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Short-Lived Isomeric States of Se^{83} and Ge^{77}

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Extractions of Br from neutron irradiated SeO_3^{2-} solutions and of As from irradiated GeS_3^{2-} solutions revealed the presence of short-lived isotopes of Se^{83} and Ge^{77} decaying by β^- -emission to 2.4-hr. Br^{83} and 40-hr. As^{77} , respectively. Direct observation of the radiations from a short-lived Se, effected by measuring the activity of Se irradiated for 20 sec. through Al absorbers, led to a half-life determination of 67 ± 3 sec. and a β -energy of 3.4 Mev. A γ -ray was also observed. Similarly, a short-lived Ge activity was found by irradiating GeS_2 with neutrons for 20 sec. and measuring the activity through Al absorbers. The half-life was determined to be 59 ± 2 sec. and the β -energy, 2.8 Mev. The agreement between the cross sections for formation of the

67-sec. Se and the 2.4-hr. Br^{83} from the short-lived Se^{83} makes it probable that the 67-sec. Se is genetically related to the 2.4-hr. Br^{83} . In a like manner it was shown that the 59-sec. Ge is probably identical with the short-lived Ge^{77} .

The presence of the 67-sec. Se^{83} activity decaying by β^- -emission to 2.4-hr. Br^{83} and the 59-sec. Ge^{77} activity decaying to 40-hr. As^{77} resolves the difficulty of the apparently high "independent" yields of Br^{83} and As^{77} in fission.

A new Se activity of 17.5 ± 0.3 sec. half-life was also found. It appears to decay by emission of γ -radiation of ~ 150 Kev. The cross section for formation of this activity by neutron activation of Se is ~ 0.6 barn.

1. INTRODUCTION

THE status of the problem of the distribution of the fission products as a function of mass number is considerably more advanced than that of an allied problem, the distribution in nuclear charge for the primary fission products of a given mass. The publication of the Plutonium Project *Table of Nuclei Formed in Fission*¹ summarizes the yield data of the fission products of U^{235} . Among the data given are the fission yields of the three "shielded nuclei," i.e. radioactive nuclei having isobaric stable nuclei of lower charge, Br^{82} , Rb^{86} , and Cs^{136} , which bear on the charge-distribution problem. Glendenin, Coryell, and Edwards² have summarized the data presently available and discussed them in terms of several possible theories. They found that the experimentally determined fractional yields of particular chain members (especially the "shielded nuclei") lay on a smooth curve of yield *versus* charge displacement from the most probable charge. For a given mass, the most probable charge was found by assuming equal charge displacements of the primary fragments of complementary chains from the stability

curve of nuclei. More recently Present³ examined the problem theoretically on the basis of a non-uniform charge distribution in the nucleus and found that the experimental data on independent fractional yields approximated a smooth (error) curve when plotted with the aid of the theoretical results.

From a consideration of the ratio of neutrons to protons for nuclei in the heavy and intermediate mass regions, it is clear that the average fission fragment will be several charges removed from stability, that is, it will emit several successive β^- -particles before becoming a stable nucleus. Moreover, from the very low yields of the "shielded nuclei," it may be inferred that the distribution of nuclear charge for a given mass number must fall off sharply from the maximum value, at least on the high charge side. It may be concluded then, that direct formation of a large fraction of the chain yield on a nucleus near stability is likely to be uncommon. Two apparent discrepancies have been found, however; namely 40-hr. As^{77} ^{1,4} and 2.4-hr. Br^{83} .^{1,5} In each of these cases the fission yield of

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¹ Issued by the Plutonium Project, J. Am. Chem. Soc. **68**, 2411 (1946); Rev. Mod. Phys. **18**, 441 (1946).

² L. E. Glendenin, C. D. Coryell, and R. R. Edwards, Clinton Laboratory Memo CL-LEG No. 1, July 25, 1946.

³ R. D. Present, Clinton Laboratory unclassified report Mon P-235, January 13, 1947 (recently published in Phys. Rev. **72**, 7 (1947)).

⁴ E. P. Steinberg and D. W. Engelkemeir, Metallurgical Laboratory Report, CC-2310, January 1, 1945; Plutonium Project Record Vol. 9B, 7.2.1 (1946).

⁵ L. E. Glendenin, Clinton Laboratory Reports CN-2839, June, 1945, Mon N-15, September, 1945; Plutonium Project Record Vol. 9B, 7.3.1 (1946).

the nucleus was found to be considerably higher than that of its immediate precursor, 12-hr. Ge^{77} and 25-min. Se^{83} , respectively. A possible interpretation might be that these two nuclei are formed in relatively high yields as primary fission fragments.

However, since such a conclusion conflicts with the simple considerations given above, Glendenin and co-workers² proposed the following possible mechanism to account for the observed yields. They suggested that Ge^{77} and Se^{83} have short-lived isomeric states, which decay by β^- -emission to As^{77} and Br^{83} , and that these isomeric states are formed in relatively high yield in fission, thus leading to a high yield of apparently "independently" formed As^{77} and Br^{83} . They suggested also that the ~ 1 -min. Se activity found in neutron irradiated Se by Edwards⁶ might possibly be the short-lived isomeric state of Se^{83} . It was the purpose of the present work to find evidence for short-lived states of Se^{83} and Ge^{77} , decaying by β^- -emission to 2.4-hr. Br^{83} and 40-hr. As^{77} , respectively, and if possible to determine their half-lives and energy characteristics.

2. NEUTRON IRRADIATIONS OF Se

2.1. Irradiations of $\text{SeO}_3^{=}$ Solutions and Br Extractions

Selenium was bombarded in the Argonne heavy water pile, and Br^{83} was looked for as soon as possible after bombardment. Since Br^{83} cannot be formed directly from Se by neutron bombardment, Br^{83} found very soon after bombardment must come either from 25-min. Se^{83} , or a short-lived isomeric state of Se^{83} . The amount of Br^{83} growing from the 25-min. Se^{83} can be determined and corrected for. The remainder then represents the yield of a short-lived state, and demonstrates the existence of this state.

The experiments were carried out in the following manner. A solution of Se in the form of $\text{SeO}_3^{=}$ (pH about 4) was irradiated for two minutes in the pneumatic tube of the pile. To an aliquot of the irradiated solution, 2 ml of standardized BrO_3^- carrier (~ 10 -mg Br/ml) was

added, and Br separated by the tested method of Edwards, Gest, and Davies,⁷ with slight modifications. The first step is the reduction of BrO_3^- to Br^- with H_2S for two minutes to insure complete exchange between the carrier and radio-Br. The solution is then filtered to remove precipitated Se and sulfides, and poured into a separatory funnel containing 25-ml CCl_4 and an excess of KMnO_4 solution in 5N HNO_3 to oxidize the Br^- to Br_2 , which is extracted into the CCl_4 layer. The H_2S reduction was begun about one and one-half minutes after the end of the irradiation and the total time elapsed to the completion of the extraction was usually four minutes. Thus the uncertainty in the time of isolation of the Br^{83} from Se is short compared to the half-life of the 25-min. state. The time of Br isolation was somewhat arbitrarily taken to be the end of the H_2S reduction—normally three minutes after the end of irradiation.

In order to show that the conditions under which this procedure was tested for radiochemical exchange held in this system, namely, that BrO_3^- was still present at the time of the H_2S reduction, it seemed important to show that $\text{SeO}_3^{=}$ itself does not reduce BrO_3^- rapidly and completely in the solution of pH 4 used; (it has been shown not to do so in neutral solution⁷). To this end, 2-ml BrO_3^- carrier was added to 5-ml stock $\text{SeO}_3^{=}$ solution, and allowed to stand for five minutes. The solution was then oxidized with KMnO_4 , as above. Considerable Br_2 appeared, indicating appreciable reduction by $\text{SeO}_3^{=}$. The aqueous solution was then completely reduced with NaHSO_3 , and reoxidized with KMnO_4 . Again a large quantity of Br_2 was found, showing that the reduction is not complete in five minutes. Since the BrO_3^- and $\text{SeO}_3^{=}$ solutions are in contact only a few seconds before the H_2S reduction begins, it seems safe to assume complete exchange of radio-Br with BrO_3^- in this procedure.

After discarding the aqueous phase, the CCl_4 layer containing Br_2 is extracted with 20 ml of water containing six drops of 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$. The CCl_4 phase is discarded, and HNO_3 and KMnO_4 added to the aqueous phase to reoxidize

⁶ R. R. Edwards, unpublished work reported in Clinton Laboratory Memo CL-LEG No. 1, July 25, 1946.

⁷ R. R. Edwards, H. Gest, and T. H. Davies, Clinton Laboratory Report CC-3390, July, 1946; Plutonium Project Record Vol. 9B, 3.3.5 (1946).

the Br⁻ to Br₂, which is extracted with CCl₄. The CCl₄ phase is then treated with 20 ml of water containing six drops of 1M NaHSO₃, and discarded. The aqueous phase is acidified with HNO₃, and boiled to remove HSO₃⁻ ion. The solution is cooled, and AgNO₃ solution added to precipitate AgBr. The precipitate is filtered on a weighed filter disk, washed with water, alcohol, and ether, and finally dried, weighed, and mounted.

The counting was done with a standard Eck and Krebs argon-ethanol Geiger-Müller tube and a Columbia-type scaler. The tube had an estimated wall thickness of about 30 mg/cm².

To determine the active Br growing from the 25-min. Se, the following procedure was employed. An aliquot of the irradiated solution was boiled with about 20 ml of 6N HCl to reduce any radio-Se in higher valence states to SeO₃⁼.⁸ Metallic Se was precipitated by passing SO₂ through the cold solution for 70 sec. The Se was collected on a coarse sintered glass funnel. This removed the bulk, but not all, of the Br⁸³ activity. A second cycle was therefore necessary, the Se being redissolved in cold, concentrated HNO₃. The solution was boiled down to remove HNO₃ and finally made up to 6N HCl. The Se was again precipitated, filtered, and redissolved, after which the solution was carefully neutralized with NH₄OH. The Se separations were performed at a time sufficiently long after the end of the irradiation to insure complete decay of the short-lived Se⁸³. Any Br now present in the separated Se solution must have grown from the 25-min. Se⁸³ present at the time of the second Se isolation. After about two hours' decay of the Se⁸³, BrO₃⁻ carrier was added and the procedure for Br isolation was performed.

In this procedure both Se precipitations must be quantitative. In practice it proved difficult to ascertain this and also to free the Se completely of Br⁸³ even by two precipitations, so that the activity of Br⁸³ formed from the 25-min. Se⁸³ was determined only approximately. Samples of Se separated long after the end of irradiation yielded Br activity far in excess of that which should have grown from the 25-min. Se as determined from earlier Se separations. This

excess Br is probably contamination introduced from the initial solution because of the relatively greater activity of Br in the stock solution compared to that which grows from 25-min. Se samples separated after a few half-lives' decay.

After a number of preliminary experiments, consistent results were obtained in Br extraction studies. Four such experiments are reported in Table I. The Br samples isolated from the irradiated Se stock solution at a time t_{Br} from the end of the irradiation are listed as Br-1, Br-2, etc., whereas the Br samples isolated at a time t_{Br} from the Se samples, previously purified from

TABLE I. Br⁸³ activity from neutron-irradiated Se solutions.

Experiment	Sample	t_{Se}	t_{Br}	Activity Br ⁸³ (c/m) at an arbitrary time (normalized for yield and volume of solution)	A_{Se}^{∞} (c/m)	A_{Se*}^{∞} (c/m)
1	Se-1 Br	49	176	480	5.78×10^6	—
	Se-2 Br	99	220	208	8.05×10^6	—
	Br-1	—	3	5680	(3×10^6)	2.52×10^6
	Br-2	—	10	6960	(3×10^6)	3.06×10^6
	Br-3	—	18	7680	(3×10^6)	3.35×10^6
	Br-4	—	133	7860	(3×10^6)	3.19×10^6
	Se-1 Br	61	225	178	2.84×10^6	—
	Se-2 Br	111	234	24.2	1.27×10^6	—
2	Se-3 Br	206	320	56.4	2.88×10^6	—
	Br-1	—	3	3650	(2×10^6)	1.64×10^6
	Br-2	—	9	4720	(2×10^6)	2.10×10^6
	Br-3	—	14	4480	(2×10^6)	1.98×10^6
	Br-4	—	185	5320	(2×10^6)	2.19×10^6
	Se-1 Br	53	216	100	1.59×10^6	—
	Se-2 Br	154	311	46.8	7.55×10^6	—
	Br-1	—	3	2870	(2.1×10^6)	1.59×10^6
3	Br-2	—	9	3820	(2.1×10^6)	2.09×10^6
	Br-3	—	15	4010	(2.1×10^6)	2.16×10^6
	Br-4	—	65	4260	(2.1×10^6)	2.18×10^6
	Br-5	—	208	4180	(2.1×10^6)	2.09×10^6
	Se-1 Br	86	230	170	5.8×10^6	—
	Se-2 Br	126	240	215	1.79×10^6	—
	Br-1	—	172	12580	(6×10^6)	6.26×10^6
	Br-2	—	178	12590	(6×10^6)	6.27×10^6
4	Br-3	—	184	12200	(6×10^6)	6.07×10^6

A_{Se}^{∞} = Saturation activity of Br⁸³ from 25-min. Se⁸³. Values in parentheses were assumed for A_{Se*}^{∞} calculations.
 A_{Se*}^{∞} = Saturation activity of Br⁸³ from short-lived Se⁸³ (assuming a half-life short compared to ~30 sec.).
 t_{Se} = Time (min.) elapsed from end of irradiation to purification of Se.
 t_{Br} = Time (min.) elapsed from end of irradiation to isolation of Br.

⁸ C. W. Stanley, Plutonium Project Record Vol. 9B, 3.3.1 (1946).

the Se stock solution at a time t_{Se} , are listed as Se-1 Br, Se-2 Br, etc.

The equation relating the value of A_{Br} , the activity of Br isolated from Se (Se-Br samples) and measured at arbitrary counting time t_c normalized for chemical yield and aliquot volume, to A_{Se}^∞ , the saturation value of activity of 25-min. Se^{83} , is:

$$A_{Br} = A_{Se}^\infty (1 - e^{-\lambda_1 T}) (\lambda_2 / [\lambda_1 - \lambda_2]) \times [e^{-\lambda_2(t_{Br} - t_{Se})} - e^{-\lambda_1(t_{Br} - t_{Se})}] \times e^{-\lambda_1 t_{Se}} e^{-\lambda_2(t_c - t_{Br})}, \quad (1)$$

where λ_1 is the decay constant of Se^{83} (0.0277 min.⁻¹), λ_2 is the decay constant of Br^{83} (0.00481 min.⁻¹), T is the time of irradiation (2 min.), and the end of irradiation is the reference point for the measurement of time of purification of Se (t_{Se}), of time of isolation of Br (t_{Br}), and of counting (t_c). From the trend of values of A_{Se}^∞ and knowledge of comparisons between the irradiations, the selected values of A_{Se}^∞ , given in parentheses in Table I, were chosen for the various experiments on gross yield of Br^{83} to aid in the estimation of A_{Se}^∞ , the saturation activity of short-lived Se^{83} , under the assumption that the half-life of this species is less than 30 sec. The values of A'_{Br} , the activity of Br separated from the Se stock solution (Br samples) are

given as:

$$A'_{Br} = A_{Se}^\infty (1 - e^{-\lambda_1 T}) (\lambda_2 / [\lambda_1 - \lambda_2]) \times (e^{-\lambda_2 t_{Br}} - e^{-\lambda_1 t_{Br}}) e^{-\lambda_2(t_c - t_{Br})} + A_{Se}^\infty (1 - e^{-\lambda_2 T}) e^{-\lambda_2 t_c}. \quad (2)$$

Since the four experiments in Table I were carried out under different bombarding conditions, the saturation activities are expected to be different.

The results of Table I, showing the high activity of 2.4-hr. Br^{83} grown from the short-lived Se^{83} compared to that grown from the 25-min. Se^{83} , establish the existence of a short-lived isomeric state of Se^{83} , which is formed by neutron capture from Se^{82} . The cross section is roughly tenfold higher than that of the 25-min. state, and the nucleus decays by β^- -emission to the 2.4-hr. Br. This is evident from the lack of substantial growth of activity in the Br samples separated at varying times from the end of irradiation (Table I).

The values obtained for the saturation activity of the 25-min. Se (A_{Se}^∞ , Table I) were erratic because of the combination of causes discussed above. However, the uncertainty introduced by this into the much larger cross section of the short-lived state is small. This may easily be seen from the high degree of internal consistency of the Br samples taken after more than five minutes. The differences here are well within an experimental error of ~ 5 percent.

The first sample, isolated after three minutes, shows a value of A_{Se}^∞ about 20 percent lower than the average of the later samples in each irradiation where such a sample was taken. This shows that the short-lived nucleus has a half-life which is not negligibly short compared to ~ 30 seconds as was assumed in the calculations, and in fact after ~ 3 minutes decay not all of the Br has been formed from the short-lived state. The estimate for the half-life from these extraction experiments is about 1 to 1.5 minutes.

2.2. Irradiations of Se Metal. Identification of the Short-lived State of Se^{83}

Irradiations of spectroscopically pure Se metal were performed in a search for the short-lived state of Se^{83} . After twenty-second irradiations, Se samples were counted through varying thicknesses of Al absorber and a period of ~ 1 min.

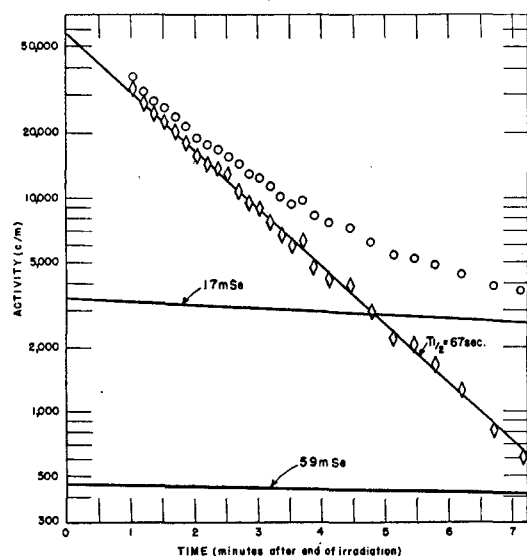


FIG. 1. Decay curve of Se metal irradiated for 20 seconds. Counted through 511-mg Al/cm² added absorber. ○ original points. ◇ subtracted curve, activities of 17-min. Se and 59-min. Se determined from later part of curve.

half-life appeared as the absorber thickness was increased. This activity is probably identical with that found by Edwards⁶ in Se irradiation experiments. The activity of the ~ 1 -min. Se increased relative to that of the 17-min. Se⁸¹ as the absorber thickness increased, an optimum value being reached at ~ 600 mg Al/cm². The half-life was determined by counting samples through Al of about the optimum absorber thickness; the value so determined was 67 ± 3 sec. A typical decay curve of the 67-sec. Se is given in Fig. 1. The absorption characteristics of the 67-sec. Se were determined by following the decay of irradiated Se samples through varying thicknesses of Al and normalizing the irradiations by the intensity of the 17-min. component and its known absorption characteristics. With a value of 1.5 Mev for the 17-min. Se⁸¹ β -energy,^{1,5} the β -energy of the 67-sec. Se activity was found to be 3.4 Mev by a Feather comparison method⁹ in which the range of β -particles of one substance is determined in terms of that of another standard substance by a comparison of the absorption curves. The Al absorption curves of the 17-min. Se⁸¹ and the 67-sec. Se are given in Fig. 2. The γ -radiation of the 67-sec. Se was observed by measuring the activity through 2.05-g Pb/cm² and comparing with the relative 17-min. Se activity through this absorber. The value of the γ -component in Al in Fig. 2 was assumed to be the same as that found in Pb since corrections for the relative counting efficiencies of the γ -radiation in Al and Pb could not be made without knowledge of the energy of the γ -radiation.

The genetic relation of the 67-sec. Se to the 2.4-hr. Br formed from the short-lived state of Se was not proved by rapid extractions of Br from Se because of the time required for the Br extractions. The activity of the 67-sec. Se was shown, however, to be genetically consistent with the activity of the Br grown from the short-lived Se state when both activities were compared to that of the 17-min. Se⁸¹, used as a reference standard. In a 20-sec. irradiation the ratio of the activity at the end of the irradiation of the 67-sec. Se to that of the 17-min. Se was 0.31. The ratio of the saturated activities after

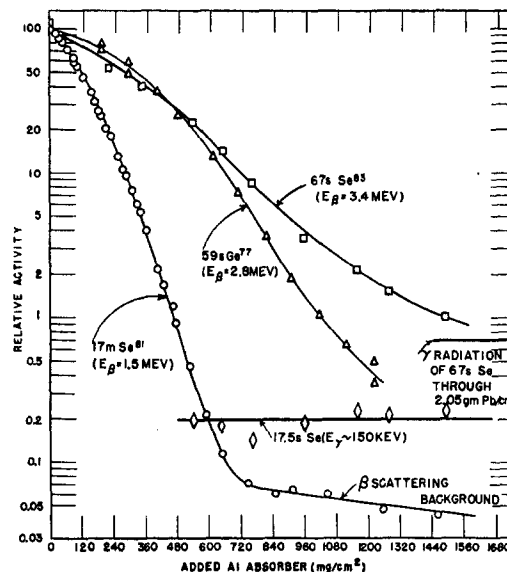


FIG. 2. Aluminum-absorption curves of 17.5-sec. Se, 67-sec. Se⁸³, 17-min. Se⁸¹, and 59-sec. Ge⁷⁷. Absorber thickness at zero added Al estimated at 35 mg/cm². \circ 17-min. Se⁸¹. \square 67-sec. Se⁸³. \diamond 17.5-sec. Se. \triangle 59-sec. Ge⁷⁷.

correcting for absorption was 0.020. The ratio of the activity of the 2.4-hr. Br grown from the short-lived Se to the 17-min. Se after a 2-min. irradiation was 0.0015, and after correcting for absorption the ratio of the saturated activities was 0.016. The agreement between these two ratios is strong evidence for the identity of the 67-sec. Se and the short-lived Se. Conclusive evidence for the mass assignment of 83 to the 2.4-hr. Br formed from the 67-sec. Se exists in the fact that the half-life and absorption characteristics of this Br activity are identical with those of the 2.4-hr. Br⁸³ grown from the 25-min. Se⁸³.

A comparison of the maximum possible decay energy of 3.14 Mev of the 25-min. Se⁸³, obtained by adding the β -energy of 1.5 Mev and the three γ -energies of 0.17, 0.37, and 1.1 Mev,^{1,5} with the decay energy of the 67-sec. Se of at least 3.4 Mev, since the γ -energy was not determined, leads to the assignment of the 67-sec. Se as an upper state of the 25-min. Se. The 67-sec. Se⁸³ decays by β^- -emission to the 2.4-hr. Br⁸³ and if isomeric decay occurs to the 25-min. Se, its probability is less than ~ 10 percent of the disintegrations since the ratio of the two states in neutron irradiation was found to be about 10 to 1.

⁹ N. Feather, Proc. Camb. Phil. Soc. **34**, 599 (1938).

2.3. Cross Section for Formation of the 25-min. Se^{83}

The neutron capture cross section of Se for the formation of the 25-min. Se^{83} as found by Seren, Friedlander, and Turkel¹⁰ was determined by measurement of the 2.4-hr. Br^{83} activity. Since it has now been shown that the bulk of the Br activity grows from the 67-sec. Se^{83} and not from the 25-min. Se^{83} , the cross section for formation of the 25-min. Se^{83} is about one-tenth of that reported, or ~ 0.0004 barn relative to a cross section for the 17-min. Se^{81} of 0.25 barn. The cross section for formation of the 67-sec. Se^{83} is 0.0043 barn in agreement with the value found by Seren *et al.* for the 2.4-hr. Br.

2.4. U^{235} Fission Yields of 25-min. Se^{83} and 2.4-hr. Br^{83}

The U^{235} fission yields of 25-min. Se^{83} and 2.4-hr. Br^{83} reported by Glendenin^{1,5} are 0.21 percent and 0.40 percent, respectively. The difference in yield of the 2.4-hr. Br and 25-min. Se of 0.19 percent can now be attributed to the yield of the 67-sec. Se^{83} . The fission yield of the 67-sec. Se relative to that of the 25-min. Se was redetermined by irradiation of UO_2Cl_2 and analysis for Se and total Br. Three Se samples were isolated 35 min., 75 min., and 108 min. after the end of the irradiation. The 2.4-hr. Br was allowed to grow into the Se and was counted. The average value of the saturation activity of 25-min. Se^{83} found was $1.31 \times 10^7 \text{ c/m} \pm 7$ percent. Two Br samples were isolated 19 min. and 106 min. after the end of the irradiation and the value of the saturation activity of the 2.4-hr. Br grown from the 67-sec. Se was obtained by correcting for the 2.4-hr. Br grown from the 25-min. Se, and was found to be $1.68 \times 10^7 \text{ c/m} \pm 7$ percent. Assuming a fission yield of 0.21 percent for the 25-min. Se, the yield of the 67-sec. Se is 0.27 percent, giving a total yield of 2.4-hr. Br^{83} of 0.48 percent. The discrepancy between the yield of the 67-sec. Se in this experiment and that reported by Glendenin arises from the rapid separation of Br in the earlier experiments before the complete decay of the 67-sec. Se.

¹⁰ L. Seren, H. Friedlander, and S. Turkel, Metallurgical Laboratory Report CP-2081, August 26, 1944.

2.5. Identification and Characteristics of a 17.5-sec. Se

The decay curves of Se irradiated for 20 sec. and measured through Al absorbers of thickness greater than $\sim 600 \text{ mg/cm}^2$, revealed another short-lived Se activity whose half-life was found to be 17.5 ± 0.3 sec. This activity appeared in equal yield both in technical-grade and spectroscopically pure Se. A typical decay curve is given in Fig. 3. The absorption curve of the 17.5-sec. Se was determined in the same manner as that of the 67-sec. Se, namely, by comparing the activity of the 17.5-sec. Se with that of the 17-min. Se through various absorbers and normalizing to the Al-absorption curve of the 17-min. Se. As is seen in Fig. 2, the absorption characteristics of the 17.5-sec. Se are those of a γ -ray. The energy of the γ -ray is estimated roughly at ~ 150 Kev from measurements made with absorbers of $1117 \text{ mg Al/cm}^2 + 209 \text{ mg Pb/cm}^2$ and 2.05 gm Pb/cm^2 .

A rough value of the cross section of Se for formation of the 17.5-sec. Se calculated relative to 0.25 barn for formation of the 17-min. Se, and assuming a counting efficiency for the γ -ray of ~ 0.1 percent and no internal conversion, is ~ 0.6 barn.

2.6 Summary of Se-Br Experiments

Extractions of Br from neutron-irradiated SeO_3^{2-} solutions revealed the presence of a short-lived state of Se^{83} decaying by β^- -emission to 2.4-hr. Br^{83} . The half-life was estimated to lie between 1 and 1.5 minutes. The cross section for formation of the short-lived state was found to be about ten times greater than for the 25-min. Se^{83} . Direct observations of the radiations from a short-lived Se, effected by measuring the activity of Se irradiated for 20 sec. through Al absorbers, led to a half-life determination of 67 ± 3 sec. and a β -energy of 3.4 Mev. A γ -ray was also observed. There is good reason to believe that a genetic relationship exists between this 67-sec. Se and the 2.4-hr. Br^{83} because of the good agreement found between the cross sections for formation of the 67-sec. Se and the 2.4-hr. Br^{83} formed from the short-lived Se. Energy considerations lead to the assignment of the 67-sec. Se as an upper state of 25-min. Se^{83} .

Experiments were performed on the relative fission yields of the 25-min. Se^{83} and the 67-sec. Se^{83} and a value of 0.27 percent for the 67-sec. Se^{83} was determined, assuming a yield of 0.21 percent for 25-min. Se^{83} . The total fission yield of Br^{83} is, then, 0.48 percent.

A new Se activity of 17.5 ± 0.3 sec. half-life was discovered in the course of this work. It appears to decay by emission of γ -radiation of ~ 150 Kev. The cross section for formation of this activity is ~ 0.6 barn.

The presence of the 67-sec. Se^{83} activity decaying by β^- -emission to 2.4-hr. Br^{83} resolves the difficulty of the apparently high "independent" yield of Br^{83} in fission.

3. NEUTRON IRRADIATIONS OF Ge

3.1. Irradiations of Ge Solutions and As Extractions

Irradiations of Ge solutions were performed in a manner similar to that used for Se. The experiments were designed to determine whether all of the 40-hr. As^{77} present in solution after irradiation comes from the 12-hr. Ge^{77} , or if a short-lived isomeric state of Ge^{77} is a possible source. Extractions of 40-hr. As^{77} at varying times after the end of the irradiation make it possible to measure the activity of As growing from the 12-hr Ge and from any short-lived Ge^{77} formed from the neutron capture of Ge^{76} .

Liquid GeCl_4 was the first compound tried for irradiation because of its high Ge content, an advantageous condition for measurable activities from short irradiations. It was found, however, that tracer As was lost from this solution by adsorption or volatilization at a rate which was sufficiently rapid to obscure the results. A concentrated Ge solution, prepared by dissolving GeS_2 in $\text{NH}_4\text{OH}-\text{NH}_4\text{HS}$ solution, was then tried and was shown to be a satisfactory medium for recovery of As tracer.

The procedure for separating Ge and As activities is that of Winsberg¹¹ with certain modifications. The separation of Ge from As is effected by distilling the Ge as GeCl_4 from a conc. HCl solution in the presence of chlorine gas. The pentavalent As is involatile. After the

Ge distillation is completed, the residual Cl_2 is displaced by air, Cu_2Cl_2 is added to reduce the As to the trivalent state, and the As is distilled as AsCl_3 . The detailed procedure used in these experiments follows. A suitable aliquot of the irradiated sulfide solution is placed in an all-glass still with a 50-ml boiler and an arrangement for passing gas through the solution throughout the distillation. The aliquot is washed down with water and 2-ml As carrier (10-mg As/ml) added, followed by 10-ml conc. HCl. Chlorine gas is passed through the still and receiver (40-ml ice water in a 100-ml centrifuge tube, surrounded by an ice-salt mixture); the sulfides of Ge and As, precipitated from the basic sulfide solution by the addition of conc. HCl, dissolve slowly. Some free sulfur remains suspended in the solution. Distillation is begun in a stream of Cl_2 and continued until about 5 ml of solution remains in the still. Under these conditions Ge, but not As, distills. The time of purification of Ge or isolation of As is taken as the midpoint of the first Ge distillation, which lasts about five minutes. Two more distillations are then performed by adding 4-ml Ge carrier (5-mg Ge/ml in 6N HCl) and 6-ml conc. HCl to the residue; each time the distillation is con-

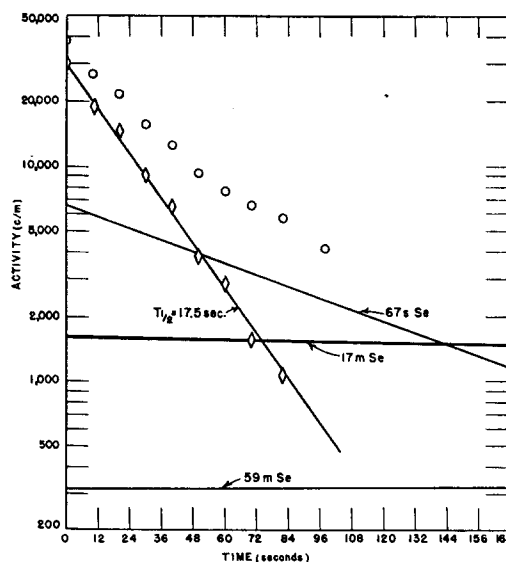


FIG. 3. Decay curve of Se metal irradiated for 20 seconds. Counting started 1 min. after end of irradiation. Counted through 1431-mg Al/cm^2 added absorber. \circ original points. \diamond subtracted curve, activities of 17-min. Se, 59-min. Se, and 67-sec. Se, determined from later part of curve.

¹¹ L. Winsberg, Metallurgical Laboratory Memo MUC-NS No. 200, January, 1945; Plutonium Project Record Vol. 9B, 8.2 (1946).

TABLE II. As⁷⁷ activity from neutron-irradiated Ge solutions.

Experiment	Sample	t_{Ge}	t_{As}	Activity As ⁷⁷ (c/m) at an arbitrary time. (Nor- malized for yield and volume of solution)	A_{Ge}^{∞} (c/m)	A_{Ge}^{∞} (c/m)
1 (2-hr. irradiation)	As-1	0.28	0.28	5070	4.22×10^5	—
	As-2	4.07	4.07	6340	(4.22×10^5)	4.83×10^5
	As-3	24.93	24.93	8480	(4.22×10^5)	3.10×10^5
	As-4	70.32	70.32	10680	(4.22×10^5)	3.32×10^5
	Ge As-1	2.60	23.35	3310	—	3.71×10^5
	Ge As-2	2.60	69.07	5330	—	3.86×10^5
Graphical analysis						
2 (1-hr. irradiation)	As-1	0.23	0.23	10750	5.94×10^5	5.28×10^5
	As-2	2.27	2.27	11320		
	As-3	4.22	4.22	12780		
	As-4	22.40	22.40	12690		
	As-5	26.78	26.78	11610		
	As-6	47.45	47.45	9590		
	As-7	72.73	72.73	6720		
	As-8	76.99	76.99	6526		
	Ge-1 As	0.23	24.23	8160	4.90×10^5	
	Ge-3 As	4.22	28.22	5700		
	Ge-4 As	22.40	46.40	2160		
	Ge-5 As	26.78	50.78	1658		
	Ge-6 As	47.45	71.45	487		

A_{Ge}^{∞} = Saturation activity of As⁷⁷ from 12-hr. Ge⁷⁷.
 A_{Ge}^{∞} = Saturation activity of As⁷⁷ from short-lived Ge⁷⁷. Values in parentheses were used for A_{Ge}^{∞} calculations.
 t_{Ge} = Time (hrs.) elapsed from end of irradiation to purification of Ge.
 t_{As} = Time (hrs.) elapsed from end of irradiation to separation of As.

A_{Ge}^{∞} = Saturation activity of As⁷⁷ from 12-hr. Ge⁷⁷.

$A_{\text{Ge}*}^{\infty}$ = Saturation activity of As⁷⁷ from short-lived Ge⁷⁷. Values in parentheses were used for A_{Ge}^{∞} calculations.

t_{Ge} = Time (hrs.) elapsed from end of irradiation to purification of Ge.

t_{As} = Time (hrs.) elapsed from end of irradiation to separation of As.

tinued until 5 ml remains in the still. The receiver is changed after each distillation. After the completion of the Ge distillations, a new receiver containing 10-ml H₂O is put in place, a stream of air passed through, and 5-ml saturated Cu₂Cl₂ in conc. HCl and 2-ml conc. HCl are added. The solution is distilled until a solid precipitate appears in the still, 5-ml conc. HCl are then added, and the solution is distilled again until solid appears. Both distillates containing As are condensed in the same receiver. The As is precipitated by passing H₂S through the distillate. The precipitate is filtered, dried, and mounted. The factor by which As is freed from Ge contamination in this procedure is about 300, which is quite sufficient for this work.

Samples of Ge activity isolated for As growth from 12-hr. Ge⁷⁷ were obtained from the first Ge distillate. The Ge was precipitated by H₂S, filtered, dried, weighed, and redissolved in NH₄OH-NH₄HS solution. An aliquot of As

carrier was added, and the solution allowed to stand for 40-hr. As growth. The As was isolated by the procedure outlined above. The factor by which Ge is freed of As impurity in the first Ge distillation was never measured directly, but a lower limit of 100 can be assigned from the experimental data.

The results of the As-extraction studies are given in Table II. The As samples isolated from the irradiated Ge sulfide solution at a time $t_{\text{Ge}} (= t_{\text{As}})$ from the end of the irradiation are listed as As-1, As-2, etc., and the As samples isolated at a time t_{As} from the Ge samples, previously purified from the Ge sulfide solution at a time t_{Ge} , are listed as Ge-1 As, Ge-2 As, etc. Calculations of the results of experiment 1 in Table II are made in the same manner as those for Table I, with hours used as the units of time.

The value of the saturation activity of As⁷⁷ from the short-lived Ge⁷⁷ ($A_{\text{Ge}*}^{\infty}$) of experiment 1 of Table II was calculated from the first As sample extracted 0.28 hr. after the end of the irradiation. This value was used in correcting the As activities of later extractions for the As present at the end of irradiation. The saturation activity of As⁷⁷ grown from the 12-hr. Ge (A_{Ge}^{∞}) as determined from the As samples was found to agree favorably with that found from the Ge-As samples. The extraction data of the second experiment were complete enough to be subjected to graphical analysis and again good agreement was found between the two independently determined A_{Ge}^{∞} values. A graphical representation of the Ge-As data of this experiment is given in Fig. 4, in which the genetic relationship of the 40-hr. As⁷⁷ to the 12-hr. Ge⁷⁷ is clearly represented. The ratio of $A_{\text{Ge}*}^{\infty}$ to A_{Ge}^{∞} from these two experiments of 1.1 establishes the existence of a short-lived isomeric state of Ge⁷⁷, formed by neutron capture of Ge⁷⁶, which decays by β^- -emission to 40-hr. As⁷⁷. An upper limit of 3 min. to the half-life of the short-lived Ge⁷⁷ was determined by extractions of As performed 8 min. to 40 min. after the end of irradiation from a Ge solution irradiated for 2 min. The variation in activity of the samples isolated in this time interval could be accounted for by growth from the 12-hr. Ge⁷⁷.

3.2. Irradiations of GeS₂. Identification of the Short-lived State of Ge⁷⁷

A search for the short-lived state of Ge⁷⁷ was made by irradiations of GeS₂ prepared from GeCl₄. Samples of GeS₂ were irradiated for twenty seconds and counted through Al absorbers. An activity decaying with a half-life of 59 ± 2 sec. was observed as the absorber thickness increased, being most pronounced at ~ 400 mg Al/cm² (Fig. 5). Preparations of GeS₂ of varying purity showed the presence of the 59-sec. activity as well as the low activity from the 89-min. Ge⁷⁵ and the 37-min. Cl³⁸ formed from the Cl impurity in the GeS₂. Irradiations of S showed that this was not the source of the 59-sec. activity. The absorption characteristics of the 59-sec. Ge were determined by following the decay of irradiated samples through sets of two Al absorbers differing by about 200-mg Al/cm², the activity through one absorber being used for normalization of the activity through the other. The Al-absorption curve of the 59-sec. Ge is given in Fig. 2; its β -energy is 2.8 Mev as determined by a Feather comparison method⁹ with the 17-min. Se⁸¹. The low activities of the samples through thick Al absorbers make it

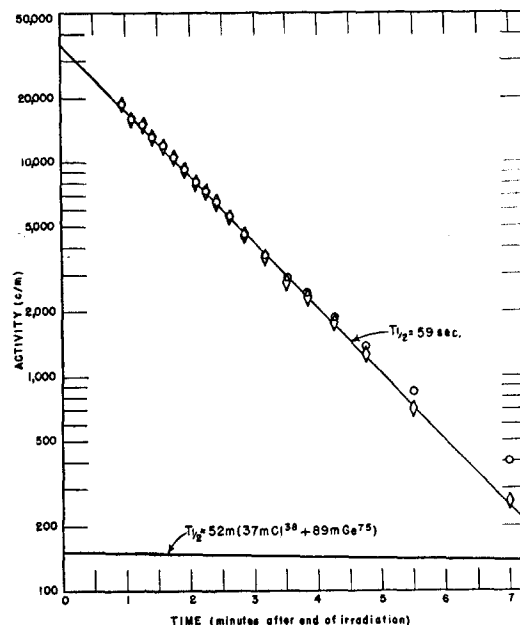


FIG. 5. Decay curve of GeS₂ irradiated for 20 seconds. Counted through 405-mg Al/cm² added absorber. ○ original points. ◇ subtracted curve, activity of 89-min. Ge⁷⁵ and 37-min. Cl³⁸ (from Cl impurity) determined from later part of curve.

improbable that there is hard γ -radiation present in high intensity.

The activity of the 59-sec. Ge was shown to be genetically consistent with that of the 40-hr. As formed from the short-lived state of Ge by a comparison of these activities with the activity of 89-min. Ge⁷⁵. The ratio of the 59-sec. Ge activity to the 89-min. Ge⁷⁵ activity at the end of a 20-sec. irradiation was 3.99; the ratio of the saturated activities corrected for absorption, 0.045. The ratio of the 40-hr. As from the short-lived Ge to the 89-min. Ge⁷⁵ at the end of a 2-min. irradiation was 4.32×10^{-4} ; the ratio of the saturated activities corrected for absorption, 0.037. It is very probable, from the agreement of the ratios of the saturated activities, that the 59-sec. Ge and the short-lived Ge decaying to 40-hr. As are identical. The 40-hr. As from the 59-sec. Ge was shown to be the same species as the 40-hr. As⁷⁷ from the 12-hr. Ge⁷⁷ by the identity of the half-lives and absorption characteristics.

A definite energy assignment of the 59-sec. Ge⁷⁷ relative to the 12-hr. Ge⁷⁷ cannot be made since the total decay energy of neither nucleus has been determined.

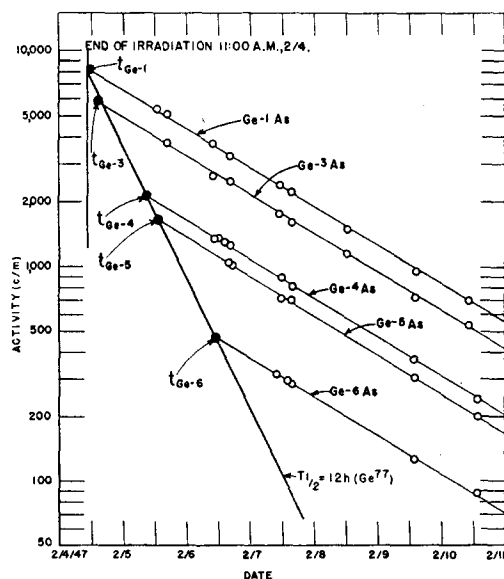


FIG. 4. Decay curves of 40-hr. As⁷⁷ samples extracted from Ge samples separated from Ge solution, showing genetic relationship of 40-hr. As⁷⁷ to 12-hr. Ge⁷⁷ (data of Table II). ○ Measured activity of Ge-As samples. ● Extrapolated activity of Ge-As samples at t_{Ge} .

3.3. Cross Section for Formation of the 40-hr. As^{77}

The cross-section of Ge for formation of the 12-hr. Ge^{77} by an (n, γ) process was determined to be 0.0055 barn by Seren, Sturm, and Moyer.¹² Since the 40-hr. As^{77} is formed in two ways, from 12-hr Ge^{77} and 59-sec. Ge^{77} , its formation cross section is the sum of the cross sections of the 12-hr. Ge^{77} and the 59-sec. Ge^{77} , whose cross section was found to be about 10 percent higher than that of 12-hr. Ge^{77} in these experiments, or 0.011 barn. The cross section of 0.0155 barn given by Seren *et al.* for the formation of the 40-hr. Ge^{77} is undoubtedly too high since it contains the contribution of the 40-hr. As^{77} (0.011 barn), an activity which was found after the Ge cross section work was done.

3.4. Summary of Ge-As Experiments

The presence of a short-lived state of Ge^{77} decaying by β^- -emission to 40-hr. As^{77} has been

¹² L. Seren, W. Sturm, and W. Moyer, Metallurgical Laboratory Report CP-1389, February 24, 1944.

shown by As extractions of GeS_3 solutions irradiated with neutrons. The cross section for formation of the short-lived state was found to be about 10 percent larger than that of the 12-hr. Ge^{77} . A short-lived Ge activity was found by irradiating GeS_2 with neutrons for 20 sec. and measuring the activity through Al absorbers. The half-life was determined to be 59 ± 2 sec. and the β -energy, 2.8 Mev. The agreement between the cross sections for formation of the 59-sec. Ge and the 40-hr. As^{77} from the short-lived Ge^{77} makes it probable that the 59-sec. Ge is genetically related to the 40-hr. As^{77} .

The presence of the 59-sec. Ge^{77} activity decaying by β^- -emission to 40-hr. As^{77} resolves the difficulty of the apparently high "independent" yield of As^{77} in fission on the assumption that the excess fission yield of As^{77} is due to 59-sec. Ge^{77} .

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The Mechanism of Processes Initiated by Excited Atoms

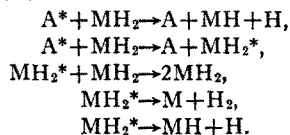
III. Photo-Sensitized Hydrocarbon Reactions

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The photo-sensitized reactions of the hydrocarbons are discussed in terms of the following reaction scheme, in which A^* indicates the photo-sensitizing atom and MH_2 the hydrocarbon:



The first and fifth reactions are followed by polymerizations. Expressions for the quenching rate, the rate of formation of M, and the rate of formation of polymer, are obtained in terms of the original rate constants, and a

number of special cases of practical interest are treated. The relative rates of the reactions are discussed with reference to the experimental data, particular regard being paid to the energy relationships, the general kinetic behavior, and the influence of temperature. Evidence is adduced in favor of the following: (1) the strength of the C-H bond in ethylene is about 100 kcal., (2) there is a triplet-excited state of acetylene with an excitational energy of 10-30 kcal., (3) conversion of a large amount of electronic energy into vibrational energy proceeds with difficulty, the process taking place much more readily when some of the energy can be taken up as electronic energy of the colliding molecule.

INTRODUCTION

APPLICATIONS of the theory of chemical change to the elucidation of reaction mechanisms have for the most part followed one of two

general paths. The first of these consists of the detailed quantum-mechanical calculation of the rates of simple processes, and the comparison of the results with experiment; the second is the