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# A Radiochemical Investigation of Short-lived Selenium and Bromine Fission Products

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SELENIUM AN
BROMIDE
FISSION
PRODUCTS

SATTIZAHN

| NAME AND ADDRESS | DATE |
|---|---|

# A RADIOCHEMICAL INVESTIGATION OF SHORT-LIVED SELENIUM AND BROMINE FISSION PRODUCTS

By

James Edward Sattizahn, Jr.

A Dissertation Submitted to the Graduate Faculty
In Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in Chemistry

The University of New Mexico
1957

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DOCTOR OF PHILOSOPHY

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DATE May 16, 1957

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# CHAPTER I

# INTRODUCTION

## Discovery of Fission

From a sample of uranium bombarded with neutrons, Hahn and Strassmann,[1] in 1939, separated four radioactive products which followed alkaline earth chemistry and were therefore tentatively attributed to isotopes of radium. Each of these products decayed to a daughter activity which could be precipitated along with lanthanum; the daughter activities were then assumed to be isotopes of actinium. Subsequently, by accepted methods of fractional crystallization and precipitation, the "radium" and "actinium" isotopes were identified unequivocally as isotopes of barium and lanthanum, respectively. Within a relatively short time there were found more such radioactive products, which were identified as isotopes of elements between bromine and lanthanum. This startling result could be explained only by the assumption that the uranium nucleus, after capture of a neutron, split into two fragments of similar mass. Thus, by radiochemical methods, the phenomenon of nuclear fission was discovered. Within a year of the original discovery of Hahn and Strassmann, about fifty more radioactive fission-product nuclides had been isolated.

By 1941, extensive physical and chemical studies had revealed the nature and implications of the fission phenomenon; during the period 1941-1945 fission radiochemistry was pursued intensively under wartime secrecy, and when in 1946 the results of this work were finally released and published,[2] the number of known fission products had been extended to over 160.

## Fission Products

A typical fission event can be represented as follows:

$$ {}_{92}U^{235} + {}_{0}n^{1} \longrightarrow [\,{}_{92}U^{236}\,] \longrightarrow {}_{37}Rb^{93} + {}_{55}Cs^{141} + 2\,{}_{0}n^{1} \qquad (I\text{-}1) $$

The only stable isotopes of mass 93 and mass 141 are ${}_{41}Nb^{93}$ and ${}_{59}Pr^{141}$, respectively. Therefore, each of the primary fragments shown above is four elements removed from stability and must in the course of time decay by successive emission of four $\beta^-$ particles. The two fission-product chains are represented by the equations

$$ {}_{55}Cs^{141} \xrightarrow{\beta^-} {}_{56}Ba^{141} \xrightarrow{\beta^-} {}_{57}La^{141} \xrightarrow{\beta^-} {}_{58}Ce^{141} \xrightarrow{\beta^-} {}_{59}Pr^{141} \qquad (I\text{-}2) $$

and

$$ {}_{37}Rb^{93} \xrightarrow{\beta^-} {}_{38}Sr^{93} \xrightarrow{\beta^-} {}_{39}Y^{93} \xrightarrow{\beta^-} {}_{40}Zr^{93} \xrightarrow{\beta^-} {}_{41}Nb^{93}. \qquad (I\text{-}3) $$

There is no a priori reason why the elements formed in equation (I-1) could not have been ${}_{41}Nb^{93}$ and ${}_{51}Sb^{141}$. In this case, the ${}_{41}Nb^{93}$ is known to be stable, whereas the ${}_{51}Sb^{141}$ would be eight successive $\beta^-$ decays removed from stability. Indeed, it has been found that a given fission-product chain does not always start at the same element. The relative probabilities of formation of these primary fragments have been studied at some length and are still of much interest.

It is apparent that, except for the first member of a decay chain, a fission product may be formed either directly in fission as a primary fragment or indirectly by decay of its predecessor.

## Fission Yields

An important factor in the development of a picture of the fission process is the determination of the relative probabilities of production of the various fission products. These probabilities, the so-called "fission yields", were first measured by Anderson, Fermi and Grosse[3] and by Mousa and Goldstein.[4] A number of reviews covering more recent investigations are available.[5,6]

The independent yield of a fission product is defined as the per cent of the fission events in which it is the primary fission fragment. The cumulative yield of a fission product is defined as the sum of the independent yields of its predecessors plus its own yield. The total chain yield, a measure of the probability that fission products of a given mass will be found in fission, is defined as the sum of all the independent yields of the mass chain in question. It is the latter two, the cumulative and total yields, that are most often tabulated in the literature.

## Mass Distribution

The first members of a fission-product decay chain are far removed from stability and their decay in most cases is so rapid (half-lives from a fraction of a second to a few minutes) that direct measurement of their yields is practically impossible with present chemical techniques. Consequently, few independent yields of the early members have been determined. The total chain yield, however, can be measured by either radiochemical or mass spectrometric methods if only the latter members of the chain (reasonably long-lived or stable) are investigated. Because the independent yields

of the last members of a fission-product chain (from thermal fission) are relatively small, the cumulative yield is essentially a measure of the total chain yield.

A plot of the mass number on a linear scale against the total chain yield on a logarithmic scale is called a mass-yield or mass-distribution curve. Such a curve for the thermal fission of $U^{235}$ is given in Figure I-1.[6] The characteristic feature of this curve is that asymmetric fission (separation into unequal masses) is much more probable than symmetric fission (separation into equal masses).

It is to be noted that since each fission event results in the production of two fission chains the total yields of all fission chains must add up to 200 per cent.

## Nuclear Charge Distribution

Because a fission chain consists of approximately seven elements, questions arise as to 1) which element has the highest probability of being formed as a primary fragment and 2) what will be the distribution of the other elements about this most probable one.

Of the many postulates suggested for determining the most probable initial nuclear charge for a given mass chain, the one by Glendenin, et al.,[7,8] appears to fit best the experimental data. These investigators introduced the hypothesis that the most probable mode of fission is that which gives rise to equal charge displacement from stability. Thus,

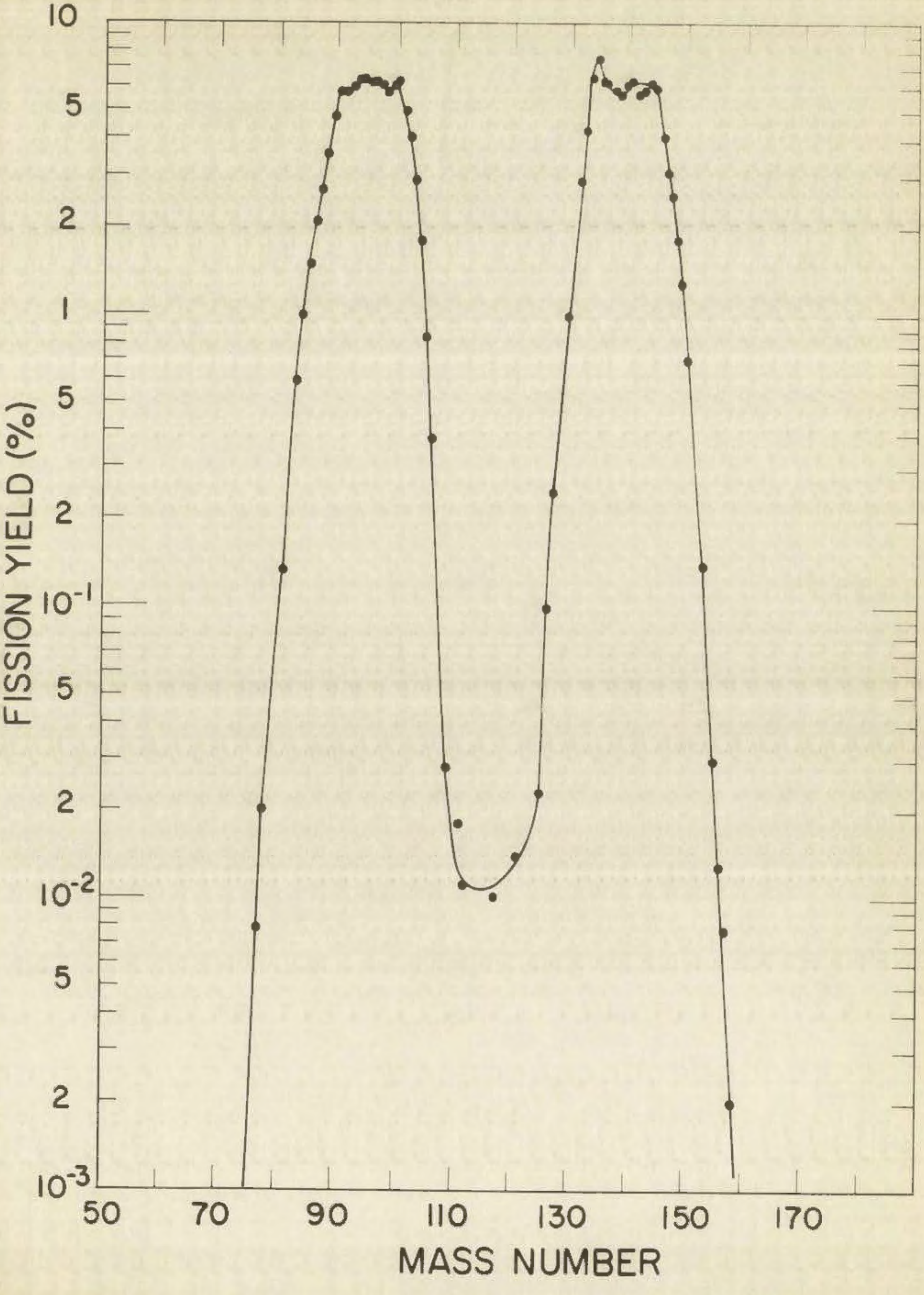

Figure I - 1. Yield-mass curve for slow neutron-induced fission of $U^{235}$.

$$Z_A - Z_p = Z_A^* - Z_p^* \qquad \text{(I-4)}$$

where $Z_p$ and $Z_p^*$ are the most probable charges of the complementary fission fragments and $Z_A$ and $Z_A^*$ are the most stable charges for mass numbers A and A*. Also, $Z_p + Z_p^*$ must equal the atomic number of the nuclide undergoing fission. The use of equation (I-4) can be illustrated by referring to equation (I-1) which represents a possible mode of fission. In this instance, $Z_A$ is 41, $Z_p$ is 37, $Z_A^*$ is 59, and $Z_p^*$ is 55, and the charge displacement for each of the two chains is 4. The essence of the equal charge displacement hypothesis, then, is that other charge distributions for pairs of fragments such as

$${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{38}Sr^{93} + {}_{54}Xe^{141} \left(\begin{matrix} Z_A - Z_p = 3 \\ Z_A^* - Z_p^* = 5 \end{matrix}\right) \qquad \text{(I-5)}$$

or

$${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{36}Kr^{93} + {}_{56}Ba^{141} \left(\begin{matrix} Z_A - Z_p = 5 \\ Z_A^* - Z_p^* = 3 \end{matrix}\right) \qquad \text{(I-6)}$$

are less probable than that which gives equal displacements for the heavy and light fragments.

$Z_A$ or $Z_p$ need not necessarily be integral numbers. If $Z_p$ were 36.5, the most probable fragment would be krypton or rubidium, with equal probabilities.

The distribution of the nuclear charge, Z, for a given mass chain about the most probable charge, $Z_p$, was assumed by Glendenin to be a smooth symmetrical curve for all mass numbers. The charge distribution curve for

fission fragments from the thermal fission of $U^{235}$, based on the limited number of independent yields available, is plotted in Figure I-2.[6]

## Single Particle Model and Nuclear Shell Theory

An adequate description of the decay of a radioactive nucleus must include, in addition to its half-life, the types and abundances of all the radiations resulting from the decay. This information and its interpretation is commonly presented in the form of a "decay scheme", similar in many respects to the atomic energy level diagrams employed in optical spectroscopy. For beta emitters the description of the radiations involves the measurement of the energy and abundance of the beta and gamma rays. The interpretation involves a description of the beta and gamma transitions in terms of the initial and final nuclear levels. Although a complete theoretical treament of the nucleus, as of the electron atmosphere around it, is a task far from being solved, the problem was remarkably simplified with the development, in 1949, of a nuclear model and the means of dealing with it. The model is called the single particle model and its treatment nuclear shell theory. This theory, the result of independent work by M. E. Mayer[9] and by Haxel, Jensen and Suess,[10] embodied the following ideas:

1. That nucleons tend to occupy shells in the nucleus in a manner similar to that of the extra-nuclear electrons about the nucleus; protons and neutrons are each associated with an independent set of shells.

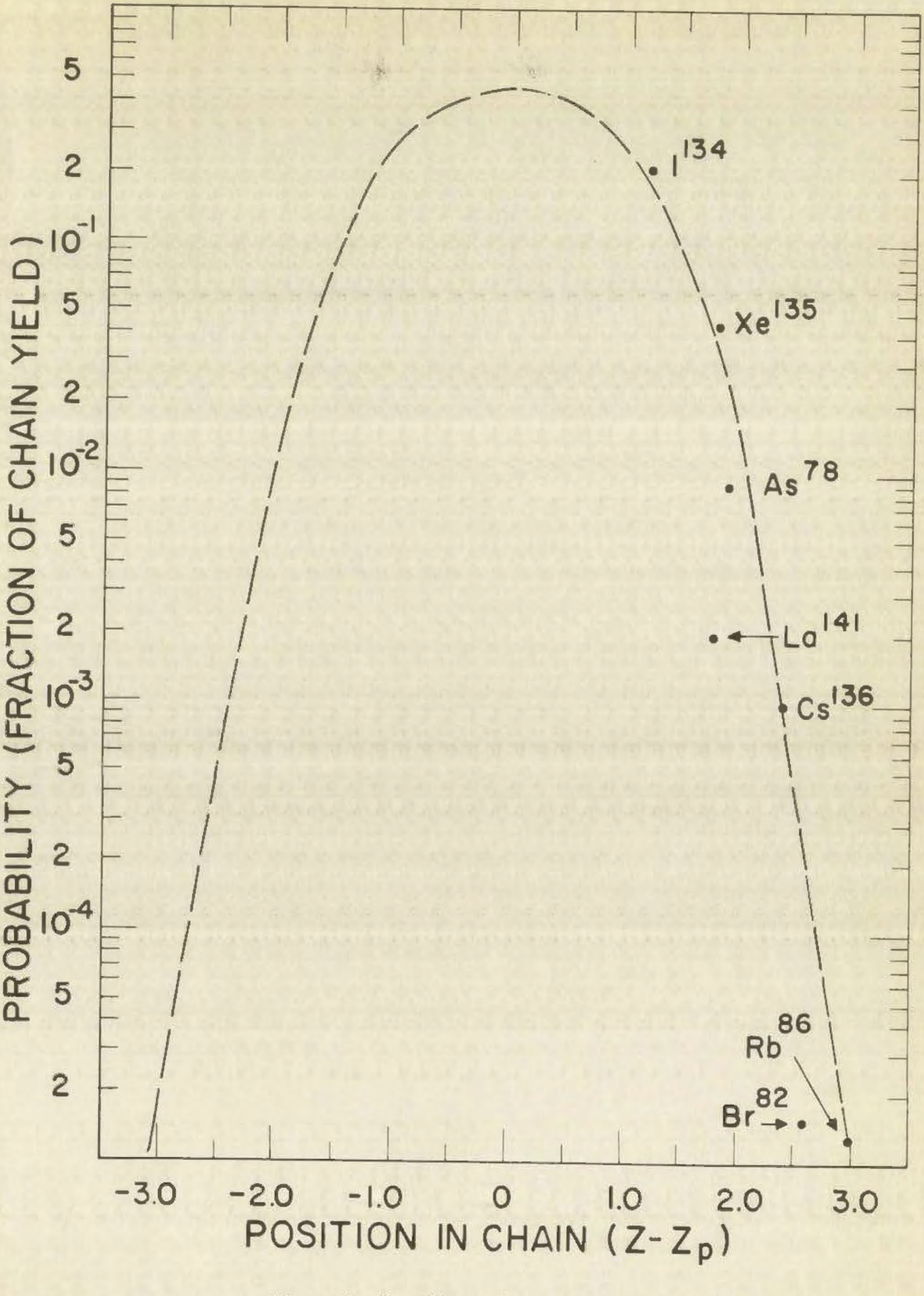

Figure I - 2. Charge distribution curve.

PRECIPITATION EFFECT ON GRAIN YIELD

[illegible]

2. The nucleons, like extra-nuclear electrons, tend to pair off, and once having paired, contribute little to the behavior of the subsequent nucleons. Nuclei which have completely closed neutron or proton shells have unusual stability as do their atomic counterparts, the rare gases.

3. Two of the fundamental properties of a nucleus, its spin and parity, are those of the last unpaired nucleon, or in cases where both a neutron and proton remain unpaired, a suitable combination of their spins and parities.

The "spectroscopic" state of the last odd nucleon is given by its orbital type (s, p, d, etc., corresponding to its azimuthal quantum numbers, $\ell = 0$, 1, 2, etc.) and its total angular momentum, the latter being the algebraic sum of its orbital angular momentum and its intrinsic spin. Thus, for example, a nucleon in a "d" state can have total angular momentum $j = 5/2$ or $j = 3/2$ depending on whether the intrinsic spin (always 1/2) is aligned parallel to its orbital angular momentum, $j = 2 + \frac{1}{2} = 5/2$, or antiparallel to its orbital angular momentum, $j = 2 - \frac{1}{2} = 3/2$.

The number of nucleons which can occupy a particular state is given by the familiar multiplicity rule $N = 2j + 1$. Thus there can be $2 \times 5/2 + 1 = 6$ nucleons in a $j = 5/2$, say $d_{5/2}$, state and likewise $2 \times 3/2 + 1 = 4$ nucleons in a $d_{3/2}$ state.

The nucleonic level sequence has been worked out theoretically and the results are summarized in Figure I-3. As already pointed out in 3, above, an important feature of the single particle model is that the spin and parity

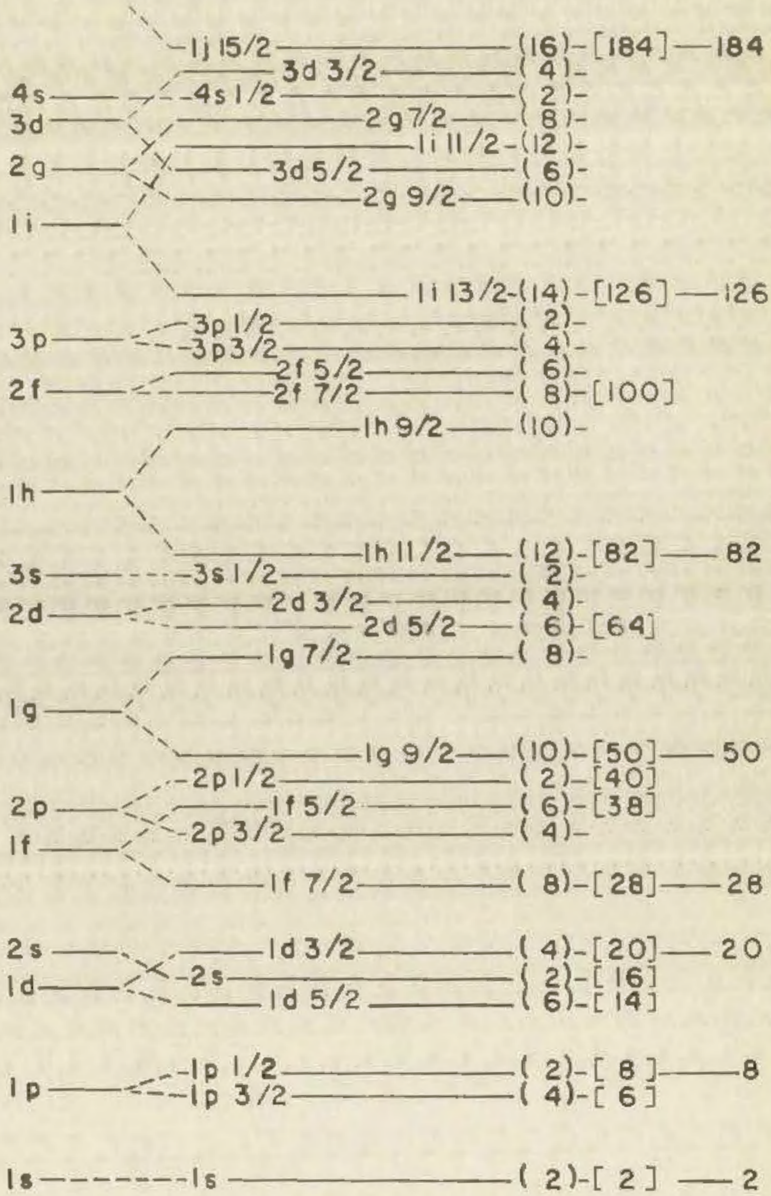

Figure I - 3. Schematic diagram of nuclear levels.

of the nucleus are those of the last unpaired nucleon; all the other nucleons are paired and therefore make no contribution. The foregoing treatment and table may be illustrated by the following examples:

$_3Li_4^7$ has 3 protons and 4 neutrons. Two of the neutrons occupy the $s_{\frac{1}{2}}$ state. The remaining two are in the next higher state, $p_{3/2}$. Since the neutrons are paired off, they may be considered "inert". On the other hand, two of the protons are paired off in the $s_{\frac{1}{2}}$ state, but the remaining proton, unpaired, is in a $p_{3/2}$ state. Hence the $Li^7$ nucleus is designated by the sincle particle model as $p_{3/2}$.

$_{20}Ca_{21}^{41}$ has 20 protons and 21 neutrons. The protons are all paired off, as are the first 20 neutrons. The remaining neutron is in an $f_{7/2}$ state. Thus, the $Ca^{41}$ nucleus in its most stable (ground) state may be designated as $f_{7/2}$. Excitation of the nucleus could raise the odd neutron to a higher state such as $f_{5/2}$ or $p_{3/2}$.

Because of complete pairing, even proton-even neutron nuclei have a spin of zero in their ground states. Odd proton-odd neutron nuclei are not as easily predictable. In general, the spin and parity of an odd proton-odd neutron nucleus result from a suitable combination of the states of the odd proton and the odd neutron; the ways in which this combination may occur are given by Nordheim's Rule.[11] This rule says that if $j_1 + j_2 + \ell_1 + \ell_2$ is an even number the resultant spin, I, is $|j_1 - j_2|$. If $j_1 + j_2 + \ell_1 + \ell_2$ is an odd number then the resultant spin, I, is probably large, approaching $j_1 + j_2$. It should be pointed out that the nucleons do not always fill the states in the precise order given in Figure I-3. For example, in the region from 38 to 50 nucleons the $p_{1/2}$ and $g_{9/2}$ states are so near in energy that in some

cases the odd particle may be in the $g_{9/2}$ state and in other cases in the $p_{1/2}$ state. With this somewhat oversimplified picture, together with selection rules for beta and gamma disintegrations, it is possible to describe the decay of most beta-emitting nuclei. The selection rules are stated in terms of spin and parity. Thus, the spins of the two nuclei $Li^7$ and $Ca^{41}$ are 3/2 and 7/2, respectively. The parity is a symmetry property of the wave functions used in the theoretical treatment of atoms and nuclei, and will not be explained here. For the purpose of this discussion let it suffice that parity of a nucleus may be even (+) or odd (-). The parities of the nuclear levels are given by the following simple diagram:

| Parity | Levels | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| even (+) | s | | d | | g | | i | |
| odd (-) | | p | | f | | h | | j |

Certain classes of beta decay processes are expected on theoretical grounds to proceed relatively rapidly; they are designated as "allowed" transitions. Others which are expected to proceed more slowly are designated as "forbidden". The beta decay selections rule are:

Allowed : spin change 0 or ± 1, no change in parity

1st forbidden: spin change 0, ± 1, ± 2, change in parity,

or in the shorthand notation ordinarily used,

allowed : $\Delta j = 0, \pm 1$ (no)

1st forbidden: $\Delta j = 0, \pm 1, \pm 2$ (yes)

Spin changes greater than those shown above are still more highly forbidden.

For the purpose of this work, gamma transitions in which the spin change

is $\leq 2$ may be considered to proceed instantaneously. Where the spin is $\geq 3$, on the other hand, the gamma transitions proceed sufficiently slowly so that a nucleus may exist in an excited state long enough to be separated chemically and measured. Where a nucleus can exist in either of two states sufficiently long-lived to be recognized by standard radiochemical techniques, the two states are said to be isomers. A long-known example of isomerism is the nucleus $Pa^{234}$. The parent $Th^{234}$ can decay to either of two states of the $Pa^{234}$. One, with a half-life of 1.18 minutes, is known classically as $UX_2$, and the other, with a half-life of 6.7 hours, is known as UZ. The common notation for representing isomeric states above the ground state is by a superscript m (for metastable); e.g., $Br^{80}$ (18 minute) is the ground state and $Br^{80m}$ (4.5 hour) is the excited state. The problem of ascertaining which of two isomers is in the ground state is quite complex when the only mode of decay for each state is the emission of a beta particle. In this case it is usually necessary to establish experimentally the complete decay scheme before a definite level assignment can be made. On the other hand, if the metastable state decays primarily by gamma emission or internal conversion, then the genetic relationship can sometimes be established by means of a hot-atom reaction. The hot-atom reaction is based on incorporating the isomer in a chemical compound and depending on either the gamma emission imparting sufficient recoil energy to the daughter nucleus to break the chemical bond or internal conversion leaving the daughter nucleus in such a high state of electronic excitation as to break the chemical bond. The separated daughter activity is then isolated in some appropriate manner and identified.

## Beta Decay and the Fermi Function

The first successful treatment of the theory of continuous beta particle spectra was described, in 1934, by Fermi[12]. According to this theory the probability that a nucleus will emit a beta particle of energy between W and W + dW is given by the formula

$$P(W)dW = \text{constant } x|M|^2 \text{ x } F(Z,W)W\ (W^2-1)^{\frac{1}{2}}(W_o-W)^2dW \qquad (I\text{-}7)$$

where W and $W_o$ are the beta-particle energy and the maximum beta-particle energy, respectively, both expressed in terms of "total energy", i.e., kinetic energy plus rest-mass energy. In this system, W is customarily expressed in units of $mc^2$, the rest-mass energy of the electron, 0.511 Mev. Thus, for example, W = 1 corresponds to an electron at rest, W = 2 corresponds to an electron with 0.511 Mev kinetic energy, etc. F(Z,W) is a function containing the coulombic effect of the nuclear charge on the beta particle. This function is known as the Fermi function and is tabulated in standard reference works.[13] In terms of beta spectrometer measurements, P(W)dW is proportional to the beta counting rate for the energy interval W to W + $\Delta$W. In practice $\Delta$W is taken small enough so that the above equation can be written to a very good approximation in terms of $\Delta$W. Equation (I-7) can be rearranged to the form:

$$\sqrt{\frac{\text{counts/min}}{F(Z,W)W(W^2-1)^{\frac{1}{2}}}} = \text{constant' } x(W_o - W). \qquad (I\text{-}8)$$

The maximum beta energy, $W_o$, is obtained by plotting W against the left-hand member of equation (I-8); the intercept on the W axis represents $W_o$. The experimental parameters are W, corresponding to the energy setting of the instrument, and counts per minute, the counting rate at this energy setting. The left-hand member is then computed from observed counts per minute and W,

using tabulated values of $F(Z,W)$. The resulting plot is known variously as a Fermi plot, Kurie plot or F-K plot.

Equation (I-7) expresses the probability of beta emission within the energy interval W to W + dW. Integration of this equation over all values of W gives an expression for the total probability of beta emission, ordinarily expressed as λ in the differential active law:

$$\text{disintegrations per unit time} \quad A = \frac{-dN}{dt} = \lambda N \tag{I-9}$$

Hence from equation I-7

$$\lambda = \int p(W)dW = \text{const} \times |M|^2 \times \int_1^{W_0} F(Z,W)W(W^2-1)^{\frac{1}{2}}(W_0-W)^2 dW \tag{I-10}$$

The integral $\int_1^{W_0} F(Z,W)W(W^2-1)^{\frac{1}{2}}(W_0-W)^2 dW$ is usually designated as "f".

With the adoption of this abbreviation

$$\lambda = \text{const} \times |M|^2 \times f. \tag{I-11}$$

But,

$$\lambda = \frac{\ln 2}{t} = \text{const} \times |M|^2 \times f \; ; \tag{I-12}$$

rearranging,

$$ft = \frac{\ln 2}{\text{const} \times |M|^2} \tag{I-13}$$

Thus, beta transitions of similar matrix elements, $|M|$, should have the same ft value irrespective of atomic number or energy, since neither parameter is contained in the constant.

The product ft, then, should be a measure of the "allowedness" or

"forbiddenness" of a beta transition. It is found, in practice, to range from about $10^3$ in allowed transitions, to greater than $10^{12}$ in highly forbidden transitions. Because of this rather wide range, it has been found more convenient to express the product as its logarithm to the base 10, log ft.

The degree of forbiddenness of a transition can be estimated from log ft values which are easily calculable, according to the method of Moszkowski,[14] from the observed half-life and the value of $W_o$ obtained from equation (I-8). In practice $E_o$, the maximum kinetic energy, is used instead of $W_o$, where $W_o = \frac{E_o}{0.511} + 1$. The approximate range of log ft for each of the types of transitions (allowed, first forbidden, etc.) is tabulated in Table I-1.

## Short-lived Nuclides

An examination of recent tables of the nuclides will show that the known fission products range from ${}_{30}Zn^{72}$ to ${}_{65}Tb^{161}$, i.e., at least 90 fission mass chains are represented. In a few instances fission chains have been followed so far back as to allow unequivocal inclusion of at least seven members in the chain. Assuming all chains consist of at least seven members, it is clear that approximately 630 different nuclides may be formed in fission. To date only 200 fission-product nuclei have been identified, the remaining nuclei defying detection by virtue of their short half-lives. For all but a few special cases, such as isotopes of xenon and krypton, which can be swept mechanically out of fission-product solutions, it is very difficult to perform a chemical isolation of a short-lived fission product before it has decayed away. On the

TABLE I-1

Selection Rules for Beta Decay

| Type | $\Delta I$ | Parity Change | log ft |
|---|---|---|---|
| Allowed (favored) | 0 or 1 | No | 3 |
| Allowed (normal) | 0 to 1 | No | 4 to 7 |
| Allowed ($\ell$-forbidden) | 1 | No | 6 to 9 |
| First forbidden | 0 to 1 | Yes | 6 to 8 |
| First forbidden (unique) | 2 | Yes | 9 |
| Second forbidden | 2 | No | 10 to 14 |
| Second forbidden (unique) | 3 | No | ~ 14 |
| Third forbidden | 3 | Yes | 18 |
| Third forbidden (unique) | 4 | Yes | ~ 20 |

other hand these short-lived isotopes, usually far removed from stability, are of considerable potential interest from the viewpoint of nuclear structure and of the fission process. The identification and characterization of these short-lived nuclides is one of the major challenges for radiochemists. The problem is two-fold: 1) the removal of the fission-product mixture from its site of production and the chemical isolation of the element of interest, over a period of seconds to minutes; 2) the rapid measurement of beta and gamma spectra and the separation by half-life and other means of the radiations of each of the active nuclides originally contained in or growing into the sample.

The most easily accessible nuclear property and the one usually first to be measured is the half-life. The half-life of a short-lived radioisotope can be found by either a direct or indirect approach. The indirect approach is of value only if it is possible to measure the radiations from the daughter or possibly the granddaughter. This method is sometimes designated as a "milking technique" and in essence consists of separating the daughter, at timed intervals, from its short-lived parent. After completion of the rapid separations, the daughter activity can be counted in a more leisurely manner. A semi-log plot of the activity of each of the separated samples as a function of its time of separation yields the half-life of the short-lived parent. This technique is limited to the determination of the half-life and does not yield any information concerning the radiation characteristics of the short-lived parent.

As the name implies, the direct approach consists of chemically separating the short-lived nuclide from the other fission products and then

observing the decay directly by various counting techniques; the determination and the energy and abundance of the beta and gamma groups is also possible. The direct approach has two facets of equal importance. The first is concerned with developing chemical procedures which will assure the rapid and complete separation of the nuclide in question from all other elements that are fission products. The second is concerned with developing instruments and counting techniques which will separate the short-lived activity from other radioisotopes of the same element, in many respects the most difficult problem of the two.

Fortunately, the rapid development of instrumentation in recent times has made possible the investigation of problems of a kind which would have been regarded as out of the question ten years ago. Two outstanding developments have been scintillation counting and multi-channel pulse analysis. The former has made it possible to count gamma rays with high efficiency and to determine their energy in a simple manner. The latter has made it possible to record simultaneously and separately the electrical pulses of different energies received from the scintillation apparatus and thereby to record with one measurement the entire beta or gamma spectrum of a radionuclide. Finally, the development of shell theory since 1949 has provided a conceptual framework which has lent some order to what was, as little as ten years ago, a more or less chaotic set of nuclei and nuclear energy levels, so that the radiochemist now knows a little better what he is looking for.

## Scope of Investigation

This investigation had as its objective a radiochemical exploration of that portion of the fission product region which includes the short-lived radioisotopes of selenium and bromine of mass number $\geq 84$. The field of interest is the area enclosed by the cross-hatching in Figure I-4, which shows the state of knowledge of the fission isotopes of these elements at the time the investigation was undertaken.

From an examination of the published data on these isotopes and from semi-theoretical considerations along the lines outlined in the section on theory, a number of immediate problems became apparent. These problems and the factors involved were the following:

1) The anomalous fission yield of $Br^{84}$.

A comparison of the fission yield of stable $Kr^{84}$ (1.02%), determined mass spectrometrically[15,16,17], with the fission yield reported for the 32-minute $Br^{84}$ (0.65%), determined radiochemically,[18] revealed an evident discrepancy. Although discrepancies in fission yield measurements are not uncommon, the discrepancy in this case was of such a magnitude, almost a factor of 2, as to warrant further examination. The fission yield of $Kr^{84}$, determined physically, was believed to be accurate to within ± 5%. The measurement of the fission yield of $Br^{84}$, on the other hand, was liable to errors both in the chemistry and in the counting of the sample.

The discrepancy between the fission yields could be explained by assuming that the 32-minute activity does not include all the $Br^{84}$ nuclei, i.e., there could be an isomer of $Br^{84}$ which escaped the attention of the investigator. This possibility is consistent with the expectations from nuclear shell

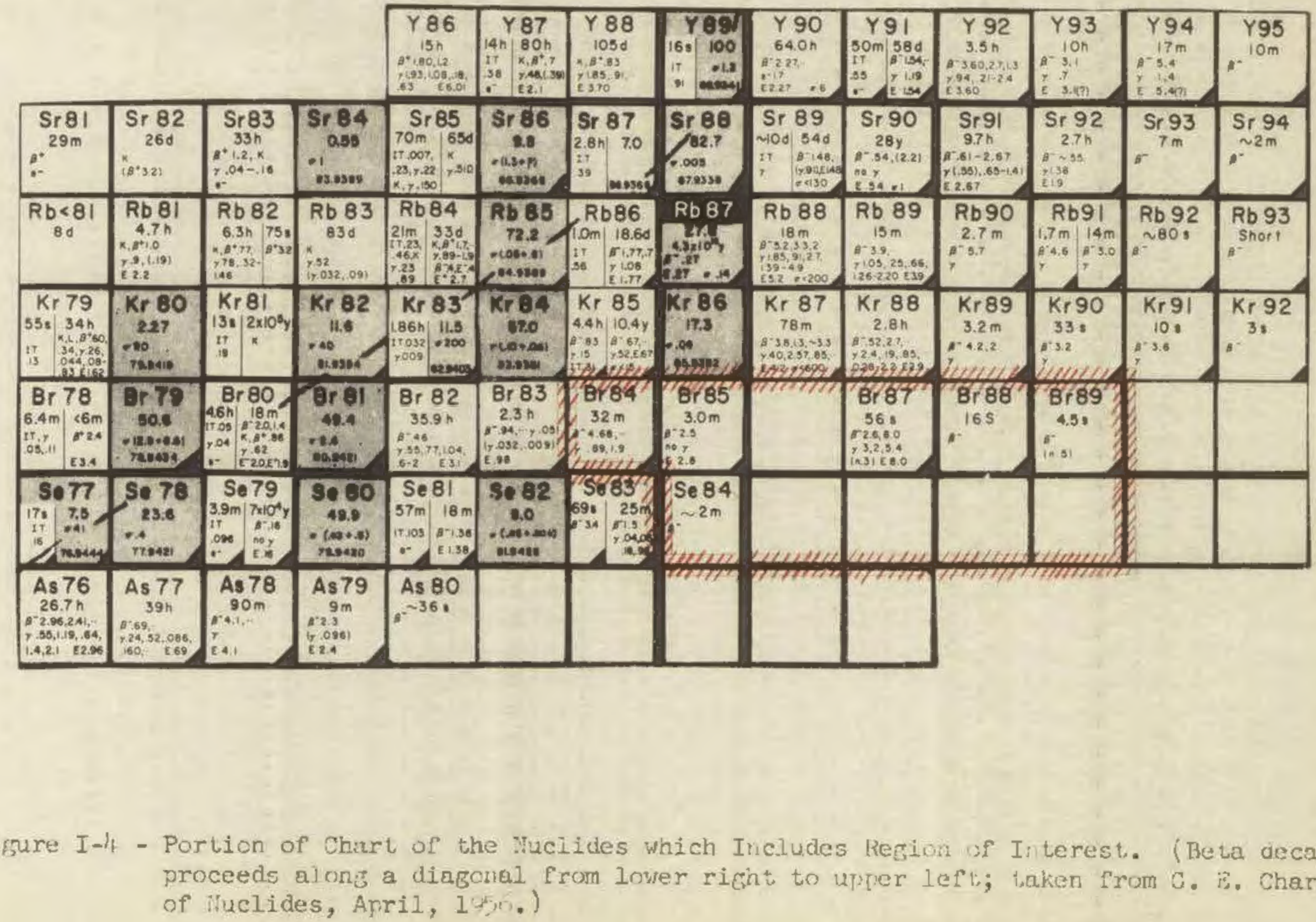

Figure I-4 - Portion of Chart of the Nuclides which Includes Region of Interest. (Beta decay proceeds along a diagonal from lower right to upper left; taken from G. E. Chart of Nuclides, April, 1956.)

theory. Combinations by Nordheim's rule of the most probable odd-proton orbitals, $p_{3/2}$ and $f_{5/2}$, with the most probable odd-neutron orbitals, $p_{1/2}$ and $g_{9/2}$, give the following results:

| | | | Resultant | |
|---|---|---|---|---|
| Odd Proton | Odd Neutron | $\ell_1 + \ell_2 + j_1 + j_2$ | Spin | Parity |
| $p_{3/2}$ | $p_{1/2}$ | $1+1+3/2+1/2 = 4$ | $\lvert 3/2-1/2 \rvert = 1$ | + |
| $p_{3/2}$ | $g_{9/2}$ | $1+4+3/2+9/2 = 11$ | $\leq \lvert 3/2+9/2 \rvert = 6$ | - |
| $f_{5/2}$ | $p_{1/2}$ | $3+1+5/2+1/2 = 7$ | $\leq \lvert 5/2+1/2 \rvert = 3$ | + |
| $f_{5/2}$ | $g_{9/2}$ | $3+4+5/2+9/2 = 14$ | $\lvert 5/2-9/2 \rvert = 2$ | - |

From these considerations it would be predicted that the ground state and first few excited states of $Br^{84}$ embrace the levels 1+, 2 -, ≤ 3 +, and ≤ 6 -. The ground state of $Kr^{84}$ may be safely taken as 0 +. The high probability that the most energetic beta group of the 32-minute state represents a direct decay to the ground state of $Kr^{84}$ indicates that the former state is the 1 + or the 2 - level. Of the possibilities 1 + and 2 -, the former would appear to be eliminated because the observed half-life of this beta group is several hundred-fold longer than expected for a 1 + ⟶ 0 + transition of this energy. On the basis of known log ft values, the 2 - is a good choice. The only difficulty with the choice of 2 -, according to Duffield and Langer,[19] is that the shape of the high-energy beta spectrum is inconsistent with a 2 - ⟶ 0 + transition. However, because of the low probability of other level assignments, it is believed that the $Br^{84}$ (32-minute) level is indeed 2-, and that the inconsistency of the beta spectrum is the result of experimental error.

Of the remaining low-lying levels predicted for $Br^{84}$, the ≤ 6 - level is the most interesting. As pointed out on page 13, gamma transitions of spin difference ≥ 3 are associated with isomerism. For isomerism actually to occur it is generally necessary that there be no states of intermediate spin between the initial and final isomeric states. These conditions could possibly be satisfied with the foregoing predicted energy levels for $Br^{84}$.

If, then, on the assumption that the 32-minute activity represents the ground state of $Br^{84}$, some or all of an hitherto unknown isomeric state were to decay by beta emission, a determination of the fission yield of $Br^{84}$ based only on measurement of the 32-minute activity (as was the case) would be in error. In short, it appeared worthwhile to look for an isomer of $Br^{84}$ to explain the discrepancy in fission yield.

2) The existence of $Br^{86}$.

The low-lying levels of $Br^{86}$ can be deduced in a manner similar to that described above as for $Br^{84}$. The nuclide $Br^{86}$ has 35 protons and 51 neutrons. The most probable odd-proton shells are the same as those of $Br^{84}$, i.e., $f_{5/2}$ and $p_{3/2}$. The most probable odd-neutron shells, however, are $d_{5/2}$ and $g_{7/2}$ (cf. Figure I-3). Combination of the odd-proton and odd-neutron orbitals according to Nordheim's rule results in the following nuclear levels:

| Odd Proton | Odd Neutron | $l_1 + l_2 + j_1 + j_2$ | Resultant Spin | Parity |
|---|---|---|---|---|
| $p_{3/2}$ | $d_{5/2}$ | $1+2+3/2+5/2 = 7$ | $\leq \lvert 3/2+5/2 \rvert = 4$ | - |
| $p_{3/2}$ | $g_{7/2}$ | $1+4+3/2+7/2 = 10$ | $\lvert 3/2-7/2 \rvert = 2$ | - |
| $f_{5/2}$ | $d_{5/2}$ | $3+2+5/2+5/2 = 10$ | $\lvert 5/2-5/2 \rvert = 0$ | - |
| $f_{5/2}$ | $g_{7/2}$ | $3+4+5/2+7/2 = 13$ | $\leq \lvert 5/2+7/2 \rvert = 6$ | - |

It may be seen that all four predicted low-lying states are of odd parity. On the other hand, the ground state of the daughter, $Kr^{86}$, is almost certainly 0 +; moreover, it has been observed empirically that for most even-even nuclei, the first and second excited states are 2 + and 2 +, respectively, or 2 + and 4 +, respectively. It follows that a beta transition from any of the $Br^{86}$ levels, regarded as probable ground states, to any of the three lowest-lying states of $Kr^{86}$ must involve a change of parity. Consequently, these higher-energy beta transitions must be at least first forbidden.

It is now possible to make a crude guess as to the half-life of $Br^{86}$. First of all, various empirical and semi-empirical means exist for the prediction of the total decay energy of a radionuclide. The consensus of these predictions is that the total decay energy of $Br^{86}$ should be approximately 8 Mev. Secondly, if the ground state of $Br^{86}$ is taken as 0 -, then the beta transition from the ground state of $Br^{86}$ to the ground state of $Kr^{86}$ will be $\Delta j = 0$ (yes), corresponding to the more rapid of the first-forbidden transitions. With the reasonable assumption of log ft = 6.5 for this transition (cf. Table I-1), and $E_\beta = 8$ Mev, the calculated half-life is approximately 30 seconds. The choice of any of the other possible levels for the ground state of $Br^{86}$ would result in the beta decay proceeding predominantly to an excited level of $Kr^{86}$, and thus presumably to a longer half-life. Although the half-life of 30 seconds seems to be a reasonable lower

limit for the highest-energy beta transitions, it is possible that the half-life of $Br^{86}$ could be somewhat shorter owing to additional beta transitions to other excited states of $Kr^{86}$. For excited states of even parity only, this shortening might amount to a factor of 2 or 3. For cases where some of the excited states of $Kr^{86}$ are of odd parity and suitable spin, allowed beta transitions to these levels may be possible and the half-life may be shortened by a factor of 10 or more. Unfortunately, so little is known or predictable about the higher states of $Kr^{86}$ that the relative contributions of these alternatives cannot be estimated. However, because at least the higher-energy beta transitions are forbidden there is a reasonable possibility that $Br^{86}$ will be of long enough half-life ($\geq$ 30 seconds) to allow discovery via radiochemical techniques. This point represents an application of the general principle that with high-energy beta emitters of this kind, it is sometimes possible to predict with reasonable certainty that a half-life will be very short; it is far more difficult to predict that a half-life will be long, but the prediction that it may be long is in itself of some value. Because $Br^{86}$ falls in the latter category, it appeared worthwhile to make a search for it.

### 3) The existence of $Se^{84}$, $Se^{85}$, $Se^{86}$ and $Se^{87}$.

The half-life of $Se^{84}$ has already been reported by Manhattan Project workers as approximately 2 minutes. However, a careful scrutiny of the reports cited revealed neither the experimental details nor any of the data on which this figure was based. It was stated that rapid selenium separations had been carried out and that some $Br^{84}$ (32-minute) had been found to grow from the selenium. The useful information from the standpoint of the present investigation was that the half-life of $Se^{84}$ is in the range

of 2 minutes, a time long enough to allow more careful $Br^{84}$ milking experiments.

In the case of $Se^{85}$, $Se^{86}$, and $Se^{87}$, as with $Br^{84}$ and $Br^{86}$ discussed previously, the present state of knowledge of the energy levels of nuclei in this region does not permit a reliable prediction as to half-lives. Nevertheless, shell theory considerations do suggest some fragments of information which are of value in experiments involving a search for these isotopes. First of all, the theory predicts that the ground state of $Se^{85}$ is either $g_{7/2}$ or $d_{5/2}$. Similarly, the ground state of $Br^{85}$ should be $p_{3/2}$ or possibly $f_{5/2}$, and the first few excited states should contain levels of the type $p_{1/2}$ and $g_{9/2}$. Because it is somewhat hazardous to assign definite single particle configurations to these levels, a more reasonable conjecture is that levels of the nature $5/2$ -, $1/2$ -, $9/2$ + and probably also $7/2$ + and $5/2$ + comprise the first few excited states of $Br^{85}$. The semi-empirical mass formula of Levy[20] predicts a total beta decay energy of 6.3 Mev for $Se^{85}$. Comparison of similar predictions with total decay energies in nearby nuclei for which the total decay energies have been measured experimentally indicate that this decay energy should be corrected upward to about 7 Mev. This latter value, then, will be taken as a "best guess" for the total beta decay energy of $Se^{85}$.

With the assumption of this energy value and of the statements above concerning the nature of the energy levels of $Se^{85}$ and $Br^{85}$, some conclusions can now be drawn. If the ground state of $Se^{85}$ is $d_{5/2}$, the beta decay to a $p_{3/2}$ ground state of $Br^{85}$ must be first forbidden. If the ground state of $Se^{85}$ is $g_{7/2}$, the decay to the $p_{3/2}$ ground state of $Br^{85}$ is also first forbidden but of longer half-life (log ft approximately 9); the beta decay

to the $f_{5/2}$ level will be first forbidden but at least ten-fold more rapid than to the $p_{3/2}$ level.

Assuming a log ft = 7 for either $d_{5/2} \longrightarrow p_{3/2}$ or $g_{7/2} \longrightarrow f_{5/2}$ and a beta energy of 7 Mev, one finds from the lot ft nomographs of Moszkowski[14] a half-life of approximately 3 minutes. However, this state of affairs is likely to be strongly modified by the possible presence of 5/2 +, 7/2 +, and 9/2 + excited states in $Br^{85}$. For example, in $Rb^{87}$, which is expected to have a shell structure similar to $Br^{85}$, an excited level believed to be 7/2 + or 9/2 + occurs at 3.0 Mev above the ground state. If, as is likely to be the case, a suitable even-parity level exists at about the same distance above the ground state of $Br^{85}$, the predominant mode of decay of $Se^{85}$ will be by beta emission to this level. With this assumption the half-life for the latter beta branch may be estimated. Log ft for this allowed transition may be estimated as about 5.5 and the beta energy may be estimated as 7 - 3 = 4 Mev. The corresponding half-life then comes out to be about 1 minute, and the resultant half-life from this mode of decay and from the more energetic one mentioned above would be about 45 seconds. The foregoing assumptions and chain of reasoning cannot be regarded as providing a "prediction" in the usual sense of the word, but do indicate the approximate half-life range one can expect for $Se^{85}$.

The $Se^{87} \longrightarrow Br^{87}$ decay is expected to involve a set of nuclear levels similar to those in $Se^{85} \longrightarrow Br^{85}$. The $Se^{87}$ decay energy is estimated to be approximately 0.5 Mev greater than that of $Se^{85}$. The excited levels of $Br^{87}$ may tend to be more closely spaced than in $Br^{85}$, but the magnitude of this effect is impossible to predict. By methods similar to those used in the above paragraph for $Se^{85}$, the allowed beta branch of $Se^{87}$ may be estimated to

have a half-life of 40 seconds and the combination of this and the most energetic branch will result in a half-life of about 30 seconds. Again, this value is only indicative of the half-life range in which one may look for $Se^{87}$.

The lack of definite knowledge of even the ground state spin and parity of $Br^{86}$, let alone the excited states, makes a prediction of the half-life of $Se^{86}$ essentially impossible. One reasonable conclusion can be drawn, however: the limitation of the ground state of $Br^{86}$ to 0 -, 2 -, 4 -, or 6 - (Table I-1) implies that the beta transition from the ground state of $Se^{86}$ (assumed to be 0+) to the ground state of $Br^{86}$ is at least first forbidden. An interesting consequence of the fact that the ground state of $Se^{86}$ is 0 + is that it can decay by allowed transitions only if there exist 1 + levels in $Br^{86}$. An examination of the level scheme postulated for $Rb^{88}$, an analogue of $Br^{86}$, shows that the first 1 + state occurs at 2.4 Mev above the ground state. If the $Br^{86}$ is conjectured to have its first 1 + state at approximately 2.4 Mev above the ground state, and if the total decay energy of $Se^{86}$ is estimated to be 4.8 Mev, the allowed beta branch has an energy of 2.4 Mev. With the log ft taken as 4.3, as for the analogous transition in $Kr^{88} \longrightarrow Rb^{88}$, the half-life of the $Se^{86} \longrightarrow Br^{86}$ transition would be about 30 seconds.

# CHAPTER II

## EXPERIMENTAL FACILITIES AND TECHNIQUES

The experimental facilities for the purposes of this discussion may be divided into three categories: the reactor, the chemistry laboratories and the instruments.

The reactor used was the Los Alamos Water Boiler.[21] It is a research-type reactor and is provided with a pneumatic tube by means of which capsules containing samples may be blown into and out of the core region. With the reactor at full power (25 K.W.) the thermal neutron flux at the inner terminal of the tube was $5 \times 10^{11}$ $cm^{-2}sec^{-1}$. This pneumatic tube is known commonly as the "rabbit".

The chemical operations were done in either of two laboratories: the first was located approximately 70 feet from the face of the reactor. Under normal conditions chemical processing of the sample could be started 15 seconds after the end of the irradiation. The second laboratory was located in the main chemistry building about two miles away. Samples were transported by motor vehicle, and chemical processing could be started about 8 minutes after end of irradiation.

On a few occasions it was necessary to have a source of high-energy neutrons. The source was the Los Alamos Cockcroft-Walton accelerator, which produces approximately 14-Mev neutrons by the ${}_1D^2 + {}_1T^3 = {}_2He^4 + {}_0n^1$ reaction.

Simple chemistry and counting were carried out in a laboratory near the Cockcroft-Walton accelerator. More complex chemistry and counting were done

in the main chemistry building located about 2 miles away.

Radiation counting was carried out using two types of instruments: beta proportional counters and scintillation counters. The Los Alamos beta proportional counters[22,23,24] are relatively insensitive (a few tenths of a per cent) to gamma rays. With the sample mounting system used, beta counting efficiencies up to about 40 per cent were available. The dead-time loss of these counters was approximately 7 microseconds; in practical terms this means a dead time loss of 2.3 per cent at 200,000 counts per minute. Sets of aluminum absorbers were available for the qualitative differentiation of beta-ray groups.

Gamma and beta spectra were measured by scintillation counting. The gamma-counting system consisted of various sizes of NaI(Tl) crystals coupled to DuMont 6292 photomultiplier tubes, with the output of the latter feeding through a Los Alamos Model 101 preamplifier and Los Alamos Model 101A amplifier to a Los Alamos Model 2 100-channel pulse height analyzer. This analyzer sorts the incoming electrical pulses into 100 groups (channels) according to their size. While a sample is being counted, the pulse analyzer system records the number of pulses entering each channel in a memory circuit. At the end of the counting period the accumulated data are printed on a paper tape which shows the number of counts which have recorded in each of the channels. The time required to print out these data is about 2 minutes, during which time the recording circuit must remain inoperative. Since the scintillator and amplifier circuits are much faster than the analyzer, it is the latter which limits the practical usable counting rate. Its average dead-time loss is about 1 per cent at 60,000 total pulses per minute.

The manner in which gamma spectra are measured by scintillation systems may be described to a good approximation by the following statement. Because the quantity of light released by the crystal is very nearly proportional to the energy of the gamma ray deposited in the crystal, and the size of the pulse sent out of the photomultiplier is very nearly proportional to the light it receives, the series of numbers printed out by the pulse analyzer system constitutes a histogram of the energies deposited by the gamma rays in the crystal. Thus, if over a period of time a number of monoenergetic gamma rays enter the NaI(Tl) crystal they will be sorted and registered as the gamma ray spectrum of the source.

The beta spectrum is obtained by means of the same equipment as described above except that the NaI(Tl) crystal is replaced by a trans-stilbene crystal. The latter is more sensitive to beta radiation and is essentially transparent to gamma rays.

The laborious computations required for the analysis of the beta spectrum were done by the IBM Electronic Data Processing Machine, Type 704.

# CHAPTER III

# CHEMICAL PROCEDURES

Five types of chemical separations were employed in this work: 1) the radiochemical isolation of bromine from fission-product mixtures; 2) the separation of radioselenium, more or less pure, from fission-product mixtures; 3) the separation of bromine daughters from their selenium parents; 4) the separation, by Szilard-Chalmers process, of ground-state bromine isomers from the upper isomers which decay by isomeric transition, and 5) the quantitative determination of $Mo^{99}$.

Three separate procedures were designed for the radiochemical isolation of bromine. The first of the procedures was relatively slow and gave quantitative results, i.e., the radiochemical yield was measured and the absolute activity of the bromine could be determined from it. The second was much more rapid, but qualitative; its radiochemical yield was estimated to be about 30 per cent but was not measured. The third was almost as rapid as the second,and as with the first, the chemical yield was measured. The choice of procedure, then, depended on the demands of the particular experiment. Where the principal object was the determination of the fission yield, either the first or the third was used. The second was used in the search for new bromine isotopes, and the primary concern was the very rapid isolation of bromine activities from fission products without particular regard to yield.

The procedure used for the separation of selenium was essentially qualitative rather than quantitative. The only object was the very rapid

separation of some of the fission-product selenium so that measurements could be made of the bromine daughters that grew from it.

Three separate procedures were designed for the separation of bromine daughters from their selenium parents. The first was applicable for determining selenium half-lives ≥ 1 minute. The second was developed to measure selenium half-lives as short as 15 seconds. The third was essentially the same as the second except for an additional chemical step which was introduced to remove the last traces of contamination.

Only one procedure was used for the identification of an isomeric state of bromine. The object was the rapid separation of the ground state radioactive bromine formed from the decay of the upper isomer.

In those procedures where the absolute activity of fission-product bromine was measured, it was also necessary to analyze for a fission product whose fission yield had been determined. The fission yield of the radionuclide $Mo^{99}$ is well known and a procedure exists which will give quantitative results, i.e., the radiochemical yield can be measured and the absolute activity of the molybdenum can be determined from it.

## Quantitative Determination of Radiobromine

### Outline of Procedure

The chemical procedure used for the separation of bromine from other fission products is that of Glendenin, Edwards, and Gest,[25] as modified by Wahl and Ramaniah.[26] The latter irradiated uranium metal with thermal neutrons and dissolved the metal in a solution of hydrochloric acid and bromide carrier.

They showed that the isotopic exchange between the radioactive bromine isotopes formed in the uranium and the bromide carrier present during the solution process was rapid and complete. Bromine was separated from the other fission products (with the exception of iodine) by first oxidizing the bromide to bromine with ceric ion and extracting it into carbon tetrachloride. The bromine was then extracted into an aqueous solution of sodium hydrogen sulfite as bromide. Iodine was removed by adding iodide carrier, oxidizing to iodine with sodium nitrite and extracting into carbon tetrachloride. The bromide was then oxidized with potassium permanganate, extracted into carbon tetrachloride and finally extracted into aqueous sodium hydrogen sulfite. Silver bromide was precipitated by adding silver nitrate, and the sample was prepared for counting. The chemical yield was about 65 per cent.

## Procedure

The irradiated uranium metal (93% $U^{235}$) was dissolved in a solution consisting of 5 ml. of concentrated hydrochloric acid, 1 ml. of bromide carrier (0.25 millimoles) and 3 ml. of molybdenum carrier (0.25 millimoles); the number of fissions that occurred in the uranium was determined from an analysis of the $Mo^{99}$ (66.4 hours) activity. After dissolution of the uranium, 3 per cent hydrogen peroxide was added dropwise until the solution became clear, indicating the conversion of U(III) and U(IV) to U(VI). After adjustment of the volume to 15 ml. with water, 2 $\underline{f}$ ceric nitrate in 1 $\underline{f}$ nitric acid was added dropwise to oxidize the bromide to bromine. The bromine was then extracted with three 10-ml. portions of carbon tetrachloride. The water layer was set aside for the determination of $Mo^{99}$. A few drops of 0.1 $\underline{f}$ sodium hydrogen sulfite and 10 ml. of water were added to the combined carbon

tetrachloride layers. After shaking, the carbon tetrachloride layer was discarded. To the water layer was added 1 ml. of 6 f nitric acid and 1 ml. of potassium iodide carrier (0.08 millimoles). A few drops of 0.1 f sodium nitrite was used to oxidize the iodide ion to iodine (bromide is not oxidized to bromine by nitrous acid). The iodine was extracted with three 10-ml. portions of carbon tetrachloride. These layers were discarded and once again 0.08 millimoles of iodide ion was added to the water layer. After addition of sodium nitrite the iodine was extracted using four 10-ml. portions of carbon tetrachloride which were also discarded. The bromide ion in the water layer was oxidized to bromine with 2 ml. of 6 f nitric acid and an excess of 0.1 f potassium permanganate. The bromine was extracted with three 10-ml. portions of carbon tetrachloride and the water layer was discarded. To the combined carbon tetrachloride layers was added 10 ml. of water and a few drops of 0.1 f sodium hydrogen sulfite (a minimum amount was used to reduce the bromine to bromide). After shaking, the carbon tetrachloride layer was discarded. One milliliter of 6 f nitric acid was added to the water layer containing the bromide ion. After dilution to 15 ml. with water, the solution was boiled for a few minutes to expel the sulfur dioxide. Two milliliters of 0.1 f silver nitrate was added and the solution heated for a minute to coagulate the silver bromide. The precipitate was filtered with suction on a tared, 26-mm-diameter Whatman No. 41 H paper with the paper clamped between a ground-edge glass chimney, 3½" high and 18 mm. i.d., and a Hirsch funnel without sides and its surface ground flat. The precipitate was washed with 5 ml. of 6 f nitric acid, 10 ml. of water, two 5-ml. portions of acetone and finally 5 ml. of ether. The filter paper containing the precipitate was dried in the oven at 110° for 10 minutes, allowed to cool for 20 minutes, weighed, mounted on double-sided Scotch tape placed in the center of a 2½" x 3-1/4" x 1/16" dural plate, and then covered

with Mylar film (1.76 mg./cm.$^2$).

### Rapid Qualitative Separation of Radiobromine

### Outline of Procedure

The method of Hahn and Strassman[27] was used for the fast separation of active bromine from the other fission products. First, the irradiated uranium salt was transferred to a distillation flask containing bromide carrier and 3 f sulfuric acid. The bromide carrier was oxidized to bromine with an equivalent amount of sodium bromate and the evolved bromine was swept into a receiving vessel by bubbling air through the solution. The most likely contaminant in addition to krypton and xenon would be iodine. Stehney and Sugarman[28] showed that less than one per cent of the iodine came over in twenty seconds, whereas as much as three per cent came over in sixty seconds. No steps were taken to assure complete isotopic exchange between fission-product bromine and carrier bromine. The procedure is, therefore, only qualitative and is designed primarily as an aid in searching for new short-lived isotopes of bromine.

### Procedure

Irradiated uranyl nitrate hexahydrate was added to a distillation flask containing a solution consisting of 10 ml. of 3 f sulphuric acid and 1 ml. of bromide carrier (0.19 millimoles). The solution was stirred rapidly for a few seconds with a ten-mil platinum wire and then carrier bromate (0.04 millimoles) was added. The evolved bromine was swept into a receiving vessel by gently

heating the flask and bubbling nitrogen gas through the solution. The bubbling time was limited to fifteen seconds. The distilled bromine was collected in a specially designed separatory funnel called the "Ultramax",* which serves equally well as a centrifuge tube. The separatory funnel contained a solution consisting of 5 ml. of 1 *f* nitric acid, 2 ml. of .2 *f* ferrous sulfate and 0.5 ml. of iodide carrier (0.04 millimoles). The distillation tube was removed and the iodide carrier was oxidized to iodine with 1 ml. of 0.3 *f* sodium nitrite. Ten milliliters of carbon tetrachloride was added and the iodine extracted into the organic layer. After centrifugation of the solution the water layer was added to a centrifuge tube containing 20 ml. of a solution 1 *f* in nitric acid and 0.19 *f* in silver nitrate. The solution was heated for a few seconds to coagulate the silver bromide, and the precipitate was then filtered, washed and mounted as described on page 35. The sample was ready for counting about three minutes after the end of the irradiation.

The procedure was tested by irradiating a piece of uranium and then allowing it to stand for a week. By this time all the bromine activities had decayed, but other fission products, particularly the $I^{131}$, were still present. By analyzing for $Mo^{99}$ it was determined that $2 \times 10^{12}$ fissions had taken place. However, no activity was detected using the above procedure, indicating that the separation from other fission products was excellent.

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*Manufactured by the Fisher and Porter Company. Catalogue No. 1735.

## Rapid Quantitative Determination of Radiobromine

### Outline of Procedure

This procedure was developed by combining the best features of the rapid qualitative method (page 36) and the slower quantitative method (page 33) for determining radiobromine.

Isotopic exchange was effected by dissolving irradiated uranium metal in a distillation flask containing a solution of bromide carrier in 3 f hydrochloric acid. The bromide carrier was oxidized to bromine with ceric nitrate and the evolved gas was swept into a receiving vessel by bubbling nitrogen through the solution. The rest of the procedure was essentially that described on page 36, except for one major modification. It was found that chloride was carried over during the distillation of the bromine and was not eliminated by any of the subsequent steps. As a result, the final silver bromide precipitate contained a few milligrams of silver chloride. For this reason it was necessary to introduce an ammonium carbonate wash of the final precipitate. The silver chloride dissolved rapidly, whereas the silver bromide remained unchanged.

### Procedure

The irradiated uranium metal (93% $U^{235}$) was transferred to a distillation flask containing a warm solution consisting of a mixture of 3 ml. of molybdenum carrier (0.31 millimoles) in 6 f hydrochloric acid and 3 ml. of bromide carrier (0.75 millimoles). After the metal had dissolved, the solution was cooled for thirty seconds in an ice-water bath. Hydrogen peroxide (3%)

was added dropwise until the solution became clear, indicating the conversion of U(III) and U(IV) to U(VI). The bromide carrier was oxidized to bromine with 0.8 ml. of 1 f ceric nitrate. After the distillation apparatus was assembled, the bromine gas was swept into a separatory funnel by gently heating the distillation flask and bubbling nitrogen through the solution for thirty seconds. The separatory funnel contained 20 ml. of carbon tetrachloride and 5 ml. of 1 f nitric acid. The bromine dissolved in the carbon tetrachloride layer, which was then separated and transferred to another separatory funnel containing 10 ml. of a solution 1 f in nitric acid and 0.08 f in iodide carrier. Four milliliters of 0.1 f sodium nitrite was added to oxidize the iodide carrier to iodine and reduce the bromine to bromide. The carbon tetrachloride layer containing the iodine was then discarded. The iodine was extracted from the water layer with 20 ml. of carbon tetrachloride. The water layer was transferred to a 40 ml. centrifuge tube and heated to boiling. The bromide was precipitated with the addition of 3 ml. of silver nitrate (0.28 millimoles). The silver bromide precipitate was filtered onto a No. 41 H Whatman filter paper by means of a glass chimney-fritted funnel arrangement. The precipitate was washed with 10 ml. of a saturated solution of ammonium carbonate, 5 ml. of water, 5 ml. of 6 f nitric acid, 5 ml. of water and finally with acetone. After the filter paper was dry, the sample was mounted as described on page 35 and then counted. In order to determine the chemical yield it was necessary to remove the silver bromide after the counting was completed and weigh the precipitate.

The number of fissions that took place in the uranium was determined by analyzing the solution remaining in the distillation flask for $Mo^{99}$.

## Radiochemical Determination of Molybdenum

### Outline of Procedure

The procedure used for the determination of $Mo^{99}$ was developed by Barnes and Lang.[29] The separation of molybdenum from fission products was based primarily on the behavior of molybdenum (VI) on an anion-exchange resin. Molybdenum (VI) was absorbed on the resin from hydrochloric acid solutions of concentrations 5 f to 9 f. The resin was washed with a mixture of dilute hydrochloric and hydrofluoric acids and subsequently with 3 f ammonium hydroxide to remove most of the interfering ions. Molybdenum was eluted from the columns with 6 f ammonium acetate, precipitated with alpha benzoinoxime, converted by ignition to molybdenum oxide and weighed. The chemical yield was about 70 per cent.

### Procedure

The sample used for the analysis of the $Mo^{99}$ activity came from either the water layer as is indicated in the procedure on page 33 or from the solution left in the bromine distillation flask as indicated in the procedure on page 38. In either case, the sample was first transferred to a 40 ml. centrifuge tube and 3 ml. of concentrated nitric acid was added. The volume was adjusted to 20 ml. with water and the molybdenum was precipitated by adding 10 ml. of alpha benzoinoxime (2% solution in ethanol). After centrifugation the supernatant liquid was discarded and the precipitate filtered onto a No. 41 H Whatman filter paper. The precipitate was washed with 1 f nitric acid and ignited for about fifteen minutes at 550° C. The molybdenum oxide was then dissolved by heating with three drops of concentrated sulfuric acid.

Five milliliters of 6 f hydrochloric acid and 1 ml. of bromine water were added and the solution was heated to boiling and then transferred to a Dowex 1-X8, 50-100 mesh, anion resin column (1 cm. O.D. x 8 cm. in length). The hydrochloric acid was allowed to drain off. The column was washed with 2 ml. of 6 f hydrochloric acid. When the liquid level reached the top of the resin, 10 ml. of a hot solution, 0.1 f in hydrochloric acid and 0.1 f in hydrofluoric acid, was added. When the level of this wash reached the top of the resin 5.0 ml. of 3 f ammonium hydroxide was added. When this wash reached the top of the resin the molybdenum was removed by washing the column with 2 ml. of hot 6 f ammonium acetate. Two milliliters of concentrated ammonium hydroxide was added to the eluate which was collected in a 40 ml. centrifuge tube. Five milligrams of Fe(III) was added and the solution boiled for one minute with stirring. After centrifugation the supernatant liquid was added to an ice-cold mixture of 6 ml. of concentrated nitric acid and 1 ml. of bromine water. The solution was cooled in an ice bath for about five minutes and then 10 ml. of alpha benzoinoxime was added. The precipitate was collected on a No. 41 H Whatman filter paper and washed with 5 ml. of 1 f nitric acid. The filter paper and precipitate were transferred to a porcelain crucible and ignited at 550° C for an hour. After cooling, the precipitate was ground to a fine powder. Two drops of ethyl alcohol were used to slurry the powder and then the precipitate was transferred, using 5 ml. of ethyl alcohol, onto a previously washed, dried and weighed filter paper using a stainless steel filter chimney and a ground-off Hirsch funnel. The precipitate was washed with ethyl alcohol, dried at 110° for ten minutes, weighed and mounted on an aluminum plate using two-sided Scotch tape and finally covered with Mylar film.

## Investigation of Isomeric States

### Outline of Procedure

A method was developed for investigating possible isomeric states of bromine based upon the reaction of bromine with phenol. The bromine evolved in the distillation procedure on page 36 was swept into a water solution containing 5 mg. of phenol. The bromine reacted immediately with the phenol to form tribromophenol bromide. An excess of sodium hydrogen sulfite was added to transform the compound into tribromophenol, a white crystalline precipitate. The precipitate was washed with 0.01 f nitric acid containing bromide carrier and then dissolved in benzene. The benzene solution was transferred to a separatory funnel and extracted with successive portions of 0.01 f nitric acid solutions containing bromide carrier. Silver bromide was precipitated from each of the extracted water layers and prepared for counting.

### Procedure

Irradiated uranyl nitrate hexahydrate was transferred to a distillation flask containing a solution of 10 ml. of 3 f sulfuric acid and 1 ml. of bromide carrier (0.19 millimoles). The solution was stirred for a few seconds with a ten-mil platinum wire and then carrier bromate (0.038 millimoles) was added. The evolved bromine was swept into a 20-ml. water solution of phenol (0.5 millimoles) by gently heating the flask and bubbling nitrogen gas through the solution for tan seconds. The yield of bromine was about 20 per cent. Therefore, it was necessary to add liquid bromine carrier to precipitate the excess phenol as tribromophenol bromide. After centrifuging, the water layer was discarded. The tribromophenol bromide was changed to tribromophenol by

stirring the precipitate with 10 ml. of 0.1 f sodium hydrogen sulfite. After centrifugation the supernatant liquid was discarded. The precipitate was washed with 10 ml. of bromide carrier (0.12 millimoles) in 0.01 f nitric acid and then dissolved in 20 ml. of benzene. The benzene solution was poured into a 60-ml. Ultramax separatory funnel containing 10 ml. of bromide carrier (0.19 millimoles) in 0.01 f nitric acid. The funnel was shaken for thirty seconds and the layers were separated by centrifugation. The water layer was drained into a centrifuge tube and saved for further processing. The benzene layer was treated with five more portions of bromide solution and the water layers were drained into separate centrifuge tubes. To each of the centrifuge tubes was added 2 ml. of 0.1 f silver nitrate and the solution heated for a few seconds to coagulate the silver bromide. The precipitate was filtered, washed, and mounted as described on page 35.

## Validity of Procedure

The foregoing procedure was tested using $Br^{80m}$ (4.5 hours) which is known to decay by isomeric transition to the ground state, $Br^{80}$ (18 minutes). The nuclide $Br^{80m}$ was prepared by irradiating 100 milligrams of potassium bromide in the "rabbit" port of the Water Boiler for three minutes. The reaction giving rise to this isomer is the capture of a neutron by $Br^{79}$ (50.6% abundant). The irradiated potassium bromide was placed in the distillation flask and after an equivalent amount of bromate carrier had been added the evolved bromine was swept into the phenol solution. The chemistry from this point was exactly the same as discussed above except that the benzene layer was treated with only three portions of bromide solution, and of these three, only the third sample

was precipitated, mounted, and counted. If the chemical procedure that had been developed was adequate, an analysis of the counting data obtained from this sample should show only one component of half-life equal to 18 minutes. The nuclide $Br^{80m}$ has a high gamma-ray conversion coefficient, and the internal conversion will leave the daughter nucleus ($Br^{80}$) in such a high state of electronic excitation that it will dislodge itself from the organic molecule in which it is bound. Figure III-1 is the experimental decay curve and exhibits a 17.6 minute half-life.

## Rapid Qualitative Separation of Selenium from Fission Products

### Outline of Procedure

The following procedure is an adaptation of the method of Edwards, Gest and Davies.[30] They found that good yields of $Se^{84}$, free from other fission products, could be achieved by an isotopic exchange reaction with selenium metal in a suitable medium. They prepared a suspension of selenium metal by reducing selenite carrier in concentrated hydrochloric acid with sulfur dioxide. Neutron-irradiated uranium trioxide was dissolved in the suspension and after stirring for a few minutes the selenium was separated by filtration. The metal was dissolved in a small volume of hot concentrated nitric acid. The decay curves of the bromine fractions separated from this selenium preparation showed a moderately small amount of long-lived contamination. Evidently the selenium fission products were reduced to the Se (0) state by the sulfur dioxide in the concentrated hydrochloric acid and were collected on the surface of the selenium metal. It was necessary to use concentrated hydrochloric acid because tellurite is reduced to the metal in are dissolved, [illegible]

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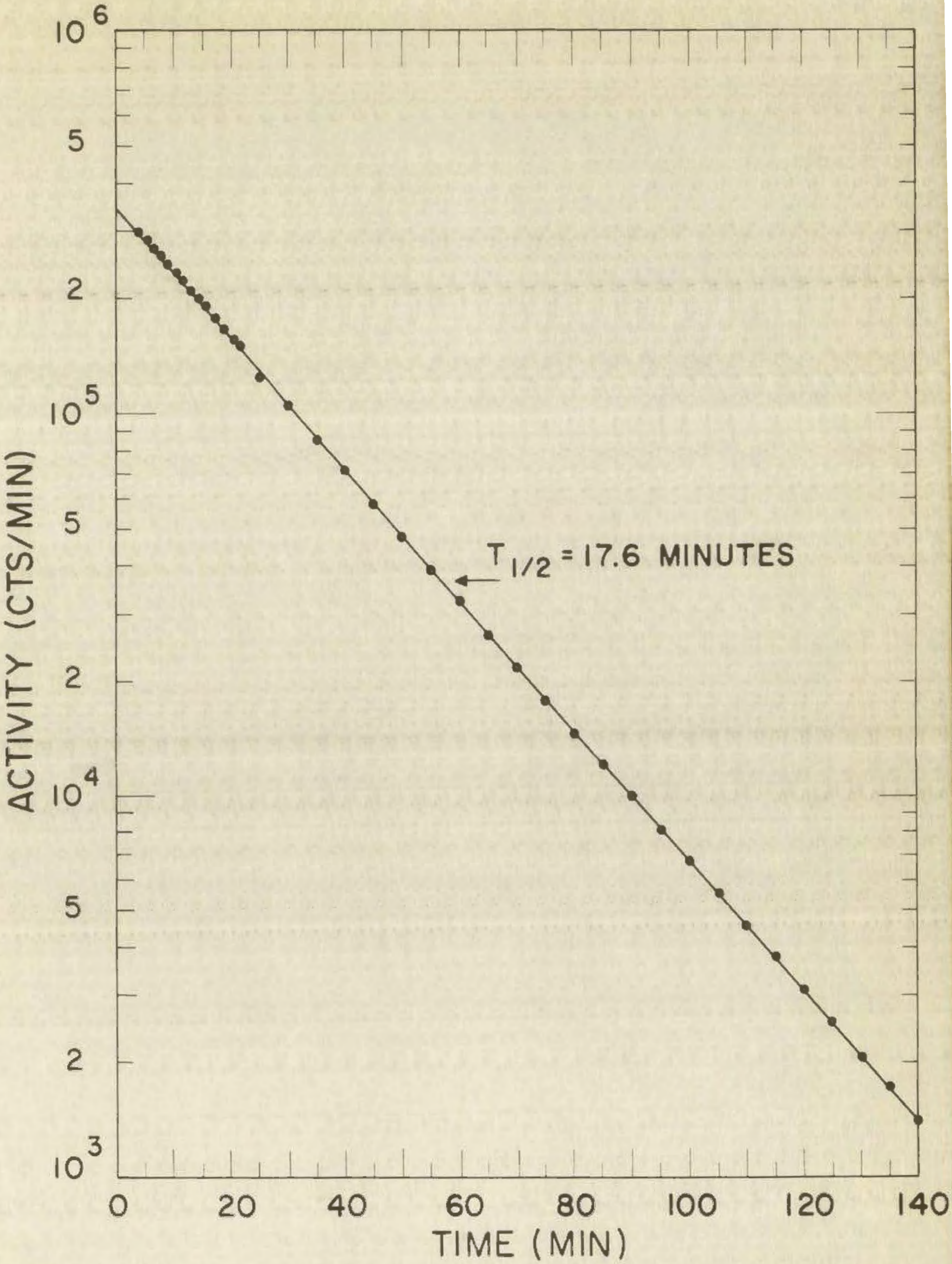

Figure III - 1. Decay of $Br^{80}$ separated from $Br^{80m}$ by a hot-atom reaction.

dilute solutions.

## Procedure

A suspension of selenium metal was prepared 15 minutes before an irradiation by reducing selenite carrier (0.13 millimoles) in 15 ml. of concentrated hydrochloric acid with sulfur dioxide. Tellurite (0.08 millimoles) was added as a hold-back carrier for the tellurium fission products. The irradiated uranium salt was dissolved in the suspension, and after stirring for thirty seconds the selenium was separated by filtration through a coarse 30-ml. Buchner-type filter funnel. The precipitate was washed with 30 ml. of concentrated hydrochloric acid and 60 ml. of water. The selenium was dissolved by either drying the precipitate and then scraping it into a 40-ml. centrifuge tube containing 3 ml. of hot concentrated nitric acid or by adding hot concentrated nitric acid directly to the filter funnel and then pouring the solution into a 40-ml. centrifuge tube. The dissolved selenium metal constituted the solution from which the daughter bromine activities were subsequently milked.

## Rapid Separation of Bromine from Selenium by Extraction

## Outline of Procedure

Edwards, Gest and Davies[30] investigated the oxidation state of the radiobromine that grew from a radioactive selenium parent, accompanied by a carrier concentration of selenite, as a function of the pH of the decay solution. It was found that about fifty per cent of the radiobromine existed as bromate at

a pH of 8 but only twenty per cent existed as bromate at a pH of 3. Adams and Gilbertson[31] had found that "selenite readily reduced bromate in the presence of small amounts of nitric acid", and therefore it is expected that all the radiobromine in a 2 f nitric acid solution of selenite should exist as bromide. If this is true, then a rapid separation of the fission-product bromine could be effected by shaking the selenite solution with carbon tetrachloride containing dissolved bromine. The exchange between bromide and bromine in aqueous solutions has already been demonstrated to be very rapid.[32]

To measure the half-life of a selenium isotope it is necessary only to measure, as a function of time, something proportional to the amount of the selenium isotope in the sample. This was done by the "milking" technique, which consists of measuring at various times, $t_1$, the amount of daughter activity (bromine) which had grown in during a time interval of length $T_1$. If the radioactive bromine is removed at time $t_1$, then the bromine activity in the sample at $t_1 + T_1$ is given by

$$A_2(t_1+T_1) = \frac{A_1(t_1)\lambda_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 T_1} - e^{-\lambda_2 T_1}\right). \qquad \text{(III-1)}$$

Subscript 1 refers to selenium and subscript 2 refers to bromine. The activity, $A_2(t_1+T_1)$, is measured by beta or gamma counting the radiobromine sample separated at $t_1+T_1$. If all the $T_1$'s were of constant value, C, then it is clear that $A_1(t_1)$ is proportional to $A_2(t_1+C)$, since the exponential in equation III-1 is a constant. Therefore, the half-life of the selenium parent can be obtained from a semilogarithmic plot of $A_2(t_1+C)$ versus $t_1$.

## Procedure

The selenite solution obtained from the rapid separation of radioselenium was diluted to 10 ml. with water, added to a 30 ml. separatory funnel containing 10 mg. of bromine in 10 ml. of carbon tetrachloride, and subsequently shaken for one minute. A stop watch was used to record the time at which the shaking stopped. The mixture was allowed to stand for thirty seconds before separation of the layers. The carbon tetrachloride solution was discarded. Another portion of bromine in carbon tetrachloride was added to the water layer and again shaken for one minute. The time interval (in this case, 1 minute) must be constant between extractions, but the choice of the length of this interval is purely arbitrary and will in general depend on the half-life of the selenium parent under investigation. After standing thirty seconds the layers were separated and the carbon tetrachloride layer saved for further processing. The extraction of bromine from the selenite solution was repeated as many times as was necessary. The carbon tetrachloride layers were treated as follows. Twenty milliliters of 1 f nitric acid were added. The layers were shaken and then the carbon tetrachloride layer was drained into a separatory funnel containing iodide carrier (0.08 millimoles) in 20 ml. of 1 f nitric acid. One milliliter of 0.3 f sodium nitrite was added to oxidize the iodide to iodine and reduce the bromine to bromide. After shaking, the organic layer was separated and discarded. The water layer was extracted again with 20 ml. of carbon tetrachloride and then transferred to a 40-ml. centrifuge tube; silver bromide was precipitated by adding 2 ml. of silver nitrate (0.18 millimoles). The silver bromide was filtered, washed, and mounted as described on page 35.

### Validity of Procedure

The foregoing procedure was tested using $Se^{83}$ (25 minutes), which is known to decay to $Br^{83}$ (2.4 hours). A sample of uranyl nitrate hexahydrate (93% $U^{235}$) weighing 8 mg. was bombarded for ten minutes in the rabbit port of the Water Boiler. The sample was transported to the main chemistry building and treated in the manner described above. The time interval chosen for the successive milking of the bromide daughters was ten minutes. The bromine activity in each fraction was measured and extrapolated back to the time of separation. A semi-logarithmic plot of the bromine activity versus the time of beginning of the growth period is shown in Figure III-2. The observed half-life of 24.8 minutes agrees quite well with the accepted value of 25 ± 1 minutes.

## Rapid Separation of Bromine from Selenium by Exchange with Silver Bromide

### Outline of Procedure

Kolthoff and O'Brien[33] have shown that freshly precipitated silver bromide exchanges rapidly with bromide at ordinary concentrations. Edwards and Gest,[34] using radiobromine tracer found that hypobromite also exchanges readily at concentrations below $10^{-10}$ f. Although their experiments were carried out in nearly neutral solutions, it is possible that rapid and complete exchange could also be achieved in a 2 f nitric acid medium.

The extraction method of separating radiobromine from its selenium parent (page 46) is not fast enough to measure selenium half-lives of less

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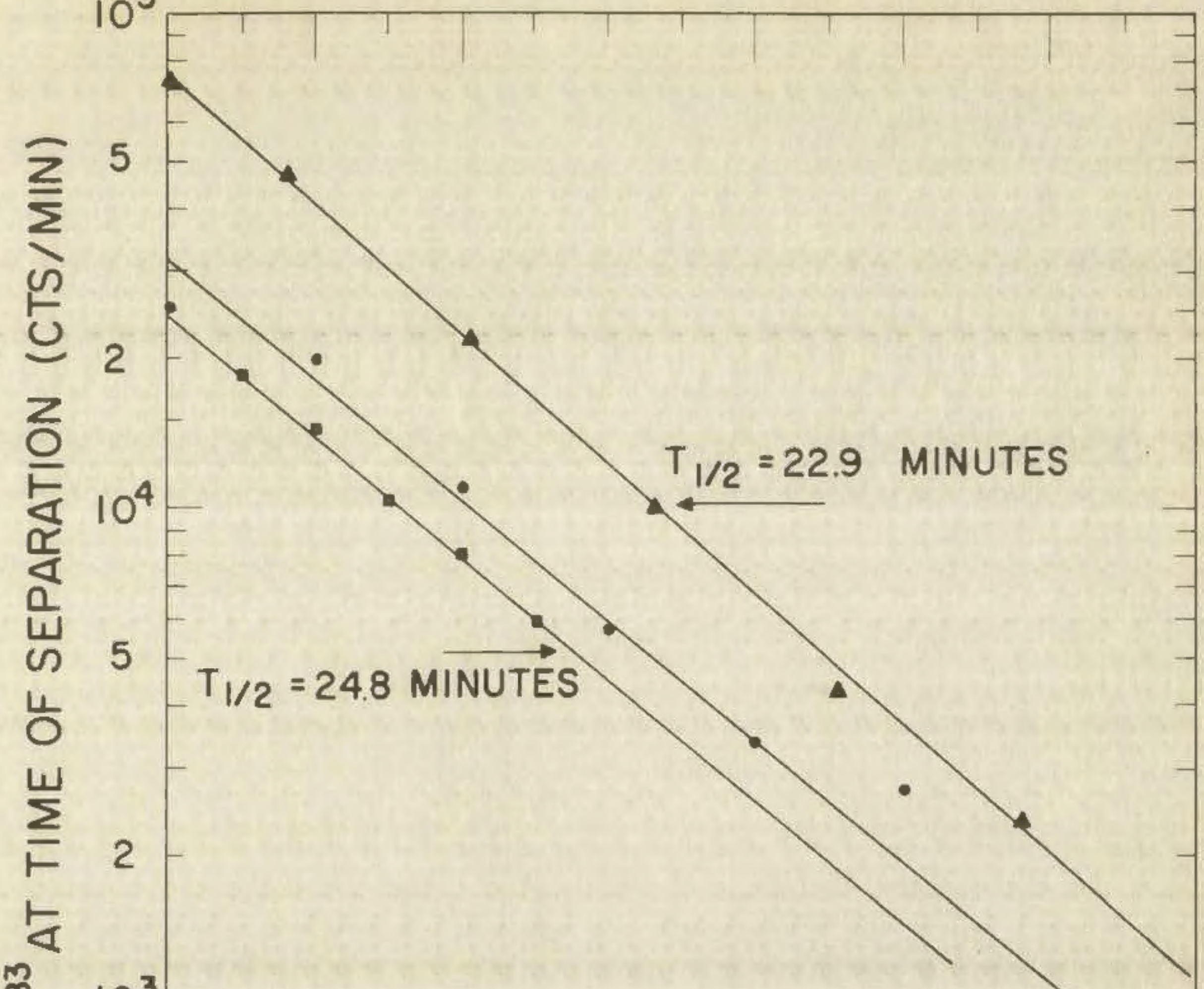

Figure III - 2. Decay curves of $Se^{83}$, computed from activities of $Br^{83}$ extracted from radioactive selenite solutions.

- ■ - Extracted with carbon tetrachloride.
- ▲ - Extracted with silver bromide.
- ● - Anion column plus extraction with silver bromide.

than a minute. The present procedure was designed specifically to determine selenium half-lives as low as fifteen seconds. It is based on the assumption that a silver bromide precipitate, mixed with the radioactive selenite solution for a few seconds, will effectively remove all the radiobromine.

### Preparation of Silver Bromide

The silver bromide precipitates were prepared as follows for all experiments:

One milliliter of bromide carrier (0.12 millimoles) was added to a 40-ml. centrifuge tube. After adjustment of the volume to 20 ml. with water, 1 ml. of 6 f nitric acid was added. The solution was heated nearly to boiling and silver bromide was precipitated by adding, with stirring, 2 ml. of silver nitrate (0.25 millimoles). The solution was allowed to stand undisturbed for one hour. The silver bromide precipitate was separated from the supernatant liquid by centrifugation. The precipitate was then washed with 20 ml. of 1 f nitric acid and finally stored in 1 ml. of 6 f nitric acid. The silver bromide was used as soon after its preparation as was possible, usually within half an hour, in order to minimize aging of the precipitate. The silver bromide was broken into fine particles with the aid of a stirring rod prior to use.

### Procedure

After the separation of the radioselenium by the method described on page 44 , the selenium metal was dissolved in 4 ml. of hot concentrated nitric

acid and then added to a 40-ml. centrifuge tube containing the freshly precipitated silver bromide in one ml. of 6 f nitric acid and 16 ml. of water. The suspension was stirred for one minute or less depending on the half-life being investigated. The silver bromide was filtered onto a No. 41 H Whatman filter contained in a ground-off Hirsch funnel-filter chimney setup. In these experiments, the Hirsch funnel was mounted on a micro bell jar so that the filtrate could be collected in a 100-ml. beaker. The beaker was quickly removed and the filtrate added to a 40-ml. centrifuge tube containing silver bromide in 1 ml. of 6 f nitric acid. The solution was stirred and then filtered as before. Again the filtrate was collected in a 100-ml. beaker and added to another silver bromide precipitate. These steps were repeated as often as desired. The silver bromide precipitates, usually three to six in number, were washed and mounted as described on page 35.

The time interval between successive additions of silver bromide and the length of time the silver bromide was stirred with the solution was kept constant for any particular experiment. Zero time was arbitrarily chosen as that instant when the silver bromide suspension was poured through the first filter. This first silver bromide sample was discarded. Some appropriate time later, e.g., one minute, the next silver bromide suspension was poured through the filter. This process was repeated, and care was taken always to keep the time interval, in this case one minute, constant. The half-life of the selenium parent was obtained from a semi-logarithmic plot of the activity in each silver bromide sample at the time of separation versus the time at which the growth period started.

## Validity of Procedure

The foregoing procedure was tested by milking $Br^{83}$ (2.4 hours) which results from the decay of $Se^{83}$ (25 minutes). A sample of uranyl nitrate hexahydrate (93% $U^{235}$) weighing 137 mg. was bombarded in the rabbit port of the Water Boiler for ten minutes. The sample was transported to the main chemistry building and treated in the manner shown above. Six samples of silver bromide were separated and counted. The time interval between separations was 25 minutes and the selenite solution was mixed with the silver bromide for one minute before filtration. The first silver bromide was inadvertently separated after only a sixteen-minute growth period. The observed activity was normalized to a 25 minute time interval using the known half-lives of $Se^{83}$ and $Br^{83}$ and is plotted as the first point in Figure III-2. The observed half-life is 22.9 minutes, which agrees reasonably well with the accepted value of 25 ± 1 minutes and certainly indicates that the method of milking with pre-formed silver bromide precipitates is an acceptable one.

In order to obtain the true counting rate of the silver bromide samples, it was necessary to correct each of them for a long-lived contaminant (about 30 hours). The contamination in most cases amounted to about 20 per cent of the original counting rate. Although this correction appeared to be a serious one, further consideration of the problem proved it to be relatively unimportant. The selenium isotope, $Se^{83}$, used to test the procedure has a fission yield of 0.22%. This is about a factor of five less than the $Se^{84}$ yield (1%) and about a factor of seven less than the $Se^{85}$ yield (1.5%). Assuming that the amount of contamination remains the same when these latter isotopes are investigated,

the relative contribution to the total beta count will be reduced by at least a factor of five. An even more important consideration is that the half-lives of $Br^{84}$ (32 minutes) and $Br^{85}$ (3.0 minutes) are from 6 to 60 times shorter than the $Br^{83}$ (2.4 hours) used in this test experiment. This combination, greater abundance of the selenium isotopes and shorter half-lives of the daughters, will reduce materially the contribution of the contaminant to the total observed beta activity.

However, in spite of the fact that the contribution from this longer-lived contaminant was considered negligible, an investigation was initiated to identify and eliminate this unknown activity. The most likely element to follow through the chemical procedure would be tellurium. It is possible that one or two per cent of the radiotellurium would be carried on the selenium metal,and the iodine daughters that grow from the decay of the tellurium would be carried on the silver bromide precipitate. To investigate this possibility the gamma rays from one of the contaminated silver bromide precipitates were counted using a 1½" x 1½" NaI(Tl) crystal. The gain on the amplifier was set to cover a range of 50 to 775 Kev, and the gamma spectrum was recorded on the multichannel analyzer. A prominent gamma peak that decayed with about an 18-hour half-life was observed at 537 Kev. This radiation could very well correspond to the known 528-Kev gamma of $I^{133}$ (20.9 hours). The parent of this iodide isotope is $Te^{133m}$ (63 minute) with a 4.9 per cent fission yield. The $I^{133}$ decays to $Xe^{133}$ (5.27 d) which would account for the lengthening of the half-life. On the basis of these results a procedure was developed which would specifically eliminate tellurium activity.

## Rapid Separation of Bromine from Selenium by Anion Resin Column and Exchange with Silver Bromide

### Outline of Procedure

Tellurium in 3 f hydrochloric acid is strongly adsorbed on an anion resin column, whereas selenium is only slightly adsorbed.[35] It was found that if tellurite carrier (0.08 millimoles) in 3 ml. of 3 f hydrochloric acid was added to a resin column and forced through rapidly (20 seconds) by means of air pressure, a small amount of the tellurite passed through the column. However, if the 3 f hydrochloric acid solution of tellurite was heated prior to its addition to the column, no tellurite was detected in the eluted solution. On the other hand, selenite under the same conditions did not appear to adsorb on the column. No macro quantity of tellurite was used in the actual experiment because it is known that adsorbability decreases with increased loading of the resin. Kraus and Nelson[35] say, "In general, adsorbability decreases with increased loading. This effect is small up to about 1 per cent loading but may amount to a 5 to 20 fold decrease between 1 and 20 per cent loading".

The procedure developed here differs from the preceding one only in that a specific step was introduced to remove tellurium activity, namely, the resin column.

### Preparation of Resin and Column

The resin used in this experiment was AG-1-X8, 50-100 mesh, supplied by the Bio-Rad Laboratories, 800 Delaware, Berkeley, California, who purify and

grade the resins manufactured by Dow Chemical Company. The resin was stored in concentrated hydrochloric acid until ready for use. The anion column was fabricated by fusing a 15-ml. conical centrifuge tube to a 9-cm. length of eight millimeter-outside diameter (6 mm I.D.) tubing drawn to a tip. The anion column was prepared for use by placing a small plug of glass wool in the tip of the column and adding an excess of resin slurry. The resin was allowed to settle to a column of the desired length (7 to 8 cm.); the excess resin and liquid were withdrawn. It is important that the resin be added all at once and not by several additions of slurry, to avoid "channeling" through the column. The resin was then washed with two 15-ml. portions of 3 f hydrochloric acid.

## Procedure

The irradiated uranium salt was dissolved in 3 ml. of hot 3 f hydrochloric acid and then transferred to the top of the resin column. The liquid was forced through the column by means of air pressure (about 2 lb./sq. in.); the time required was about twenty seconds. The liquid was collected in a 40-ml. centrifuge tube containing a suspension of selenium metal in 15 ml. of concentrated hydrochloric acid (the suspension of selenium metal was prepared 15 minutes before an irradiation by reducing selenite carrier (0.12 millimoles) in 15 ml. of concentrated hydrochloric acid with sulfur dioxide). After stirring for thirty seconds, the selenium was separated by filtration, with suction, through a coarse 30-ml. Buchner-type filter funnel. The precipitate was washed with 30 ml. of concentrated hydrochloric acid and 60 ml. of water, and dissolved by adding 4 ml. of hot concentrated nitric acid directly

to the funnel. The resulting solution, which formed instantly, was poured quickly into a 40-ml. centrifuge tube containing the freshly precipitated silver bromide in 1 ml. of 6 f nitric acid and 16 ml. of water. The suspension was stirred for one minute or less and then the silver bromide was separated by filtration onto a No. 41 H Whatman filter paper contained in a ground-off Hirsch funnel-filter chimney setup. The Hirsch funnel was mounted on a micro bell jar so that the filtrate could be collected in a 100-ml. beaker. The beaker was quickly removed and the filtrate added to a centrifuge tube containing silver bromide in 1 ml. of 6 f nitric acid. The chemical steps which followed were the same as described in the procedure on page 49. The time interval between silver bromide separations was kept constant and the counting data analyzed in the same manner as before.

## Validity of Procedure

The foregoing procedure, designed specifically to remove tellurium activity, was tested using $Se^{83}$ (25 minutes) which is known to decay to $Br^{83}$ (2.4 hours). A 75-mg. sample of uranyl nitrate hexahydrate (93% $U^{235}$) was bombarded in the rabbit port of the Water Boiler and then returned to the main chemistry building. This sample was treated in the manner described above. The time interval between silver bromide separations was 20 minutes and the selenite solution was mixed with the silver bromide for one minute before filtration. Seven silver bromide precipitates were mounted and counted. Each of the samples decayed with approximately the correct half-life. A long-lived contaminant amounting to 0.2 per cent of the original counting rate was evident. The introduction of the resin-column step had reduced the contamination

by a factor of 100 and verifies the assumption that radiotellurium was being carried through the procedure.

Figure III-2 is a semi-logarithmic plot of the activity in each silver bromide sample at the time of separation versus the time of the beginning of the growth period. The observed half-life is 25 minutes.

## Separation of Radioactive Bromine from Rubidium Nitrate

### Outline of Procedure

The radioactive bromine was produced by a ${}_{37}Rb^{87} + {}_{0}n^{1} \longrightarrow {}_{35}Br^{84} + {}_{2}He^{4}$ reaction. By reference to Figure I-4 it is seen that the probable contaminants will be $Rb^{84}$ and $Rb^{86}$ produced by the (n,2n) reaction on $Rb^{85}$ and $Rb^{87}$, and $Kr^{85}$ and $Kr^{87}$ produced by the (n,p) reaction on $Rb^{85}$ and $Rb^{87}$. Two methods were used to separate the bromine activity from the rubidium and krypton radionuclides. The first method consisted of dissolving the rubidium nitrate in dilute nitric acid containing bromide carrier. Silver bromide was precipitated by adding silver nitrate. The precipitate was filtered, washed, and mounted in the standard manner. The second method consisted of dissolving the rubidium salt in dilute nitric acid and then adding carbon tetrachloride containing bromine carrier. The layers were mixed by shaking and the organic layer containing the radioactive bromine was separated. The bromine was then extracted into an aqueous solution of sulfurous acid as bromide. Silver bromide was precipitated as before by adding silver nitrate. Both methods proved satisfactory for separating bromine activity free from contaminants.

## Procedure (First Method)

The rubidium salt (normal or enriched in one isotope)* was removed from behind the target of the Cockcroft-Walton accelerator and dissolved in 20 ml. of 0.1 f nitric acid containing 0.18 millimoles of bromide carrier as hydrobromic acid. Two milliliters of 0.1 f silver nitrate was added and the solution heated for a few seconds to coagulate the silver bromide. The silver bromide was filtered, washed, and mounted as described on page 35.

## Procedure (Second Method)

The rubidium salt, irradiated at the Cockcroft-Walton accelerator, was dissolved in 10 ml. of 3 f nitric acid and the solution added to 20 ml. of carbon tetrachloride containing 20 mg. of $Br_2$. The layers were mixed by shaking for 30 seconds and after allowing 30 seconds for the layers to separate, the carbon tetrachloride was drained into a separatory funnel containing 20 ml. of 1 f nitric acid. The layers were again mixed and allowed to separate as before. The organic layer was drained into a separatory funnel containing 10 ml. of 1 f nitric acid. Sulfur dioxide was bubbled through the solution to reduce the bromine to bromide. After shaking, the carbon tetrachloride layer was discarded. Two milliliters of 0.1 f silver nitrate was added to the water layer and the solution heated for a few seconds to coagulate the silver bromide. The silver bromide was filtered, washed, and mounted as before.

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*The enriched rubidium isotopes were obtained from the Isotopes Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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## CHAPTER IV

## EXPERIMENTAL RESULTS

### Discovery of a 6-Minute Bromine Activity

An examination of the bromine row on the isotopic chart (Figure I-4) shows that, of the bromine fission products, mass number 86 is the first for which no isotope is known. The first phase of the present investigation was a search for this isotope. At the same time, in view of the discrepancy in fission yields between $Br^{84}$ and $Kr^{84}$, the possibility of observing an isomer of $Br^{84}$ was kept in mind.

From the isotope chart (Figure I-4) and from the individual summaries of nuclear properties (Tables IV-1 through IV-5), it is evident that the set of bromine fission products represented by $Br^{83}$ (2.3 hours), $Br^{84}$ (32 minutes), $Br^{85}$ (3.0 minutes), $Br^{87}$ (56 seconds) and $Br^{88}$ (16 seconds), is a formidable mixture in which to look for still other activities by beta counting. Gamma counting, on the other hand, provides an avenue of attack. Neither $Br^{83}$ nor $Br^{85}$ have any detectable prominent gamma rays. The nuclide $Kr^{85}$, daughter of $Br^{85}$, has a 0.3-Mev gamma ray but its half-life, 4.6 hours, is long enough to permit an accurate determination of its contribution to the total activity. On the other hand, with even the most rapid bromine separations available (about 2 minutes), the nuclide $Br^{88}$ (16 seconds) will have decayed sufficiently so that it will not be detectable at the time of counting. The remaining known isotopes, $Br^{84}$ (32 minutes) and $Br^{87}$ (56 seconds) can easily be distinguished from one another because of the difference in their half-lives.

The first experiment was designed to measure the gamma spectrum of $Br^{84}$.

The gamma rays from $Br^{84}$ are present in all rapidly-separated samples of fission-product bromine and essentially constitute a "base line" which must be subtracted from the total gamma count in a search for any shorter-lived components. The experiment was performed as follows:

A 20-mg. sample of uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated in the rabbit port of the pile for three minutes, and the radioactive bromine was separated as described on page 36. The sample was then mounted for counting on the gamma scintillator pulse analyzer system described on page 30, and a series of gamma spectra were measured as the sample decayed. The individual measurements consisted of 3-minute counts (with an additional 2 minutes required for print-out of data), the first one starting at 30 minutes after end of irradiation; a total of 13 successive spectra were taken. A semi-logarithmic plot of the counting rate versus the channel number of the analyzer for gamma spectra taken at four different times are shown in Figure IV-1.

The semi-logarthmic technique for plotting gamma-spectra is often a valuable visual aid in the identification of short-lived gamma emitters. As may be recognized, on this type of plot successive gamma spectra have the same apparent shape when only a single half-life is involved. If the counting periods are of equal duration and are taken at equal intervals, the plots appear as a series of curves of the same shape, each curve displaced downward a constant distance from its predecessor. If, on the other hand, the gamma spectrum is a composite of the spectra of two activities of different half-lives, the successive curves have different shapes; those portions of the over-all spectrum corresponding to the shorter-lived member will be displaced

Table IV-1

Nuclear Properties of Selenium-80 and Bromine-80

| Nuclide | Se$^{80}$ | Br$^{80m}$ | Br$^{80}$ |
|---|---|---|---|
| Half-life* | Stable | 4.5 h (a,b)<br>4.58 h (c)<br>4.4 h (d) | 18.5 m (b)<br>18 m (r,e) |
| Radiations and energies, Mev. | | $\gamma_1$ 0.0363 (f)<br>0.037 (g)<br>$\gamma_2$ 0.0481 (f)<br>0.0489 (g) | $\beta_1^-$ 1.38 - 14% $\beta_2^-$ 1.99 - 78% (h)<br>1.38 - 14% 2.04 - 78% (f)<br>1.97 (i)<br>$\beta^+$ 0.862 (f) $\gamma$ 0.62 (k)<br>0.868 (j) 0.62 (f)<br>0.62 (l) |
| Basis of mass assignment | | 1. Parent of 18m Br by chemistry (m,n,o,p)<br>2. Br$^{79}$ (thermal n,$\gamma$) (b)<br>3. Br$^{79}$ (5-Mev d,p) (b)<br>4. Br$^{81}$ (17-Mev $\gamma$,n) (a)<br>5. Se$^{80}$ (8-Mev p,n) (q) | 1. Br$^{79}$ (thermal n,$\gamma$) (b)<br>2. Br$^{79}$ (5-Mev d,p) (b)<br>3. Br$^{81}$ (17-Mev $\gamma$,n) (a)<br>4. Se$^{80}$ (2.9-Mev p,n) (d) |

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Ref. continued on page 63

*
s = seconds
m = minutes
h = hours

Table IV-1

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(l) J. Laberrique-Frolow, H. Langevin and R. Bernas, Compt. rend. 238, 677 (1954).
(m) E. Segrè, R. S. Halford and G. T. Seaborg, Phys. Rev. 55, 321 (1939).
(n) D. DeVault and W. F. Libby, Phys. Rev. 58, 688 (1940).
(o) R. E. Siday, Proc. Roy. Soc. 178A, 189 (1941).
(p) G. Kayas, J. Phys. radium 11, 195 (1950); Ann. Phys. 7, 802 (1952).
(q) L. L. Woodward, D. A. McCown and M. L. Pool, Phys. Rev. 74, 870 (1948).
(r) H. Wäffler and O. Hirzel, Helv. Phys. Acta 21, 200 (1948).

Table IV-2

Nuclear Properties of Selenium-83 and Bromine-83

| Nuclide | $Se^{83m}$ | $Se^{83}$ | $Br^{83}$ |
|---|---|---|---|
| Half-life* | 67s (a)<br>69s (b) | 25m (c)<br>26m (b) | 2.30h (d)<br>2.45h (e)<br>2.3h (f)<br>2.3h (k)<br>2.4h (g,h) |
| Radiations and energies, Mev. | $\beta^-$ 3.4 (a)<br>$\gamma$ Observed (a)<br>No I.T. not parent of 25m Se (a,b) | $\beta^-$ 1.5 (c,b)<br>$\gamma$ .176 (b)<br>.37 (c)<br>.95 (b) | $\beta^-$ .94 (g)<br>.94 (i)<br>$\gamma$ .046 (j)<br>.051 (d) |
| Basis of mass assignment | 1. Se (pile n,$\gamma$) (b)<br>2. Parent of 2.3h Br, chemistry (a) | 1. Se (pile n,$\gamma$) (b)<br>2. Se (5.5-Mev d,p)(e,k)<br>3. Parent of 2.3h Br, chemistry (e,k,a,l) | 1. Se (5.5-Mev d,n) (e,k)<br>2. Rb (16-Mev $\gamma,\alpha$) chemistry (m)<br>3. Parent of 1.9h Kr, chemistry (k) |

(a) J. R. Arnold and N. Sugarman, J. Chem. Phys. 15, 703 (1947).

(b) W. C. Rutledge, J. M. Cork and S. B. Burson, Phys. Rev. 86, 775 (1952).

(c) L. E. Glendenin, National Nuclear Energy Series, C. D. Coryell and N. Sugarman, editors, Radiochemical Studies: The Fission Products, Div. IV, Vol. 9, 590 (Editor's note, McGraw-Hill Book Co., New York (1951).*

(d) P. Swinbank and J. Walker, Proc. Phys. Soc. 66A, 1093 (1953).

(e) A. H. Snell, Phys. Rev. 52, 1007 (1937).

(f) F. Strassmann and O. Hahn, Naturwiss. 28, 817 (1940).

(g) S. Katcoff, B. Finkle, and N. Sugarman, NNES 9, 591 (1951).

(h) R. B. Duffield and L. M. Langer, Phys. Rev. 81, 203, 298A (1951).

*Hereafter references from this source will be abbreviated, e.g., NNES 9, 590 (1951).

References continued on page 65

### Table IV-2

### References (Cont'd.)

(i) S. C. Fultz and M. L. Pool, Phys. Rev. 86, 347, 631A (1952).
(j) A. C. Helmholtz, Phys. Rev. 60, 415 (1941).
(k) A. Langsdorf, Jr. and E. Segré, Phys. Rev. 57, 105 (1940).
(l) R. R. Edwards, H. Gest and T. H. Davies, NNES 9, 237 (1951)
(m) R. N. H. Haslam and H. M. Skarsgard, Phys. Rev. 81, 479, 660A (1951).

Table IV-3

Nuclear Properties of Selenium-84 and Bromine-84

| Nuclide | $Se^{84}$ | $Br^{84}$ | |
|---|---|---|---|
| Half-life* | ~ 2m (a) | 33m (b)<br>32m (c)<br>30m (d) | |
| Radiations and energies, Mev. | | $\beta_1^-$ 1.72 - 35% (c)<br>$\beta_2^-$ 2.53 - 16% (c)<br>$\beta_3^-$ 3.56 - 9% (c)<br>$\beta_4^-$ 4.68 - 40% (c)<br>$\beta_4^-$ 4.5 (e) | $\beta_4^-$ 5.3 (b)<br>$\beta_4^-$ 4.76 (f)<br>$\gamma_1$ .89 (j)<br>$\gamma_2$ 1.89 (j) |
| Basis of mass assignment | 1. Separation of Br at short times after fission shows parent of 33m Br has a short half-life (g) | 1. Rb (fast n,$\alpha$) chemistry (h)<br>2. U(n,f) chemistry (i,d)<br>3. If the 33m Br is an isomeric state then the ground state has $t/\frac{1}{2} < 30s$, chemistry (c) | |

(a) L. E. Glendenin, NNES 9, 590, editor's note (1951).
(b) S. Katcoff, B. Finkle and N. Sugarman NNES 9, 587 (1951).
(c) R. B. Duffield and L. M. Langer, Phys. Rev. 81, 203 (1951).
(d) F. Strassmann and O. Hahn, Naturwiss. 28, 817 (1940)
(e) H. J. Born and W. Seelmann-Eggebert, Naturwiss. 31, 201 (1943).
(f) N. R. Johnson and G. D. O'Kelley, Bull. Am. Phys. Soc. II 2, 24 (1957).
(g) R. R. Edwards, H. Gest, and T. H. Davies, NNES 9, 237 (1951).
(h) H. J. Born and W. Seelmann-Eggebert, Naturwiss. 31, 86 (1943).
(i) R. W. Dodson and R. D. Fowler, Phys. Rev. 55, 880 (1939).
(j) L. M. Langer and R. B. Duffield, quoted by C. M. Huddleson and A. C. Mitchell, Phys. Rev. 88, 1350 (1952).

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* s = seconds
m = minutes
h = hours.

Table IV-4

Nuclear Properties of Selenium-85 and Bromine-85

| Nuclide | $Se^{85}$ | $Br^{85}$ |
|---|---|---|
| Half-life* | | 3.00 (a)<br>3.00 (b,c) |
| Radiations and energies, Mev. | | $\beta^-$ 2.5 (a)<br>no strong $\gamma$ (a) |
| Basis of mass assignment | | Parent 4.4h Kr, chemistry (c,a) |

(a) N. Sugarman, J. Chem. Phys. 17, 11 (1949)
(b) F. Strassmann and O. Hahn, Naturwiss 28, 817 (1940).
(c) H. J. Born and W. Seelmann-Eggebert, Naturwiss. 31, 59, 86 (1943).

*s = seconds
m = minutes
h = hours

Table IV-5

Nuclear Properties of Selenium-87 and Bromine-87

| Nuclide | $Se^{87}$ | $Br^{87}$ |
|---|---|---|
| Half-life* | | 55.6s neutrons detected (a)<br>55.0s neutrons detected (b)<br>56.1s neutrons detected (c) |
| Radiations and energies, Mev. | | $\beta^-$ 2.6 - 70% (d) $\gamma$'s 2-4 (d)<br>8.0 - 30% (d) 5.4 (d)<br>Delayed neutrons (e)<br>2% (f,d)<br>Energy of neutrons .25 (a)<br>.30 (g) |
| Basis of mass assignment | | U(n,f) parent of 78m Kr chemistry (h,c) |

(a) D. J. Hughes, J. Dabbs, A. Cahn and D. Hall, Phys. Rev. 73, 111 (1948).
(b) W. C. Redman and D. Saxon, Phys. Rev. 72, 570 (1947)
(c) N. Sugarman, J. Chem. Phys. 17, 11 (1949).
(d) A. F. Stehney and N. Sugarman, Phys. Rev. 89, 194 (1953).
(e) A. H. Snell, J. S. Levinger, E. P. Meiners, Jr., M. B. Sampson and R. G. Wilkinson, Phys. Rev. 72, 545 (1947).
(f) J. S. Levinger, E. P. Meiners, M. B. Sampson, A. H. Snell and R. G. Wilkinson, NNES 9, 603 (1951).
(g) M. Burgy, L. A. Pardue, H. B. Willard and E. O. Wollan, AECD-16; Phys. Rev. 70, 104A (1946).
(h) W. Seelmann-Eggebert and H. J. Born, Naturwiss. 31, 59 (1943).

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* s = seconds
m = minutes
h = hours

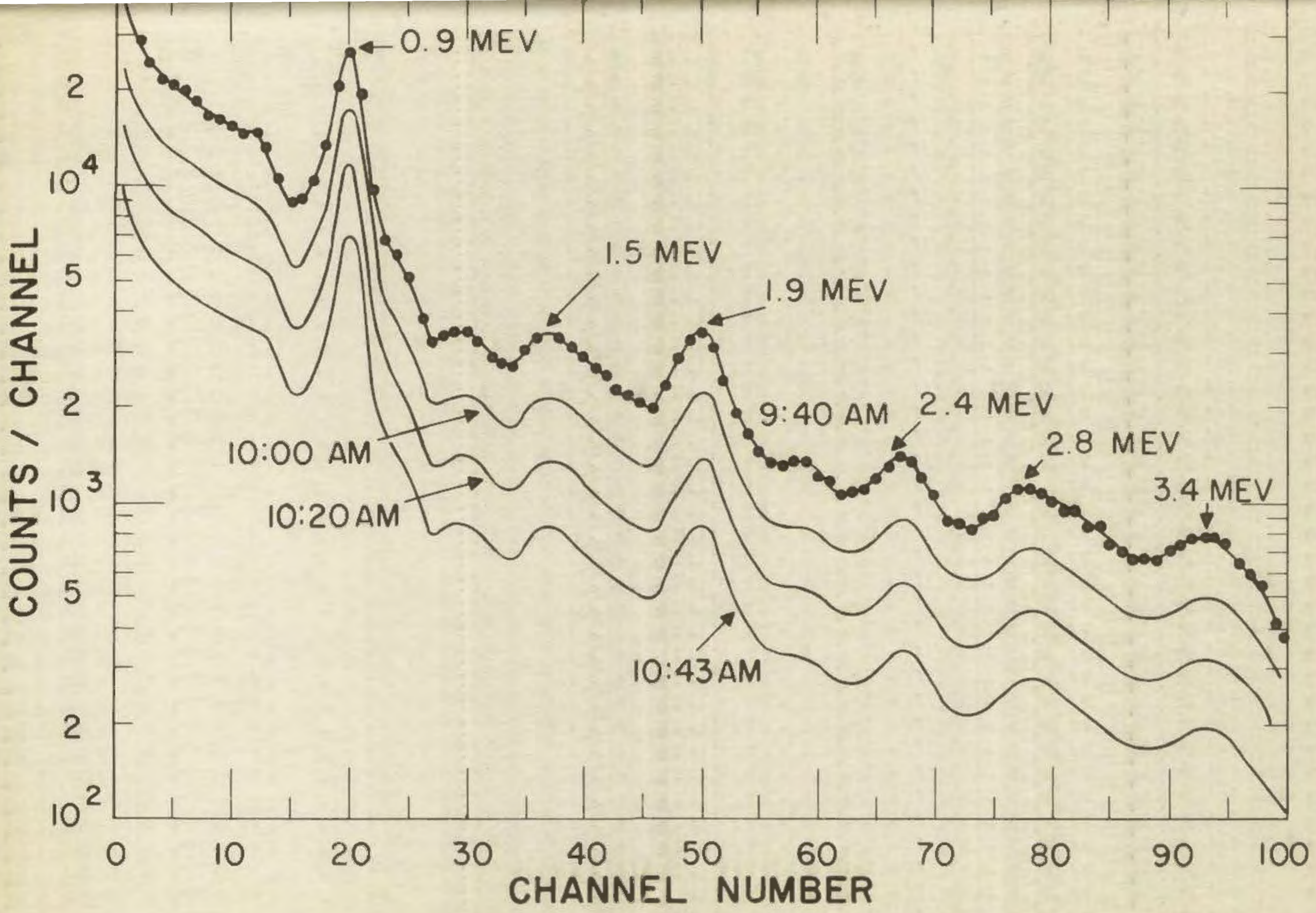

Figure IV - 1. Successive gamma scintillation spectra of 32-minute $Br^{84}$ source. 2" × 2" NaI(Tl) crystal, 3-minute counts, data shown only for first curve.

downward more than those of the longer-lived member.

In the present case, all the peaks over the entire spectrum decayed with a half-life of 33 ± 1 minutes, indicating that only $Br^{84}$ was present.

Following the establishment of the gamma-spectrum base line contributed by the 32-minute $Br^{84}$, as described above, the next experiment was set up to explore for possible new isotopes of bromine of half-life $\geq 3$ minutes. A 20-mg. sample of uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated for 10 seconds in the rabbit port of the Water Boiler. The sample was returned to the laboratory near the reactor, where the radioactive bromine was separated and prepared for counting as described on page 36. The distillation of bromine was started 49 seconds after the end of irradiation and was continued for 15 seconds. The silver bromide precipitate, mounted on an aluminum plate, was then returned to the main chemistry building and counted with the scintillation system described on page 30. A 2" x 2" NaI(Tl) crystal was used to detect the radiation, and the gate trigger discriminator of the 100 channel analyzer was set at thirteen. The purpose of cutting out the first 13 channels of the analyzer was to reduce the total counting rate below the point where coincidence corrections would be necessary. Expressed in terms of energy, this means that no pulse corresponding to a gamma of 650 kilovolts or less was recorded by the analyzer. The first count was started 11 minutes after the end of irradiation, and, as in the preceding experiment, a series of 3-minute counts was taken. Figure IV-2 is a semi-logarithmic plot of the counting rate versus the channel number of the analyzer for four different times. It will be noticed that the spectrum is not decaying uniformly with the half-life of $Br^{84}$ (32 minutes). There is definite evidence for a shorter-lived component. The decay of the sample was followed for about two and one-half hours until finally only the

32-minute $Br^{84}$ was present.

A semi-logarithmic plot of the counting rate in each channel, versus the time at which the count was taken, could be resolved into two components. Figure IV-3 shows the gamma spectrum of the shorter-lived component with the 32-minute activity subtracted. The positions of the photopeaks indicate that this new activity has a spectrum similar to that of the 32-minute $Br^{84}$, suggesting the possibility of a shorter-lived isomer.

An estimate of the half-life of the new activity was ascertained from a semi-logarithmic plot of the total number of counts under each photopeak versus the time at which the count was taken. Figure IV-4 is a plot of the 1.5-Mev peak as a function of time; there is striking evidence for the presence of a 6-minute activity.

The next series of experiments was concerned with the identification and characterization of the 6-minute bromine activity. This task was carried out in three steps: 1) the precise determination of the half-life of $Br^{84}$; 2) the mass assignment and identification of the 6-minute activity, and the accurate determination of its half-life; and 3) the measurement of the radiations of the 6-minute activity.

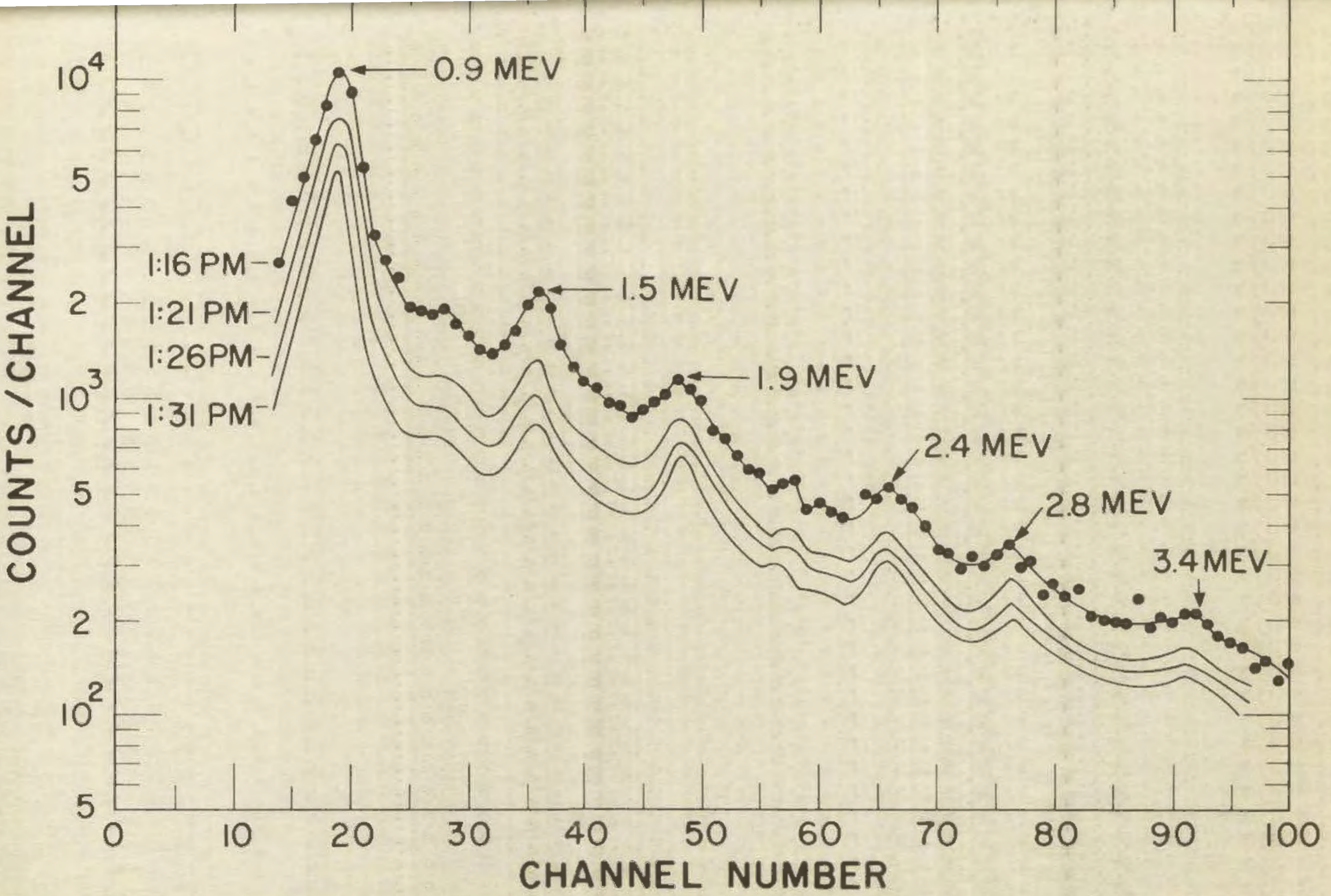

Figure IV - 2. Successive gamma scintillation spectra of fission product bromine. 2" × 2" NaI(Tl) crystal, 3-minute counts, first count 11 minutes after end of irradiation, data shown only for first curve.

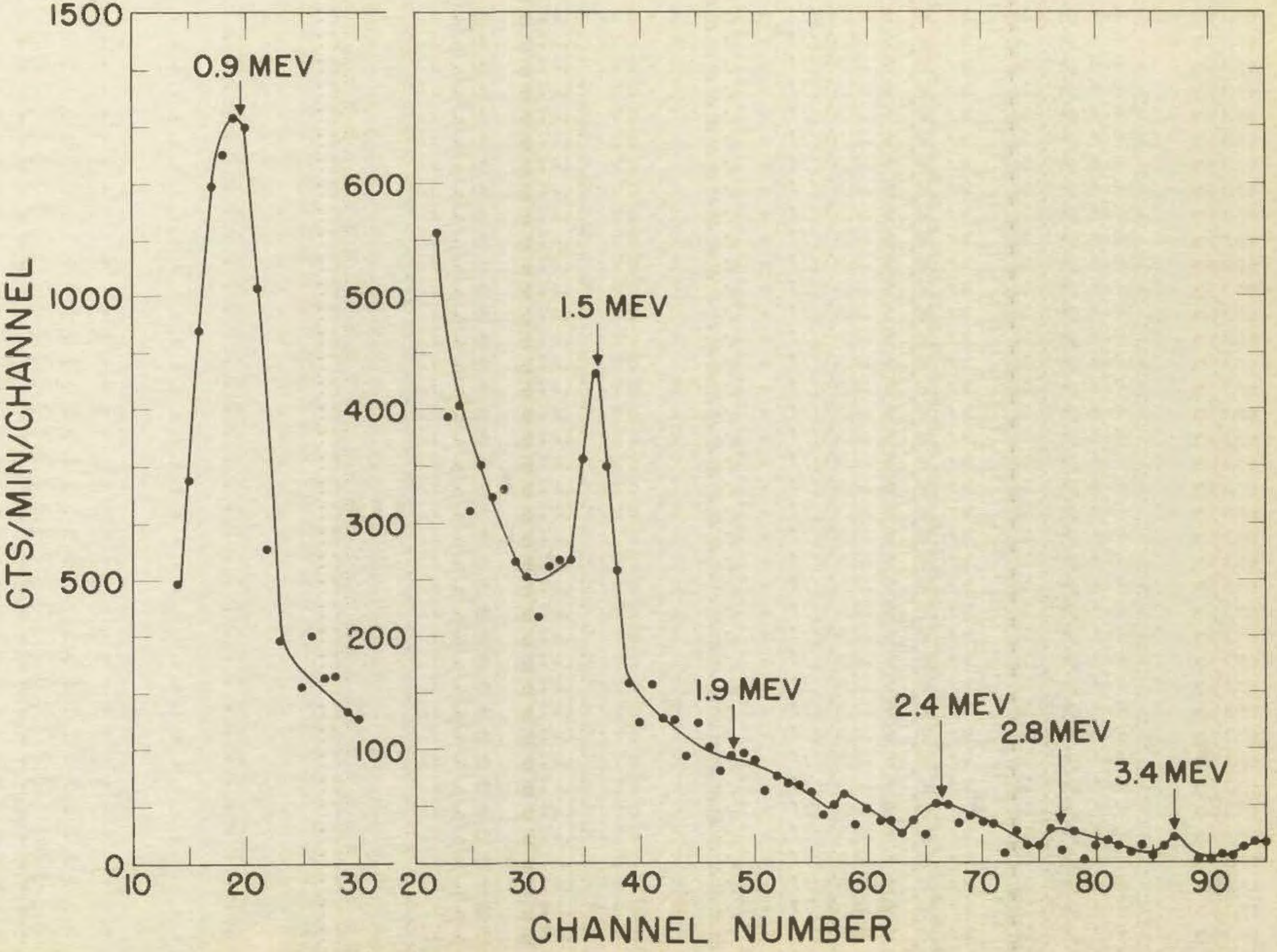

Figure IV - 3. Gamma scintillation spectrum of 6-minute bromine from fission products, by subtraction of 32-minute component from first curve of Figure IV - 2.

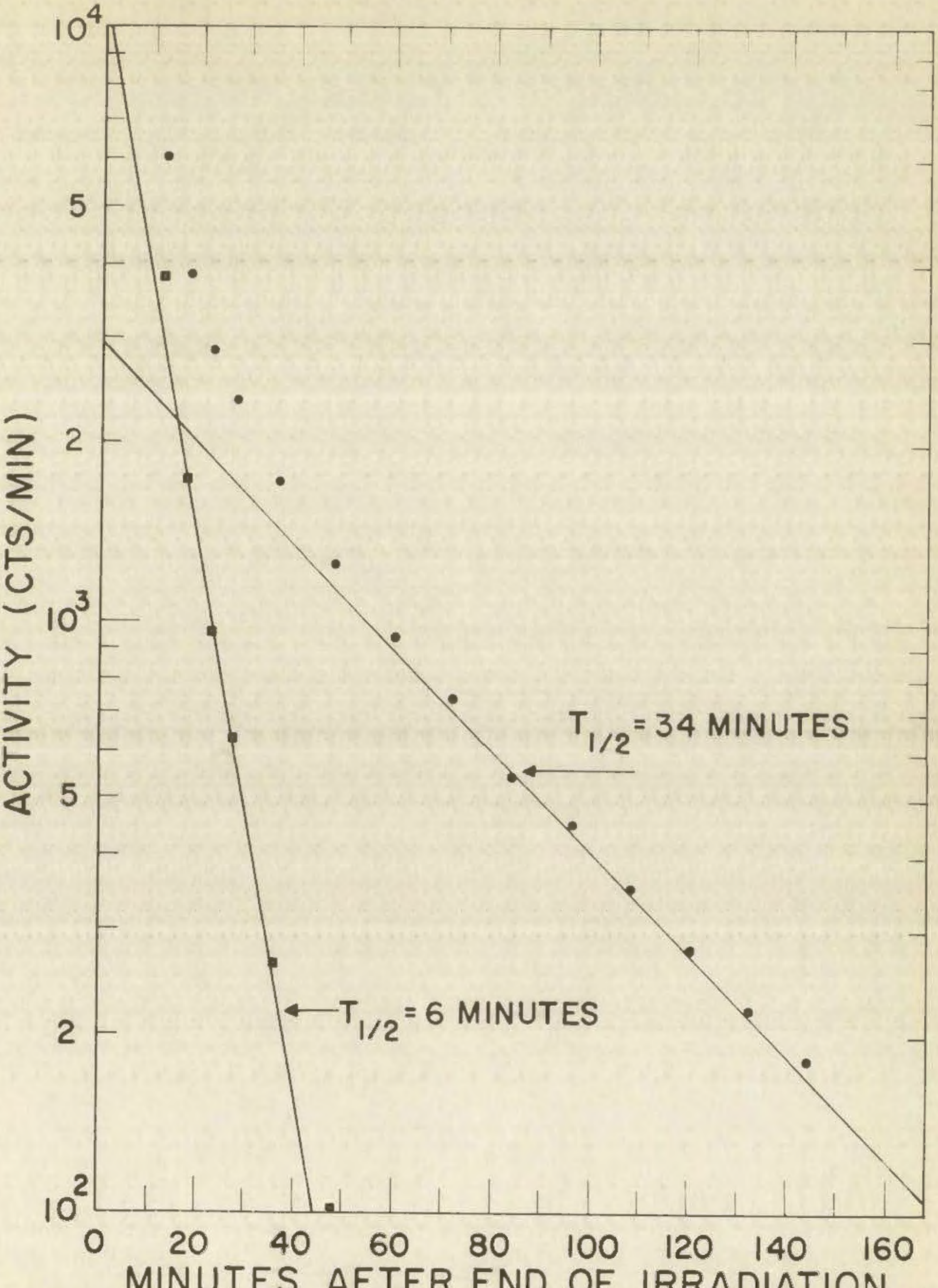

Figure IV - 4. Decay of 1.5-Mev photopeak from gamma scintillation spectra of fission-product bromine.

## Redetermination of the Half-life of the 32-Minute $Br^{84}$

As mentioned previously, the gamma rays from $Br^{84}$ (32 minutes) were present at all times and constituted essentially a "base line" which had to be subtracted from the total count before any shorter-lived components could be identified. The following experiment was designed to measure accurately this "base-line" half-life.

Two 50-mg. pieces of uranium metal (93% $U^{235}$) were irradiated in the rabbit port of the Water Boiler and the radioactive bromine was separated by means of the procedure on page 53. The final silver bromide precipitate contained $Br^{83}$ (2.4 hours), $Br^{84}$ (32 minutes), and $Kr^{83m}$, the 1.9-hour daughter of $Br^{83}$. By reference to Figure I-4, it is seen that $Br^{83}$ decays by emission of beta rays of 0.94-Mev maximum energy and that $Br^{84}$ decays by emission of beta rays of 4.68-Mev maximum energy. Hence, it was possible to determine the half-life of $Br^{84}$ by counting its beta rays through an aluminum absorber of sufficient thickness to eliminate the radiations from the 2.4-hour $Br^{83}$. This method was used in preference to resolving the compound decay curve which results when no absorber is used. The absorber chosen was 444 mg./cm.$^2$ thick, sufficient also to eliminate essentially all the radiation from $Kr^{83m}$. Except for some bremsstrahlung, which has a very low counting efficiency in beta counters, the radiation entering the counter was only that from the decay of $Br^{84}$. The gross decay curve shown in Figure IV-5 indicates that from 35,000 counts per minute down to background only one component was present.

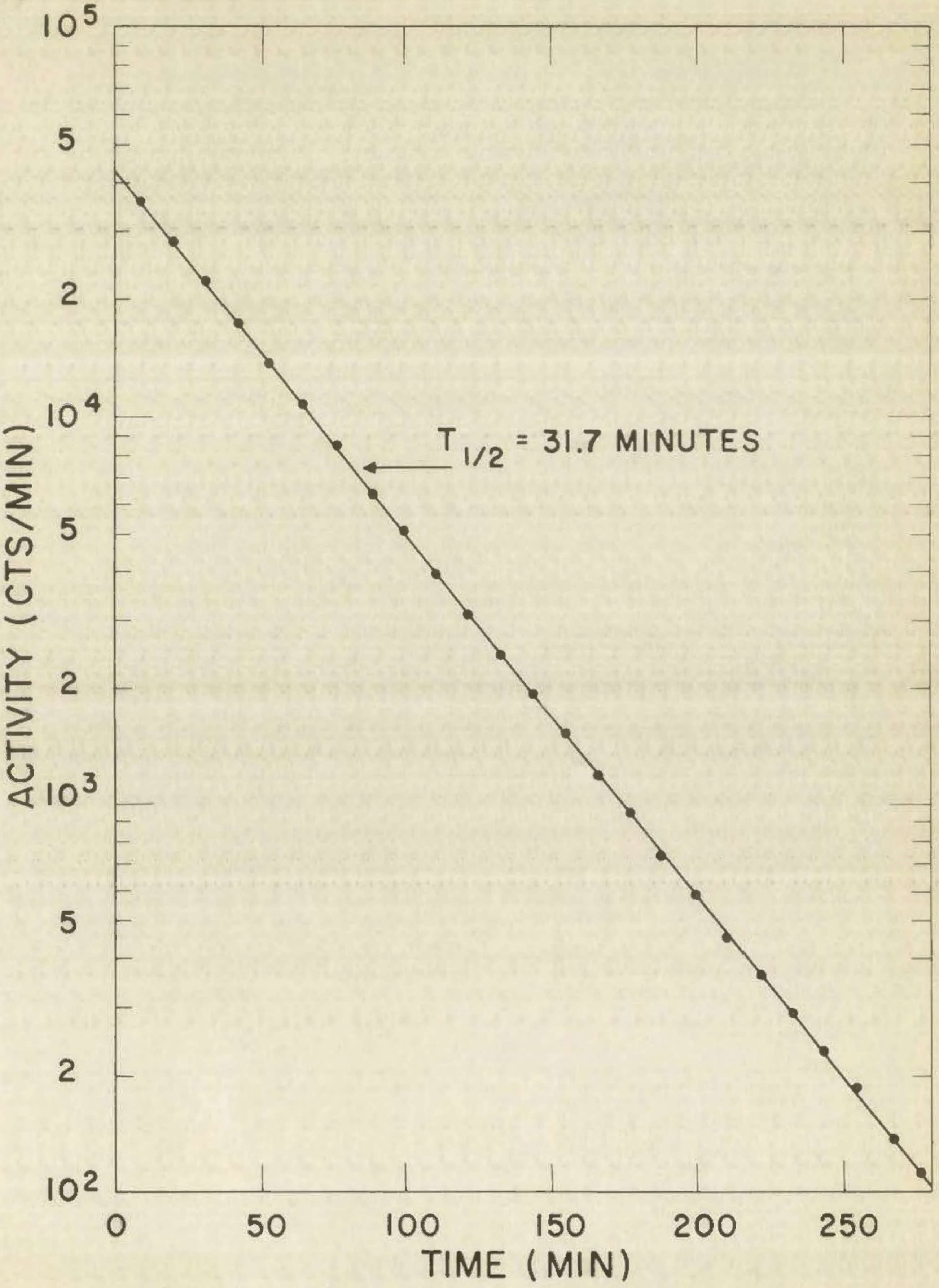

Figure IV - 5. Beta decay of $Br^{84}$, counted through 444 mg. /cm.$^2$ of aluminum.

The decay constant for $\text{Br}^{84}$ was calculated by least-squares fit of the counting data.[*] The least squares calculation leads not only to the value of the decay constant, but also to its standard deviation. The results, in terms of half-lives, are: 31.693 minutes, std. dev. 0.029 min; 31.719 min; std. dev. 0.036 min; weighted average 31.704 minutes with standard deviation 0.022 minutes.

For all calculations thereafter, the half-life of $\text{Br}^{84}$ was taken as 31.7 minutes.

### Identification of the 6-Minute Activity as an Isomer of $\text{Br}^{84}$

It was apparent that if the new 6-minute bromine activity was, as suspected, an isomer of $\text{Br}^{84}$, it could also be produced by a ${}_{37}\text{Rb}^{87} + {}_{0}\text{n}^{1} \longrightarrow {}_{35}\text{Br}^{84} + {}_{2}\text{He}^{4}$ reaction. Accordingly, arrangements were made to irradiate samples of rubidium with fast neutrons. The source of high-energy neutrons was the Los Alamos Cockcroft-Walton accelerator, which produces approximately 14-Mev neutrons by the ${}_{1}\text{D}^{2} + {}_{1}\text{T}^{3} \longrightarrow {}_{2}\text{He}^{4} + {}_{0}\text{n}^{1}$ reaction. Rubidium nitrate

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[*] The decay constant was calculated by least-squares fit of the counting data to an equation of the form

$$A(t_1) = A(0)e^{-\lambda t_1}.$$

A(0) and $\lambda$ were the parameters estimated; $A(t_1)$ is the average activity observed for a period of counting beginning at time $t_1$. In this experiment, all of the periods were the same and there was only one activity, so that no correction for decay during a counting period was needed. The error in $t_1$ was negligible. The standard deviation of each $A(t_1)$ was calculated from well-known properties of the Poisson distribution. Each $A(t_1)$ was given a weight equal to the reciprocal of the square of its standard deviation. Because $\lambda$ enters the equation in a non-linear way, it was necessary to iterate the least squares calculation. This iteration is feasible only on electronic data processing machines, such as the IBM Electronic Data Processing Machine, Type 704 which was used for this calculation. The iteration was continued until there was agreement in the eighth decimal place.

was selected as the target material because it is easily dissolved in water and the interfering activities can be easily removed. Three samples of this salt, varying in isotopic abundance of $Rb^{87}$, were bombarded with high-energy neutrons. The first experiment used normal rubidium (27.8% $Rb^{87}$), the second used enriched rubidium (89.62% $Rb^{87}$), and the third used depleted rubidium (0.9% $Rb^{87}$). In this manner, any activities produced could be associated definitely with $Rb^{87}$ or with $Rb^{85}$.

In the first experiment, 150 mg. of the normal rubidium nitrate was placed behind the target of the Cockcroft-Walton accelerator and irradiated with fast neutrons for four minutes. The sample was then removed rapidly and the bromine activity was isolated by the first procedure outlined on page 59; the bromine sample was counted on a methane-flow beta proportional counter. A series of counts was made, starting at 8 minutes after the end of irradiation, and extending through three days.

An analysis of the decay curve showed components of half-lives 6 minutes, 31.7 minutes and 35.9 hours. The 31.7-minute activity was due to $Br^{84}$, the 35.9-hour activity to $Br^{82}$. The latter was produced by the reaction $_{37}Rb^{85} + {_0}n^1 \longrightarrow {_{35}}Br^{82} + {_2}He^4$. Normal rubidium consists of 27.85% $Rb^{87}$ and 72.15% $Rb^{85}$. Assuming equal cross sections for the $(n,\alpha)$ reactions on both isotopes of rubidium, one would expect that the ratio of observed activities of 31.7-minute $Br^{84}$ and 35.9-hour $Br^{82}$ would be 26.3 at end of irradiation. The actual value obtained was 26.8. The ratio of the 6-minute activity to the 31.7-minute activity at end of irradiation was about two.

The second experiment was a repeat of the first, except that the target material was 88 mg. of rubidium nitrate enriched in $Rb^{87}$, and the time of

irradiation was 5 minutes. The isotopic analysis was 10.38% $Rb^{85}$ and 89.62% $Rb^{87}$. The $Rb^{87}/Rb^{85}$ ratio, then, was 8.63, a ratio 22.4-fold greater than in the first experiment. The first count was started at about 4 minutes after the end of irradiation.

The decay curve, plotted in Figure IV-6, showed the same three components, but in different relative amounts. The zero-time ratio of 31.7-minute activity to 35.9-hour activity was 540; the calculated ratio, assuming equal cross sections was 590. This result is remarkably close in view of the fact that the sample contained only 10 counts per minute of the 35.9-hour activity at end of irradiation. The zero-time ratio of 6-minute activity to 31.7-minute activity was again about two.

In the third experiment, the source material, which consisted of 167 mg. of rubidium nitrate highly enriched in $Rb^{85}$, was irradiated for 1.5 minutes. The isotopic analysis was 99.1% $Rb^{85}$ and 0.9% $Rb^{87}$. The first count was taken at 4 minutes and 45 seconds after the end of irradiation. This investigation had also a secondary purpose: a search for a short-lived isomer of $Br^{82}$.

The expected ratio of 31.7-minute activity to 35.9-hour activity was 0.62. The observed 35.9-hour activity was 240 counts per minute. On this basis, about 150 counts per minute of 31.7-minute activity and 300 counts per minute of 6-minute activity should have been present at the end of irradiation. The gross activity in the early counts was in the range expected, but the statistical scattering of the counting data made an accurate resolution of the two shorter-lived components essentially impossible. The first one-minute count of the sample contained about 300 counts due to the shorter-lived bromines and 340 counts due to background and long-lived bromine activity. No prominent short-

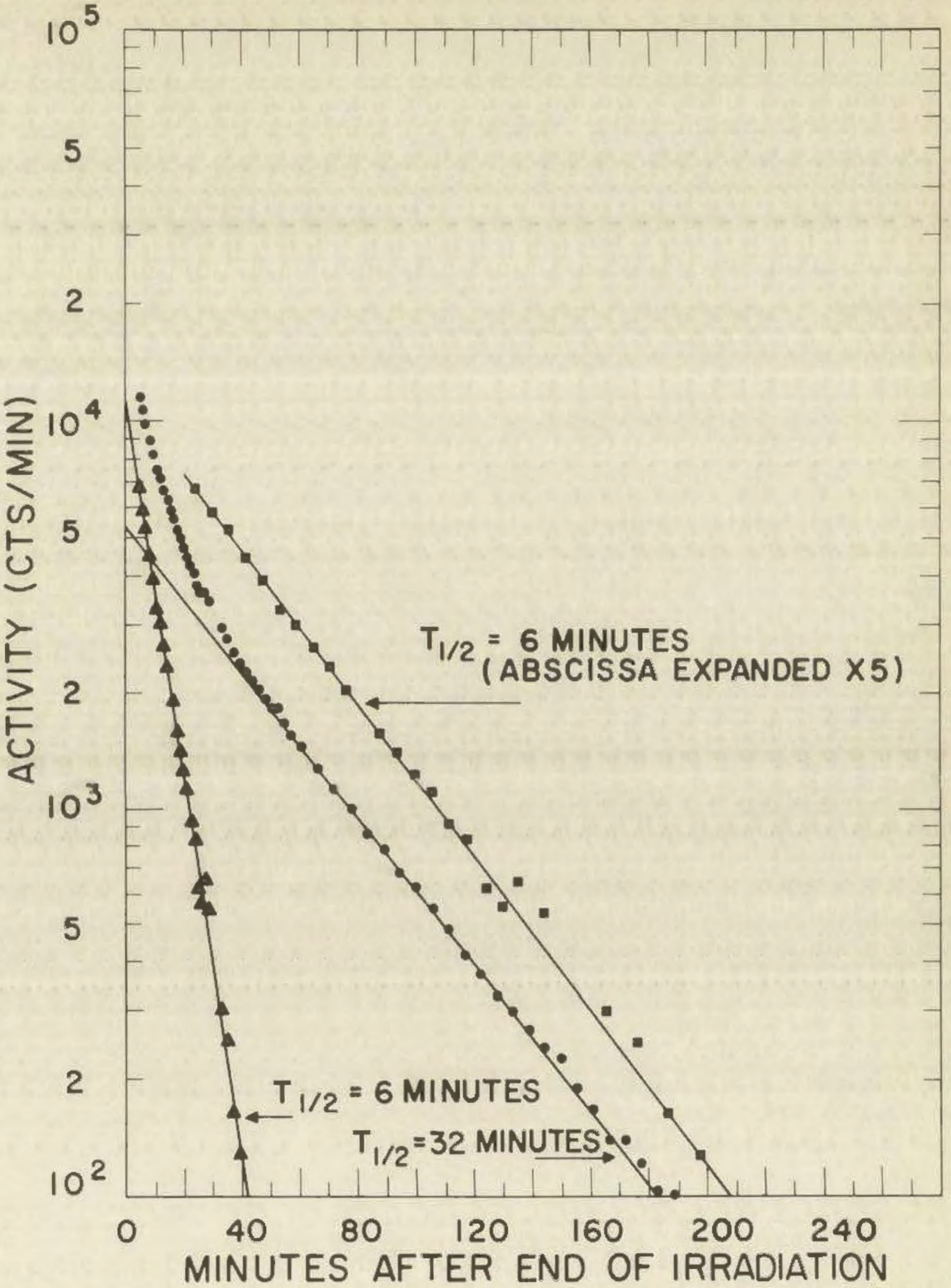

Figure IV - 6. Beta decay of bromine from 14-Mev neutron irradiation of enriched $Rb^{87}$.

lived activity was observed. With the assumption of equal cross sections for the formation of the 35.9-hour $Br^{82}$ and any short-lived beta-emitting isomer of $Br^{82}$, it was estimated that the latter, if it exists, must have a half-life less than one minute.

Thus, the three experiments described above show that the 6-minute activity is associated with $Rb^{87}$ because the 6-minute/31.7-minute activity ratio does not depend on the enrichment of the $Rb^{87}$. Also, because the only bromine-producing reactions expected from 14-Mev neutrons on rubidium isotopes are of the $(n,\alpha)$ type, it may be safely concluded that the 6-minute activity is an isomer of $Br^{84}$.

## Half-life of the Short-lived Isomer of $Br^{84}$

The determination of the half-life of the short-lived isomer of $Br^{84}$ was based on a statistical analysis of the decay curves of two samples of bromine separated from rubidium nitrate (89.62% $Rb^{87}$) irradiated with 14-Mev neutrons. One of the samples has been discussed previously and its decay curve is shown in Figure IV-6. As a precautionary measure, a more elaborate chemical separation procedure was employed for the second sample. This sample was processed by the second mthod described on page 59 and was beta-counted in the same manner as the first.

The decay constant was calculated by least-squares fit of the counting data.*

The results in terms of half-lives are: 5.91 minutes, std. dev. 0.20 minutes; 6.08 minutes, std. dev. 0.12 minutes; weighted average 6.04 minutes with standard deviation 0.06 minutes.

For all future calculation the half-life of this isomer of $Br^{84}$ will be taken as 6.0 minutes.

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*The counting data from each of the samples was treated by a least-squares fit to an equation of the form $A(t_i) = A_1(0)e^{-\lambda_1 t} + A_2(0)e^{-\lambda_2 t} + A_3(0)e^{-\lambda_3 t}$. Subscript 1 refers to 6-minute $Br^{84}$, subscript 2 refers to 31.7-minute $Br^{84}$ and subscript 3 refers to 35.9-hour $Br^{82}$. The procedure was essentially the same as for 31.7-minute $Br^{84}$ (page 77) except that average activities were corrected for decay during the period of each count to give activities, $A(t_i)$, at beginning of counting period. The activity due to each isotope was estimated for the beginning of each counting period. Each of these estimated activities was multiplied by $(1 - e^{-\lambda_j\tau})/(\lambda_j\tau$, $j = 1, 2, 3$, and $\tau$ is the length of the counting period. Estimated values of $\lambda_j$ were used. The sum of these products was divided by the sum of the estimated activities to give an approximate correction factor. Errors in estimating activities and decay constants tend to cancel since the factors $(1 - e^{-\lambda_j\tau})/\lambda_j\tau$ are always near unity. Observed counts per minute were divided by these correction factors to obtain instantaneous activities at the beginning of counting periods. The procedure, followed by the least-squares calculation, should be iterated to give better estimates for the correction factor. However, the correction factor was never a large number, so the error involved in not iterating the calculation for the correction factor was regarded as being very small.

## Radiations of the 6.0-Minute $Br^{84}$

The gamma spectrum of the 6.0-minute $Br^{84}$ was measured with the gamma-scintillation counting equipment described in Chapter II. A $1\frac{1}{2}''$ x $1\frac{1}{2}''$ NaI(Tl) crystal was mounted in a lead housing $2''$ thick and was covered with 500 mg./cm.$^2$ of aluminum. The sample and standards were mounted on a $1/16''$ dural plate positioned 4 mm. above the aluminum absorber.

The energy scale of the scintillation system had been calibrated previously with gamma rays from 0.280 Mev ($Hg^{203}$) to 1.333 Mev ($Co^{60}$), and the pulse height was known to vary almost linearly with gamma energy.

The $Br^{84}$ source was prepared from a sample of enriched $Rb^{87}$ (as the nitrate) irradiated at the Cockcroft-Walton accelerator and processed by the first procedure on page 59. Because the 31.7-minute $Br^{84}$ was unavoidably present in sources of the 6.0-minute $Br^{84}$, it was necessary to measure first the spectrum of the mixture and then, after the 6.0-minute activity had died out, a series of spectra of the 31.7-minute component. By extrapolation of the latter back to the time of the first spectrum, the 31.7-minute component could be subtracted out. The radiochemical purity of the sample with respect to possible short-lived contaminants was verified by recording additional gamma-spectrum measurements while the 6.0-minute $Br^{84}$ was still present. A plot of these spectra (logarithm of counts per channel versus channel number) after subtraction of the 31.7-minute $Br^{84}$ component showed that all the prominent short-lived photopeaks decayed at the same rate (Figure IV-7). This rate corresponded to a half-life of 6 minutes (Figure IV-8).

In the energy range covered, 0.150-2.73 Mev, photopeaks were found at 0.44 ± 0.01, 0.88 ± 0.01, 1.46 ± 0.02 and 1.9 ± 0.3 Mev. The 1.9-Mev peak was

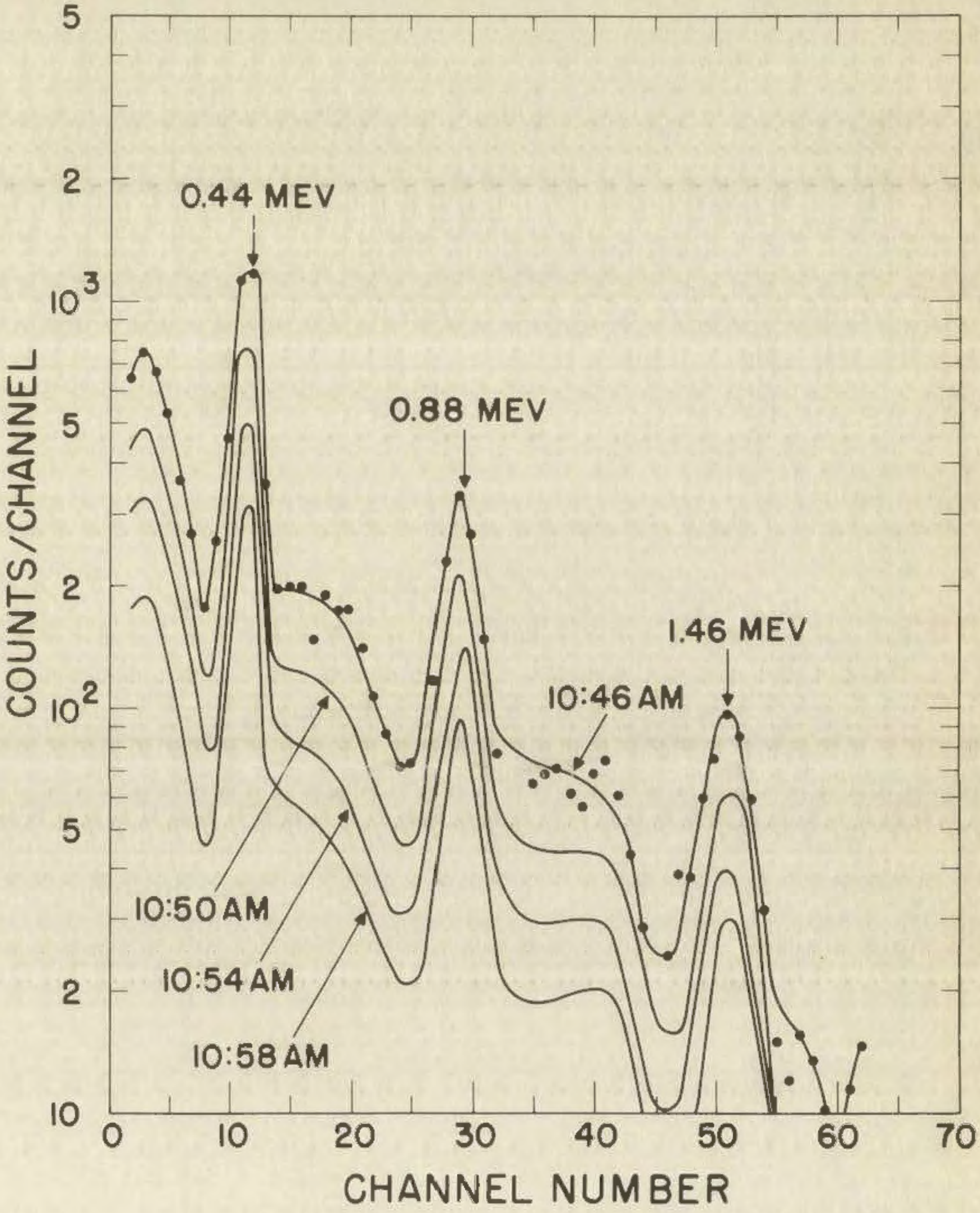

Figure IV - 7. Successive gamma scintillation spectra of bromine from 14-Mev neutron irradiation of $Rb^{87}$, after subtraction of 31.7-minute component. $1\frac{1}{2}'' \times 1\frac{1}{2}''$ NaI(Tl) crystal, 2-minute counts.

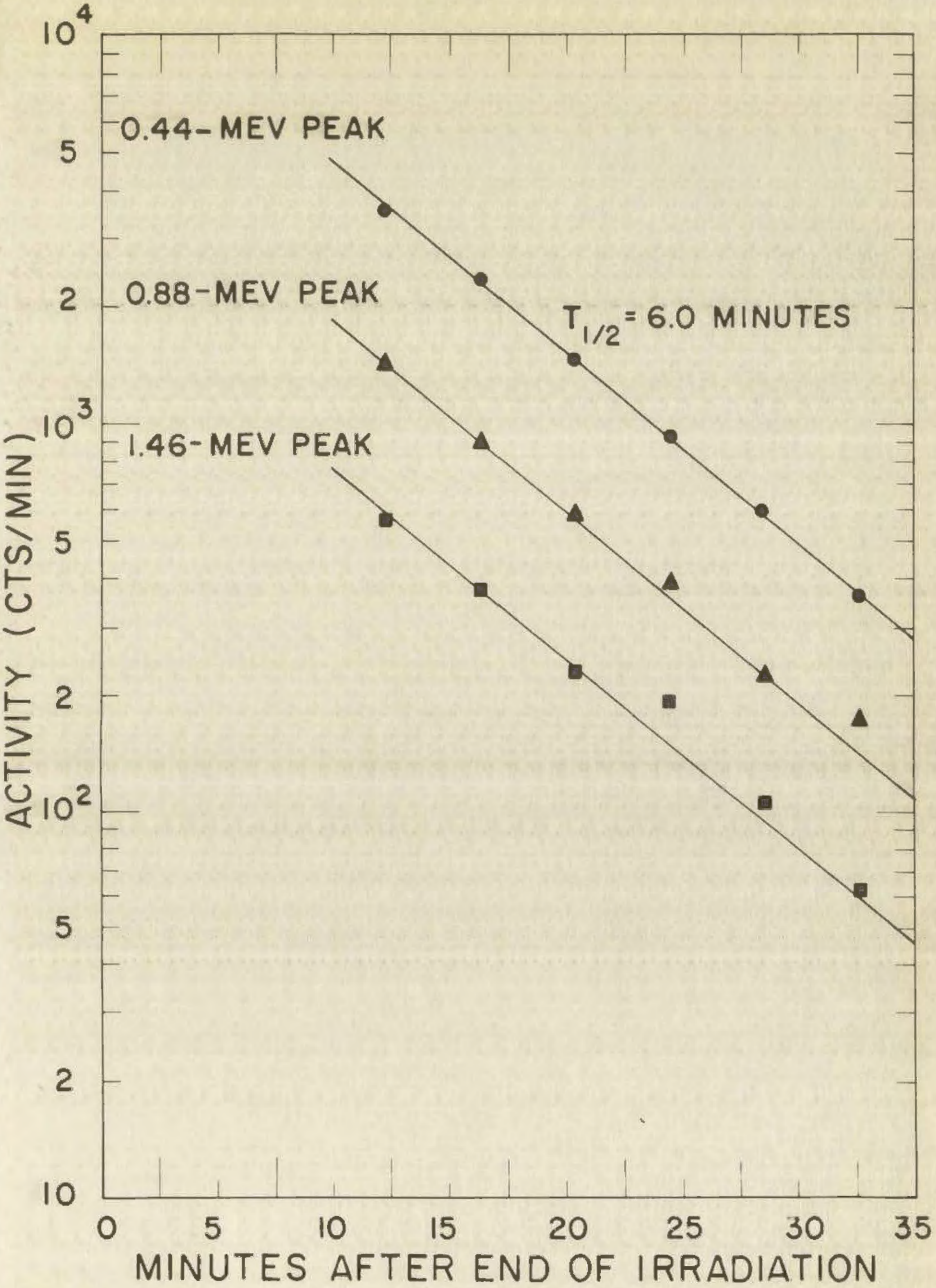

Figure IV - 8. Decay of principal photopeaks from gamma scintillation spectra of bromine produced by 14-Mev neutron irradiation of $Rb^{87}$.

too weak to show in the scale of Figure IV-7, although the points on which it was based appeared to be statistically significant.

This gamma spectrum may be compared with the spectrum, taken with a 2" x 2" NaI(Tl) crystal, of the 6-minute bromine activity isolated from fission products (Figure IV-3). It will be noted that the latter spectrum exhibits definite photopeaks at 0.9 and 1.5 Mev, plus possibly others at 1.9, 2.4, 2.8 and 3.4 Mev. The 0.44-Mev photopeak lay below the lower-energy limit of the measurement.

The data from the 0.15-2.73 Mev spectra were also used, in conjunction with beta-counting data from the same sample, to determine the number of each of the gamma rays per beta ray. The number of gamma rays represented by each photopeak was obtained by dividing the number of counts in the peak (a quantity proportional to the photopeak area when the spectrum is plotted on a linear scale) by the "photopeak efficiency" for the gamma ray in question. The photopeak efficiency, in turn, had been determined previously with a series of standard gamma sources of energies 0.078 Mev ($Hg^{203}$ and $Pb^{203}$), 0.290 Mev ($Hg^{203}$), 0.511 Mev ($Na^{22}$), 0.662 Mev($Cs^{137}$-$Ba^{137m}$), and 1.28 Mev ($Na^{22}$). The photopeak efficiency, which for the usual scintillation systems varies monotonically with gamma energy, was plotted versus gamma energy.

The beta spectrum was measured with a scintillator consisting of a 5/8"-long by 1-9/16"-diameter trans-stilbene crystal packed in aluminum oxide. The amplifier gain was adjusted to cover a beta-energy range of 0.24 to 5.24 Mev. The beta spectra of $Tl^{204}$ (0.765 Mev), $Y^{90}$ (2.27 Mev) and $Cl^{38}$ (4.81 Mev) were used for energy calibration.

The bromine sample used for the beta work was prepared in the same manner as in the gamma-spectrum measurement, except that only 2.8 mg. of bromine carrier was used. The final beta-spectrum source consisted of 8.4 mg./cm.$^2$ of silver bromide in a 0.5-cm. diameter circle on filter paper, mounted on a piece of cardboard and covered with one layer (9 mg./cm.$^2$) of Scotch tape. The low-Z material was used to reduce back-scattering. The mounting card was placed with the precipitate facing the crystal and almost touching it. Care was taken to mount all the standards in the same manner.

Again, as with the gamma spectra, two sets of measurements were needed, the first of the composite containing the 6.0-minute activity, and the second of the longer-lived material. Subtraction of the longer-lived component gave the net spectrum of the 6.0-minute activity (Figure IV-9). A Fermi plot of the 6.0-minute beta spectrum is shown in Figure IV-10.[*] The Fermi plot could be broken down into beta groups of maximum energies 3.2 Mev (8%), 1.9 Mev (72%) and 0.8 Mev (20%). The intensity of the 3.2-Mev component is open to question. As may be seen from the composite curve in Figure IV-9, the beta spectrum above 1.9 Mev is mainly that of the 31.7-minute $Br^{84}$. Small errors in subtracting off the latter could lead to large errors in the remainder, or even to the indication of a 6.0-minute 3.2-Mev group where none exists. The end-point energies and relative intensities calculated for the 0.8- and 1.9-Mev groups, however, are relatively insensitive to the intensity inferred for the 3.2-Mev group.

The determination of the beta ray energy groups as described above made

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[*] The quantity $\sqrt{N\eta/\epsilon f}$ is proportional to the quantity $\sqrt{\text{cts/min}/F(Z,W)W(W^2-1)^{\frac{1}{2}}}$ of equation I-8. It is the standard Fermi plot ordinate applicable to equal electron momentum intervals transformed for use of data gathered by equal energy intervals. N = cts/min, $\epsilon = W$, $\eta$ = momentum/$m_oc$, and $f = \eta^2F(Z,\eta)$, where $F(Z,\eta)$ is the Fermi function for equal momentum intervals.

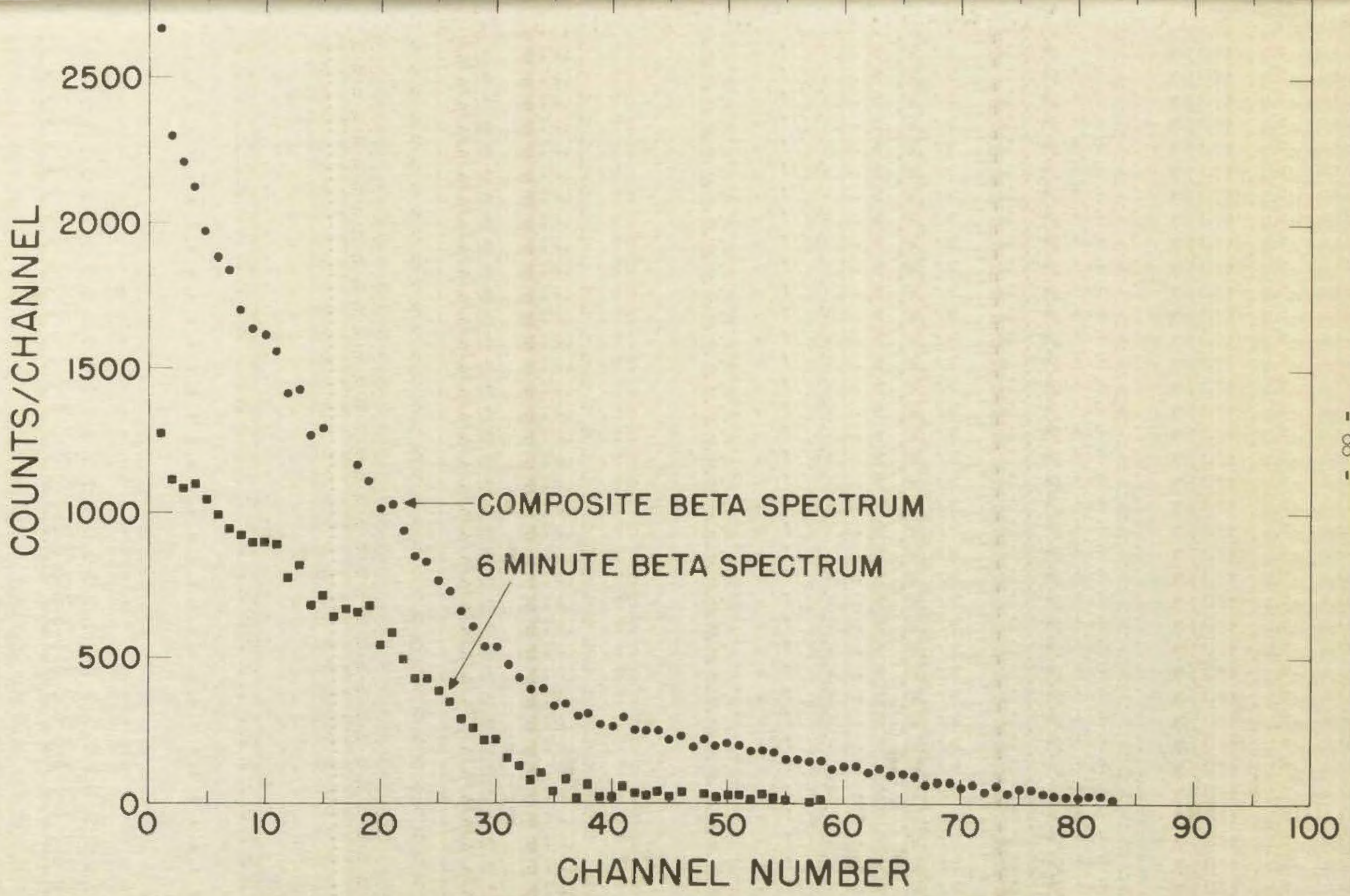

Figure IV - 9. Beta scintillation spectra of bromine from 14-Mev neutron irradiation of $Rb^{87}$.

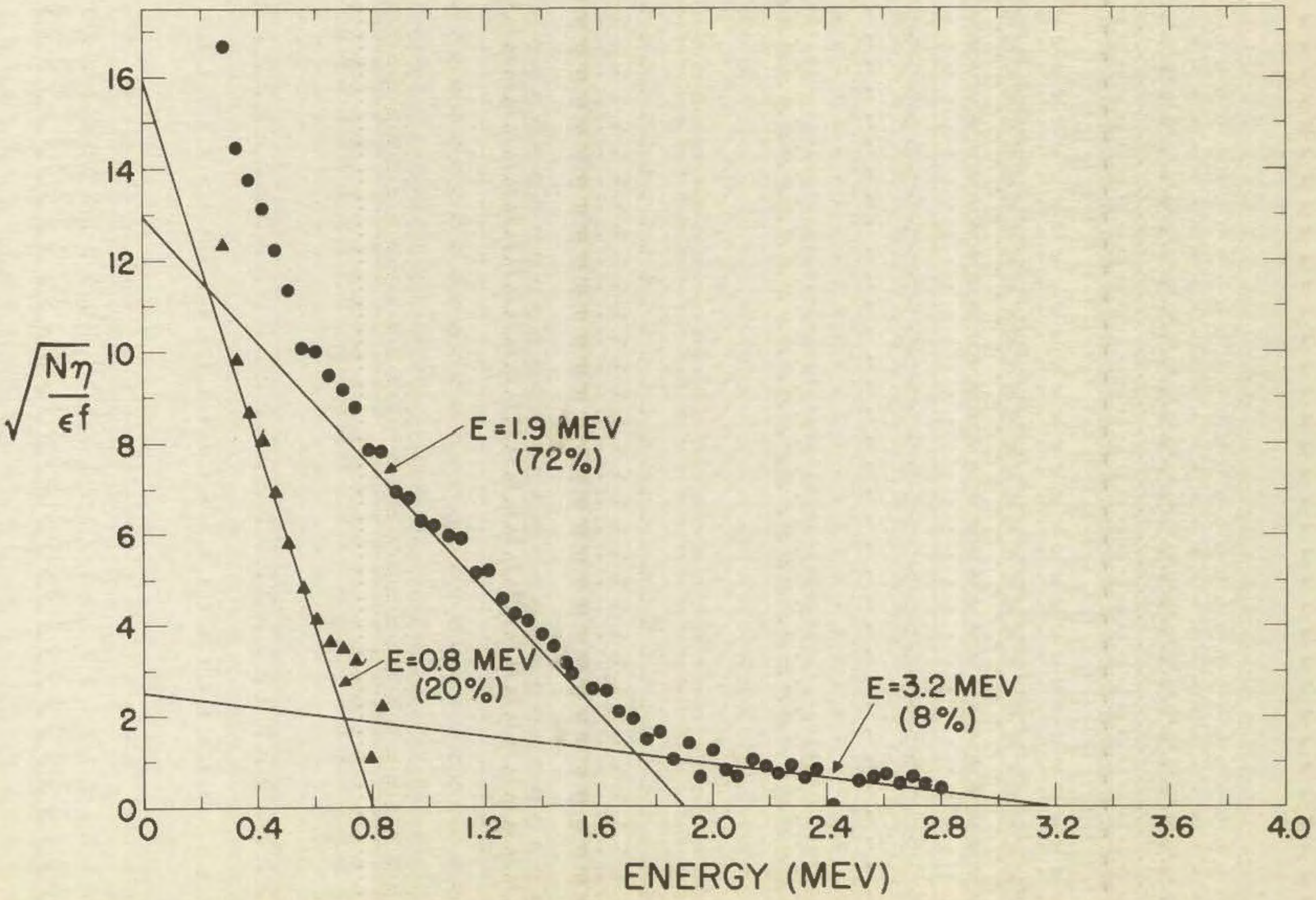

Figure IV - 10. Fermi plot of beta scintillation spectrum of 6.0-minute bromine.

possible the calculation of the beta-counting efficiency of the 6.0-minute $Br^{84}$, a datum needed for the measurement of the ratio of gammas to betas.

By beta-counting samples of a wide variety of radionuclides for which the beta-energy distribution and absolute disintegration rate were known, Prestwood and Bayhurst[36], of this laboratory, had established a functional relationship between the average beta energy of a source and its counting efficiency on the standard beta-proportional counters used in this work. Computation of the average energy of the three beta groups reported above, and insertion of this energy in the Prestwood-Bayhurst function, gave an absolute beta-counting efficiency of 0.468 for the experimental conditions employed (source thickness about 20 mg./cm.², mounted on 1/16" dural plate, and placed on first shelf of beta counter).

The ratio of gammas to betas for the 6.0-minute activity could not be measured directly on any single sample. Because the time required to make one gamma spectrum count and to print out the data was at least four minutes and because it was advisable to take a succession of gamma counts as closely spaced as possible, insufficient time was left to beta-count the sample before the 6.0-minute activity had died out. Hence, it was necessary to gamma-count one sample and beta-count another and to relate the two by comparing their 31.7-minute components.

The beta and gamma results for the 6.0-minute activity are summarized in Table IV-6. The log ft values were computed for the three beta transitions to provide a qualitative indication of their allowed or forbidden character. Owing to the extreme uncertainty in the abundance of the 3.2-Mev group, its

log ft is likely to be more nearly a lower limit than an upper limit.

Table IV-6

Radiations of the 6.0-Minute $Br^{84}$

Principal Gamma Rays

| Gamma Energy (Mev) | Photopeak Area (cts/min) | Photopeak Efficiency (cts/gammas) | Intensity (gammas/min) | Calculated betas/min | $\frac{\text{Gammas}}{\text{Betas}}$ |
|---|---|---|---|---|---|
| $0.44_0$ | 2,370 | 0.054 | 43,900 | 64,100 | 0.68 |
| $0.88_4$ | 780 | 0.0162 | 48,100 | 64,100 | 0.75 |
| 1.46 | 331 | 0.0069 | 48,000 | 64,100 | 0.75 |
| 1.89 | 45 | 0.0043 | 10,500 | 64,100 | 0.16 |

Beta Ray Groups

| Beta Energy (Mev) | Abundance (%) | log ft |
|---|---|---|
| 0.8 | 20 | 4.1 |
| 1.9 | 72 | 5.0 |
| 3.2 | (8) | (6.8) |

## Exploration for Bromine Activities of Half-life Less Than 3 Minutes

Following the identification of the 6.0-minute activity and the semi-quantitative measurement of its radiation characteristics, the exploration was extended to possible new activities of still shorter half-life. Because the experiments with fission-product bromine had indicated that the 6.0-minute activity is probably the only gamma emitter in the half-life range 3 to 30 minutes, the experiments to be described were essentially a search for new activities with half-lives in the range 0.5 to 3 minutes. The measurements involved were necessarily more qualitative, owing to the obvious difficulties associated with the rapid preparation of the samples and the recording of data from the gamma-ray spectrometer.

These experiments were conducted in a simple and more or less standardized manner. Uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated in the rabbit port of the Water Boiler for 15 seconds, the bromine was separated by the procedure on page 36 except for omission of the iodine decontamination step, and counting was begun approximately 2.5 minutes after the end of irradiation. The purified sample was counted with a scintillation system employing a 4"x 4" NaI(Tl) crystal. The large crystal was chosen because of its higher gamma ray counting efficiency, particularly in the high-energy region. The higher gamma efficiency was gained somewhat at the expense of energy resolution; the resolution of the 4" x 4" scintillator system was about 15% at the 0.662-Mev gamma line of $Cs^{137}$- $Ba^{137m}$, compared to the 8.5-9.0% resolution obtained for the same line with the $1\frac{1}{2}$" x $1\frac{1}{2}$" and 2" x 2" scintillators used for the other gamma measurements in this investigation.

Preliminary measurements of the rapidly separated bromine samples showed

a rather diffuse gamma scintillation spectrum, with definite indications of a component of half-life in the vicinity of 1 minute. The only prominent photopeak was one at about 1.5 Mev.

For the better characterization of the photopeak at 1.5 Mev, a second sample was prepared and the portion of the pulse distribution corresponding to the gamma ray energy range 1.3 to 1.6 Mev was fed to a 10-channel pulse analyzer; readings were taken at 30-second intervals starting at 3 minutes after end of irradiation and continuing until 8 minutes after end of irradiation. Simultaneously, a complete 100-channel spectrum was taken over the first 70 seconds of counting. A second 100-channel spectrum was taken, for comparison, over a two minute interval starting about 4 minutes later. The two 100-channel spectra are plotted in Figure IV-11.

The first 100-channel spectrum showed that the prominent "photopeak" at 1.5 Mev was in reality composed of two close-lying peaks, one at 1.42 Mev and one at 1.56 Mev; the second was approximately twice as intense as the first. The series of 10-channel readings, which embraced the energy region of these two peaks, showed that both decayed with a 56-second half-life over 6 half-lives.

The conclusions drawn from these data may be summarized as follows:

1. There exist short-lived bromine activities which have gamma rays of energies 1.42, 1.56, ~ 2.0, ~ 2.4, ~ 2.7 and ~ 3.2 Mev.

2. Of these gamma rays, the two most prominent, at 1.42 and 1.56 Mev, decay with a half-life of about 56 seconds.

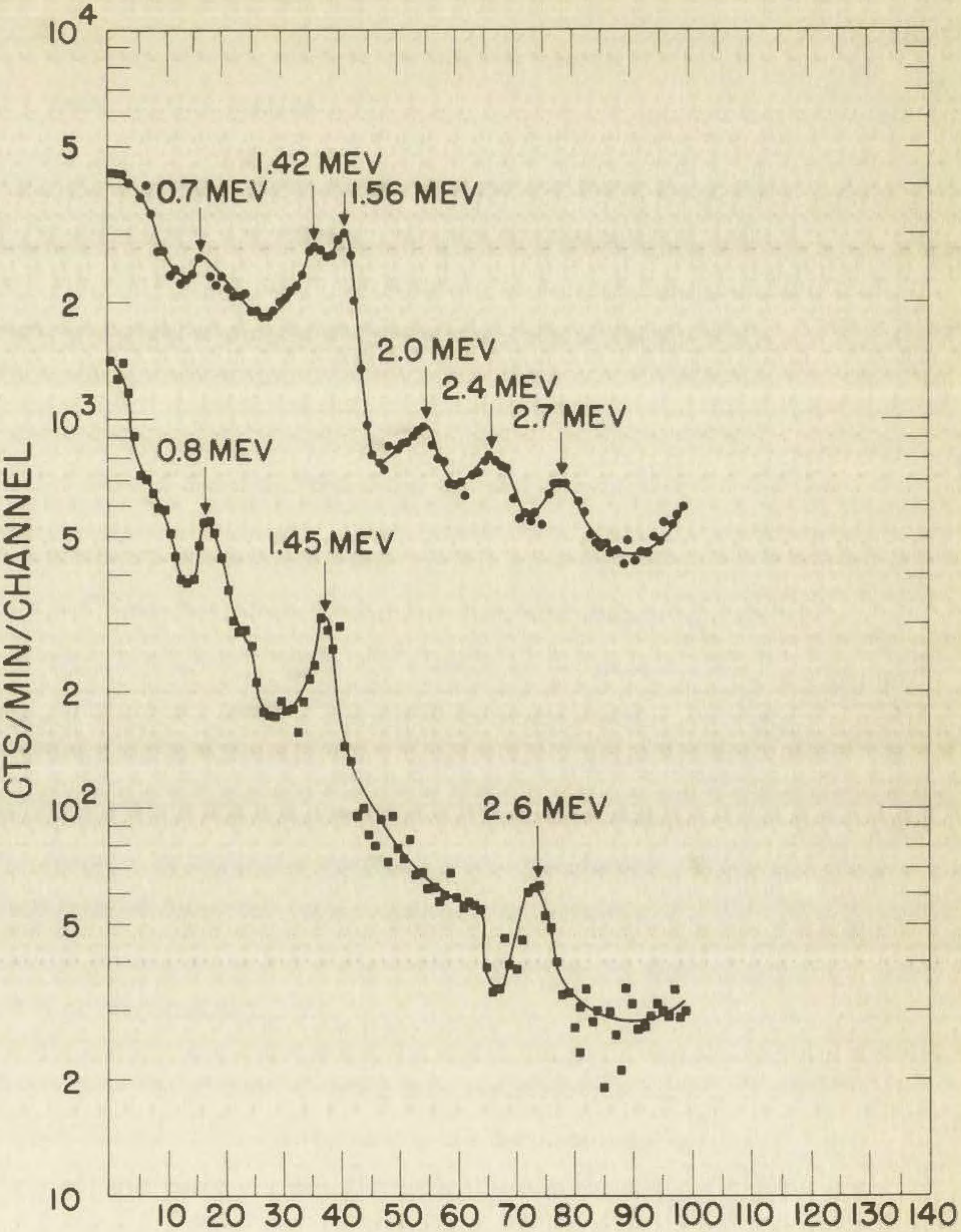

Figure IV - 11. Gamma scintillation spectra of rapidly-separated fission-product bromine, taken with 4" × 4" NaI(Tl) crystal. Upper curve: 70 second count, starting 3 minutes after end of irradiation. Lower curve: 2-minute count, starting about 7 minutes after end of irradiation.

3. The agreement of this half-life with the one reported for $Br^{87}$ suggests that at least the two high-intensity gammas arise from decay of this nuclide.

Because the scintillation system borrowed for these experiments was needed for other work, the decision was made to discontinue the investigation at this point and to shift the emphasis to an exploration for the still-unknown selenium parents of radioactive bromine nuclides.

## Lack of Isomeric Transition for 31.7-Minute $Br^{84}$

One of the first questions raised by the discovery of a short-lived isomer of $Br^{84}$ was that of its energy position with respect to the 31.7-minute isomer, i.e., which of the two isomers is the ground state of the nuclide. Duffield and Langer,[19] in their beta-spectrometer investigation of the 31.7-minute $Br^{84}$, looked for a short-lived isomeric daughter of this activity by a Szilard-Chalmers experiment. They were unable to find any isomeric daughter activity and concluded that, "the isomer, if it exists, has a half-life of less than 30 seconds, or the gamma-ray associated with the isomeric transition is not sufficiently converted to give a measurable separation of the isomers".

Inasmuch as the present investigation had developed information which Duffield and Langer did not have, namely the definite existence of an isomer, their type of experiment was repeated with improved techniques to ascertain whether the short-lived isomer was formed by isomeric transition from the longer-lived isomer. This experiment involved the hot-atom procedure outlined

on page 42, and was based on the principle that atoms of the lower isomer formed by isomeric transition from an upper state are dislodged from the molecule in which the atoms of the upper isomer are bound. (cf. page 13).

A solution of 2 x $10^6$ cts/min of 31.7-minute $Br^{84}$ was isolated from a fission-product mixture and the organic bromo-compound was prepared and washed. Then, a series of four aqueous phase separations was carried out at 5-minute intervals, and after heating, silver bromide was precipitated from each aqueous sample. The precipitates were filtered, washed, and mounted as described on page 42, and beta counting was started within five minutes after separation.

None of the samples showed any indication of a short-lived component. However, all counted initially at a rate of about 200 cts/min and decayed with about a 32-minute half-life. The counts corresponded to about $10^{-4}$ of the original 31.7-minute $Br^{84}$ activity. This residue was attributed to small quantities of the organic bromo-compound dissolved in the aqueous layers.

Although this experiment does not completely exclude the possibility that the 31.7-minute $Br^{84}$ may be the upper isomeric state, it does indicate that its decay does not proceed by an isomeric transition in which the gamma rays are appreciably internally converted.

The alternative possibility, that the 6.0-minute state decays by isomeric transition to the 31.7-minute state, was not checked experimentally. Sources of the 6.0-minute isomer of sufficient strength and purity could be prepared only by fast-neutron irradiation of rubidium, and during the time this portion

of the problem was under investigation, the services of the Cockcroft-Walton accelerator were not available.

## Half-life of $Se^{84}$

The chemical procedure used to determine the half-life of $Se^{84}$ consisted of the rapid separation of active selenium from fission products, followed by six successive extractions of the bromine daughter from the selenium solution with carbon tetrachloride. The chemical techniques are described on pages 44 and 46.

The only prior information on the parent nuclide $Se^{84}$ was that its half-life is about 2 minutes. Consequently, it was necessary that the separation of the radioselenium and the milking of bromine activity from it be done in the chemistry laboratory near the reactor as soon as possible after the end of the irradiation. The counting of the 31.7-minute bromine activity could be carried out in a more leisurely manner. For this reason, the samples were returned to the main chemistry building for beta counting. The radioactive bromine samples were placed beneath 444 mg./cm.$^2$ of aluminum absorber and were counted continuously for five hours; a plot of the resulting decay curves showed only one component, a 31.7-minute activity.

The time intervals between successive milkings were 2.5 minutes, except for the first sample, where the growth interval was only two minutes. This point has been corrected for the difference in interval using equation III-1 and assuming a half-life of 3.1 minutes for $Se^{84}$ and 31.7 minutes for $Br^{84}$.

The half-life obtained for $Se^{84}$ was 3.1 minutes.

A second experiment was performed like the first, differing only in that the bromine was milked by the silver bromide technique described on page 49. Seven silver bromide separations were performed at intervals of 2 minutes. The samples decayed with a half-life of 31.7 minutes, indicating only one component. The half-life obtained for $Se^{84}$ was 3.5 minutes.

The data from both experiments are plotted in Figure IV-12. An average half-life of 3.3 minutes was adopted for all future investigations.

## Origin of the 6.0-Minute $Br^{84}$

The two experiments above had as their primary concern the measurement of the half-life of $Se^{84}$ by measurements of the 31.7-minute $Br^{84}$ activity. They left unanswered a closely related question: whether or not the $Se^{84}$ decayed also to the 6.0-minute isomer of $Br^{84}$. A third experiment was set up to answer this question. The essential difference between this experiment and the two preceding was that both the timing of the separations and the mode of counting were chosen so as to optimize the 6.0-minute activity.

A sample of uranyl nitrate hexahydrate was irradiated for 3 minutes and the separation and clean-up of the active selenium was completed 3 minutes after the end of irradiation. The selenium was then allowed to decay for a period of 3 minutes, after which the bromine activity was extracted with carbon tetrachloride and mounted (as silver bromide) for gamma counting. The circuitry was adjusted to record all gamma radiations above 0.5 Mev, and a

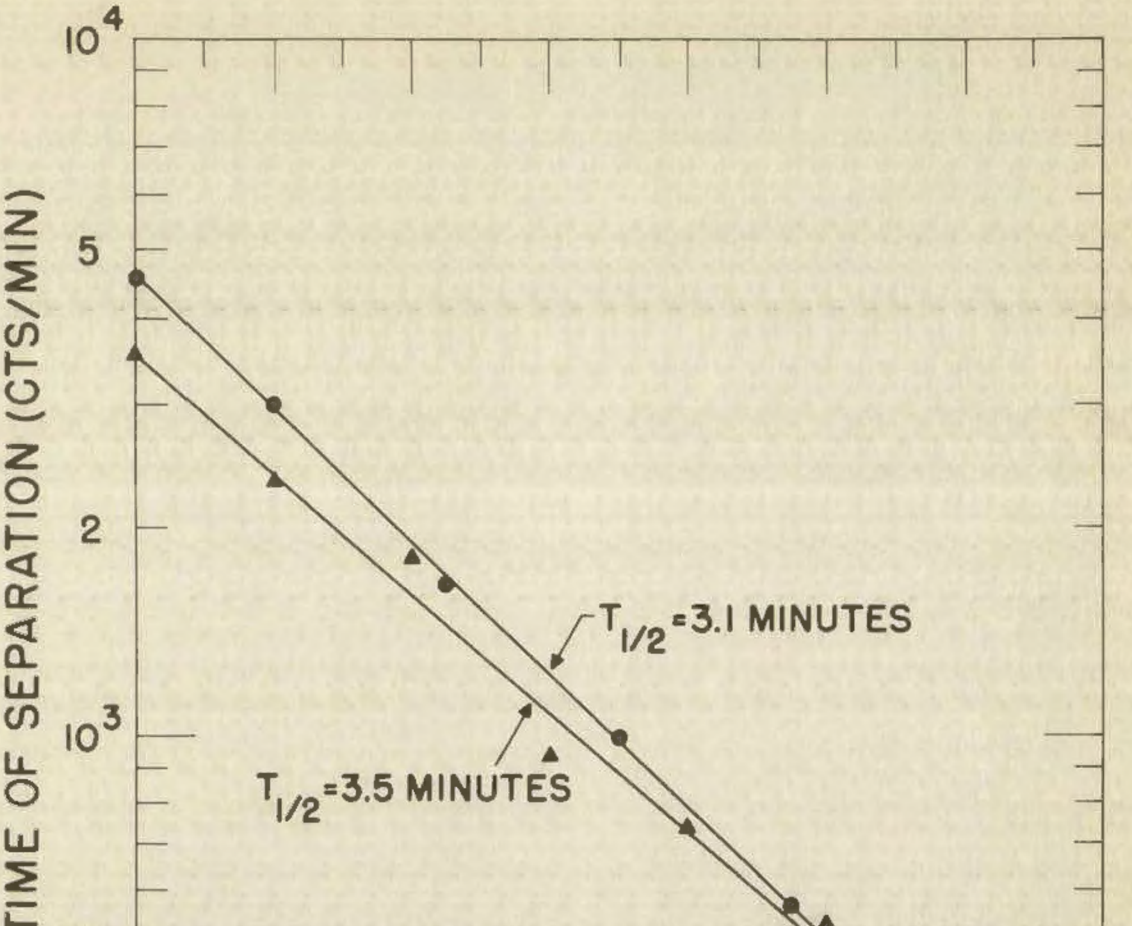

Figure IV - 12. Decay of Se$^{84}$, computed from activities of Br$^{84}$ extracted from fission-product selenium. Bromine activity beta counted through 444 mg./cm.$^2$ of aluminum.

▲ - Extracted with silver bromide.

● - Extracted with carbon tetrachloride.

series of one-minute counts was begun, starting at 11 minutes after the end of irradiation. For comparison, a second irradiation was carried out, and a similar series of gamma counts was made on the bromine activity separated directly from the fission-product mixture. The irradiation lasted 30 seconds, the bromine separation was completed 95 seconds after the end of irradiation, and counting was begun 6.5 minutes after the end of irradiation. In this run the irradiation and the bromine separation were conducted very rapidly to minimize the growth of $Br^{84}$ from $Se^{84}$. The gamma-counting data from the first and second runs are plotted in Figures IV-13 and IV-14, respectively.

As may be seen from Figure IV-13, the bromine milked from selenium exhibited a gamma half-life of 31.7 minutes only; within limits of experimental error no 6.0-minute component was observable. On the other hand, Figure IV-14 shows that the gamma decay of the directly-separated bromine consists of three components: a 32-minute period, a 5.5-minute period, and at the beginning, a 1-minute period. The first two are recognizable as the two isomers of $Br^{84}$. The third period appears to be that of $Br^{87}$.

The results of this experiment lead to the conclusion that little, if any, of the 6.0-minute $Br^{84}$ is produced by decay from $Se^{84}$, i.e., $Se^{84}$ decays preponderantly to the 31.7-minute isomer. The fact that the 6.0-minute isomer does appear in fission-product bromine implies that it is formed independently in fission.

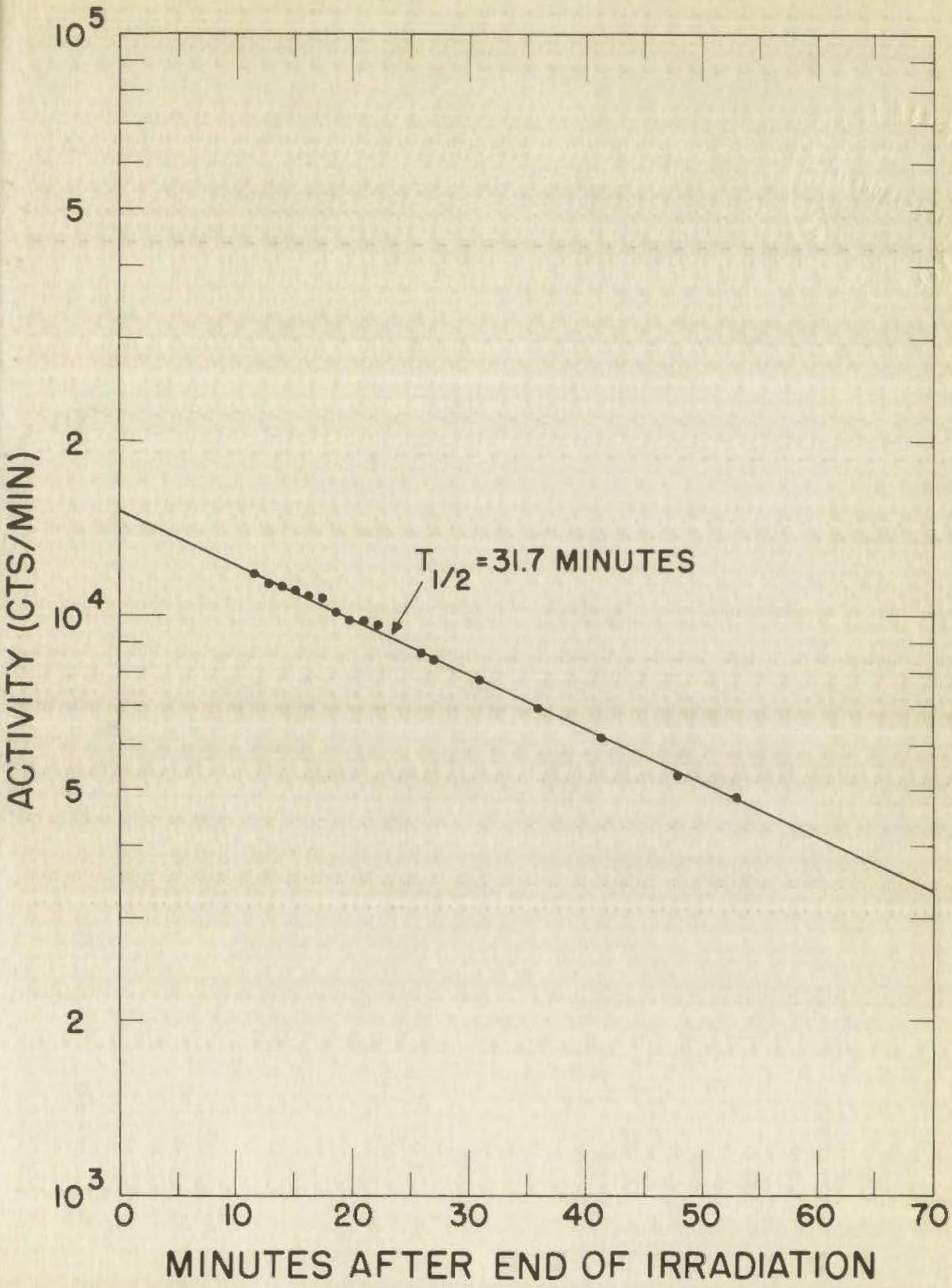

Figure IV - 13. Gross gamma decay of bromine from rapidly separated fission-product selenium.

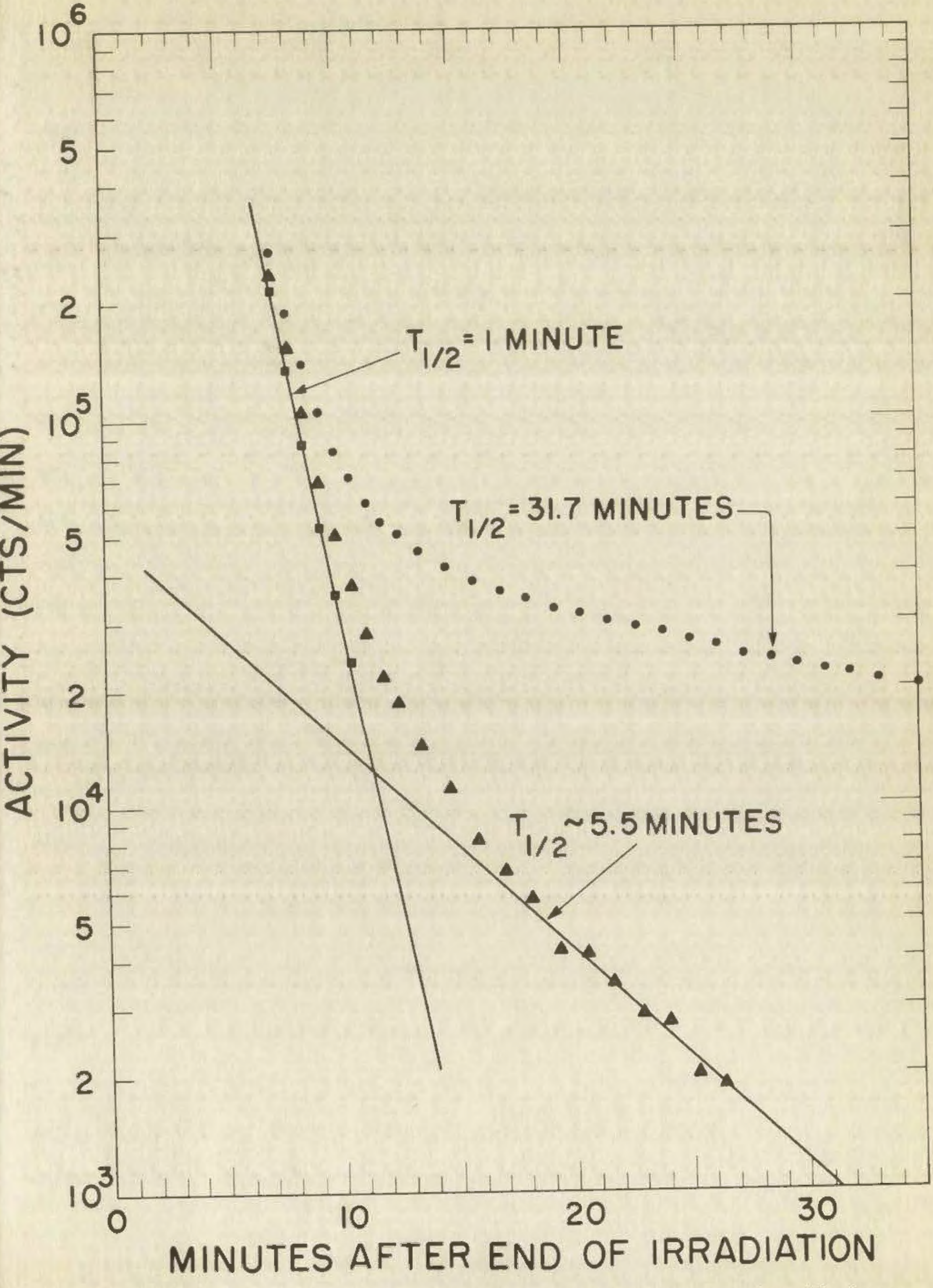

Figure IV - 14. Gross gamma decay of bromine separated rapidly from fission products.

## Half-life of $Se^{85}$

It will be recalled that, on the basis of a combination of various empirical and semi-theoretical considerations, the half-life of $Se^{85}$ was expected to be in the vicinity of 45 seconds (cf. page 26). In accordance with this expectation, a preliminary experiment was conducted to ascertain whether any $Br^{85}$ could be found in bromine extracted from rapidly separated fission-product selenium.

A 40-mg. sample of uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated for 30 seconds in the rabbit port of the Water Boiler, and the selenium was separated about 2 minutes after the end of irradiation. After a preliminary scavenging with pre-precipitated silver bromide to remove any fission-product bromine that may have accompanied the selenium, the latter was allowed to stand for 35 seconds and a second silver bromide separation was made. The first silver bromide separation occurred at 2.5 minutes after end of irradiation and the second silver bromide extraction at 3.1 minutes after end of irradiation. The second silver bromide was mounted under 354 mg./cm$^2$. of aluminum absorber and beta counting was begun 4.2 minutes after the end of irradiation.

As shown in the plot of the counting data (Figure IV-15), the decay curve of the bromine activity can be resolved into two components, one consistent with a half-life of 31.7 minutes and the other with a half-life of about 3 minutes. The radiations of any $Br^{83}$ present in the sample were eliminated by the aluminum absorber. Inasmuch as any bromine activities accompanying the selenium would have been removed with the first silver bromide extraction, it was assumed that the 3-minute component in the second precipitate

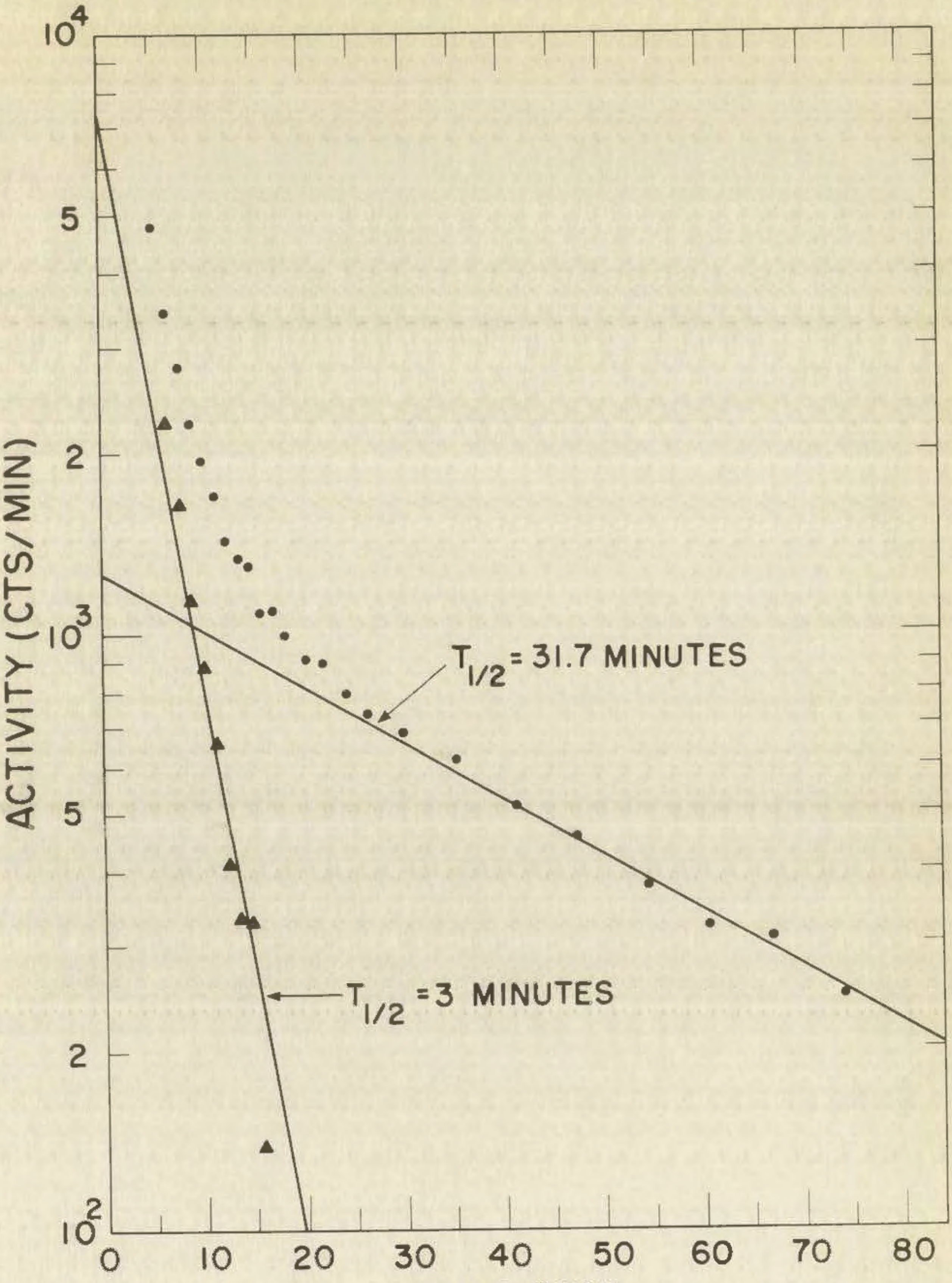

Figure IV - 15. Beta decay of bromine extracted from rapidly-separated fission-product selenium. Bromine activity beta counted through 354 mg. cm.$^2$ of aluminum.

was $Br^{85}$ and that it had grown in from a selenium parent present during the interval from 2.5 minutes to 3.1 minutes after end of irradiation.

On the basis of this evidence, it appeared that the half-life of $Se^{85}$ might be measured successfully by the silver bromide milking technique described on page 49. The relatively short half-life of the $Br^{85}$ necessitated the use of a separate beta counter for each silver bromide sample to provide sufficient data so that the 3-minute component could be reliably measured. Three identical beta counters were available.

Owing to the impossibility of obtaining complete recovery of the silver bromide in the time available between successive milkings and to non-uniformity in the adsorption of the active bromine on the silver bromide precipitate, radiochemical yields could not be obtained by the conventional weighing method. Instead, the 31.7-minute $Br^{84}$, produced at a known rate from the 3.3-minute $Se^{84}$ and present as the long-lived component in each sample, was used as a yield monitor and all the $Br^{85}$ activities were computed by reference to it.

The three beta counters limited each milking experiment to three samples. The timings of two successive identical experiments were overlapped in such a manner that the time of the third milking of the first was the same as first milking of the second.

In each run 100 mg. of uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated for 15 seconds in the rabbit port of the Water Boiler, and the selenium was separated and dissolved in the standard manner (cf. page 44). In the first run the three bromine growth periods were 103-137 seconds, 137-167 seconds, and 167-197 seconds, and in the second run the growth periods were 167-197 seconds,

197-227 seconds, and 227-257 seconds, all periods expressed in terms of time after end of irradiation. The timing of the individual silver bromide separations was considered to be known to ± 3 seconds. Each sample was counted through 272 mg./cm.$^2$ aluminum absorber, and its decay was followed by a series of 45-second counts until the 3.0-minute activity had died out. Thereafter, the 31.7-minute activity was evaluated by counting at 5-minute intervals over a period of 6 hours. The resulting decay curves were then resolved and the contributions of the 3.0-minute and 31.7-minute components were extrapolated back to the time of separation.

The data from both runs are plotted in the upper curve of Figure IV-16, which shows a $Se^{85}$ half-life of 39 seconds. The beginning of the first growth period is represented as zero time on the graph. The point at 64 seconds is actually two superimposed points; the last milking of the first run and the first milking of the last run gave identical results. The first point, representing a growth period of 34 seconds, 4 seconds longer than the others, was computed from the extrapolated bromine activity by the assumption of a $Se^{85}$ half-life of 39 seconds and a $Br^{85}$ half-life of 3.0 minutes, and the use of a correction term of the form $(e^{-\lambda_1 T_1} - e^{-\lambda_2 T_1})/(e^{-\lambda_1 T_2} - e^{-\lambda_2 T_2})$, where $T_1$ and $T_2$ are 30 and 34 seconds respectively, and the λ's have their usual meaning. This point, it will be noted, agreed very well with the others.

Although the methods employed in the preceding experiment gave a consistent set of data, it appeared worthwhile to check the final result by another experiment employing a different procedure for milking the bromine from selenium. The carbon tetrachloride extraction procedure, while not as

rapid as the silver bromide method, was still rapid enough to be applicable to a $Se^{85}$ half-life determination. In this experiment, the interval between milkings was set at 1 minute, about the limit of speed possible with this procedure. Only one set of three milkings was performed.

An 80-mg. sample of uranyl nitrate hexahydrate (93% $U^{235}$) was irradiated for 15 seconds and the selenium was separated as before. The selenium solution was added to a separatory funnel containing 0.25 millimoles of bromine dissolved in 20 ml. of carbon tetrachloride, and the layers were mixed by shaking for a few seconds and were then allowed to separate for 30 seconds. The time at which the shaking was stopped (105 seconds after the end of irradiation) was arbitrarily taken as zero time, and the carbon tetrachloride layer was discarded. Then, the selenium solution was milked three times at intervals of one minute with successive 10-ml. portions of carbon tetrachloride containing bromine. The bromine was removed from each of the carbon tetrachloride layers, converted to silver bromide, and mounted for beta counting. The 3.0-minute components from the decay curves of the individual samples were extrapolated back to their respective times of separation. The results, plotted in the lower curve of Figure IV-16, showed a $Se^{85}$ half-life of 35 seconds. This half-life compares favorably with the value obtained in the first (silver bromide method) experiment.

Notwithstanding the consistency of the results above, there remained the possibility that it was a bromine exchange that was being measured, rather than the half-life of $Se^{85}$. The possibility may be illustrated by the following hypothetical case: If the $Se^{85}$ were to decay with a half-life of 15 or 20 seconds to a chemical state of bromine which does not exchange instantaneously

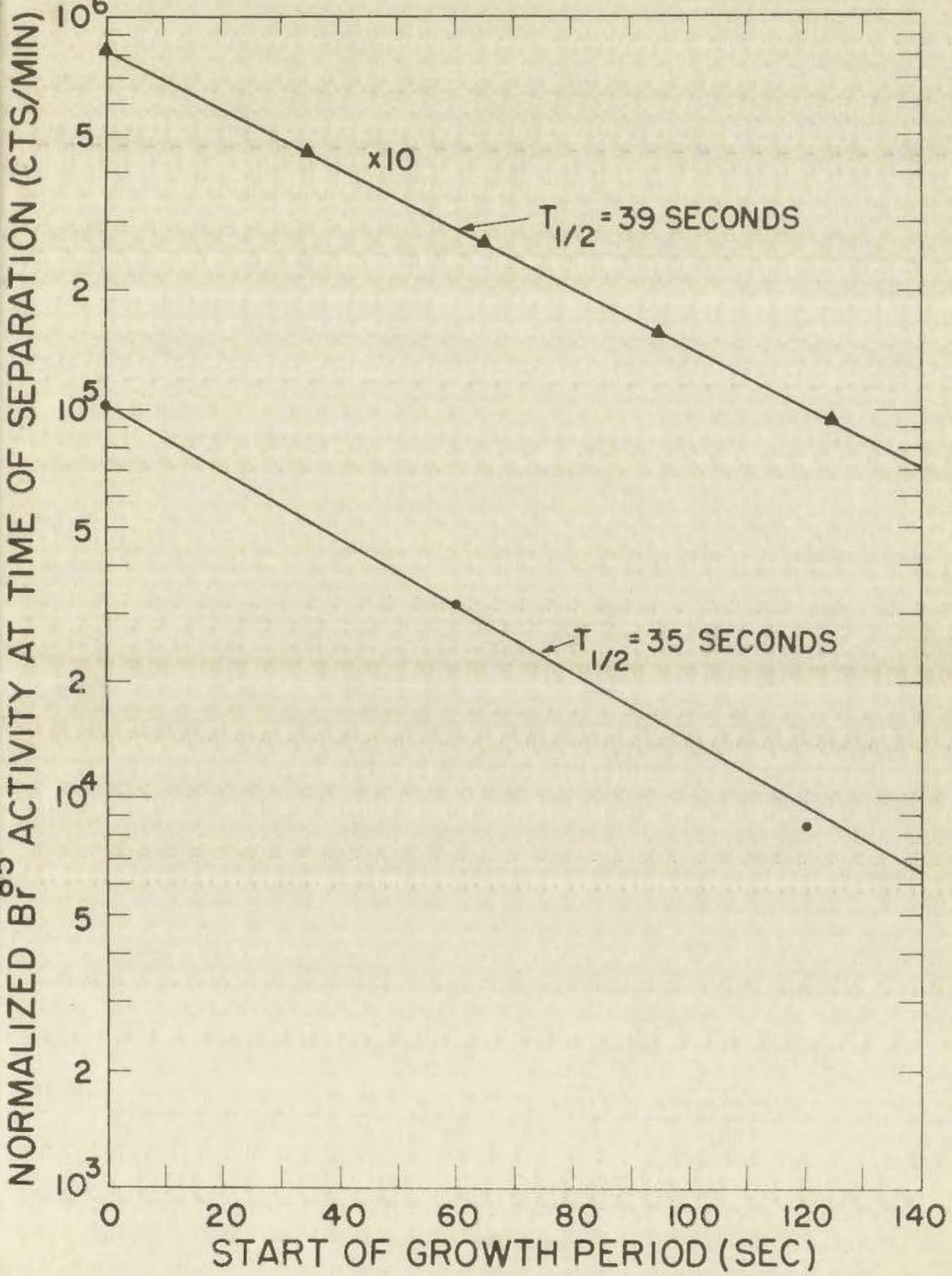

Figure IV - 16. Decay of $Se^{85}$, computed from activities of $Br^{85}$ extracted from fission-product selenium. Bromine activity beta counted through 272 mg./cm.$^2$ of aluminum.

● - Extracted with carbon tetrachloride.

▲ - Extracted with silver bromide.

with bromide ion or molecular bromine, and if the radiochemical exchange were to proceed by a first order reaction with a half-life of 40 seconds, the relative quantities of active bromine found in successive milkings would be approximately the same as if they had grown directly from a 40-second selenium parent. If such were the case, it is highly probable that the exchange reaction would be temperature sensitive. An experiment was conducted to investigate this possibility.

The experiment consisted of two silver bromide milking runs, one with hot solutions (about 80° C) and one with cold solutions (about 5° C). The results of the two runs are plotted together in Figure IV-17. As may be seen, the data from the hot run (the first three points) are consistent with the data from the cold run (the last three points). There was no indication of any temperature dependence.

On the basis of the combined results of all three experiments, including estimates of the experimental errors, the half-life of $Se^{86}$ was adopted as 39 ± 4 seconds.

### Half-life of $Se^{87}$

In exploratory experiments in which selenium was separated from fission products as rapidly as possible and bromine was separated in turn from the selenium, there was observed in the bromine extract a prominent 1-minute activity. The fact that this half-life was the same, within experimental error, as that reported for $Br^{87}$ indicated that $Br^{87}$ had grown in from the

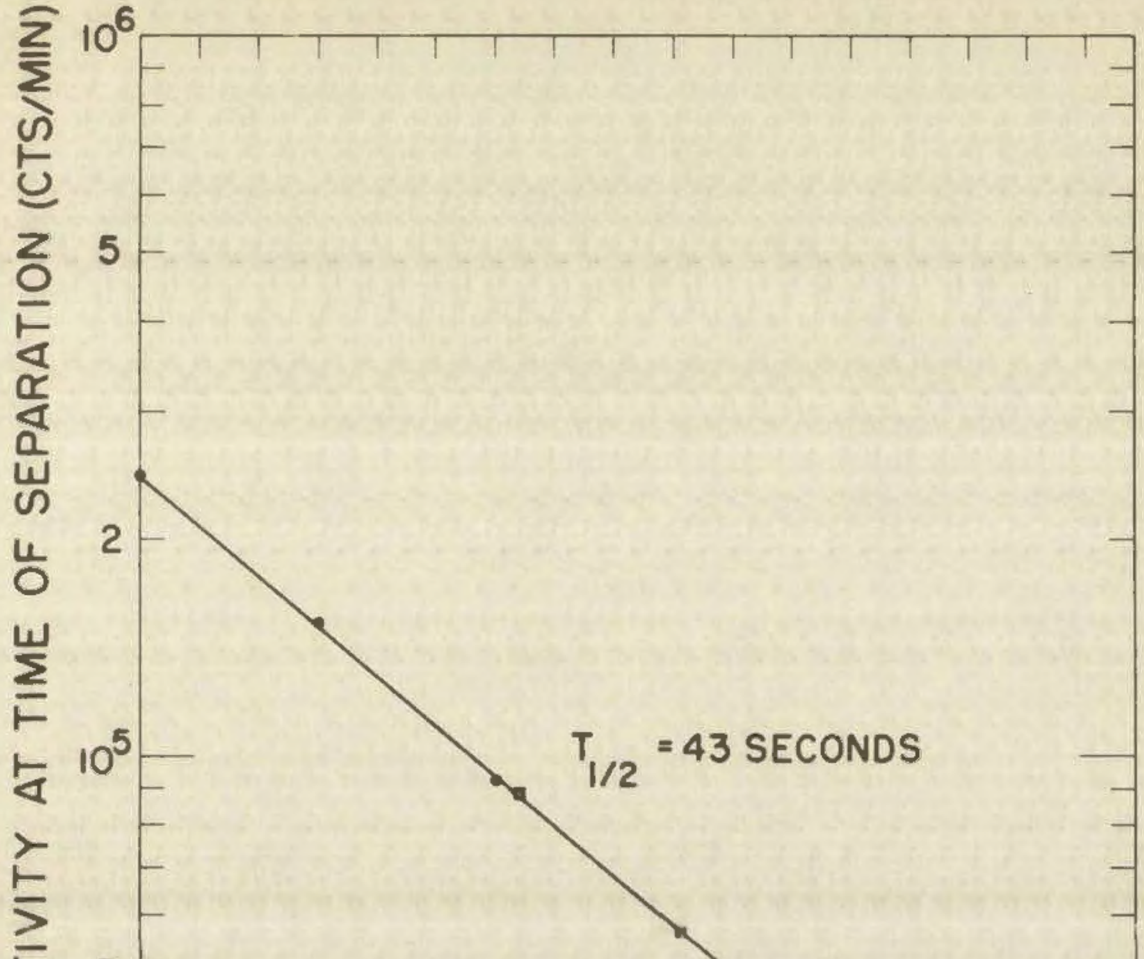

Figure IV - 17. Comparison of $Se^{85}$ half-lives, by silver bromide extractions from hot and cold solutions of fission-product selenium. Bromine activity beta counted through 272 mg. /cm. $^2$ of aluminum.

■ - Extractions at 5°C.
● - Extraction at 80°C.

selenium and hence that a measurable amount of $Se^{87}$ had survived until the time of the bromine milking.

A series of milking runs was carried out similar in chemical technique to those employed in the $Se^{85}$ experiment except for the addition of a rapid resin-column step to remove tellurium before isolation of the selenium (cf. page 55).

The half-life of the $Br^{87}$ (56 seconds) and the half-life expected for the $Se^{87}$ (about 30 seconds) were too short to allow a series of bromine samples to be extracted and counted with any degree of accuracy. Consequently, a set of four separate runs was carried out, with only one bromine sample extracted in each run. The uranium irradiation times were each 20 ± 1 seconds, and the bromine separation times were set at successively later intervals to achieve as nearly as possible the same net result as was obtained by successive milkings on a single sample in the $Se^{85}$ experiment. Unfortunately, because of the finite and inherently variable times involved in some of the chemical manipulations (e.g., filtration of silver bromide), it was found essentially impossible to maintain a constant bromine growth period. The respective bromine growth intervals were 92-115 seconds, 111-130 seconds, 120-143 seconds, and 132-159 seconds, all expressed in terms of time after end of irradiation.

The silver bromide samples were beta counted through 1310 mg./cm.$^2$ of aluminum absorber, which let through only the relatively hard betas of $Br^{87}$ and $Br^{84}$. Figure IV-18 shows a typical decay curve for one run. The individual decay curves were resolved into 1-minute and 31.7-minute components, and, as in the $Se^{85}$ experiment, the 31.7-minute $Br^{84}$ components were used in conjunction with the known $Se^{84}$ half-life to normalize the experimentally obtained

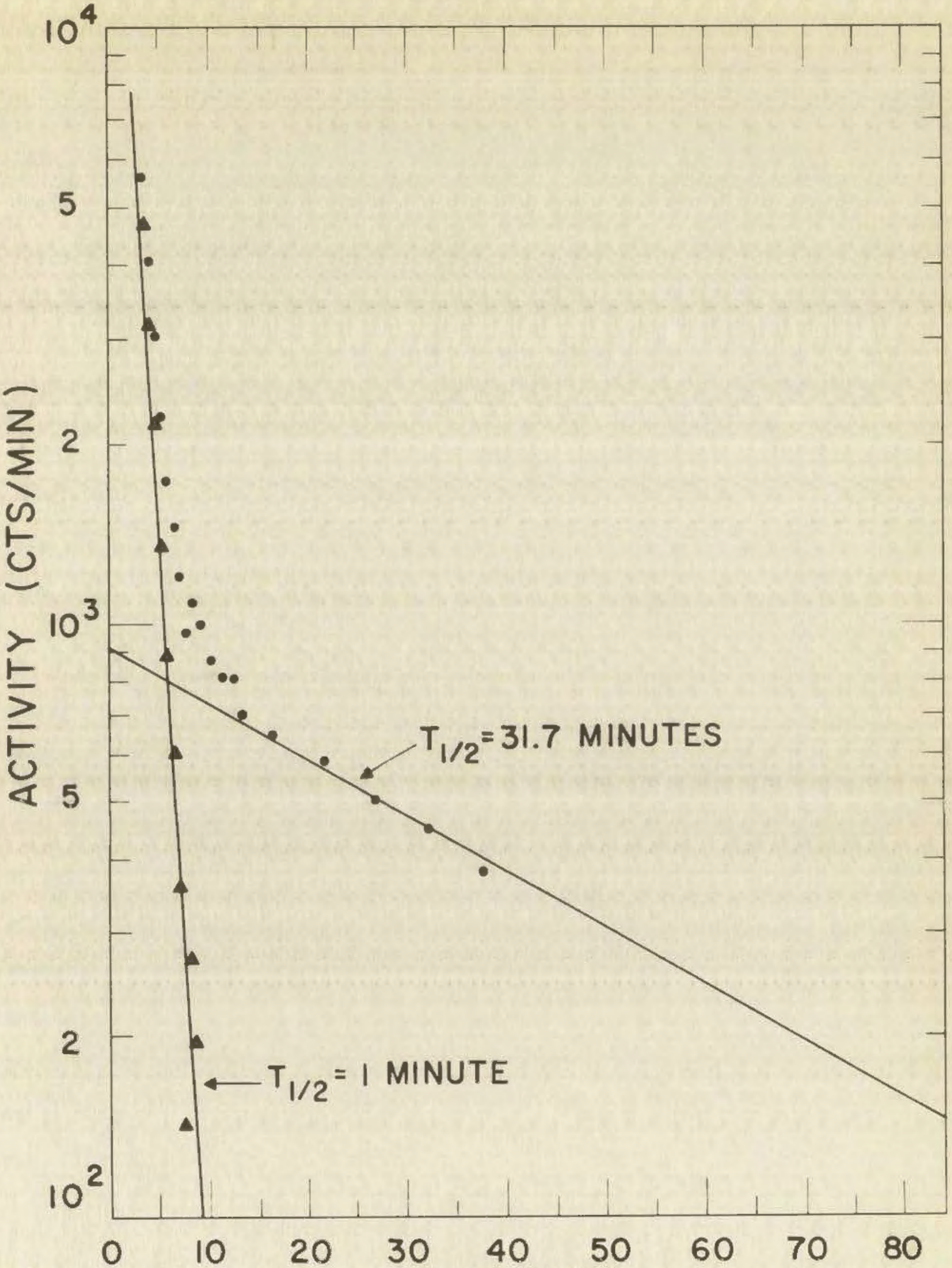

Figure IV - 18. Typical decay curve of short-lived bromine activity extracted from rapidly-separated fission-product selenium. Bromine activity beta counted through 1310 mg./cm.$^2$ of aluminum.

1-minute components to constant yield.

A preliminary plot of the 1-minute components without regard to the differences in growth period gave an apparent half-life of 15 seconds for $Se^{87}$. The known $Br^{87}$ half-life (56 seconds) and the approximate $Se^{87}$ half-life (15 seconds) were then converted to λ's and inserted in the parent-daughter expression

$$A_2(t_1 + T) = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1(t_1)(e^{-\lambda_1 T} - e^{-\lambda_2 T}) \qquad \text{(IV-1)}$$

and the relative values of $A_1(t_1)$ were plotted as a function of time $(t_1)$. The beginning of the first growth period was taken as time zero. These data are represented by the circular points in Figure IV-19. They indicate a corrected $Se^{87}$ half-life of about 17 seconds.

The results of two of the exploratory runs, conducted in the same manner except for omission of the resin column pre-treatment, are plotted as square points in Figure IV-19.

The results were not as clear-cut as those for $Se^{85}$. However, the trend is apparent and it indicates that the 1-minute activity has a selenium parent of half-life approximately 17 seconds. The two dotted lines in Figure IV-19 were drawn in to show the approximate range of uncertainty of the half-life that might be derived from the data. They gave half-lives of 15 seconds and 19 seconds. From a consideration of these measures of uncertainty and from estimates of other uncertainties in the experiment the experimental half-life was taken as 17 ± 3 seconds.

It has been assumed thus far that the 1-minute bromine activity was $Br^{87}$. However, in the light of the half-life guesses made for $Br^{86}$ and $Se^{86}$, both

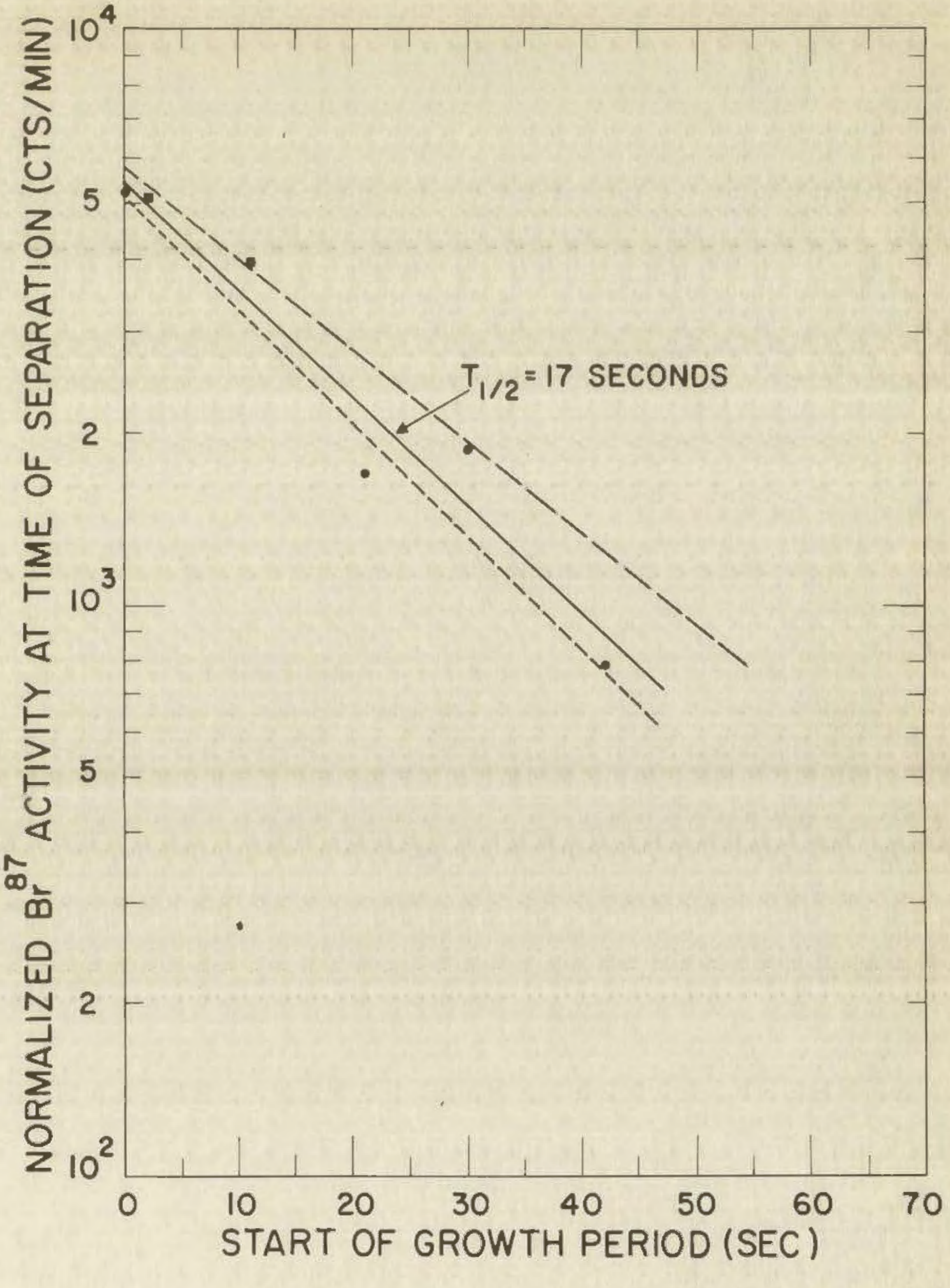

Figure IV - 19. Decay of $Se^{87}$, computed from activities of 1-minute bromine extracted from fission-product selenium. Bromine activity beta counted through 1310 mg./cm.$^2$ of aluminum. Dotted lines indicate probable limits of error in half-life.

approximately 30 seconds, one cannot entirely exclude the possibility that the 1-minute component observed in these experiments is the still-unidentified $Br^{86}$ and thus that the parent half-life measured is that of $Se^{86}$.

The fact that $Br^{87}$ decays in part to a level of $Kr^{87}$ which emits neutrons was exploited in one preliminary attempt to verify its presence in a silver bromide milking. A standard irradiation, selenium separation, and bromine extraction was carried out in the manner described above, and the silver bromide sample was transferred rapidly to a neutron counter consisting of boron trifluoride tubes imbedded in paraffin. However, the source was too weak to permit positive identification of any effect above the rather high counter background.

## Fission Yield of $Br^{84}$

A search of the literature had shown that the last measurement of the $U^{235}$ thermal fission yield of the 31.7-minute $Br^{84}$ had been performed prior to 1946 and that the result obtained was inconsistent with the fission yield reported for $Kr^{84}$ (cf. page 20). The discovery of a 6.0-minute isomer of $Br^{84}$, the determination of the half-life of $Se^{84}$, and the observation that the $Se^{84}$ decays very little, if at all, to the 6.0-minute $Br^{84}$, all reported in the present work, provided both a basis and a justification for the remeasurement of the fission yield of this nuclide. A second consideration, of equal importance, was the improvement in chemical techniques and radiation instruments during the decade since the previous fission-yield measurement.

The measurement of the fission yield of $Br^{84}$ consisted to two separate determinations, one for the 31.7-minute isomer and one for the 6.0-minute isomer.

The former was undertaken first.

This first determination involved the following sequence of steps:

1) A sample of uranium metal (93% $U^{235}$) was irradiated in the Water Boiler and dissolved in hydrochloric acid containing known weights of bromide and molybdenum carriers.

2) The bromine was separated from the solution and the residue was set aside for analysis of $Mo^{99}$. The radiochemical analyses for bromine and molybdenum followed the procedures described on pages 33 and 40 respectively.

3) The purified bromine sample was counted on the third shelf of a standard beta proportional counter, with 444 mg./cm.$^2$ of aluminum absorber between sample and counter window to cut out radiations from $Br^{83}$ and $Kr^{83m}$. Counting was started 1.5 hours after the end of irradiation, at which time the 6.0-minute isomer had disappeared. The ratio of the $Br^{84}$ counting efficiency for third shelf with absorber to the counting efficiency for first shelf without absorber (the standard condition for absolute determination of counting efficiency) was determined by comparison of counting rates for the two positions with a sample of pure 31.7-minute $Br^{84}$ which had been prepared by the $Rb^{87}$ $(n,\alpha)$ $Br^{84}$ reaction.

4) The standard counting efficiency was computed by application of the Prestwood-Bayhurst[36] function to the $Br^{84}$ beta distribution reported by Duffield and Langer.[19]

5) The counting rate of the $Br^{84}$ at an arbitrary reference time was converted to the number of $Br^{84}$ atoms produced during irradiation by a calculation which took into account the counting efficiency of the $Br^{84}$ sample, the growth of the $Br^{84}$ from its $Se^{84}$ parent, and its decay during and after the time of formation. It was assumed that the fission chain began at $Se^{84}$ and that all the 31.7-minute $Br^{84}$ came from $Se^{84}$. The pertinent mathematical equation is the one which describes the formation and decay of a radioactive daughter whose parent is formed at a constant rate during a time T:

$$A_2(t) = \frac{\epsilon F Y_2}{T} \left[ \frac{\lambda_2}{\lambda_2 - \lambda_1} (1 - e^{-\lambda_1 T}) e^{-\lambda_1 t} + \frac{\lambda_1}{\lambda_1 - \lambda_2} (1 - e^{-\lambda_2 T}) e^{-\lambda_2 t} \right] \quad \text{(IV-2)}$$

where

$T$ = duration of irradiation,

$t$ = time between end of irradiation and separation of bromine from selenium,

$A_2(t)$ = counting rate of 31.7-minute $Br^{84}$ at time $t$,

$\lambda_1$ = decay constant of 3.3-minute $Se^{84}$,

$\lambda_2$ = decay constant of 31.7-minute $Br^{84}$,

$F$ = total number of fissions,

$\epsilon$ = counting efficiency of $Br^{84} = \frac{\text{cts./min.}}{\text{dis./min.}}$,

and

$Y_2$ = fission yield of the 31.7-minute $Br^{84}$.

6) The number of fissions which had taken place in the irradiated uranium was obtained by radiochemical analysis of $Mo^{99}$, the standard

nuclide used for fission determination in this laboratory.* The $Mo^{99}$ calibration factor had been established previously by a number of careful measurements of the $Mo^{99}$ separated from samples of enriched $U^{235}$ in which known numbers of fissions had occurred. The calibration factor is ordinarily expressed as a "K-factor", the ratio of the number of fissions to the counts per minute of $Mo^{99}$, corrected for radiochemical yield and for decay during and after irradiation.

Two fission-yield runs were made, with all conditions as nearly identical as possible. In each case, 50 mg. of uranium metal (93% $U^{235}$) was wrapped in aluminum foil and irradiated in the rabbit port of the Water Boiler for 5 minutes at a power level of 60 watts. The relatively large pieces of uranium and the aluminum wrappers were chosen to minimize any loss of fission fragments by recoil out of the sample. For convenience in operation, the duration of irradiation was set at 5 minutes; under these experimental conditions it was necessary that the pile be run at 60 watts to produce a convenient quantity of $Br^{84}$. For each sample the uranium and its wrapper were dissolved together to insure recovery of all fission fragments. The experimental data are summarized in Table IV-7.

It will be noted that the two determinations agreed within less than 2.5 per cent. The accuracy was more difficult to estimate. The $Mo^{99}$ fission determination should have been accurate to ± 3 per cent; the limits of error

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*The author is indebted to Mr. C. J. Orth for the $Mo^{99}$ analysis and to Mr. J. S. Gilmore, Mr. E. J. Lang and Mr. G. W. Knobeloch for the calibration factor determinations.

applicable to the $Br^{84}$ determination are perhaps 2 or 3 fold larger. The over-all accuracy of the fission yield determination was estimated to be ± 10 per cent. Thus, the $U^{235}$ thermal fission yield of 31.7-minute $Br^{84}$ may be cited as 0.9 ± .09 per cent.

Table IV-7

Summary of Fission Yield Calculations for 31.7-Minute $Br^{84}$

| | Sample No. 1 | Sample No. 2 |
|---|---|---|
| Duration of bombardment (T) | 5 min. | 5 min. |
| Time of separation (t) | 24 min. | 26 min. |
| $Br^{84}$ activity at t, shelf 3, 444 mg./cm.$^2$ Al absorber | $1.07_0\times10^5$ cts/min. | $1.02_9\times10^5$ cts/min. |
| $Br^{84}$ activity at t, computed to shelf 1, zero absorber | $5.84_5\times10^5$ cts/min. | $3.62_3\times10^5$ cts/min. |
| $Br^{84}$ activity corrected for chemical yield | $7.77_0\times10^5$ cts/min. | $7.45_3\times10^5$ cts/min. |
| $\left[\frac{\lambda_2}{\lambda_2-\lambda_1}(1-e^{-\lambda_1 T})e^{-\lambda_1 t} + \frac{\lambda_1}{\lambda_1-\lambda_2}(1-e^{-\lambda_2 T})e^{-\lambda_2 t}\right]$ | 0.0680 | 0.0653 |
| $Br^{84}$ counting efficiency ($\epsilon$) | $0.491_5$ | $0.491_5$ |
| Number of fissions | $1.310\times10^{10}$ | $1.277\times10^{10}$ |
| Fission yield | 0.887% | 0.909% |
| | Average Fission Yield: | 0.898% |

The measurement of the fission yield of the 6.0-minute isomer of $Br^{84}$ was carried out in generally the same manner. However, the low yield of this isomer, its short half-life, and the impossibility of measuring it in fission-product bromine by beta counting necessitated a number of modifications in the procedure used for the 31.7-minute isomer. In addition to the obvious modifications associated with speeding up the chemical separation and counting schedule, a somewhat involved system of counting calibrations was employed to convert the gamma counts observed to the (hypothetical) beta counts needed.

One aspect of the experimental analysis, the part of the calculations dealing with rate of formation and decay of the 6.0-minute $Br^{84}$, was relatively simple. In the experiments concerned with the origin of the 6.0-minute $Br^{84}$, it had been established that little, if any, of this isomer was produced via decay of $Se^{84}$. For the purposes of the fission-yield work, it was assumed that 6.0-minute $Br^{84}$ was formed directly in fission.

The determination of the fission yield of the 6.0-minute $Br^{84}$ was then carried out by the following sequence of steps:

1) A sample of uranium metal (93% $U^{235}$) wrapped in aluminum was irradiated in the Water Boiler for 15 seconds and dissolved in hydrochloric acid containing known weights of bromide and molybdenum carrier.

2) The bromine was distilled from the solution and the non-volatile residue was set aside for analysis of $Mo^{99}$. The radiochemical analyses for bromine and molybdenum followed the procedures described on pages 38 and 40 respectively.

3) The bromine sample was purified and mounted, and its gamma spectrum was measured on a scintillation spectrometer employing a 2" x 2" NaI(Tl) crystal. The times of the beginning and end of the measurement were accurately known. The resultant spectrum, representing a composite of the spectra of the 6.0-minute and 31.7-minute activities, was plotted on linear scale graph paper, and the area of 0.44-Mev photopeak was measured and converted to total counts. The 0.44-Mev photopeak, which occurs in the spectrum of the 6.0-minute $Br^{84}$ only, was taken as a measure of this isomer.

4) The 0.44-Mev photopeak was calibrated in terms of beta activity of the 6.0-minute isomer by another set of measurements on a sample of the $Br^{84}$ isomeric mixture produced by the $Rb^{87}(n,\alpha)Br^{84}$ reaction. A rubidium nitrate (89.62% $Rb^{87}$) target was irradiated with fast neutrons at the Cockcroft-Walton accelerator and the bromine was separated and divided into two approximately equal portions. One portion was measured on the same apparatus used for the 6.0-minute $Br^{84}$ of fission origin; simultaneously, the other portion was counted in the standard first-shelf position of a beta proportional counter. The precise ratio of the amounts of active bromine in the two portions was established later by beta counting the 31.7-minute component. Comparison of the beta count with the area of the 0.44-Mev photopeak of the gamma count provided a calibration constant by means of which the equivalent beta count of the 6.0-minute component of the fission product source could be computed. The latter datum, expressed in counts per minute, was transformed into disintegrations per minute by application of a beta-counting efficiency calculated from the Prestwood-

Bayhurst function and the previously measured beta spectrum (cf. page 83).

5) The number of fissions that had occurred in the irradiated uranium was obtained, as before, by radiochemical analysis of $Mo^{99}$.

Two fission-yield runs were made with all important parameters kept as nearly identical as possible. In the first run 5.9 mg. of 5-mil uranium (93% $U^{235}$) foil was used and in the second run 2.9 mg. of 2-mil uranium (93% $U^{235}$) foil was used. Each was wrapped in aluminum foil and irradiated for 15 seconds in the rabbit port of the Water Boiler at a power level of 25 K.W. The size of the foils and the length of irradiation were deliberately chosen to minimize the total elapsed time between formation of the bromine and its distillation from the fission-product mixture. In particular, because the major part of the 31.7-minute isomer was presumed to come from decay of 3.3-minute $Se^{84}$, rapid removal of bromine from the fission product mixture tended to favor the 6.0-minute isomer. Also, with the duration of the irradiation chosen as 15 seconds, the correction for decay during irradiation was insignificant and could be neglected.

The pertinent mathematical expression which describes the formation and decay of a single radioactive species formed directly in fission is:

$$A(t) = \epsilon \; F \; Y \; e^{-\lambda t} \lambda \qquad \text{(IV-3)}$$

where t is the time elapsed between formation and counting of the fission product, and the other symbols have their usual meaning.

The experimental data are summarized in Table IV-8. It will be noted that the precision was quite satisfactory; the results of the two runs agree to about 4 per cent. As is usual in measurements of this kind, the accuracy is much more difficult to assess. The sequence of operations involved in arriving at a hypothetical "beta count" for the fission-produced 6.0-minute $Br^{84}$ introduced a number of sources of error which did not occur in the measurement of the fission yield of the 31.7-minute isomer. The first such source of error was the large correction for dead-time loss in gamma measurement, 18 per cent in the first run and 14 per cent in the second run. A second and more subtle source of error arose from the element of arbitrariness involved in defining the area of the 0.44-Mev photopeaks, both in the fission product $Br^{84}$ spectrum and in the $(n,\alpha)$-produced $Br^{84}$ spectrum used in the establishment of a gamma/beta calibration factor. A consideration of these and the normal errors associated with this type of experiment led to the assignment of an estimated over-all error of ± 20 per cent. Thus, the $U^{235}$ thermal fission yield of the 6.0-minute isomer of $Br^{84}$ may be cited as 0.019 ± .004 per cent.

Table IV-8

Summary of Fission Yield Calculations for 6.0-Minute $Br^{84}$

| | Sample No. 1 | Sample No. 2 |
|---|---|---|
| Duration of bombardment (T) | 15 sec. | 15 sec. |
| Time elapsed between formation and counting (t) | 18.75 min. | 15.5 min. |
| Area of 0.44-Mev photopeak at t = 0 | $545_4$ cts./min. | $490_5$ cts./min. |
| Photopeak area corrected for dead-time loss | $643_5$ cts./min. | 5592 cts./min. |
| Photopeak area corrected to 100% chemical yield | $4.92_3 x 10^4$ cts./min. | $2.70_0 x 10^4$ cts./min. |
| $Br^{84}$ activity computed to shelf 1, beta counter (beta cts./min = photopeak area x 7.83) | $3.85_4 x 10^5$ cts./min. | $2.11_4 x 10^5$ cts./min. |
| $Br^{84}$ counting efficiency ($\epsilon$) | 0.468 | 0.468 |
| $Br^{84}$ disintegration rate | $8.23_8 x 10^5$ dis./min. | $4.51_7 x 10^5$ dis./min. |
| $Br^{84}$ atoms ($\lambda$ = 0.1147/min.) | $7.18 \times 10^6$ | $3.94 \times 10^6$ |
| Number of fissions (from $Mo^{99}$) | $3.78 \times 10^{10}$ | $1.99 \times 10^{10}$ |
| Fission Yield | 0.0190% | 0.0198% |

Average fission yield 0.0194%

# CHAPTER V

## SUMMARY

The primary aim of the present investigation was the radiochemical exploration of the short-lived fission-product isotopes of bromine and selenium. The experimental results may be expressed in five categories:

1) Three new nuclear species were found: $Se^{85}$, $Se^{87}$, and an isomer of $Br^{84}$. In addition, a definite half-life value was obtained for $Se^{84}$, for which only an estimated half-life had been reported previously.

2) The gamma and beta radiations of the new $Br^{84}$ isomer were measured, and some information was obtained concerning its relationship to the other isomer and its mode of formation in fission.

3) The $U^{235}$ thermal fission yields of the isomers of $Br^{84}$ were measured.

4) The isotope $Br^{86}$ could not be definitaly identified.

5) A lower limit was estimated for the half-life of a beta-emitting isomer, if it exists, of $Br^{82}$.

In the course of this investigation a number of new techniques were developed for the chemical separation of short-lived bromine and selenium fission products and the measurement of their properties.

The experimental results are summarized in Tables V-1 and V-2. The assignments of the 31.7-minute and 6.0-minute activities as isomers of $Br^{84}$ was considered to be definitely established by the fast-neutron experiments with $Rb^{87}$ in varying degrees of enrichment. It will be recalled that shell model considerations (cf. page 22) applied to the $Br^{84}$ nucleus suggested that isomerism was possible, and that if isomerism did exist the most probable spins and parities of the two levels were 2- and 6-. The 6.0-minute activity can be assigned as the high-spin member. Three pieces of evidence support this conclusion: 1) the $Se^{84}$, presumed to have zero spin, decays to the 31.7-minute level and not to the 6.0-minute level; 2) according to Johnson and O'Kelley,[37] 25 per cent of the beta-decays of the 31.7-minute $Br^{84}$ proceed directly to the ground state of $Kr^{84}$, also presumed to have zero spin; 3) the 6.0-minute isomer has at least three high-abundance gamma rays in combination with a relatively low-energy beta spectrum. As expected, the two isomers have some gamma rays in common. The high gamma/beta ratio (about 0.7) applicable to the gamma rays of energy 0.44, 0.88, and 1.46 Mev suggests that these three gamma rays occur in cascade following the 1.9-Mev beta transition.

The choice as to which isomer is the ground state of $Br^{84}$ cannot be settled on the basis of the information available. Only one fragment of evidence exists. The 6.0-minute isomer was not observed to grow from the 31.7-minute isomer in the hot-atom experiment, which by itself tends to favor the 31.7-minute isomer as the ground state.

The sum of the fission yields of the two $Br^{84}$ isomers amounted to 0.92 ± 0.09 per cent; at almost the outer limit of the estimated experimental error, this value is consistent with the fission yield reported for $Kr^{84}$.

Table V-1

Nuclear Properties of 6.0-Minute $Br^{84}$

| Half-life | Gamma Energy (Mev) | $\frac{\text{Gammas}}{\text{Betas}}$ | Beta Energy (Mev) and Abundance | Comments |
|---|---|---|---|---|
| 6.0 ± 0.2 min. | 0.44 ± 0.01 | 0.68 | 0.8 ± 0.1 (20%) | 1. Little, if any, produced by decay of $Se^{84}$. |
| | 0.88 ± 0.01 | 0.75 | 1.9 ± 0.2 (72%) | |
| | 1.46 ± 0.02 | 0.75 | 3.2 (~ 8%) | 2. Believed to be high-spin member of isomeric pair. |
| | 1.9 ± 0.03 | 0.16 | | |

Yields of $Br^{84}$ Isomers from Thermal Fission of $U^{235}$

| Nuclide | Fission Yield | Total Fission Yield of $Br^{84}$ |
|---|---|---|
| 6.0-minute $Br^{84}$ | 0.019 ± 0.004% | 0.92 ± 0.09% |
| 31.7-minute $Br^{84}$ | 0.90 ± 0.09% | |

Table V-2

Half-lives of Fission-product Selenium Isotopes

| Isotope | Method of Bromine Extraction | Half-life Reported | Half-life Measured this Investigation | Half-life Recommended |
|---|---|---|---|---|
| $Se^{83}$ | Carbon Tetrachloride | 25 ± 1 min. | 24.8 min. | 24.2 ± 1.5 min. |
| | Silver bromide | | 22.9 min. | |
| | Resin column plus silver bromide | | 25 min. | |
| $Se^{84}$ | Carbon Tetrachloride | approx. 2 min. | 3.1 min. | 3.3 ± 0.2 min. |
| | Silver bromide | | 3.5 min. | |
| $Se^{85}$ | Carbon Tetrachloride | none | 35 sec. | 39 ± 4 sec. |
| | Silver bromide | | 39 sec. | |
| | Silver bromide from hot and cold solutions | | 43 sec. | |
| $Se^{87}$ | Resin column plus silver bromide | none | 17 sec. | 17 ± 3 sec. |

It is interesting that the $Br^{84}$-$Kr^{84}$ fission-yield discrepancy which was responsible in part for the present investigation would have been still greater if the original researcher had been aware of the 3.3-minute $Se^{84}$ predecessor.

The results of the $Se^{83}$, $Se^{84}$, and $Se^{85}$ half-life experiments show that the silver bromide technique for milking bromine gave half-lives in agreement with those from the carbon tetrachloride extraction. Inasmuch as the carbon tetrachloride method should be reasonably fool-proof, the agreement may be considered a demonstration of the quantitative validity of the silver bromide method. Hence, the half-life of $Se^{87}$, determined only by the latter, is probably valid within the limits of error indicated.

The half-life established for $Se^{84}$ in the present work showed that the original rough value obtained by Plutonium Project workers was at least in the correct range. The close agreement between the estimated half-life (45 seconds) and the observed half-life (39 ± 4 seconds) for $Se^{85}$ is noteworthy but probably fortuitous; the estimated half-life for $Se^{87}$ was in error by almost a factor of two (30 seconds predicted, 17 ± 3 seconds observed). Nevertheless, when it is born in mind that the latter "prediction" extended the semi-theoretical technique beyond its elastic limit, a significant observation still remains: even in cases where there exists no prior experimental information on nuclei of interest, the semi-empirical mass formulas and the nuclear shell model may be employed, in combination with analogies drawn from known nuclei of similar shell structure, to provide the radiochemist with an effective guide in his search for new nuclei.

# CHAPTER VI

# SUGGESTIONS FOR FUTURE RESEARCH

The present work emphasized several areas of interest which are worthy of further investigation. Some of the problems posed are of an intensive character, e.g., the detailed study of the radiations and decay schemes of nuclides already known; another group of problems, extensive in character, involves the extension of the techniques of this work to the exploration of other short-lived isotopes.

One of the most immediate problems in the first category is the establishment of the energetic and genetic relationship between the two isomers of $Br^{84}$. Attempts to milk the 6.0-minute isomer from the 31.7-minute isomer by a Szilard-Chalmers experiment gave negative results. The inverse experiment could be performed with a modification of the same procedure, carried out at greater speed. Discovery that the 31.7-minute isomer grows from the 6.0-minute isomer would establish the latter as the higher energy state. The converse is not true; the failure to find this mode of growth could mean either that the isomeric transition from the 6.0-minute state is not highly converted or that it constitutes only a very small fraction of the decays, i.e., that the decay of the 6.0-minute isomer proceeds predominately by beta emission. The same impediments, of course, could be responsible for the failure to find the 6.0-minute activity growing from the 31.7-minute activity. In any case, if no isomeric transition can be observed it may be extremely difficult to establish which of the isomers is the higher energy level.

Whether or not the isomeric relationship is established, the beta and gamma radiations of the 6.0-minute isomer, and of the 31.7-minute isomer as well, need to be examined in more detail with the ultimate object of formulating a decay scheme for both. In view of the short half-lives and the probable complexity of decay of both, such a study is a major enterprise.

The present experiments in this direction have been handicapped by low source intensity. Before the work can be pursued any further it is necessary to have sources at least 100-fold stronger. Such sources might be brought within reach either by fast-neutron irradiations of rubidium with Be-D neutrons at a cyclotron or by pile irradiations of a large sample of uranium with very rapid removal of bromine before much of the 3.3-minute $Se^{84}$ had decayed.

Perhaps the first extensive problem in need of attack is that of the still-unidentified $Br^{86}$. Here the radiochemical techniques already developed should be adequate. Granting the availability of adequate instrumentation near the pile, the gamma spectrum of the 1-minute bromine activity could be examined further along the lines initiated in the present work. Rapid gamma spectra could be taken as a function of time, and comparisons could be made between the 1-minute activity separated directly from fission products and that separated from a selenium predecessor. In addition, efficient neutron counting of the 1-minute activity proceeding from the 17-second selenium parent would establish whether or not the activity is $Br^{87}$.

The half-lives of the selenium isotopes of mass number greater than 87 might be measured by rapid separation of selenium from fission products, followed by "milking" (by gas-sweeping experiments) the granddaughters (Krypton) rather than the daughters (bromine).

An obvious extension of the silver bromide milking technique is the possible identification of some of the short-lived fission product iodine isotopes and their tellurium parents.

As may be seen by the examples selected in the preceding paragraphs, combinations of relatively simple chemical operations, with the accent on speed and with the guidance of nuclear shell considerations, may be used to seek out many of the short-lived fission-product nuclides presently unknown. Indeed, in few areas of present-day radiochemical interest are improvements in experimental technique more needed and more likely to be rewarded by discovery.

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