derived from our experiments, assuming that all the photons are caused by recombination, lie between $\rho_e = 1\times10^{-12}$ and 2×10^{-12} cm^3/sec for ion concentrations of $\approx 6\times10^{16}$/cm^3 and an electron temperature of $\approx$4500°K. It compares favorably with the calculated values by Cillie[8] of $\rho_e = 7\times10^{-13}$ to 1×10^{-12} cm^3/sec; the precise value would depend sensitively on the electron temperature.

These results disagree with those of Olsen and Huxford[9] obtained with a similar apparatus. However, their measurements were not made in a field-free region, but between the electrodes of a tube very similar to our shock discharge chamber. The effect of the field is illustrated by experiments by Miller[10] in our laboratory. When a voltage pulse is applied to the electrodes at certain intervals after the beginning of the discharge, it is found that, during the first ten microseconds, production exceeds recombination in the discharge chamber, because the pulse makes the discharge more intense.

If a pulse is applied later, the intensity drops because the rate of recombination decreases owing to the increasing electron temperature. Thus the low values of recombination coefficient observed in "active" discharges are probably a result of the continuing processes of production which maintains the ion concentration during a time interval in which it was presumed to be decaying freely.

It is planned to exploit the method outlined above to obtain data for a larger range of ion concentrations and temperatures.

ACKNOWLEDGMENT

The authors are indebted to Dr. A. von Engel for his detailed comments and criticisms on this paper.

[8] G. Cillie, Monthly Notices Roy. Astron. Soc. **92**, 820 (1931/2).
[9] H. Olsen and W. Huxford, Phys. Rev. **87**, 927 (1952).
[10] F. Miller, M. S. thesis, University of Oklahoma, 1956 (unpublished).

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Halogen Delayed-Neutron Activities*

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A gas-flow technique has been developed to make rapid chemical separations of bromine and of iodine fission products from a solution of U^{235} irradiated with thermal neutrons. The active bromine or iodine is observed by its delayed neutron emission. Analysis of the decay curves so obtained has been made by graphical and by computer methods. Four delayed-neutron periods have been found in the bromine fraction and three in the iodine. Including several already well known, the half-lives and probable mass assignments are as follows: 54.5-sec Br^{87}, 16.3-sec Br^{88}, 4.4-sec Br^{89}, and 1.6-sec Br^{90}; 24.4-sec I^{137}, 6.3-sec I^{138}, and 2.0-sec I^{139}. Shorter-lived halogens would not have been detected. The relative yields of each neutron activity in the order of decreasing half-life are, for bromine, 0.37:1.0:1.9:1.5; while for iodine they are 1.0:0.47:0.38 in the same order. If we assume that there are no other important contributors of delayed neutrons in this half-life range, the numerical values of yields for bromine may be compared directly with those for iodine with an uncertainty of a factor of 2.

I. INTRODUCTION

AFTER U^{235} or similar material undergoes fission, a neutron radioactivity may be observed. The total number of these "delayed" neutrons is about 1% of the number emitted promptly. The process has long been understood[1] in principle. The delayed neutrons are actually emitted promptly from a suitably excited nuclide, but the latter is formed by the β decay of a precursor, whose decay period thus characterizes the neutron activity. If chemical separation of fission products is made, the neutron activity follows the chemistry of the precursor. In the present work, rapid chemical separations of bromine and of iodine have been made from fission products of U^{235} which was bombarded by thermal neutrons. The neutrons are emitted from krypton and xenon isotopes, for which the bromine and iodine isotopes respectively are the delayed-neutron precursors.

Because of their importance in the control of reactors, delayed neutrons have been extensively studied[2,3]—chiefly by examining the "gross" neutron activity, i.e., that which is emitted by an activated sample of fissionable material not subjected to chemical processing. The time behavior of the gross activity usually has been described by a sum of six exponentials decaying

* Work performed under the auspices of the U. S. Atomic Energy Commission.
[1] N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426 (1939).

[2] An extensive bibliography of work to 1956 is contained in the article by G. R. Keepin, in *Progress in Nuclear Energy* (Pergamon Press, Inc., New York, 1956), Vol. I, Ser. 1, p. 201.
[3] Keepin, Wimett, and Zeigler, Phys. Rev. **107**, 1044 (1957); Smith, McVicar, Thorne, and Rose, J. Nuclear Energy **4**, 133 (1957).

with appropriate time-constants and coefficients. The coefficients vary with the type of bombardment and with the target material, but the time-constants show only small variations.[4] Although there have been suggestions that the number of delayed-neutron precursors might number considerably more than six,[5] until recently there has been no direct experimental support for this point of view. It has therefore been more usual to assume that there are indeed just six beta-active nuclides whose mean lives are just the six time-constants of the fit to the gross decay data. Such work as had been done on chemical separation[6–8] was not in obvious disagreement with this point of view. This situation changed, however, with the discovery[9] that Br^{88} is a delayed-neutron precursor, for Br^{88} has a half-life of about 16 sec for which there is no place in the scheme of six. Its delayed-neutron yield was given in I as 3.5 ± 1.5 times that of 54-sec Br^{87}, and this is too large to be considered a minor contaminant. From this one must conclude that there are at least seven major delayed neutron activities. We shall show, however, that there are at least nine. We have investigated halogen activities with half-lives longer than about one second, and find four due to bromine and three due to iodine. The gross activities whose half-lives are approximately 22, 6, and 2 sec are each shown to contain one bromine and one iodine activity. We were not able with the techniques presently available to investigate the remaining two shorter-lived groups.

The chemical technique used in the present work is a refinement of that described in I. The uranium is in an appropriate solution and is irradiated momentarily by a thermal neutron beam, after which a burst of air containing inert halogen of the species of interest passes through the vessel and carries the activity to remote neutron counting equipment. It is clear that if one wishes to examine short-lived activities by such a method, he must use a small solution volume V and high flow rate f. In the course of this work, methods were devised for increasing f/V and at each such stage evidence for shorter-lived halogen delayed-neutron precursors was obtained and reported in preliminary form.[10] In this paper we shall describe only experiments done with the latest version of the apparatus.

II. EXPERIMENTAL METHOD

The main features of the apparatus are represented schematically in Fig. 1. When the valve V_2 is opened (typically for 1.2 sec) a burst of air and halogen mixture, contained in the 3-liter flask R, is sucked through the cell Q containing the uranium solution, which was just previously irradiated with thermal neutrons. It then passes through C and into the evacuated bottle B. About 0.4 liter flows during the burst. If bromine activities are being studied, R contains about 20 mg Br_2 per liter of air, while for studies of iodine it contains air saturated with iodine vapor at room temperature. The two small vessels flanking Q are safety traps to guard against the active solution being drawn accidentally into the room. Q is made of quartz with an empty volume of 50 cm^3 and filled about two-thirds full of soft glass beads of 5-mm diameter. A tamper on top of the beads keeps them in place during the air-flow interval. The solution (4.5 ml) initially wets only the lower balls, and during the air burst is disrupted violently over these and filtered out by the upper ones. The amount of liquid transported out of the cell, for example as droplets, is very slight and was not detected in our experiments. The vessel C also contains glass balls. Prior to each run, these are wet with carbon tetrachloride and the excess drained off. The halogen dissolves in the wet surface and the emitted neutrons may be counted. The remaining gas, which contains a good deal of beta and gamma activity and may contain a small amount of rare-gas neutron activity,[11] continues to B and is pumped out between runs. A ball joint at T

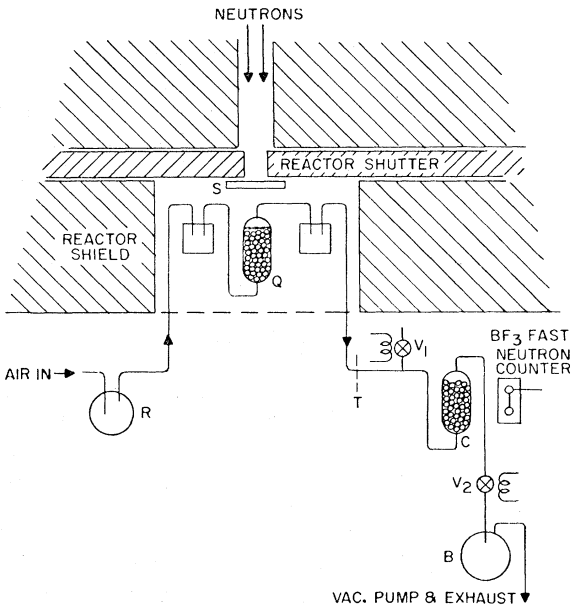

FIG. 1. Schematic diagram of gas-flow system for rapid chemical separation of fission-product halogens.

[4] Typical values of half-life and relative abundance: Keepin *et al.*, reference 3 (thermal fission of U^{235}); 56 sec, 0.03; 22.7 sec, 0.22; 6.2 sec, 0.20; 2.3 sec, 0.40; 0.61 sec, 0.12; 0.23 sec, 0.04.

[5] We are indebted to C. D. Coryell and A. C. Pappas for correspondence expressing this point of view.

[6] Snell, Levinger, Meiners, Sampson, and Wilkinson, Phys. Rev. **72**, 545 (1947).

[7] N. Sugarman, J. Chem. Phys. **15**, 544 (1947).

[8] N. Sugarman, J. Chem. Phys. **17**, 11 (1949).

[9] G. J. Perlow and A. F. Stehney, Phys. Rev. **107**, 776 (1957). This paper will be referred to as I in the subsequent text.

[10] G. J. Perlow and A. F. Stehney, Bull. Am. Phys. Soc. Ser. II, **2**, 309 (1957), and **3**, 6 (1958).

[11] We have done experiments to search for delayed-neutron precursors among the rare gas fission fragments. A weak activity was found, but because of the possibility of inadequate trapping of halogens, and of the $D(\gamma,n)$ reaction in the paraffin moderator of the neutron counter, it is not yet certain that the rare gases were responsible.

may be opened to permit the insertion of a trap for chemistry external to the pile.

The irradiation cell and its safety vessels are imbedded in paraffin except for an entrance window for neutrons, and the unit is contained in a boral box (B_4C sandwiched in aluminum) with a boral shutter (S in Fig. 1) which is operated rapidly by an air cylinder. The latter, in turn, is actuated by compressed air admitted by an electric valve controlled by a master sequence timer. The latter controls V_2 and also valve V_1, which is used to equalize pressures across the irradiated solution immediately after the air burst. The boral box is set into an opening in the thermal column of the Argonne Research Reactor CP-5 just outside of the massive and slow-moving reactor shutter, whose aperture is adjusted to regulate the initial counting rate. A thick shield isolates the box from the experimental area, and no delayed neutrons emitted from the irradiation cell are observable at the neutron counter. The neutron beam is well thermalized and has an intensity $\sim 10^{10}$ neutrons/cm^2 sec. The combined fission rate due to thermal neutrons leaking past the shutter and to fast neutrons going through the shutter was measured to be 0.3% of the rate with the shutter open. Although small, this number leads to a sizable correction to the values of the initial activity of the weak 54-sec bromine for very short irradiations. As a consequence, conclusions about this initial activity are drawn only from longer irradiations.

Counting is done by means of two BF_3 proportional counters connected in parallel and imbedded in paraffin inside a cadmium shield. The counter is adequately flat in response over the energy range from 40 kev to 1 Mev, which contains most of the delayed neutrons.[12] The counts are scaled and recorded on a Brush paper-tape recorder along with time marks from a spring-controlled clock, and a set of marks derived from the timer, valves, and shutter, which characterizes the times of the various functions. The counting system has a dead-time of one microsecond. The counter, the cell C, and a minimum of the piping into the latter, are enclosed in a neutron shield of borated paraffin to minimize background. The latter was generally about one count per second. The counting rates at the start of counting were usually several thousand per sec.

The solution for the bromine work was made with 2.1 g of U^{235} dissolved in a solution $0.5M$ in $NaBrO_3$ and $1M$ in HNO_3. The acid bromate solution oxidized iodine fission products to the nonvolatile IO_3^- form and prevented accumulation of Br^-, which would have decreased the fraction of radioactivity removable as Br_2. For the iodine fission products, the solution to be irradiated consisted of 1.4 g of U^{235} dissolved in 5.0 ml of a solution $0.3M$ in Fe^{+3}, $0.2M$ in Fe^{+2}, and $0.1M$ in H_2SO_4. In addition, 7 mg of Br^- was present as a holdback carrier. The combination of iron compounds served to oxidize I^- to volatile I_2 and to reduce Br_2 to Br^-.

Data were taken after first equilibrating the concentration of carrier halogen in the solution by passing a few liters of the gas mixture through it with the shutter closed. The shutter was then opened and an irradiation made for times varying between 0.8 sec and 8 min. The usual case was then to pull a burst of gas for perhaps 1.2 sec with a waiting interval between the end of irradiation and the operation of the valves of about 0.2 sec. This interval was increased progressively in some of the runs to test for the existence of an earlier generation of the bromine precursors.

The IBM 650 digital computer was used extensively in this work—first for the reduction and correction of the original data, and second, for the fitting of the corrected data by sums of exponentials. In addition, a certain amount of graphical analysis was done by the standard method of "peeling off" of successively shorter-lived activities. The fitting process done by the computer is a least-squares method based on a minimization procedure due to Davidon[13] and modified and adapted for the IBM 650 by Peshkin.[14] Where comparison has been made, the graphical and machine methods give similar answers, but the machine has always been able to effect an "improvement" over the graphical in the sense of least squares. The machine typically gives a wider spectrum of answers since it is less burdened by prejudice. However, if the data are equivocal from the standpoint of graphical analysis, the machine has similar difficulty and may, in fact, give nonsensical answers.

The machine calculation consists of finding values of the a_j and λ_j which minimize

$$M(a_j,\lambda_j)=\sum_{i=1}^{N}(y_i-\sum_{j=1}^{m}a_j e^{-\lambda_j t_i})^2/\sigma_i^2.$$

Here y_i is the measured counting rate at the mean time t_i, σ_i is its standard deviation as determined by counting statistics, and the λ_j and a_j are the decay constants and initial rates respectively of the various activities, of which it is assumed that there are m. The quantity

$$\chi^2 \equiv M_{\min}$$

is immediately obtained when the correct a's and λ's are found and may be used to judge the reliability of the data or of m. Defining the number of degrees of freedom k as the number N of experimental points minus the number of parameters ($\leqslant 2m$) being varied, it may be shown[15] that χ^2/k has a theoretical expectation of unity and variance $\sigma^2=2/k$, provided that the assumed function truly represents the phenomenon, and that the σ_i are the correct standard errors.

[12] R. Batchelor and H. R. McK. Hyder, J. Nuclear Energy 3, 7 (1956).

[13] W. C. Davidon, Argonne National Laboratory Topical Report ANL 5990 (to be published).

[14] M. Peshkin (private communication).

[15] H. Cramér, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, New Jersey, 1946), p. 233.

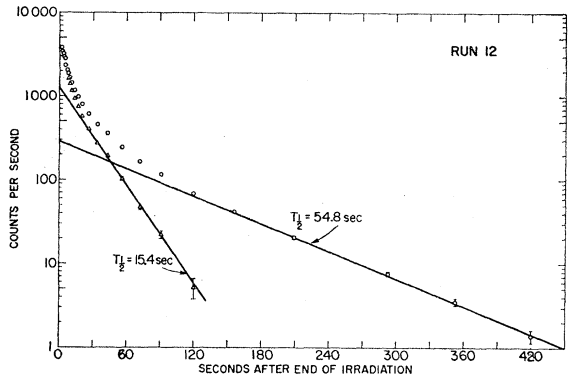

FIG. 2. Decay of the neutron activity of fission-product bromine from the fission of U^{235} by thermal neutrons following an 8-min irradiation. Circles—original counting rates; triangles—counting rates after subtraction of 54.8-sec activity.

III. THE BROMINE DELAYED-NEUTRON PRECURSORS

Figure 2 is a logarithmic plot of data from a run using bromine chemistry and an irradiation of 8 min. The zero of time on the plot, as in all data to be discussed, is the time of the end of irradiation. One may observe the graphical resolution into a component having a half-life of 54.8 sec, one of 15.4 sec and a shorter-lived remainder. Figure 3 is a similar plot of data from a shorter irradiation, 0.76 sec. Here the 54-sec and 16-sec groups are relatively weak, and are subtracted off to show that the remaining neutron activity is to be decomposed into a group having a half-life of 4.4 sec and one of 1.6 sec. Because 2 seconds transpired between the end of irradiation and the first experimental point, any component of appreciably shorter lifetime will not be apparent in the plots, but may result in introducing some error into the determination of the shortest-lived component displayed. Our data give no evidence either way on the existence of a shorter-lived bromine activity.

Table I is a summary of results from a number of runs with bromine chemistry. They have various irradiation times, but all are characterized by a very short wait (~0.2 sec) between the end of irradiation and the onset of the air burst. Counting commenced about 2 sec from the end of irradiation. Since the shutter opening was varied from run to run, the counting rates are only to be compared on a relative basis. The main tabulation consists of half-lives, T_i(sec), and their corresponding counting rates, $a_i(\text{sec}^{-1})$ referred to the end of irradiation. All of these results were obtained by the machine calculation. In many cases initial guesses of the values were obtained by graphical means. The Davidon process of minimization does not, at least in principle, require good guesses, but there are practical limitations associated with the size of numbers which may be handled by the IBM 650 during the course of a calculation, and these prevent complete freedom of choice of the initial values. The number of parameters being varied was seven. The value of 54 or 54.5 sec for T_4 was assumed and not permitted to vary. The tabulated a's have been corrected for the effect of the radiation which leaks through the shutter. The correction is serious only for a_4 and only in runs 1, 2, and 3. As a consequence, the yield ratios involving a_4 in those runs are disregarded.

The shortest-lived component, being the most difficult to measure, emerges from the machine calculation with the greatest spread in half-lives, varying between 1.0 and 2.2 sec at the extremes. The mean is 1.6±0.6 sec. We have assumed equal weighting for all runs because we have not been able to obtain probable errors with assurance from the machine calculations. The quoted limit of error attempts to take possible systematic effects into account. The same procedure is used for the errors quoted for all half-lives measured in the present work.

The next longer-lived component shows a smaller spread. The average half-life is 4.4±0.5 sec. The third group is characterized by a half-life of 16.3±0.8 sec, somewhat higher than the value 15.5±0.4 quoted in

TABLE I. Half-lives and initial activities obtained by least-squares analysis for bromine isotopes.

Run No.	Length irradiation (sec)	T_1 (sec)	a_1 (sec^{-1})	T_2 (sec)	a_2 (sec^{-1})	T_3 (sec)	a_3 (sec^{-1})	T_4[a] (sec)	a_4 (sec^{-1})	χ^2	χ^2/k
1	0.76	2.2	2190	5.4	710	16.5	170	54	28	18	1.0
2	0.76	1.6	1400	4.2	820	16.1	156	54	16	14	1.2
3	0.77	2.0	1960	4.6	1050	16.6	209	54	26	32	1.9
4	1.25	1.4	2810	4.3	2080	16.7	266	54.5	39	18	1.2
5	1.26	1.8	2430	4.2	1990	16.1	339	54.5	37	11	0.6
6	1.28	1.5	2940	4.3	2600	17.9	297	54.5	44	36	1.4
7	1.30	1.0	2340	3.6	2530	15.2	336	54.5	34	14	0.7
8	4.2	1.7	1730	4.4	1680	15.8	300	54.5	42	17	1.1
9	15.9	2.0	1860	4.8	1680	15.8	640	54.5	98	19	1.1
10	55.8	1.1	2070	4.6	1700	16.5	670	54	166	31	1.0
11	480	1.7	1760	4.4	1550	16.0	790	54.5	216	37	1.1
12	480	1.5	2420	4.4	2370	15.9	1160	54.5	290	29	1.5
Average		1.6±0.6		4.4±0.5		16.3±0.8				$\chi_{\text{total}}^2/k_{\text{total}}=1.14$ $\pm(2/k_{\text{total}})^{\frac{1}{2}}=\pm0.09$	

[a] Values assumed for this period.

I. The longest group has the assumed value of 54 or 54.4 sec.

The values of χ^2/k cluster around 1.0, for the most part within the standard deviation of about 0.3. Considering all of the data as part of one experiment, we obtain $(\chi^2)_{\text{total}}/k_{\text{total}}=1.14$, slightly higher than expectation (1 ± 0.09).

The relative fission yields of the neutron activities may be obtained by extrapolating each activity to the case of irradiation to saturation. The average half-lives of Table I were used in this way to obtain the contents of Table II, which displays yields relative to that of the 16 second group. The average values of the yields are in the ratios 1.5:1.9:1:0.37 in order of increasing half-life. The limits of error indicated in the table are the statistical ones. The spread in the individual values arises from several causes; first, the statistical uncertainties in the data; second, an uncertainty in the duration of the shortest irradiations; third, the possibility that the bromine activities might have precursors

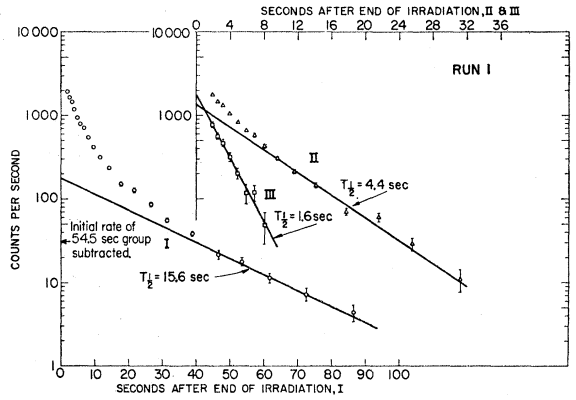

FIG. 3. Decay of neutron activity in bromine fraction after an irradiation of 0.76 sec. Graphical analysis into four components.

with appropriate lifetimes; and finally, a possible chemical effect in the solution. The latter may arise in the following way. Our chemical procedure extracts, either directly or by exchange, only those radiobromine atoms which had valence 0 or -1 while in solution. The considerable population of $+5$ presumably remains behind because of its long exchange time.[9] The number of fissions per second in our solution is $\sim10^{10}$ which produces ~5000 r/sec. During a run of several minutes with such intense local irradiation, it is possible to have a building up of chemical effects which could affect the distribution of bromine among its valence states. The effect would be more pronounced for the longer lived bromine isotopes which have a longer history of immersion in the solution. Whatever the cause, however, we consistently observe a reduced yield ratio Y_4/Y_3 for the longest irradiations.

We attempted to ascertain whether 54-sec Br itself had a precursor of lifetime great enough to be detected

TABLE II. Ratios of initial activities of bromine isotopes corrected to the case of irradiation to saturation (relative yields).

Run No.	Length of irradiation (sec)	Y_1/Y_3[a]	Y_2/Y_3	Y_4/Y_3
1	0.76	1.7	1.3	
2	0.76	1.2	1.7	
3	0.77	1.2	1.5	
4	1.25	1.2	2.3	0.45
5	1.26	1.0	1.8	0.33
6	1.28	1.4	2.7	0.46
7	1.30	1.0	2.3	0.30
8	4.2	1.2	2.0	0.44
9	15.9	1.4	1.4	0.41
10	55.8	2.8	2.3	0.44
11	480	2.2	2.0	0.27
12	480	2.2	2.0	0.25
Average		1.5±0.6	1.9±0.4	0.37±0.08

[a] Subscripts 1, 2, 3, 4 refer to 1.6-, 4.4-, 16.3-, and 54.5-sec activities, respectively.

by the present techniques.[16] This was done by making a series of successive runs with identical short irradiation intervals but longer and longer delays between the end of irradiation and the air burst. The effect of such a precursor would then appear as a growth in the initial rate of the 54-sec activity. The uncertainty in the values has thus far prevented us from drawing any conclusions.

IV. IODINE DELAYED-NEUTRON PRECURSORS

A series of runs was made using iodine chemistry and various irradiation times. The time interval between the end of irradiation and the start of each burst, the duration of the burst, and the time at which counting started, were similar to the bromine runs. A logarithmic plot of data from an irradiation of 4-min duration shows a prominent group with a half-life of 24.4 sec, and some activity of shorter life. From about 40 to 370 sec the data follow a simple exponential decrease over a range of greater than 4 decades in counting

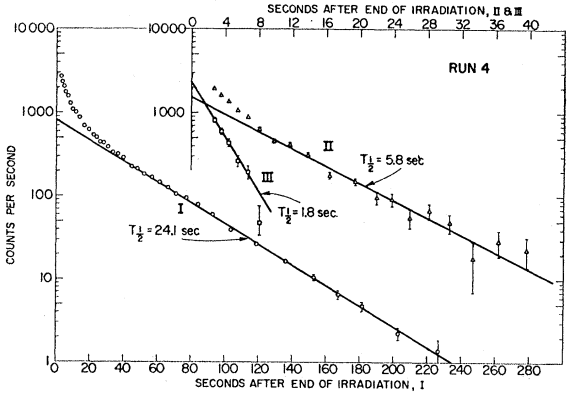

FIG. 4. Decay of neutron activity in iodine fraction after an irradiation of 2.8 sec. Graphical decomposition into three components.

[16] Sattizahn, Kahn, and Knight, Bull. Am. Phys. Soc. Ser. II, 2, 197 (1957).

TABLE III. Half-lives and initial activities obtained by least-squares analysis for iodine isotopes.

Run No.	Length of irradiation (sec)	T_1 (sec)	a_1 (sec^{-1})	T_2 (sec)	a_2 (sec^{-1})	T_3 (sec)	a_3 (sec^{-1})	χ^2	χ^2/k
1	0.88	1.8	890	5.2	520	23.2	310	33	1.1
2	1.29	2.3	1410	6.8	700	26.1	400	23	1.0
3	2.8	2.0	2750	5.8	1440	23.8	930	44	1.3
4	2.8	2.0	2400	6.0	1260	24.0	840	32	1.0
5	5.1	1.8	3890	6.4	2470	24.6	1530	27	0.8
6	5.1	1.7	4530	6.6	2600	24.8	1610	47	1.5
7	24.5	1.7	4720	6.6	4660	24.5	5430	36	1.2
8	242	2.7	3680	7.2	3800	24.4	10 600	42	1.0
Average		2.0±0.5		6.3±0.7		24.4±0.4		$\chi_{total}^2/k_{total}=1.10$ $\pm(2/k_{total})^{\frac{1}{2}}=\pm0.09$	

rate. From the absence of 54-sec activity it is clear that bromine contamination is very small.

Figure 4 is a plot of data following an irradiation of 2.6 sec. The shorter lived group is now more prominent and is graphically resolved into two components, one of 5.8 sec and one of 1.8 sec.

Table III summarizes a set of eight runs as analyzed by the machine technique. These data were taken with the pile shutter opened the same amount and should be roughly comparable from run to run when the different irradiation intervals are taken into account. The average values of the half-lives are 2.0±0.5, 6.3±0.7, and 24.4±0.4 sec. The values of χ^2/k fluctuate in the neighborhood of 1.0, mostly within the theoretical error limits of about ±0.25. Treating all eight runs as a single experiment, we have $(\chi^2)_{total}/k_{total}=1.10$. The standard error is $\pm(2/k_{total})^{\frac{1}{2}}=\pm0.09$.

The counting rates of Table III are corrected for finite irradiation time to obtain the relative yields given in Table IV. The values are reasonably consistent and we obtain for the relative yields $Y_1:Y_2:Y_3=0.38:0.47:1$, in order of increasing half-life. The errors in yield quoted in the table are the statistical ones.

V. VALIDITY OF THE RESULTS

Since the bromine and iodine lifetimes are somewhat similar, it is necessary to consider both the completeness of the chemical separation of the halogens from each other and the question of the validity of the particular number of components chosen for the analysis.

TABLE IV. Initial activities of iodine isotopes corrected to the case of saturation irradiation (relative yields).

Run No.	Length of irradiation (sec)	a_3^{sat} (sec^{-1})	Y_1/Y_3[a]	Y_2/Y_3
1	0.88	11 300	0.30	0.48
2	1.29	10 200	0.35	0.50
3	2.8	11 900	0.37	0.46
4	2.8	10 600	0.37	0.45
5	5.1	11 700	0.42	0.51
6	5.1	11 200	0.47	0.52
7	24.5	10 800	0.44	0.46
8	242	10 600	0.35	0.36
Average			0.38±0.05	0.47±0.05

[a] Subscripts 1, 2, and 3 refer to 2.0-, 6.3-, and 24.4-sec activities, respectively.

In I there is a description of a series of tests to detect the presence of fission product iodine in the air stream following bromine chemistry. The chemical procedure in the present work is the same as that of I. Since no iodine was found at that time, the tests have not been repeated. In the case of iodine chemistry, however, the data for the 4-min irradiation, already mentioned, may be used to deduce an upper limit of 4% for the countwise contamination of all bromine isotopes at $t=0$, if one ascribes all of the activity at 370 sec to 54-sec bromine. A considerably lower value may be deduced from the result of a test with an external trap. A column having an empty volume of 0.8 liter was filled with glass balls and inserted in the active side of the gas line at position T. For the first run, a "blank," the glass beads were wet with a $1M$ nitric acid solution, the excess liquid being drained off. A typical iodine type of run was then made with a 60-second irradiation, except that the air flow was allowed to persist for about 5 sec, rather than the customary 1 to 2 sec, because of the larger volume through which it had to flow. The earliest point plotted is at 7 sec after the end of irradiation. The decay plot was analyzed graphically into a 24.2-sec group with initial rate 1400 counts/sec, and a group of 5.7-sec half-life and initial rate 740 counts/sec. The run was then repeated with the solution changed to $0.5M$ $NaBrO_3$ in $1M$ HNO_3. This passes bromine freely but stops iodine. The points now fell on a line indicating about 25-sec half-life and an initial activity of only 10 counts/sec. The short-lived activity was statistically unresolvable. It was suspected that the neutrons observed here actually originated in the trap containing the BrO_3^- and leaked through the shield. To show that this was so, another run was made with the same arrangement, except that the counting vessel C was bypassed by the gas stream. The data obtained were identical with those from the previous run within statistical fluctuation. We conclude that the iodine fraction does not contain a contamination of bromine as large as 0.2%.

The separation of a complex activity into the correct number of components is always open to some doubt. No statistical test such as the "chi square" test we have

TABLE V. Results of least squares analysis of decay of iodine activity when two components were assumed to be present.

Run No.	Length of irradiation (sec)	T_1 (sec)	a_1 (sec^{-1})	T_2 (sec)	a_2 (sec^{-1})	Y_1/Y_2	χ^2	χ^2/k
1	0.88	3.5	1030	22.5	330	0.63	39	1.2
2	1.29	3.6	1710	23.0	520	0.67	35	1.5
3	2.8	4.0	2920	23.6	970	0.66	62	1.8
4	2.8	3.9	2750	23.7	910	0.65	59	1.7
5	5.1	4.7	3840	23.8	1170	0.57	51	1.5
7	24.5	5.1	6040	24.0	5730	0.56	65	2.0
8	242	4.8	6400	24.1	11 100	0.58	52	1.1
Average		4.2		23.5		0.62	$\chi_{\text{total}}^2/k_{\text{total}}=1.53$ $\pm(2/k_{\text{total}})^{\frac{1}{2}}=\pm0.09$	

adopted can detect the existence of a very weak activity or resolve two activities of similar lifetimes. In our case, however, we are strongly helped by the knowledge that each fraction counted can contain only a few neutron-active nuclides, and that the half-lives may be compared with those obtained by radiochemical methods. We cannot say with certainty that there are not five bromine delayed-neutron precursors with half-lives between 55 and 1.5 sec, although it is not likely. We can say with assurance that there are not less than four. We have, for example, subtracted off the weak 54-sec group and fitted the remaining activity with two periods by the machine techniques. Inspection of the fit and of χ^2/k causes immediate rejection of this possibility. Unfortunately the situation is by no means as clear-cut in the case of iodine. The reason is that the 24-sec group has higher yield than the combined shorter-lived groups studied, and the statistics are thereby less favorable for their resolution than was the case for the short-lived bromines.

In Table V we show the result of least-squares analysis of the iodine runs using only two components. The data are actually fitted reasonably well. The half-lives have average values of 4.2 and 23.5 sec. The former does not correspond to any known iodine isotope, but this is not necessarily ground for rejection, since the radiochemical lifetime measurements are

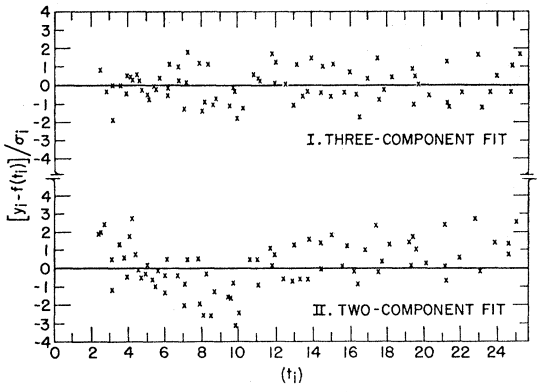

FIG. 5. Comparison of residuals (measured in units of standard error) of two-component (lower plot) and three-component least-squares fits to iodine data. Composite of runs 1–5.

difficult to make and could be in error. However, the calculated values of the half-lives are observed to increase with the length of irradiation, as they must if there are actually three components. A stronger argument for three components may be made by scrutiny of the values of χ^2/k and their comparison with the corresponding values in Table III where the fit is with three components. Only two of the eight runs qualify within the expected limit of error. The value of $(\chi^2)_{\text{total}}/k_{\text{total}}$ is objectionably high and would imply systematic error sources which we consider unreasonably large.

Further judgments concerning the number of components may be gotten by examining the fits in detail. In Fig. 5 we plot the "weighted residual" $[y_i-f(t_i)]/\sigma_i$, where $f(t_i)$ is the machine value of the counting rate at t_i. This is done separately for the fits with three components and those with two, and includes all points up to 25 sec for the first 5 runs. Whereas the three-component plot shows the expected scatter of the points about zero, the plot for two components shows the data points characteristically too high at early times, then mostly too low, and then too high again. This is what would be expected if the data truly represent three components rather than two. This is what we conclude.

VI. DISCUSSION

With the exception of 1.6-sec bromine, all of the neutron activities reported here may be identified with known fission products. Among the bromines, the 54-sec activity is well known to be Br^{87} and has been studied by chemical separation and neutron counting,[6] and by extraction of the Kr^{87} daughter from an AgBr precipitate.[8] In addition, a study has been made of its decay scheme.[17] The 16.3-sec bromine has been discussed in I. It is Br^{88}, and is especially interesting for being of odd Z-odd N character. The 4.4-sec bromine was observed by Sugarman[7] by neutron-counting after chemical separation, but the half-life assignment in that work was open to some question because the delayed-neutron character of Br^{88} was not known at that time. The present work corroborates its existence and furnishes a good measurement of the lifetime. This

[17] A. F. Stehney and N. Sugarman, Phys. Rev. 89, 194 (1953).

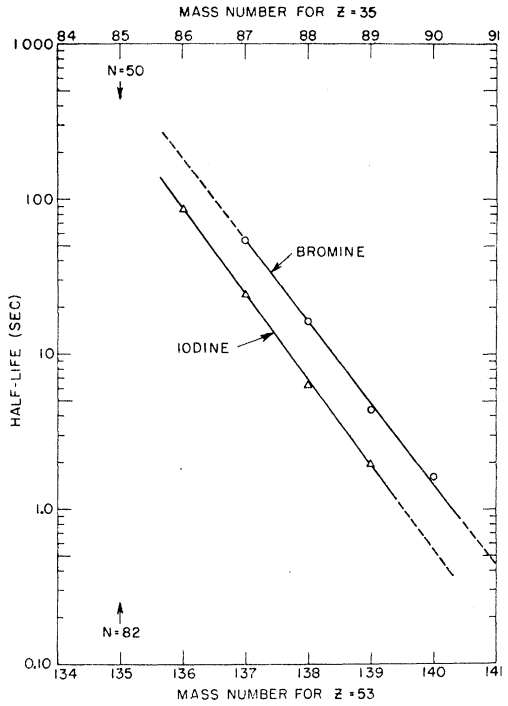

FIG. 6. Half-lives of bromine and iodine isotopes having neutron numbers in excess of closed-shell values.

isotope is frequently assigned to mass 89, although a search for mass 89 descendents following AgBr precipitation was not successful.[8] The 1.6-sec bromine has not been observed previously. It is likely to be Br^{90}, which like Br^{88} is also odd-odd.

Among the iodine activities, the 24-sec group is well known[6,8] to be I^{137}. It is interesting to note that the half-life we measure (24.4 ± 0.4) is close to the value that Snell *et al.* obtained by neutron counting after chemical separation, and higher than the 22 sec usually found in the gross activity. The difference is, of course, due to the unresolved 16-sec bromine in the latter. The 6.3-sec iodine is to be identified with I^{138}, whose half-life measured radiochemically[8] is 5.6 sec. I^{138} bears the same relationship to the closed shell of 82 neutrons that Br^{88} does to that of 50. Both contain three open-shell neutrons. The 2.0-sec iodine is to be identified with I^{139} whose half-life has been determined radiochemically[8] to be 2.7 sec.

If one examines the half-lives of all known bromine and iodine isotopes having more neutrons than a closed shell, a curious regularity is apparent when the mass assignments above are used. This is seen in Fig. 6. As neutron number is increased by one unit, the half-lives decrease by nearly the same factor for iodine and for bromine isotopes, i.e., 3.5 and 3.4, respectively.[18] While this by no means proves the correctness of the mass assignments of 4.4-sec and 1.6-sec bromine, it lends support to the conjecture.

Considering the relationship between the six periods of the gross activity and the present results, it is apparent that the "22-sec," "6-sec," and "2-sec" groups each contain one bromine and one iodine activity. It would be interesting to extend the separation techniques to shorter times and see whether the duality holds for the two gross periods which are as yet unexplored chemically.

The experiment to fix the ratio of bromine to iodine neutron activities has not yet been done. However, by assuming that there are no significant delayed-neutron activities other than bromine and iodine, and by fitting a combination of these to the gross data, one finds that 24-sec I^{137} and 16-sec Br^{88} have equal neutron yields within a factor of two.

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[18] The regularity is perhaps not so puzzling when it is considered that for these nuclei, the β-decay is presumed to proceed via a high multiplicity of branches. It is thereby characterized more by the statistics of the distribution of final allowed states than by the properties of the final ground state.