution was kept in an ice bath, concentrated NH_4OH was added slowly

until the pH had been reduced to about zero. Hydroxylamine hydrochloride was then added in excess with the solution at about room temperature until red selenium began to precipitate again. At this temperature the chemical yield is about 20 per cent at the end of 5 hours. The precipitate obtained after 5 hours was collected on filter paper, washed with water and acetone, and air-dried to constant weight. The solution from which selenium is filtered is kept at room temperature since it tends to form a gray amorphous mass at only slightly higher temperatures. The solution was refiltered 33 hours later and a total yield of 80 per cent (including the first fraction) was obtained.

Arsenic and Germanium Separations

After the selenium had been removed, the filtrate was divided into a one-fifth and a four-fifths aliquot. A few drops of 1-per cent aerosol in 95-per cent ethyl alcohol solution were added to each aliquot and H_2S was bubbled through each for about 10 minutes. The precipitates formed at this pH are As_2S_3 and GeS_2 along with any selenium still remaining. The mixed sulfides from the one-fifth aliquot were filtered, washed with water, alcohol, and ether, dried at 110° for 10 minutes, cooled for 5 minutes in air, and weighed.

The precipitate from the four-fifths aliquot was dissolved in 25 ml of concentrated NH_4OH and transferred to a glass still. While shaking the bulb of the still, which is kept at ice temperature during this period, anhydrous HCl gas was passed into the solution until it was saturated with HCl . Fifteen ml of concentrated HCl were added along with small amounts of Ga^{+++} and Zn^{++} as chlorides. Chlorine gas was bubbled through the mixture at a rate of about one bubble per second. The bulb of the still was then placed in a glycerine bath and the latter slowly brought to 115° to 120° C. The receiver for the distillate was previously filled with 15 ml of cold water with the still delivery tube extending below the water level. The receiver was kept in an ice bath during the distillation. After about 20 ml of distillate had been collected, the process was stopped and the receiver removed.

The distillate was adjusted to 6N in HCl , and GeS_2 was precipitated. The precipitate was filtered, washed, dried, and weighed as with the one-fifth aliquot mixed sulfides. The filtrate was discarded.

Five ml of a concentrated HCl solution saturated with $CuCl$ were added to the solution remaining in the still, then an additional 20 ml of concentrated HCl . While air was bubbled through the still, the distillation was repeated as for germanium. The distillate collected was treated with H_2S to precipitate As_2S_3 . The precipitate was filtered, washed, dried, and weighed as before. The filtrate was discarded as well as the residue remaining in the still.

Separation of Gallium

The filtrates from the one-fifth and four-fifths aliquots were combined and As^{+++} carrier as As_2O_3 in 6N HCl was added. Arsenous sulfide was precipitated and discarded. In order to remove gallium, the filtrate was extracted with 100 ml of ether saturated with 6N HCl and then again with a 50-ml volume. The ether layers were combined

and extracted three times with 25-ml portions of water saturated with ether. The water layers were combined and kept at about 50°C on a hot plate until all the dissolved ether had been removed. Zinc carrier as ZnCl_2 in 6N HCl was added to the aqueous solution to "holdback" any

*Since many precipitates tend to occlude or adsorb many foreign substances, it is usually necessary to add carriers not only for ions to be precipitated but also for ions to be held in solution. Such carriers are called holdback carriers.

zinc coming through the ether extraction, and the solution was made slightly alkaline to litmus with concentrated NH_4OH . Five ml of NH_4HSO_3 reagent (concentrated NH_4OH saturated with SO_2) were added, and the solution adjusted so that it was just acid to litmus. The solution was covered and boiled vigorously for 5 minutes to precipitate $\text{Ga}(\text{OH})_3$. The precipitate was filtered and the filtrate was discarded. The precipitate was washed with two 10-ml portions of hot 2-per cent NH_4NO_3 solution and then dissolved in concentrated HCl. Eight ml of 8-hydroxyquinoline reagent (10 per cent in 2M HAc) were added, then concentrated NH_4OH until the solution was slightly acid to litmus. A few ml of 6M NH_4Ac were added dropwise to complete the neutralization. When a thick yellowish-green precipitate formed and persisted, 3 ml more NH_4Ac were added. The solution was heated to about 60°C to hasten coagulation of the precipitate; a few drops of aerosol solution were added and the solution filtered while still hot. The precipitate was washed with hot water, cold water, dried at 110° for 10 minutes, cooled in air for 5 minutes, and weighed as $\text{Ga}(\text{8-hydroxyquinolate})_3$.

Eight ml of 8-hydroxyquinoline reagent were added to the HCl layer from the ether extraction in which gallium was removed. $\text{Zn}(\text{8-hydroxyquinolate})_2$ was precipitated in a manner completely analogous to that for gallium. The precipitate was dissolved in 1N HCl and reprecipitated by neutralizing the acid with 1N NH_4OH . The second precipitate was then washed, dried, cooled, and weighed as for gallium.

Discussion of Procedure

The chemical yields obtained are listed in Table 9. The receiver for the germanium distillate in the 7-per cent-yield run (run 5) was not in place during the early part of the distillation. The yields obtained in other runs were 75 and 81 per cent.

It seems quite clear that arsenic and germanium can be removed quantitatively from the bromine layer into 6N HCl since the mixed sulfides gave reproducible yields in the neighborhood of 95 per cent (in only one run was it as low as 64 per cent). The mixed sulfides were always precipitated as a check on the germanium and arsenic yields. The distillation process is necessarily inefficient when conducted over the periods of distillation time that were used in these experiments (about 30 minutes each for germanium and arsenic). Hence the yields obtained do not seem unreasonably low. The gallium yields were generally reproducible within narrow limits. The losses are believed due to small inefficiencies in the ether extraction and the subsequent extraction of the ether with water. The zinc yield is probably high since the gallium yields were never quite so large as 100 per cent. It is believed that the bulky $\text{Zn}(\text{8-hydroxyquinolate})_2$

TABLE 9

Chemical Yields

Element	Yield (Per cent)
Selenium	80 (over-all, 20 in 5 hours)
Arsenic	15 to 60
Germanium	7 to 81
Mixed sulfides	64 to 100
Gallium	74 to 81
Zinc	100
Barium	97 to 99
Iron	90 to 100
Alkali Residue	90 to 100

precipitate was not dried sufficiently. The reduction of SeO_3^{2-} to metallic selenium proceeds very slowly at room temperature in our system so that an 80-per cent over-all yield or a 20-per cent yield in 5 hours is not unreasonable. Higher temperatures were not feasible since amorphous selenium, which is quite difficult to handle in mounting, forms.

The amounts of carriers used are listed in Table 10. The weights are of the substances listed in the first column.

TABLE 10

Weights of Carriers

Substance	Weight (gm)
Selenium	0.70
AsBr_3	0.5 to 0.6
As^{+++} (holdback)	0.10
GeBr_4	0.62
Ga^{+++}	0.09
Ga^{+++} (holdback)	0.09
Zn^{++}	0.10
Zn^{++} (holdback)	0.10
Ba^{++}	0.68
Fe^{+++}	0.26

Since the major amount of the activity was found to be in the arsenic isotopes, particularly 26.8-hr. As^{76} , 40-hr. As^{77} , and 17.5-day As^{74} , every attempt was made to keep precipitates clean of arsenic contamination. Precipitating selenium, dissolving in concentrated HNO_3 , adding inactive arsenic carrier, and reprecipitating selenium produces decay curves that show no half-lives attributable to arsenic activities. The germanium-arsenic distillation produces germanium of high purity. Chemically, no arsenic was apparent since

the precipitate after H_2S treatment was completely white. Less than 1 mg of arsenic will give rise to a yellow discoloration of the sulfide precipitate. Radiochemically, germanium decay curves gave no indication of a 26.8-hr. activity. The arsenic could conceivably be contaminated with small amounts of germanium activity but percentage-wise this contamination would be negligible since germanium activities are formed in much smaller yields than arsenic. During the distillation of germanium, carrier amounts of Zn^{++} and Ga^{+++} were usually present in the still, and during the arsenic distillation Cu^{++} from oxidized CuCl was also present.

The gallium separation should be clean in that inactive As_2S_3 was precipitated from the solution before the ether extraction or the $\text{Ga}(\text{OH})_3$ precipitation. AsCl_3 , if present, would go into the ether phase. Gallium is freed from zinc by the ether extraction and is further purified by adding zinc holdback carrier and precipitating $\text{Ga}(\text{OH})_3$ under conditions in which $\text{Zn}(\text{OH})_2$ does not come down. The zinc sample may have been contaminated slightly with gallium but is probably free from arsenic contamination. The question is somewhat academic in any case since the zinc sample showed no activity.

The Mounting of Samples

Samples were either left on the filter paper on which they had been obtained or else scraped off the filter, slurried with 95-per cent ethyl alcohol and/or 1-per cent agar solution in water, and then mounted on one-half of a polystyrene sample cylinder (see Section V-D for details). Most samples were covered with cellophane to keep them from physical shifting and to keep off contaminants. Filter papers, all 9 cm in diameter, and cellophane were Scotch taped on to the sample cylinders. In general it was always attempted to put the sample directly on the sample cylinder, but in the case of extremely small samples the scraping-off process would result in high percentage losses of the sample. It was found necessary to use agar and alcohol to mount As_2S_3 , the mixed sulfides, $\text{Fe}(\text{OH})_3$, and alkali-residue samples because of their tendency to crumble. The other samples could be mounted with alcohol alone.

D. APPARATUS AND COUNTING TECHNIQUES

The Counter

The Geiger-Mueller counter used throughout this research is a cylindrical flow counter of thin-wall type, as pictured in Figure 19, 20A and 20B. The counter, based on an idea of W. F. Libby, was developed by R. L. Schuch, R. L. Wolfgang and the author. It consists of two light cylindrical brass ends, E, held apart by three brass rods, B, $1/8$ inch in diameter, spaced 120 degrees apart. Lucite plugs, L, which fit tightly into the ends of the brass cylinders eliminate sharp metallic edges and help reduce multiple-pulse formation. The diameter of the counter is 1-1/2 inches and its active length is 10 inches. The center wire, C, used early in the research was 28-gauge copper-magnet

Fig 19

3134-64

125

61

3134-65

wire; later 2-mil tungsten was used. In the counter drawing, Figure 19, J indicates de Khotinsky wax, H a solder joint onto brass cap G. Gas flows in at F through 6 mm pyrex tubing D. There is a block in the tubing so that the gas will flush out the inside of the brass cylinder E. The counter wall is grounded at E.

The wall of the counter, A, is a plastic material, similar to cellophane, with gold sputtered upon it on one side in a thin uniform layer. This is a product known commercially as "Gild-It."* The gold

*W. H. Coe Manufacturing Co., 5414 W. Madison St., Chicago, Illinois.

side is electrically conducting, and 10 inches of it have negligible resistance. The thicknesses of several samples from different lots were determined and all were found to be 2.70 mg/cm^2 . This substance has exceptional two-dimensional strength; it is difficult to crease or otherwise distort in shape.. With reasonable care a single foil will last for months of continuous use. In this research the same wall was used for about three months and was replaced not because of deterioration, but because it was thought to be contaminated with activity. A sharp edge and a rather severe blow are required to tear the wall. As a counter wall, it shows no fatigue or memory effects. Other thin foils were tried in the course of the development of the counter, such as aluminum, copper, and brass, but none approached "Gild-It" in strength with respect to thickness and in stability.

The commercial product is used as a decal and comes with a heavy paper backing. The wall is cut to shape with the backing on, and then the latter is removed by soaking in water for about five minutes. The associated paste is rubbed off, the wall is rinsed with distilled water and dried. The wall is mounted, conducting side in, on the brass endcaps and one of the three brass rods with stopcock grease. Only a thin film is required. Some of the contact brass area on the endcaps should be left free of grease since the wall must make electrical contact. The foil need not be stuck to two of the three rods. The overlap seam has been found to be sealed best by paraffin. A narrow-width metal tool (roughly comparable to the width of the seam), such as a small screw-driver or spatula, is heated gently in a yellow flame and touched to a block of paraffin. The melted paraffin that adheres to the tool is then transferred to the seam. Generally smoother seals can be made by tacking down the seam at the center first and working the paraffin in either direction. Since the foil is mostly plastic, high temperatures will cause crumpling. The tool should be at such a temperature to barely melt paraffin. The foil is readily removed by breaking the paraffin seal with a sharp-pointed instrument, like a pair of tweezers. Re-sealing can be accomplished without the further use of paraffin.

Counter Characteristics and Associated Equipment

The counter has an unshielded background of about 300 counts per minute; inside 8 inches of steel, the background rate is about 80 counts per minute; and when further shielded inside eleven anti-coincidence counters (2 inches by 17 inches), the background is about 6.0 counts per minute. Coincidence losses as determined by the use of matched Cs^{137} sources give a dead time of about 400 microseconds. For the counting rates obtained in this research these give no appreciable correction.

The background rate when anti-coincidence shielded is believed to be somewhat high. With a screen wall counter in the same shield, and with the same anti-coincidence counters and scaling circuit, the ratio of unshielded background to anti-coincidence shielded background inside 8 inches of steel is about one-hundred. With our counter this ratio is about fifty. Since the foil-wall counter is 2 inches longer than a screen wall, a somewhat smaller ratio is expected because of a larger solid angle not covered by anti-coincidence counters. It is believed that the residual background of perhaps 2 counts per minute may be traced to contamination of the foil. It is also possible that the plastic part of the foil contains natural Cl^{34} and/or K^{40} . Other possibilities are contamination in the brass rods or the lucite end caps. No real investigation of this has been made since the background rate is not uncomfortably high and the time required for such a project is prohibitive.

The counting gas that has been used throughout this research is "Q" gas, which consists principally of helium and contains a small

*Nuclear Instrument and Chemical Co., 223 W. Erie St., Chicago, Illinois

amount of butane as the quenching gas. This filling gives extraordinarily large pulses in the Geiger region. The pulse height was found to be a rather insensitive function of the flow rate beyond a certain minimum. Under normal conditions an output flow rate of about eight bubbles per 5 seconds is adequate to maintain constant pulse height over wide ambient temperature ranges and to conserve gas. The gas was passed from the tank reducing-valve through a drying tube and a needle valve to an input bubbler, through the counter and associated rubber tubing, and finally to the output bubbler. The input bubbler was used to detect leaks in the system between the two bubblers.

With the 28-gauge copper center wire the Geiger onset voltage was 1650 volts; with a 2-mil tungsten wire this was reduced to 1250 volts. A plateau determination at 5000 counts per minute using a Cs^{137} source gave a 200-volt plateau with 5-per cent slope per hundred volts. The plateaus were essentially the same with both center wires. The counter was normally operated at about 30 volts above the onset voltage. Since the pulse height is a function of the voltage and the sensitivity control, a pulse attenuator type of control, the pulse height was kept constant by keeping the voltage constant and changing the sensitivity to compensate for variations. The pulse height was observed on an oscilloscope.

The shielding arrangement and scaling circuit used were completely described by Anderson and Libby,⁴³ Martell and Libby,⁴⁴ and Kalkstein.⁴⁵

⁴³E. C. Anderson and W. F. Libby, Phys. Rev., 81, 64 (1951).

⁴⁴E. A. Martell and W. F. Libby, Phys. Rev., 80, 977 (1950).

⁴⁵M. I. Kalkstein, Ph.D. Thesis, Univ. of Chicago, 1951.

Briefly, the shield is made of 1-inch-thick hot-rolled steel plates, stacked on 8-inch I beams. The 12-inch by 12-inch by 28-inch opening

for the counter and associated equipment has 8 inches of shielding in all directions. A door that is operated by an electrically controlled hydraulic jack completes the equipment. The scaling circuit is of a conventional anti-coincidence design in which pulses from the sample counter are inverted and mixed with those from the anti-coincidence counters. Only pulses unique to the sample counter are registered in the output circuit. These pulses are fed into a cyclotron specialties kind of mechanical register. At the counting rates experienced in this research some register coincidence losses have been observed. Counting rates above 200 counts per minute have been corrected by the use of a correction graph, Figure 21.

The samples to be counted are mounted on split polystyrene cylinders of 1-7/8 inch inside diameter, Figures 20A and 20B. The two halves of the cylinders are hinged with Scotch electrical tape. Two lucite half-moon supports on either end of the lower half cylinder are held in place with Scotch tape. The counter rests on these supports. Within counting statistics reproducible geometry between sample and counter is obtained in this way. The counter and sample cylinder are placed in a semi-cylindrical lucite mount 4 inches in diameter, Figures 20A and 20B. Sufficiently long pieces of rubber tubing are attached to the ball joints such that the mount can be withdrawn from the shield and sample cylinders changed without disconnecting the gas line.

The physical geometry of the counter-sample cylinder system was determined in two separate experiments. With some of the indium metal sample used by Martell and Libby,⁴⁴ the natural In^{115} β^- of 630 kev was counted. A sample of thickness 327 mg/cm² and area 154 cm² gave a counting rate of 15.6 ± 0.7 counts per minute. Correcting for absorption in the counter wall and self-absorption and using Martell and Libby's⁴⁴ absolute disintegration rate of 10.9 disintegrations per minute per gm, we calculate the geometry and efficiency of the counter to be about 0.40. Using KCl, we found the activity to be 45.8 ± 1.1 counts per minute for a sample of thickness 1.8 mg/cm² and area 64 cm². This results in a geometry and efficiency factor of 0.36 if the disintegration rate of K^{40} is 32.5 disintegrations per second per gm of potassium.⁴⁶

⁴⁶ A. D. Suttle, private communication.

It is possible to calculate the geometry if one knows the distance from the sample to the counter and it is assumed that end losses are negligible. Since our samples were generally short in comparison with the 10-inch sensitive portion of the counter, this is thought to be a valid procedure. The calculated value is 39 per cent. Because the distance from the counter wall to sample is not known accurately, this value will be used only as an order-of-magnitude calculation to confirm the observed values. Actually the sample is not a constant distance from the counter wall during a count since the wall pulsates with a frequency equal to that of the output bubbler. The amplitude of the pulse is about a millimeter near the middle of the counter.

Backscattering was determined for the polystyrene sample cylinders by counting 54-min. In^{116} and 26.8-hr. As^{76} with and without a sample cylinder. The samples (both as sulfides) were collected on 9-cm filter

Fig 21

paper to a thickness of about 1.3 mg/cm^2 . The filter paper was then mounted on a ring of copper wire so shaped that it would fit closely inside a sample cylinder. An auxiliary wire support was used to hold the filter paper and ring the same distance from the counter as they would be in the sample cylinder. These two determinations gave a mean result that the observed count rate was 1.14 ± 0.01 times as high with the sample cylinder as that without. This result is comparable to that found by other observers.⁴⁷ Actually our measure

⁴⁷R. G. Fluharty, *Nucleonics*, 2, No. 5 (1948).

ments "without backing" involves the use of filter paper of about 8 mg/cm^2 so that the results are not strictly comparable.

When the counter was first constructed, a few trial determinations were made with soft radiation to check the efficiency. A sample of C^{14} that was enriched about twofold above the natural level could be counted even without anti-coincidence shielding. Natural Rb^{87} was counted with anti-coincidence shielding and an absorption curve was run. The latter corresponded within counting error with that obtained by Suttle⁴⁶ on a screen wall counter. With the thin wall, large effective counting area (about 300 cm^2), and ease of changing samples, we believe this counter to be of considerable value in any work in which soft radiation must be counted, particularly if relatively large samples must be used. The simplicity of construction, stability of operation, and inexpensiveness of construction and operation make it an exceedingly handy tool.

Counting Methods

If the counter had not been in use prior to the time a count was to be taken, the counter was flushed at a rapid bubble rate (about 20 per second) until pulses began to appear on the oscilloscope. The bubble rate was then reduced to the standard one of about 2 per second and flushing was continued until the pulse height remained constant for several minutes. The pulse height was then adjusted to a standard height by the sensitivity control and counting was begun. The pulse height was watched quite carefully during the first 15 minutes or so of counting since pulses too small are not registered by the output circuit and those too large are not cancelled by the anti-coincidence pulses. The bubble rate was also checked periodically to insure reasonable constancy.

If the counter had been in use--that is, gas had been flowing--the sample cylinders were changed and the pulse height was checked again before the counting was begun. At regular intervals the onset voltage, plateau, and background rate without anti-coincidence shielding were checked. No appreciable variations were detected during the entire period of this research.

When aluminum absorption curves were run, it was found that the background with absorber was always higher than that without absorber in spite of repeated cleaning of the absorbers with nitric acid. Part of this rise is ascribed to contamination of the aluminum and the remainder to the Crane effect⁴⁸ due to some unavoidable handling or

⁴⁸H. R. Crane, *Phys. Rev.*, 75, 985 (1949); M. L. Wiedenbeck and H. R. Crane, *Phys. Rev.*, 75, 1268 (1949).

rubbing of the aluminum surface. To compensate for possible Crane-effect "decay," sample and background were counted for approximately equal lengths of time under the same handling conditions.

Absorption curves taken on a simple β spectrum, that is, one β , give linear plots on semi-log graph paper. This is in contrast to the concave-downward sort of plot commonly obtained. The straight line is believed to result from the intimate contact of sample, absorber, and counter. Because of the linearity the energy is easily determined. Libby and Suttellel, ⁴⁴, ⁴⁹ have determined the relationship of half-

⁴⁹A. D. Suttle and W. F. Libby, private communication.

thickness to range for a wide range of energies. The relationship is a constant equal to $1/13.5$. Knowing this value for the range, one can read the energy from Glendenin's range-energy curve.⁵⁰

⁵⁰L. E. Glendenin, Nucleonics, 2, No. 1, 25 (1948).

Background counts were taken on a sample cylinder that had an inactive sample mounted in a manner similar to that of the active sample. Filter paper was used when the active sample was so mounted. The background was counted at least once a day and daily fluctuations corresponded to those expected. This was a further check on the operating stability of the counter.

In a number of cases, the activity counted was in the range of 2" to 10 counts per minute. Against a background of 6 counts per minute, this meant long counting periods. For several weeks counting was maintained on a 24-hour-per-day schedule, 8 hours each being devoted to two samples and one background count. The time of day at which the background was taken was varied every other day to compensate for systematic errors.

The general practice has been to allow the counter to run continuously, counting background if there were no samples to be counted, since the counter would then be available for immediate use. The amount of "Q" gas used is quite small under these circumstances; the standard 100-cubic-foot cylinder lasts about a month.

In the case of some of the arsenic and selenium samples it was believed that some soft radiation might be present, such as 76-day As^{73} or 127-day Se^{75} , both of which decay by K capture. To check this possibility the samples were removed from the polystyrene sample cylinders and mounted on the brass sample cylinders of a screen wall counter. If orbital-capture activities and soft conversion electrons were present in any appreciable amount the observed counting rate would be expected to be much higher since there is no intervening wall between counter and sample. The results are given in Section V-E. The technique of counting on a screen wall counter has been completely described by many others^{14,15} so that no further mention will be made here.

E. RESULTS

Methods

In order to calculate the yield of a particular isotope, it was necessary to determine its absolute disintegration rate. This was done first by extrapolating the resolved decay curves to the end of the bombardment. Then the resulting value was corrected for external absorption due to the 2.7 mg/cm² cellophane covering and/or the 2.7 mg/cm² counter wall. The corrected count rate was then substituted into the following equation which corrected for chemical yield, self-absorption, backscattering, physical geometry, and efficiency:

$$D = \frac{0.693Iw}{Agybx_{1/2} [1 - \exp(-0.693\frac{x}{x_{1/2}})]}$$

In this equation D is the absolute disintegration rate (exclusive of counting efficiency); I is the extrapolated count rate corrected for external absorption; w is the weight of the sample in mg and A its area in cm²; g is the physical geometry and efficiency factor while b is the backscattering factor; y is the chemical yield based on the weight mounted; $x_{1/2}$ is the half-thickness of the beta radiation, and x is the average thickness of the sample, both in mg/cm². In the cases of activities whose identities were not clearly established, as in some of the group precipitates, for example, no self-absorption correction was made, and an arbitrary 3-per cent correction for external absorption was applied.

Earlier a description of the methods used for the calibration of the counter is presented. The constants applicable to the counter are physical geometry and efficiency = 0.38 (the mean of the indium and potassium results) and backscattering factor = 1.14. Thicknesses, weights, and areas of samples, types of mountings, chemical yields, and thicknesses of external absorber are listed in Appendix IV. In the case of activities where half-thicknesses were known from absorption curves run on our counter, these values were used. For other activities the literature values of the energy⁵¹ were used and the

⁵¹Way, Fano, Scott and Thew, Nuclear Data, Nat. Bur. Standards (U.S.) Circ. 499, 1950; G. T. Seaborg and I. Perlman, Rev. Mod. Phys., 20, 585 (1948):

range determined from Glendenin's graph.⁵⁰ The half-thickness was calculated from the range by the use of the Libby-Suttle formula, 19,44,49 which gives it as 1/13.5 of the range. In all cases the thickness of the sample was calculated from the weight and area. It was assumed that the samples were of uniform thickness, a reasonable premise in view of the appearances. No correction was made for the agar sometimes present in milligram quantities.

Results

The quantity A_0 is defined as the disintegration rate expected if every meson interacting with a bromine nucleus resulted in the isotope in question. The value of A_0 is obtained from the A_0/N graphs presented in Appendix III. A complete explanation of the method of calculation is presented earlier. The counting efficiencies are estimated from literature values of energy, branching ratios, and other pertinent data. The counting efficiencies relative to a 630 Kev β^- and literature values of half-lives⁵¹ of all isotopes identified are listed in Table 11. The indicated errors in counting efficiencies show the disagreement in the literature on the branching ratio of those isotopes. The percentage yield is defined by the equation

$$\text{yield (per cent)} = \frac{D \times 100}{A_0 \times \text{counting efficiency}}$$

Table 12 lists the yields that have been obtained for chemically separated samples.

In Table 13 are listed the yields of activities from the mixed sulfides precipitates of runs 2, 3, and 4. None of the results of run 1 are included since the total activity was so low that decay curves were difficult to resolve, and no real information was obtained from the run. Two factors probably contributed to the lowness of the yields. The irradiation bottle was not washed, and the length of samples was insufficient to stop the 145 Mev π^- , although it is adequately long for 122 Mev π^- .

Table 14 gives the mean yields of the various activities calculated in two different ways. The average in column (2) are based on only one value per isotope (or half-life) per run. The relative weighting factors of the yields determined for the chemically separated and unseparated samples for germanium and arsenic isotopes are four-fifths and one-fifth. If all values are weighted equally for the two types of samples, the mean yields are as indicated in column (3). In the case of germanium activities in the mixed sulfides, the values 0.6 per cent yield for Ge^{69} and 0.3 per cent for Ge^{75} were assumed, and the arsenic yields for the 40-hr. and 90-min. activities were obtained by difference. The errors shown in columns (2) and (3) represent standard deviations of the several results. They are not meant to imply the accuracy of this investigation. In column (4) the mean yields of column (2) are assigned errors believed to be the experimental errors of this research. In the section on errors in this chapter the considerations that led to these error assignments will be discussed at some length.

The yields obtained in group precipitates except for the mixed-sulfides sample-run yields, which are listed in Table 13, are indicated in Table 15. These values were all obtained in run 2. Counting rates obtained in a comparable control run (deflecting magnet off) are also listed.

Upper limits on yields for activities other than arsenic, germanium, selenium, or gallium have been grouped according to half-life and chemical nature and are shown in Table 16.

TABLE 11

Half-Lives and Counting Efficiencies

Isotope	Half-life	Estimated Relative Counting Efficiency
Se ⁷²	9.5 d	... ^a
Se ⁷³	6.7 hr.	0.33 + 0.67 ^b - 0.03 ^c
As ⁷¹	50 hr.	0.05 ^d
As ⁷¹ + As ⁷⁷	50 hr., 40 hr.	1.0 ^e
As ⁷²	26 hr.	0.35 ^b
As ⁷² + As ⁷⁶	26 hr., 26.8 hr.	1.0 ^e
As ⁷⁴	17.5 d	0.75 ^f
As ⁷⁶	26.8 hr.	1.0
As ⁷⁷	40 hr.	1.0
As ⁷⁸	90 min.	1.0
Ge ⁶⁹	39.6 hr.	1.0 + 0.08 - 0.67 ^b
Ge ⁷⁵	82 min.	1.0
Ga ⁶⁸	68 min.	1.0
Ga ⁷²	14.1 hr.	1.0
Ga ⁷³	5.0 hr.	1.0

^aThirty-five per cent counting efficiency was assumed for the 26-hr. As⁷² daughter.

^bH. Hopkins, Phys. Rev., 77, 717 (1950).

^cF. R. Scott, Phys. Rev., 84, 659 (1951).

^dMei, Mitchell, and Huddleston, Phys. Rev., 79, 237 (1950).

^eThe 40-hr. and 26.8 hr. experimental periods in arsenic are each the sum of two activities, and the over-all counting efficiency of each pair is taken as 1.0 for the purposes of calculation. Corrections will be made later.

^fJohansson, Cauchois, and Siegbahn, Phys. Rev., 82, 275 (1951).

^gC. M. Huddleston and A. B. Smith, Phys. Rev., 84, 289 (1951).

TABLE 12

Yields of Chemically-Separated Samples

Run No.	Isotope	Half-life Exp.	I (cpm)	D (dpm)	A ₀ (dpm)	Yield (per cent)
3	As ⁷⁴	17.5 d	16.3	119	2,180	7.3
	As ⁷¹ , As ⁷⁷	40 hr.	119	874	22,400	3.9
	As ⁷² , As ⁷⁶	26.8 hr.	340	2440	32,900	7.4
	As ⁷⁸	92 min.	364	2610	268,000	1.0
	Ge ⁶⁹	40 hr.	33.4	137	22,400	0.6
	Ge ⁷⁵	95 min.	208	862	265,000	0.33
4	As ⁷⁴	17.5 d	14.5	285	4,600	8.3
	As ⁷¹ , As ⁷⁷	40 hr.	94	1860	47,100	4.0
	As ⁷² , As ⁷⁶	26.8 hr.	255	4990	68,600	7.3
	Ge ⁶⁹	41 hr.	55	263	46,000	0.6
	Ge ⁷⁵	95 min.	294	1410	453,000	0.31
	Ga ⁷²	14.1 hr.	203	643	122,100	0.5
	Ga ⁷³	5.0 hr.	301	952	276,000	0.35
	Ga ⁶⁸	69 min.	1690	5300	456,000	1.2
5	As ⁷⁴	17.5 d	39.2	305	5,980	6.8
	As ⁷¹ , As ⁷⁷	40 hr.	258	2028	60,600	3.3
	As ⁷² , As ⁷⁶	26.8 hr.	705	5385	87,500	6.1
	Se ⁷²	9.5 d	31.7	354	11,100	3.2
	Se ⁷³	6.7 hr.	256	2870	278,000	3.1
	Ga ⁷²	14.1 hr.	190	1030	156,000	0.7
	Ga ⁷³	5.0 hr.	253	1377	337,000	0.4
	Ga ⁶⁸	68 min.	1270	6860	590,000	1.2

TABLE 13

Yields from Mixed-Sulfides Samples

Run No.	Isotope	Half-life Exp.	I (cpm)	D (dpm)	A ₀ (dpm)	Yield (per cent)
2	As ⁷⁴	17.5 d	14.1	50	876	7.6
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	117	422	9,520	4.4
	As ⁷⁶ , As ⁷²	26.8 hr.	304	1050	14,200	7.4
	Se ⁷³	7 hr.	224	703*	50,500	4.2
	As ⁷⁸ , Ge ⁷⁵	75 min.	1010	3480	187,000	1.8
3	As ⁷⁴	17.5 d	10	117	2,180	7.2
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	49.2	579	22,400	2.6
	As ⁷⁶ , As ⁷²	26.8 hr.	116	1330	32,900	4.0
	Se ⁷³	7 hr.	106	1224*	107,800	3.4
	As ⁷⁸ , Ge ⁷⁵	78 min.	219	2510	268,000	0.9
4	As ⁷⁴	17.5 d	17.5	205	4,600	6.0
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	150	1775	47,100	3.8
	As ⁷⁶ , As ⁷²	26.8 hr.	412	4740	68,600	6.9

*One-hundred-per cent chemical yield was assumed; no carrier was present.

TABLE 14
Mean Yields of Isotopes

Isotope (1)	Mean Yields (per cent)		
	(2)	(3)	(4)
As ⁷⁴	7.3 ± 0.5	7.1 ± 0.8	7.3 ± 1.8
As ⁷⁷ , As ⁷¹	3.8 ± 0.4	3.3 ± 0.7	3.8 ± 0.9
As ⁷⁶ , As ⁷²	6.7 ± 0.5	6.3 ± 1.3	6.7 ± 1.7
As ⁷⁸	0.9 ± 0.1	0.9 ± 0.2	0.9 ± 0.3
Ge ⁶⁹	0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.15
Ge ⁷⁵	0.3 ± 0.05	0.3 ± 0.05	0.3 ± 0.08
Ga ⁷²	0.6 ± 0.07		0.6 ± 0.15
Ga ⁷³	0.4 ± 0.04		0.4 ± 0.1
Ga ⁶⁸	1.2 ± 0.05		1.2 ± 0.4
Se ⁷²	3.2 ± 0.5		3.2 ± 0.9
Se ⁷³	3.6 ± 0.5		3.6 ± 1.0

TABLE 15

Yields of Group Precipitates, Sample and Control Runs

Chemical Identity	Isotope Assignment	Half-life Exp.	I (cpm)	D (dpm)	A ₀ (dpm)	Counting Efficiency	Yield (per cent)
Sample Run							
BaSO ₄		10 hr.	10	26	36,200	1.0	0.07
Fe(OH) ₃		14.5 hr.	79	220	25,400	1.0	0.9
		100 min.	752	2090	157,000	1.0	1.3
Alkali residue	Br ⁸² (?)	35 hr.	11	31	10,900	1.0	0.3
	Br ⁸⁰ (?)	3 hr.	134	372	102,800	1.0	0.4
Control Run							
Mixed sulfides		All > 90 min.	13	33			
BaSO ₄			2	5			
Fe(OH) ₃		13 hr.	9	26			
Alkali residue	Br ⁸² (?)	35 hr.	10	29			

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TABLE 16

Maximum Yields of Group Precipitates

Half-Life	Chemical Nature	Maximum Yield (per cent)
30 min. - 10 d	Follows BaSO_4	0.1
14 hr.	Follows $\text{Fe}(\text{OH})_3$	0.9
100 min.	Follows $\text{Fe}(\text{OH})_3$	1.3
14 d	Follows $\text{Fe}(\text{OH})_3$	0.4
1 d	Follows $\text{Fe}(\text{OH})_3$	0.1
6 hr. - 10 d	In alkali residue	0.02
60 hr.	Cu^{67}	0.2
12.9 hr.	Cu^{64}	0.2

Results of Auxiliary Experiments

In order to determine the effect of secondary reactions due to neutrons in π^- capture, several auxiliary experiments were performed. In run 5 a piece of indium foil 6 cm by 20.3 cm in area and 164 mg/cm² thick was wrapped around the outside of the bromine sample bottle at the end farthest from the deflecting magnet. The foil was so placed that an edge faced the meson beam. When the irradiation was over, the foil was wrapped around an Eck and Krebs cylindrical counter of 30 mg/cm² wall, and the activity was followed until the count rate was about 50 counts per minute. Then the sample was transferred to a polystyrene sample cylinder and counted on the foil-wall counter. A 54 min. activity observed was attributed to ^{116}In , and the extrapolated count rate on the foil-wall counter corrected for external absorption was 1.1×10^5 counts per minute. Correcting for saturation, self-absorption, and geometry, one calculates the disintegration rate to be 1.3×10^6 disintegrations per minute. If it is assumed that the major contribution to the count rate is from the 27,000 barn cross-section at the neutron resonance energy for ^{115}In of 1.44 ev, the neutron flux at that energy is about $4.8 \times 10^2 \text{ cm}^{-2}\text{min}^{-1}$.

For a bottle area of about 725 cm² (18 cm long, 10 cm diameter, flat ends assumed) and a uniform neutron flux, one calculates the neutron to π^- flux ratio to be about 0.5. The π^- intensity was about 43,000 per watt minute at a mean wattage of 14 or about 6×10^5 per minute. If the average cross-section for neutron activation of indium is as low as 10^{-23} cm^2 , the neutron to π^- ratio is 1350. No real judgment of the neutron flux can be made since a background rate-- that is, the ^{116}In activation that would result without bromine in the

the bottle--is not known. It has been reported⁵² that for every π^-

⁵²V. C. Tongiorgi and D. A. Edwards, Bull. Am. Phys. Soc., 27, No. 3 (1952).

capture, lead emits about seven neutrons with an energy less than 10 Mev. A reasonable guess as to the neutron flux might then be about $4.8 \times 10^3 \text{ cm}^{-2}\text{min}^{-1}$, which would correspond to a neutron to π^- ratio of about five.

In run 6 about 30 ml of bromine was irradiated with high energy neutrons inside the cyclotron pit. A mixed-sulfides precipitation was performed as in previous runs and 6.7-hr. Se^{73} , 9.5-day Se^{72} , and 26.8-hr. As^{76} were found in considerable yield. The cross-section for the formation of the latter activity could not be calculated since it was found that the polyethylene used to monitor the neutron flux was not sensitive down to the threshold for the (n, α) reaction on Br^{79} . It was expected that one could calculate the contribution of the (n, α) reaction to the meson-induced yield of As^{76} and As^{78} if the cross-sections for the reactions $\text{Br}^{79}(n, \alpha)\text{As}^{76}$ and $\text{Br}^{81}(n, \alpha)\text{As}^{78}$ could be determined. The neutron flux was to be taken from the indium foil experiment.

In run 7 a bromine sample of regular size was placed behind 56.7 gm/cm^2 of copper absorber, 10 per cent more than the range of 122 Mev π^- in copper. The yields of activities, based on mesons, found in a mixed-sulfides group precipitate are listed in Table 17. The estimated error in these yields is on the order of 50 per cent because of the low count rates. There is some ambiguity in the interpretation of these results since the mesons are captured in copper. However, the path-length in bromine seen by neutrons formed in copper is roughly one-half the path-length when captured in bromine, so that order-of-magnitude judgments can be made.

TABLE 17

Yields in Run 7

Isotope	Half-Life Exp.	I (cpm)	D (dpm)	A_0 (dpm)	Yield (per cent)
As^{74}	17.5 d	1.7	4	2,020	0.25
As^{77}	40 hr.	25.3	61	21,300	0.3
As^{76}	26.8 hr.	32	74.5	31,800	0.25

The question of secondary reactions was finally settled in run 8 in which six solid bromine disks were irradiated. The disks were each 4.7 cm thick and about 10 cm in diameter. The surface density was about 15 gm/cm^2 in each disk so that each was 27 per cent of the range of a 122 Mev π^- in bromine. The disks were numbered consecutively

from 1 to 6 with number 1 closest to the magnet. The activities found in a mixed-sulfides precipitate, and their yields based on mesons are listed in Table 18 and 19. The A_0 values in Table 18 are the expected disintegration rate for an isotope of given half-life formed in 100-per cent yield, based on the total number of mesons absorbed in samples 1 through 4. These A_0 values do not give the disintegration rate per mesons absorbed in each sample. The same A_0 values are used in samples 5 and 6, beyond the π -range, since the effect of secondary reactions relative to the total number of mesons absorbed is desired. The yield-range relationship is shown in Figure 19 and discussed later.

Upper Limits on Yields of Short-Lived Activities

The 75-min. activity in the mixed sulfides of run 2 may have been a mixture of 44-min. Se^{70} , 82-min. Ge^{75} , 90-min. As^{78} , and 52-min. As^{70} . A yield of 0.8 per cent with 25-per cent counting efficiency for a half-life of about 50 minutes would give 200 counts per minute at the end of the bombardment or about 100 counts per minute at the time of the first count. This amount could have been detected in our decay curves. The combined yield of Se^{70} and As^{70} is expected, then, to be less than 0.8 per cent.

In short-lived germanium activities the 140-min. Ge^{66} decays to 9.4-hr. Ga^{66} which has a hard β^+ . With 25-per cent counting efficiency the maximum yield is estimated at 0.2 per cent. This corresponds to a count rate of 50 counts per minute about 8 hours after the end of the run. This amount of 9.4-hr. activity could surely be seen in the germanium decay curve. A reasonable upper limit for 23-min Ge^{67} cannot be set from a consideration of the 78-hr. Ga^{67} daughter activity. Assuming a counting efficiency of 1 per cent for Ga^{67} , 2 counts per minute upper limit for long-lived activity in the germanium sample, saturation activity for Ge^{67} , and about 25-per cent over-all counting geometry, the upper limit is 40 per cent, which is meaningless for our purposes. However, by considering the short-lived activities in run 2, we set an upper limit of 1.3 per cent for the yield of Ge^{67} , assuming that we could have seen 50 counts per minute of 23-min. activity at the time of the first count (about 80 minutes after the end of the run). A counting efficiency of 100 per cent and over-all geometry of 25 per cent have been assumed.

In gallium the maximum yield for 9.4-hr. Ga^{66} is set at 0.3 per cent assuming that 40 counts per minute of 9.4-hr. activity could be seen by our methods. No limits can be set for 15-min. Ga^{65} , 20-min. Ga^{70} , and 48-min. Ga^{64} since the first count in the most favorable case was about 8 hours after the end of the run.

Errors

Errors in the yields are estimated from the following sort of considerations. The extrapolated count rates are believed to be good in general to about 10 per cent although the uncertainty in resolution of some of the decay curves, however, is large. The separation of 40-hr. and 26.8-hr. arsenic activities is subject to considerable error. Errors due strictly to counting are believed less

TABLE 18
Yields in Run 8

Sample No.	Isotope	Half-Life Exp.	I (cpm)	D (dpm)	A ₀ (dpm)	Yield (per cent)
1	As ⁷⁴	17.5 d	15.7	38	4,370	1.2
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	96.5	236	42,700	0.6
	As ⁷⁶ , As ⁷²	26.8 hr.	227	540	58,700	0.9
2	As ⁷⁴	17.5 d	18.4	44	4,370	1.4
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	113	273	42,700	0.65
	As ⁷⁶ , As ⁷²	26.8	268	623	58,700	1.1
3	As ⁷⁴	17.5 d	26.4	65	4,370	2.0
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	163	406	42,700	1.0
	As ⁷⁶ , As ⁷²	26.8 hr.	384	926	58,700	1.6
4	As ⁷⁴	17.5 d	37.1	93	4,370	2.8
	As ⁷⁷ , As ⁷¹ , Ge ⁶⁹	40 hr.	229	585	42,700	1.4
	As ⁷⁶ , As ⁷²	26.8 hr.	537	1330	58,700	2.3
5	As ⁷⁶	26.8 hr.	50	127	58,700	0.2
6	As ⁷⁶	26.8 hr.	22	50	58,700	0.09

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TABLE 19

Total Yields in Run 8

Isotope	Total Yield* (per cent)
As ⁷⁴	7.4
As ⁷⁷ , As ⁷¹	3.7
As ⁷⁶ , As ⁷²	5.9

* The yields in samples 5 and 6 have not been included in the total.

than 10 per cent. Geometry is reproducible to less than that and fluctuations in the counter itself are believed negligible. The determination of the chemical yield in a few cases has a considerable uncertainty. This is especially true in the case of the light arsenic precipitates. The general weighing error is estimated at 2 per cent or less but could be as much as 15 per cent for the arsenous sulfide sample in run 4.

The internal consistency of the results of this research is reflected in Table 14 in which the mean values of yields and their standard deviations are given. The further consideration of whether the calculated yields correspond to absolute yields based on the number of mesons absorbed depends on the reliability of the meson measurements. In no run was the sample irradiated at the location where the beam was monitored by the scintillation counters. The usual position was in front of the counters inside the cubical iron shield.

The change in monitoring scintillation counters between runs 5 and 6 introduces further uncertainty. The second pair would be expected to see more mesons (and perhaps have a higher background) than the first pair since a 3-inch back counter of the latter pair has been replaced by a 4-inch one. Further, each counter of the second pair used more efficient light-gathering methods such that each was about 98 per cent efficient⁵³ at the extreme edges. Since the measured yields in run 8 corresponded quite closely to the mean of previous

⁵³R. Martin, private communication.

runs, it might be assumed that the methods of measuring mesons, old and new, are consistent. However, Sugarman, in the meson-induced fission of mercury,⁵⁴ and Turkevich, in the meson-activation of an NH_4NO_3 solution,⁵⁵ find that under the new arrangement (12 feet of

⁵⁴N. Sugarman, private communication.

⁵⁵A. Turkevich, private communication.

steel shielding, 4 inch by 5 inch magnet-pole opening, new counters) they obtain varying yields depending on the position of their samples

along the line between magnet and counters. The activation per meson that they observe, if their samples are as close to the magnet as possible, corresponds to values obtained under the old arrangement (6 feet of steel shielding, 2 inch by 3 inch magnet-pole opening, old counters). However, when their samples are placed near the counters, their apparent yields are lower by about a factor of two. It is perhaps fortuitous then, that irradiations in the new arrangement at the magnet gave yields comparable to the old at the counters. In neither case do we really know how many mesons are striking the sample. The calculated yields are then relative. It will be shown later, however, that these relative yields correspond to photographic plate data quite closely, implying that the meson measurements are probably as good as the other parameters entering into the yield calculation.

The standard deviation in several measurements of the number of mesons per watt-minute in each run is given in Appendix III. The spread in general is about 5 per cent.

In the calculation of yields the observed activity should be corrected for a small amount of background activity that is induced when the deflecting magnet is off. This correction is not clearly known for each isotope, but the result of run 2 indicates that for the activities that follow the mixed sulfides or $\text{Fe}(\text{OH})_3$, the correction is about 3 per cent of the total activity after the short-lived activities have died out. In any case the correction has been neglected. The reported 5 ± 4 per cent contamination of the π^- -beam²⁶ has not been corrected for either. Since these corrections are in opposite directions, they tend to compensate for each other. Their net effect should be much smaller than other errors in these determinations.

Estimated counting efficiencies may be the largest single source of errors; a factor of three is possible in a few cases (see Table 11). Generally the decay schemes and branching ratios of K-capture isotopes are not too well known. In those cases of K-capture decay only, counting efficiencies have been estimated by calculating the photoelectric cross-section in helium and cellophane (i.e., carbon) for the x-rays in question. Helium is the principal constituent of our counting gas, and the wall of the counter is mostly a cellophane-like plastic.

Errors from impure bromine samples were generally of no consequence. The group-precipitates analysis shows that the only meson-induced activities that we obtain in any but negligible amounts fall within a few atomic numbers of bromine. A high neutron flux plus macro amounts of arsenic, germanium, or gallium impurity could affect the results. In our runs the only purification step after each use of the bromine was to re-extract it with 6N HCl. The impurities of arsenic, germanium, and gallium remaining after the purification extraction were less than 5 mg of each. The indium-foil results imply that the neutron flux at the indium resonance energy is probably about $4.8 \times 10^{-2} \text{min}^{-1}$. If the capture cross-sections of As^{75} , Ge^{74} , and Ga^{71} for 1.44 ev neutrons are taken as equal to the thermal cross-sections, and a run such as run 5 is selected as the worst case, the end-of-bombardment disintegration rates are 2.2×10^{-3} disintegrations per minute per mg of arsenic, 5.9×10^{-3} disintegrations per minute per mg of germanium and 1.4×10^{-3} disintegrations per minute per minute per mg of gallium for As^{76} , Ge^{75} , and Ga^{72} , respectively. This is for a 358-minute

irradiation at about 6×10^5 mesons per minute. Even if these calculations are wrong by a factor of one hundred in flux or cross-section, we need not be concerned because we have used the same samples of bromine over and over again.

The total effect of these errors in the calculated yields is estimated at 25 to 35 per cent. In Table 14, column (4) the experimental error for each isotope has been assigned. Possible counting efficiency errors for Se^{73} and Ge^{69} have not been included.

The Effects of Secondary Reactions

In the solid bromine run 0.2-per cent and 0.1-per cent yields (where the percentages are based on mesons) of 26.8-hr. arsenic activity created presumably by an (n, α) reaction, were found in samples 5 and 6 which were beyond the range of π^- in bromine. If it is assumed that that neutrons are given off isotropically from π^- capture, then the total contribution of neutron-induced reactions to the previously calculated yield of 26.8-hr. arsenic activity (6.7 per cent) is about 6 per cent of the total 26.8-hr. yield. The (n, α) reaction on bromine also leads to As^{78} so that it is expected that the meson yield of As^{78} will be reduced to 0.8 per cent. No 40-hr. or 17.5-day activities were seen in the solid bromine run beyond the meson range although these were observed in run 7. The maximum contributions of neutron-induced reactions to the yields of 17.5-day As^{74} and 40-hr. As^{77} and As^{71} are seen from run 7 to be about 4 per cent and 5 per cent of the respective total yields. The corrected mean yields of arsenic isotopes and their estimated experimental errors are listed in Table 20.

TABLE 20

Corrected Mean Yields of Arsenic Isotopes

Isotope	Neutron Uncorrected Yield (per cent)	Corrected Yield (per cent)
As^{74}	7.3 ± 1.8	7.0 ± 1.8
$\text{As}^{77}, \text{As}^{71}$	3.8 ± 0.9	3.6 ± 0.9
$\text{As}^{76}, \text{As}^{72}$	6.7 ± 1.7	6.3 ± 1.7
As^{78}	0.9 ± 0.3	0.8 ± 0.3

The yields of other isotopes observed in π^- activation should not be affected by neutron-induced reactions. Cross-sections for interfering reactions such as $\text{Br}^{79}(n, p\bar{n})\text{Se}^{73}$ or $\text{Br}^{79}(n, \alpha p)\text{Ge}^{75}$ are expected to be very low. It should be mentioned that not all activation observed beyond the range of π^- 's need be neutron-induced. It has been shown that μ^- produce stars also.²³ About 60 per cent of slow μ^- are captured in photographic emulsions before decay. Of these some 8 per cent produce stars, the majority of which are one-prong stars. Since the range of μ^- in bromine is about 15 per cent more than

that of π^- , a small amount of activation might be expected.

Empirical Isotopic Yields of Arsenic Isotopes

It is proposed that the yields of all the arsenic isotopes can be obtained if the following general assumptions are made:

- (1) The interaction of a π^- with Br^{79} is the same as that with Br^{81} .
- (2) The isotopic yields fall on a smooth curve, and the yield of a given isotope is comparable to those of adjacent mass number.
- (3) The yields for a given process are the same for both bromine isotopes.

The yield of each arsenic isotope depends on the yields of two reactions. For example, As^{78} is formed from $\text{Br}^{79}(\pi^-, p)$ and $\text{Br}^{81}(\pi^-, p2n)$. Since Br^{79} and Br^{81} are approximately equal in abundance, the As^{78} yield is the sum of the single-reaction yields. This sum has been found experimentally to be equal to 0.8 per cent. Similarly the sum of the $(\pi^-, p4n)$ and $(\pi^-, p6n)$ reaction yields is equal to 7.0 per cent, the 17.5-day As^{74} yield. The 26.8-hr. yield of 6.3 per cent is the sum of the yields of 26.8-hr. As^{76} and 26-hr. As^{72} . The As^{76} yield is made up of the $(\pi^-, p2n)$ and $(\pi^-, p4n)$ yields while the As^{72} yield is the sum of the $(\pi^-, p6n)$ and $(\pi^-, p8n)$ yields. If the counting efficiency of As^{72} is designated as n and the single-reaction yields of (π^-, p) , $(\pi^-, p2n)$, $(\pi^-, p4n)$, $(\pi^-, p6n)$, and $(\pi^-, p8n)$ are designated as x , y , z , u , and v respectively, the statements above can be summarized as follows:

$$x + y = 0.8$$

$$z + u = 7.0$$

$$y + z + n(u + v) = 6.3$$

The value of n is taken as 0.35 (see Table 11), and x and v are both assumed to be small, say 0.1 per cent. This assumption will be partially justified below. Then $y = 0.7$, $z = 4.8$ and $u = 2.2$. The resultant isotopic yields are As^{78} - 0.8 per cent, As^{76} - 5.5 per cent, As^{74} - 7.0 per cent, As^{72} - 2.3 per cent, and As^{70} - 0.1 per cent. The As^{70} yield is estimated on the assumption that the $(\pi^-, p10n)$ yield should be less than the $(\pi^-, p8n)$ yield. Since the latter yield is already small, the As^{70} yield should also be quite small.

The same technique cannot be applied to the yields of reactions in which an odd number of neutrons are emitted. No yields of this type are unambiguously known. Since the counting efficiency of As^{71} is low, the major contribution to the 40-hr.-activity count rate must be from As^{77} . Yields of odd neutron reactions have been assigned by interpolating between values calculated for even neutron-reaction yields. The yields of single reactions leading to arsenic isotopes are given in Table 21. The isotopic yields are the sums of pairs of these reactions and are calculated in Table 22.

TABLE 21
Empirical Single-Reaction Yields

Reaction	Yield (per cent)	Reaction	Yield (per cent)
(π^-, p)	0.1	$(\pi^-, p5n)$	3.5
pn)	0.4	p6n)	2.2
p2n)	0.7	p7n)	1.1
p3n)	3.1	p8n)	0.1
p4n)	4.8	p9n)	0
		p10n)	0

TABLE 22
Arsenic Isotopic Yields

Isotope	Yield (per cent)	Isotope	Yield (per cent)
As ⁷⁸	0.8	As ⁷³	4.6
As ⁷⁷	3.5	As ⁷²	2.3
As ⁷⁶	5.5	As ⁷¹	1.1
As ⁷⁵	6.6	As ⁷⁰	0.1
As ⁷⁴	7.0		

If the (π^-, p) yield were as large as 0.3 per cent, the yields of (π^-, p) , (π^-, pn) , and $(\pi^-, p2n)$ would be nearly equal. This would not be in keeping with the rest of the curve since it rises sharply at $(\pi^-, p3n)$. There is more arbitrariness in assigning the $(\pi^-, p8n)$ yield as 0.1 per cent. From the slope of the curve, Figure 22, one would guess that the yield of As⁷⁰ ought to be 0.5 per cent or less which would mean that the yield of $(\pi^-, p8n)$ ought to be about 0.4 per cent or less.

Empirical Isotopic Yields of Other Elements

For other elements isotopic-yield assignments are much less clear since there are fewer radioactive isotopes that we have identified. Assuming as a first approximation that the shapes of their yield curves are the same as that of arsenic, we have fitted the arsenic yield curve to the experimentally known selenium and germanium points. The experimental gallium width seems much broader, and the arsenic curve does not fit all. Consequently an arbitrary curve, much flatter, has been drawn in. The curves and experimental points are shown in

Fig 22
84

3134.88

3/34-89

fig 23

Figure 22. The vertical lines through the experimental points indicate the estimated experimental error. The points at which the curves have been fitted are as follows:

- (1) Selenium - Se^{73} , 3.6 per cent; Se^{72} , 3.2 per cent.
- (2) Germanium - Ge^{69} , 0.6 per cent; Ge^{75} , 0.3 per cent; Ge^{67} , <1.3 per cent; Ge^{66} , <0.2 per cent.
- (3) Gallium - Ga^{73} , 0.4 per cent; Ga^{72} , 0.6 per cent; Ga^{68} , 1.2 per cent; Ga^{66} , <0.2 per cent.

The smooth-curve yields, added for each mass number and for each element, are shown in Table 23.

TABLE 23

Smooth-Curve Isotopic Yields

Mass Number	Selenium	Arsenic	Germanium	Gallium	Total
78	1.3	0.8	...	...	2.1
77	3.5	2.9	...	...	6.4
76	6.0	5.2	...	...	11.2
75	7.3	6.8	0.3	...	14.4
74	7.0	7.0	2.7	...	16.7
73	4.3	4.6	4.9	0.4	14.2
72	2.5	2.5	5.5	0.6	11.1
71	1.3	1.2	4.7	1.1	8.3
70	0.4	0.1	2.0	1.4	3.9
69	...	...	0.6	1.5	2.1
68	...	...	...	1.2	1.2
67	...	...	...	0.7	0.7
66	...	...	...	0.2	0.2
Totals	33.6	31.1	20.7	7.1	92.5

Comparison with Plate Studies

In order to correlate these data with prong distributions obtained in photographic plates, it is necessary to correct the emulsion data for the occurrence of alpha particles. Menon and associates³³ state that 30 ± 4 per cent of all prongs are due to alphas rather than protons. Their prong distribution before and after correction as compared with this research is shown in Table 24. The agreement is good except for arsenic. In the evaporation theory (see below, this chapter) the relative emission probabilities of protons to alphas are in the ratio 5 to 1 for a reasonable nuclear temperature associated with π^- capture. This suggests that perhaps only 15 per cent of prongs are alphas, in which case the agreement becomes quite good. These comparisons are not altogether valid since our results are for capture at all energies up to 122 Mev while Menon's data are for capture at rest. The prong distribution for π^- capture in flight as compared to π^- capture at rest (see Table 6) shows a higher percentage of three-

and four-prong stars and a lower percentage of two-prong stars. The one- and two-prong percentages are relatively unchanged.

TABLE 24
Comparison with Prong Distributions

Change in Atomic Number (1)	Percentages			
	(2) ^a	(3) ^b	(4) ^c	(5) ^d
0	34	34	34	34
1	33	23	29	31
2	22	26	23	21
3	5	11	7	7
4	5	5	5	..
5	1	1	2	..
Totals	100	100	100	93

^aAll prongs are protons.

^bThirty per cent of prongs are alpha particles.

^cFifteen per cent of prongs are alpha particles.

^dThis research.

Capture of π^- Mesons in Flight

In run 8, the solid-bromine irradiation, it was found that the mixed-sulfides decay curves of the front four samples were parallel within experimental error. We conclude that the relative amounts of 26.8-hr., 40-hr., and 17.5-day arsenic activities formed are the same for fast or slow capture (i.e., capture in flight or capture at rest). Because of the difficulty of resolving cleanly a 26.8-hr. activity from a 40-hr. one, the relative amounts may actually differ by 25 per cent from sample to sample, and this difference would not be seen. However, there was no systematic difference in slopes and no regularities could be observed. The total yield of each of the three activities checked quite closely with the mean value obtained in previous runs.

In Figure 23 the yield in the 1th sample of the three activities obtained has been plotted against residual range as the meson leaves the sample. The energy corresponding to this range is also indicated. The fraction of total activity found in the fourth sample was 38 per cent, 39 per cent, and 38 per cent, respectively, for the 26.8-hr., 40-hr., and 17.5-day activities. If the capture cross-section of bromine for fast π^- mesons is geometrical, 1.13 barns, then one would expect about 38 per cent to be captured in flight, that is, in samples 1 to 3 plus part of 4, and about 62 per cent to be captured at rest in 4. This is for the ideal case in which there is no

scattering. The yield should drop exponentially in the first three samples and rise sharply at sample 4. Since our yields seem to increase slowly in going from samples 1 to 3, probably scattering has occurred to a considerable extent. That is, if the path length of the meson in bromine because of scattering is a great deal more than the straight-line path, some mesons may have come to rest in sample 2, for example, instead of reaching sample 4.

Comparison with Evaporation Model

If one plots the total yield of a given mass number against mass number, it will be seen that $A = 74$ has about a 20 per cent higher yield than either 73 or 75 and yields for the remainder of mass numbers drops off rapidly. The number of nucleons that must be emitted to obtain $A = 74$ is five or seven depending on whether Se^{79} or Se^{81} is the excited nucleus. Considering six to be the mean number of nucleons emitted and the nuclear excitation energy to be 140 Mev, we have applied evaporation theory⁵⁶ to the excited selenium nuclei Se^{79} and Se^{81} to determine what the yields of various isotopes will be. The nuclear temperature T can be calculated approximately from the following equation:⁵⁷

⁵⁶V. F. Weiskopf, Phys. Rev., 52, 295 (1937).

⁵⁷Y. Fujimoto and Y. Yamaguchi, Prog. Theor. Phys., 5, 787 (1950).

$$T^2 \cong 10 X / A$$

where X is the excitation energy in Mev and A is the mass number. In this calculation T has been taken as 4 Mev.

Let the mean life of the excited selenium nucleus be τ corresponding to a total width or emission probability Γ , and the widths for the emission of individual particles be Γ_n, Γ_p and Γ_α for the emission probabilities of neutrons, protons and alphas. The mean number of nucleons emitted will be

$$\int_0^\infty \left(\frac{\Gamma_n + \Gamma_p + 4\Gamma_\alpha}{\tau} \right) e^{-\frac{t}{\tau}} dt = \frac{\Gamma_n + \Gamma_p + 4\Gamma_\alpha}{\Gamma}$$

where τ is the mean life. The ratio of particle widths are estimated from Coulomb barrier considerations and the ratio $\Gamma_n : \Gamma_p : \Gamma_\alpha$ is equal to $1 : \exp(-6.4/4) : \exp(-12.8/4)$ or $25 : 5 : 1$. The Coulomb barrier for protons in a nucleus of $A = 80$ is 6.4 Mev; the temperature is 4 Mev. Setting the mean number of nucleons lost at six,

$$\frac{\Gamma_n + \Gamma_p + 4\Gamma_\alpha}{\Gamma} = 6 \text{ and combining } (25 + 5 + 4) \frac{\Gamma_\alpha}{\Gamma} = 6, \text{ we get } \frac{\Gamma_p}{\Gamma} = \frac{6}{34}, \frac{\Gamma_\alpha}{\Gamma} = \frac{30}{34} \text{ and } \frac{\Gamma_n}{\Gamma} = \frac{150}{34}. \text{ It follows from the above}$$

analysis the $\frac{\Gamma_1}{\Gamma}$ is the mean number of particles of type i that are emitted. A Poisson distribution will apply to the emission of the particles. Consequently the yield of the isotope from Se^{79} or Se^{81} that requires the emission of ν_n neutrons, ν_p protons, ν_α alpha particles will be

$$\frac{\left(\frac{150}{34}\right)^{\nu_n} \left(\frac{30}{34}\right)^{\nu_p} \left(\frac{6}{34}\right)^{\nu_\alpha}}{\nu_n! \nu_p! \nu_\alpha!} e^{-\frac{186}{34}}$$

It is implicit in this theory that there is a means of carrying off excess energy by ways other than particle emission. In every π^- -capture at rest at least 140 Mev (rest mass of π^-) of excitation energy is fed into the capturing nucleus. The emission of a single neutron, for example, has a probability corresponding to 0.9 per cent. Since boiling off a neutron de-excites a nucleus only about 8 Mev in binding energy plus about 2kt kinetic energy on the average, the remaining energy must somehow be lost unless the resultant nucleus is to undergo further boiling off.

Since each isotope can be made in two days (i.e., from Se^{79} or Se^{81}) an average of the two individual yields has been taken to represent the yield. The calculated distribution is shown in Table 25. The yield of individual isotopes agrees quite well for arsenic, selenium, and gallium but not as well for germanium. Evaporation predicts a much broader and flatter distribution than the curve that we have fitted. However, the fitted germanium curve is in considerable doubt; only two points are known with reasonable certainty.

TABLE 25
Evaporation Model Distribution, Non-Cooling, $T = 4$ Mev.

Mass Number	Selenium	Arsenic	Germanium	Gallium	Total
81	0.2	...	...	...	0.2
80	0.9	...	...	...	0.9
79	2.3	...	...	...	2.3
78	3.9	2.0	0.4	...	6.3
77	5.3	3.4	0.9	...	9.6
76	5.9	4.7	1.7	...	12.3
75	5.5	5.2	2.5	...	13.2
74	4.2	4.8	3.0	...	12.0
73	2.9	3.8	2.9	1.3	10.9
72	1.7	2.5	2.6	1.4	8.2
71	0.9	1.5	2.0	1.4	5.8
70	0.4	0.8	1.4	1.2	3.8
69	...	...	0.9	0.9	1.8
68	...	...	0.4	0.6	1.0
67	...	...	0.2	0.3	0.5
66	...	...	0.1	0.2	0.3
65	...	...	...	0.1	0.1
Totals	34.1	28.7	19.0	7.4	89.2

Fujimoto and Yamaguchi⁵⁷ take into account the cooling of the nucleus as particles are emitted. For the case of the emission of neutrons, protons, and alphas from a nucleus of mass number 100 and an excitation energy of 100 Mev, they calculate the mean number of neutrons, protons, and alphas emitted to be 4.7, 1.0, and 0.27 respectively. The calculations are sufficiently approximate, such that their results can probably be applied to our nucleus of mass number 80 without appreciable error. The dependence on mass number in these calculations is primarily in the binding energy of a nucleon, the nuclear temperature, and the Coulomb barrier. The isotopic distribution obtained is given in Table 26. This is clearly no better a fit than the non-cooling case. If an excitation energy of 140 Mev is used the mean number of neutrons, protons, and alphas becomes about 5.9, 1.5, and 0.5 respectively or a total of 9.4 nucleons as the mean number emitted. This is too high to fit the experimental data.

TABLE 26
Evaporation Model Distribution with Cooling, $T_0 = 3.5$ Mev

Mass Number	Selenium	Arsenic	Germanium	Gallium	Total
81	0.1	...	...	...	0.1
80	0.6	...	...	...	0.6
79	1.5	...	...	...	1.5
78	2.9	1.5	0.3	...	4.7
77	4.1	2.9	0.8	...	7.8
76	4.7	4.1	1.6	...	10.4
75	4.6	4.7	2.4	...	11.7
74	3.8	4.6	3.1	...	11.5
73	2.7	3.8	3.4	1.9	11.8
72	1.7	2.7	3.2	2.2	9.8
71	0.9	1.7	2.5	2.0	7.1
70	0.5	0.9	1.8	1.6	4.8
69	...	...	1.2	1.1	2.3
68	...	...	0.7	0.7	1.4
67	...	...	0.4	0.4	0.8
66	...	...	0.2	0.2	0.4
65	...	...	...	0.1	0.1
Totals	28.1	26.9	21.6	10.2	86.8

In the non-cooling model the emission of deuterons and tritons was considered in conjunction with neutrons, protons, and alphas. Deuteron emission increases the yields of higher A isotopes and decreases lower A yields in the case of arsenic isotopes. Triton emission has such a small width that it does not sensibly affect the distribution. Other permutations were attempted to obtain a better fit: higher and lower temperatures, larger and smaller mean number of nucleons emitted.

The best fit with experimental points was obtained with $T = 3$ Mev, corresponding to an excitation energy of 72 Mev. The emission

of neutrons, protons, alphas, and deuterons was considered, and the mean number of ejected nucleons was taken as six. The deuteron width was estimated to be 0.9 times the alpha width.⁵⁷ The calculated distribution is given in Table 27 and shown graphically in Figure 24. Experimental isotopic yields and their estimated errors are also indicated. The arsenic points would fit the curve much better at mass numbers 71, 72, 76, and 77 if the As⁷⁶ and As⁷⁷ yields were reduced and the As⁷¹ and As⁷² yields were increased. It will be recalled that the measured 40-hr. yield was the sum of the As⁷¹ and As⁷⁷ yields. If we have incorrectly divided the total 40-hr. activity between As⁷¹ and As⁷⁷, it is quite possible that the evaporation-model curve fits the experimental points closely. The same considerations apply to the As⁷² - As⁷⁶ pair. After the arsenic deviations are taken care of in this way, the only experimental points that are more than twice experimental error from the theoretical curve are Ge⁷⁵ and Ga⁶⁸. The fit then is in general quite good.

TABLE 27
Evaporation Model Distribution, Non-Cooling, T = 3 Mev

Mass Number	Selenium	Arsenic	Germanium	Gallium	Total
81	0.2	...	...	...	0.2
80	0.8	...	...	...	0.8
79	2.2	...	...	...	2.2
78	4.2	1.3	0.2	...	5.7
77	6.2	2.6	0.4	...	9.2
76	7.6	3.9	0.9	...	12.4
75	7.7	4.9	1.4	...	14.0
74	6.7	5.0	1.8	...	13.5
73	5.0	4.4	2.0	0.44	11.8
72	3.3	3.4	1.9	0.53	9.1
71	2.0	2.3	1.5	0.55	6.4
70	1.1	1.4	1.1	0.45	4.0
69	...	...	0.7	0.40	1.1
68	...	...	0.4	0.24	0.6
67	...	...	0.2	0.17	0.4
66	...	...	0.1	0.10	0.2
65	...	...	0.05	0.05	0.1
Totals	47.0	29.2	12.6	2.9	91.7

We consider now the hypothetical case in which bromine has but one stable isotope of mass A. The single-reaction yields* have been

*It should be clear that the isotopic yields of Table 27 were calculated by averaging the yields of appropriate pairs of single reactions in Table 28.

calculated from the evaporation model and are shown in Table 28. The reactions shown are meant to designate only the total number and type of nucleons ejected. In the calculations the emission of alphas and deuterons has been included.

Fig 24

Fig 25

TABLE 28
Single-Reaction Yields

Reaction	Yield	Reaction	Yield	Reaction	Yield	Reaction	Yield
π^- , n	1.6	π^- , p	0.2	π^- , 2pn	0.3	π^- , 3p3n	0.3
2n	4.0	pn	1.0	2p2n	0.8	3p4n	0.5
3n	6.7	p2n	2.5	2p3n	1.4	3p5n	0.6
4n	8.4	p3n	4.2	2p4n	2.0	3p6n	0.6
5n	8.4	p4n	5.4	2p5n	2.3	3p7n	0.5
6n	7.0	p5n	5.4	2p6n	1.9	3p8n	0.3
7n	5.0	p6n	4.6	2p7n	1.5	3p9n	0.3
8n	3.1	p7n	3.3	2p8n	1.0	3p10n	0.2
9n	1.7	p8n	2.1	2p9n	0.6	3p11n	0.1
10n	0.9	p9n	1.2	2p10n	0.3	3p12n	0.04
11n	0.6	p10n	0.6	2p11n	0.2		
				2p12n	0.1		

The single reaction yields are plotted on a contour map in Figure 25. One is tempted to describe a path followed in the emission of nucleons from π^- capture, but there is some doubt whether the evaporation model used correctly describes the process. Only qualitative general conclusions should be drawn. The contour lines indicate the highest yields to be in regions of maximum nuclear stability. The total yield for each atomic number drops sharply past two z units from the target nucleus.

The results of the evaporation-model calculation suggests that only about 70 Mev of the absorbed energy is available for evaporation. An interaction model that might be considered, then, is one in which the rest energy from π^- capture is transferred to two or three nucleons. If their energies are sufficiently high and their momenta are properly directed, they may escape from the nucleus. Since some of the energy is available for evaporation, however, perhaps only two nucleons escape the nucleus in the primary process. The kinetic energy of the third and probably a portion of the kinetic energies of the two escaping lead to the excitation of the nucleus. Even a qualitative interpretation is difficult since capture in our studies has occurred at all kinetic energies of the absorbed mesons up to 122 mev.

The fit we have obtained by the arbitrary choice of the nuclear temperature and the mean number of nucleons emitted may not represent reality but should give some basis for predicting yields in π^- capture by other elements. It should be noted that the calculation is more properly made for the excited nuclei Se⁷⁷ and Se⁷⁹ or perhaps As⁷⁷ and As⁷⁹ rather than for Se⁷⁹ and Se⁸¹. This arises because of the two primary nucleons postulated to be lost before evaporation begins. One of these must be a neutron. The other may be a neutron or a proton. When this calculation was performed, the mean number of evaporated nucleons was taken as four, and the distributions were calculated for the case of Se⁷⁷, Se⁷⁹ and As⁷⁷, As⁷⁹ as the excited nuclei. The

distribution in the former case was weighted two-thirds and in the latter case one-third. The weighting factor arises from the following considerations: If the two escaping particles are considered to be those formed in the primary interaction, then the emission of two neutrons is favored over a neutron and a proton by a factor of about two.

The calculated weighted distribution for the emission from the excited nuclei of lower mass number is quite similar to that obtained in Table 27. Within our experimental error either set of curves could be considered a reasonable fit. An inspection of the calculated width (emission probabilities) indicates that alpha particle emission is much less favored than photographic plate data would imply. The ratio of numbers of protons to alphas is 8.5 in the evaporation model as compared to the value 3.3 found by Menon.³³ The total yield per element in the evaporation model does not agree with prong distributions. Almost half the total yield in our model is found in selenium. In photographic plates the corresponding zero-prong stars occur in about 34 per cent of heavy-nuclei capture.³³

Comparison with Spallation

The study of spallation in middle-weight nuclei^{58,59} leads to the

⁵⁸Cunningham, Hopkins, Lindner, Miller, O'Connor, Perlman, Seaborg, and Thompson, Phys. Rev., 72, 739 (1947); Miller, Thompson, and Cunningham, Phys. Rev., 74, 347 (1948); H. Hopkins, Phys. Rev., 77, 717 (1950); M. Lindner and I. Perlman, Phys. Rev., 78, 499 (1950).

⁵⁹Batzel, Miller, and Seaborg, Phys. Rev., 84, 671 (1951).

following general conclusions about the high-energy interaction of the bombarding nucleon with nucleons in a nucleus:

(1) A large majority of the spallation products results from reactions in which only a fraction of the total energy of the incident particle is left with the nucleus.

(2) The distribution of the yields of the reaction products is in agreement with a picture of high-energy nuclear reactions involving nuclear transparency⁶⁰ and the idea that the nuclear reactions involve

⁶⁰R. Serber, Phys. Rev., 72, 1114 (1947).

excitation following collisions and energy transfers between the impinging particle and the individual nucleons of the target nucleus.

Spallation yields are highest in the elements near the target in atomic number. In general, for a given element the yield is a maximum in the region of maximum nuclear stability. However, for elements near the target in atomic number, the maximum yield is shifted slightly toward the neutron-deficient isotopes; for those far away in atomic number, the maximum yield lies in the neutron-rich region.

It is seen that these same conclusions might be applied to π^- capture. While it is difficult to compare, for example, the results of 340-Mev protons on copper⁵⁹ with those of 122-Mev π^- mesons on bromine, it is thought that spallation-like processes probably occur in π^- capture. In comparing spallation with π^- capture, we find some evidence for a different shape in the yield curves and a different rate of decrease of yield with atomic number, but our experimental errors are such that the differences may not be real.

APPENDIX I

RANGE-ENERGY RELATION OF π MESONS

The range-energy curves for π mesons shown in Figure 26 were calculated from W. A. Aron's³⁶ range-energy curves of protons in copper and silver. The rate of energy loss of an energetic particle depends only on the velocity of the particle. The range of a particle is a function of the rate of energy loss. The energies of a π meson and a proton of the same velocity are related by the equation

$$E_{\pi} = \frac{m_{\pi}}{m_p} E_p .$$

where E and m are kinetic energy and mass, respectively. Their range, for a given velocity of both particles are given by

$$R_{\pi} = \frac{m_{\pi}}{m_p} R_p$$

Hence if a range-energy curve for protons is available, it is possible to calculate a range-energy curve for mesons or other particles. This, of course, is limited to relatively heavy particles that show no large amount of scattering.

APPENDIX II

PREPARATION OF BROMINE DISKS

A pyrex plate 6 inches by 6 inches by 1/4 inch was covered with a thin film of silicone stopcock grease and placed on a cake of dry ice somewhat larger in area than the plate. A pyrex ring 10 cm in diameter and 4.7 cm in height was placed on top of the plate, and powdered dry ice was packed around the ring. A small amount of liquid bromine, precooled in ice water, was slowly poured into the ring until the layer was about 1/8-inch thick. This was allowed to freeze solid.

Fig 2.6

Then the packed dry ice was removed, and the plate and ring were placed on a wire gauze support such that the ring and plate assembly could be raised from or lowered into a trough containing liquid nitrogen. The assembly was placed in liquid nitrogen until temperatures had more or less equilibrated. Then with the assembly out of the liquid nitrogen bath, more precooled bromine was added (about 1/2 inch additional). The assembly was returned to the liquid nitrogen bath until the bromine had frozen solid.

This procedure was repeated until the top level of the ring had been reached. The last freezing step was done carefully since the center remains liquid for quite a long while even though a hard crust forms on top. When it was certain that the center was not liquid, the assembly was taken out of the liquid nitrogen bath and the wire gauze was removed. Then by twisting sharply on the ring, the solid bromine and the ring were freed from the plate. Silicone grease was found to be necessary in order to remove the plate. Otherwise the bromine tends to separate from the ring, and the solid bromine remains on the plate. It was found to be preferable to start the freezing with dry ice because liquid nitrogen boiled violently on the first addition of even pre-cooled bromine and the initial seal of ring to plate was difficult to make. Because this violent boiling of the liquid nitrogen also tends to sweep out bromine fumes, it was desirable to add bromine when the assembly was out of the liquid nitrogen bath.

APPENDIX III

SUMMARY OF IRRADIATION DATA

Tables 29 (shown on the following page) and 30 summarize the irradiation data of this research. Figure 27 gives the meson intensity at 2-minute intervals in a typical run. Run 2 was selected as typical since it showed neither the most nor least fluctuation in intensity during an irradiation. Figures 28 through 33 are A_0/N graphs. To calculate the A_0 value for any isotope, determine the A_0/N value corresponding to the half-life of the isotope. Multiply by the number of mesons per watt-minute as given in Table 29.

TABLE 30

Other Irradiations

Run No.	Type	Date	Time of Irrad.	Target
6	High energy neutrons Synchrocyclotron pit	1/30/52	30 min.	Liq. Br ₂
9	Thermal neutrons Radium-beryllium source	11/14/51	36 hrs.	As ₂ S ₃
10	8 Mev deuterons Small cyclotron	12/5/51	1 hr.	Ga ₂ O ₃

TABLE 29
Meson Irradiations

Run No.	Energy of π^- (Mev)	Date	Time of Irrad. (min.)	Magnet Pole Gap (in.)	Mesons per watt-min. $\pm \sigma$	Total No. Mesons	Scin. Counters
1	145	10/18/51	60	2 x 3	14,100 $\pm$ 1,000	6.68 x 10 ⁶	Old
2	122	11/5/51	120	2 x 3	30,200 $\pm$ 1,700	3.36 x 10 ⁷	Old
3	122	11/7/51	224	2 x 3	29,100 $\pm$ 2,600	8.06 x 10 ⁷	Old
4	122	11/27/51	318	2 x 3	35,400 $\pm$ 2,200	1.71 x 10 ⁸	Old
5	122	12/13/51	358	2 x 3	42,700 $\pm$ 1,800	2.09 x 10 ⁸	Old
7	122	2/28/52	180	2 x 3	29,200 $\pm$ 1,000	7.36 x 10 ⁷	New
8	122	4/15/52	702	4 x 5	71,600 $\pm$ 2,400	1.31 x 10 ⁸	New

202

6.6
3134.123

MESON INTENSITY (NO. PER MIN IN THOUSANDS)

400
300
200
100

0

10

20

30

40

50

60

70

80

90

100

110

120

TIME (MINUTES)

Fig 6

9134-104

Fig 28

3138-105

Fig 9.1

3/34-10

3/34-10

100%

9/28/82

100%

3/34-108

3/34-108

3/34-108

3134-109

APPENDIX IV

SUMMARY OF CHEMICAL DATA

Table 31 summarizes the data pertaining to the samples that were separated in the various runs. The explanation of columnar headings and abbreviations used is as follows:

Column (1) indicates the number of the run. The symbols S and C stand for sample run (magnet on) and control run (magnet off). The six disks of run 8 are numbered 1 through 6.

Column (2) is the chemical nature of the solid that was mounted on the sample cylinder. The mixed sulfides are represented by M. S. and the alkali residue by A. R. The 8-hydroxyquinolate group has been indicated by the symbol X. Selenium samples were precipitated twice in the same run. The numbers pertaining to Se(2) include similar numbers of Se(1); that is, Se(2) is the total for all selenium samples of run 5.

Column (3) lists the nature of the carrier added and the column (4) its weight in mg. Column (5) indicates the weight mounted in mg of the substance listed in column (2). Column (6) gives the per cent chemical yield based on the weight mounted.

Columns (7) and (8) give the area of the sample in cm^2 and the thickness in mg/cm^2 respectively. Column (9) indicates the type of mounting. The symbol 1 means that the sample was on a 9-cm filter-paper backing while 2 means that the sample was placed directly on the sample cylinder.

Column (10) gives the thickness of external absorber in mg/cm^2 that is seen by the sample.

TABLE 31

Chemical Yields and Sample Dimensions

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
2S	BaSO ₄	Ba ⁺⁺	680	1030	90	100	10.3	2	2.7
	M. S.	AsBr ₃	500						
		GeBr ₄	620	371	90	80	4.64	2	5.4
	Fe(OH) ₃	Fe ⁺⁺⁺	260	780	83	100	7.8	2	2.7
	A. R.			7500		100	75	2	2.7

TABLE 31--Continued

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
2C	BaSO ₄	Ba ⁺⁺	680	1010	87	100	10.1	2	2.7
	M. S.	AsBr ₃	590	402	90	78	5.15	2	5.4
		GeBr ₄	620						
	Fe(OH) ₃	Fe ⁺⁺⁺	260	750	83	100	7.5	2	2.7
	A. R.			6000		100	60	2	2.7
3	As ₂ S ₃	AsBr ₃	600	75	32.1	63.6	1.18	1	5.4
	GeS ₂	GeBr ₄	745	147	56.8	77.4	1.90	2	5.4
	M.S.	AsBr ₃	600	99	20.0	63.6	1.65	1	5.4
		GeBr ₄	745						
4	As ₂ S ₃	AsBr ₃	790	36	11.7	63.6	0.57	1	5.4
	GeS ₂	GeBr ₄	620	105	48.6	82.2	1.28	2	5.4
	M. S.	AsBr ₃	790	105	20.0	63.6	1.65	1	5.4
		GeBr ₄	620						
	GaX ₃	Ga ⁺⁺⁺	93	503	75.0	126	3.99	2	5.4
5	As ₂ S ₃	AsBr ₃	610	72	30.1	65.9	1.1	2	5.4
	GeS ₂	GeBr ₄	620	12	6				
	M. S.	AsBr ₃	610	50	11.3	62	0.81	2	5.4
		GeBr ₄	620						
	Se(1)	Se	700	146	20.8	63.6	2.30	1	5.4
	Se(2)	Se	700	352	50.3	63.6	5.53	1	5.4
	GaX ₃	Ga ⁺⁺⁺	93	293	43.7	87	3.37	2	5.4
	ZnX ₂	Zn ⁺⁺	100	608	92.6	87	7.0	2	5.4
7	M. S.	AsBr ₃	680						
		GeBr ₄	620	480	100	190	2.84	2	5.4
8-1	M. S.	AsBr ₃	240						
		GeBr ₄	155	142	95	69	2.06	2	5.4
8-2	M. S.	AsBr ₃	240						
		GeBr ₄	155	144	97	88	1.63	2	5.4

TABLE 31--Continued

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
8-3	M. S.	AsBr ₃ GeBr ₄	250 155	147	96	57	2.59	2	5.4
8-4	M. S.	AsBr ₃ GeBr ₄	250 155	142	93	72	1.96	2	5.4
8-5	M. S.	AsBr ₃ GeBr ₄	230 155	130	90	65	2.00	2	5.4
8-6	M. S.	AsBr ₃ GeBr ₄	240 155	140	94	71	1.98	2	5.4