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Short-Lived Halogen Fission Products†

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Half-life values have been determined for some short-lived Br and I fission products. The chemical isolation of Br from irradiated uranyl nitrate led to a half-life for Br^{85} of 3.00 ± 0.05 min. The energy of the β -radiation of Br^{85} was found to be 2.5 Mev by Feather analysis of the Al absorption curve. The half-lives found for Br^{87} and Br^{88} by extraction of the Kr daughter activities from AgBr precipitates were 56.1 ± 0.7 sec. and 15.5 ± 0.3 sec., respectively, on the basis of a 3-min. half-life for Br^{85} . Attempts to measure the half-lives of Br^{89} and Br^{91} by extraction of the descendant Sr activity were unsuccessful because of the absence of activity. The identity in half-lives of Br^{87} and the 55.6-sec. Br delayed neutron emitter makes it probable that the mass assignment of the delayed neutron emitter is 87.

The half-life of I^{137} was found to be 19.3 ± 0.5 sec. by extraction of Xe^{137} from AgI precipitates, on the assumption of constant chemical yield of the Xe extraction. Isolation of Cs^{138} both from the gas separated from AgI precipitates and from the precipitates directly led to a half-life determination for I^{138} of 5.9 ± 0.4 sec. Extractions of Ba^{140} yielded a value of 2.7 ± 0.1 sec. for the half-life of I^{139} . The absence of Ba^{140} activity in AgI precipitates made it impossible to determine the half-life of I^{140} . Because of the agreement in half-lives of I^{137} and the 22.0-sec. I delayed neutron emitter it is probable that the two are identical.

The low retention of the decay products of the short-lived halogens by the silver halide precipitates led to an estimate of 20 sec. for the "setting" time of the precipitate.

1. INTRODUCTION

EXPERIMENTS have been performed on the search for new short-lived fission products of Br and I and the determination of the mass numbers of the three longer-lived delayed neutron emitters identified as isotopes of Br and I. The fission chains showing the region of investigation in the light and heavy groups of fission products as given in the table of "Nuclei Formed in Fission"¹ are listed in Table I.

In these experiments a solution of uranyl nitrate containing Br^- or I^- carrier is irradiated for a fixed time after which AgBr(I) is precipitated from the active solution. The AgBr(I) precipitate collected by filtration is examined for known fission products which could arise from the decay of active Br or I isotopes; e.g., Kr and Xe, Rb and Cs, Sr and Ba. The activity levels of these decay products will be determined by the neutron flux, time of irradiation, and quantity of uranium irradiated, and by the time of precipitation after the end of irradiation and the half-life of the halogen activity. In experiments performed under standard conditions where only the

time of precipitation is varied, the variation in activity of a decay product will be a measure of the half-life of its halogen ancestor. For example, in chain of mass 85, the half-life of the Br isotope is 3 min. The initial activity of the 4.5-hr. Kr^{85} found in the precipitate should decrease one-half for each 3 min. elapsed between the end of irradiation and precipitation of AgBr, provided the loss of Kr from the precipitate is constant from experiment to experiment and the chemical operations are performed quantitatively. In practice it is rather difficult to perform some of the operations quantitatively so that the chemical yield must be determined in another way. This is discussed more fully under the specific isotopes studied.

The co-precipitation of radioactive ancestors or descendants of the halogens on the silver-halide precipitates would affect the measured half-lives. Fission yields and half-life considerations make it unlikely that Se or Te parents of the halogen activities would seriously interfere with these measurements. Contamination of the precipitates by descendant activities, Kr or Xe, Rb or Cs, Sr or Ba, would be expected to be small and would affect only those measurements where the descendant activity in the precipitate is small relative to the total descendant activity present. A discussion of this effect is given later in the pertinent cases (cf. Sections 8 and 9).

† This document is based on work performed at the Argonne National Laboratory, Chicago, Illinois, operated by the University of Chicago for the Atomic Energy Commission.

¹ "Nuclei Formed in Fission," issued by the Plutonium Project, J. Am. Chem. Soc. 68, 2411 (1946); Rev. Mod. Phys. 18, 513 (1946).

TABLE I.* Fission chains investigated for Br and I ancestry.**

Mass 85:	3.0-min. Br → 4.5-hr. Kr → Stable Rb
Mass 86:	~10-yr. Kr → Stable Kr
Mass (87):	55.6-sec. Br → v. short Kr
Mass 87:	50-sec. Br → 75-min. Kr → 6.3×10^{10} -yr. Rb → Stable Sr
Mass 88:	3-hr. Kr → 17.8-min. Rb → Stable Sr
Mass 89:	2.6-Min. Kr → 15.4-min. Rb → 53-da. Sr → Stable Y
Mass 90:	~33-sec. Kr → short Rb → 25-yr. Sr → 65-hr. Y → Stable Zr
Mass 91:	9.8-sec. Kr → short Rb → 9.7-hr. Sr → 51-min. Y
	57-da. Y → Stable Zr
Mass 135:	<2-min. Te → 6.7-hr. I → 13-min. Xe
Mass (136):	1.8-min. I → 9.2-hr. Xe → $> 2.5 \times 10^4$ -yr. Cs → Stable Ba
Mass (137):	22.0-sec. I → v. short Xe
Mass 137:	30-sec. I → 3.4-min. Xe → 33-yr. Cs → Stable Ba
Mass 138:	17-min. Xe → 32-min. Cs → Stable Ba
Mass 139:	41-sec. Xe → 7-min. Cs → 85-min. Ba → Stable La
Mass 140:	16-sec. Xe → short Cs → 12.8-da. Ba → 40.0-hr. La → Stable Ce

* Uncertain mass assignments are given in parentheses.

** See reference 1.

Another effect which could alter the half-life observed for the halogen species is a time-dependent exchange between the halogen carrier added (Br^- or I^-) and the halogen activity in higher valence states. A serious perturbation in

the observed half-life would occur only when the exchange constant is of the same order as the radioactive decay constant of the halogen. The concentrations used in these experiments are: $(\text{H}^+) \cong 0.01 M$, $(\text{Br}^-) \cong 0.01 M$, and $(\text{I}^-) \cong 0.01 M$. Using these concentrations and assuming the well established rapid exchange of Br^- with Br_2 , one calculates an effective exchange constant for carrier Br^- with radio-Br as BrO_3^- from kinetic data on the interaction of Br^- with BrO_3^- to give Br_2 .² This constant proves to be much smaller than the radioactive decay constants of the Br isotopes studied. The exchange constant of carrier I^- and radio-I as IO_3^- from reactions analogous to those of Br is much larger than the radioactive decay constants of the I isotopes studied. Although kinetic information on the reaction of I^- or Br^- with other oxidation species of halogens is not known, it would be fortuitous if the effective exchange constants were of the same order as the decay constants.

Observations made on the 4.5-hr. Kr^{85} , 75-min. Kr^{87} , 2.8-hr. Kr^{88} and its 17.8-min. Rb^{88} daughter led to determination of the half-lives of Br^{87} and Br^{88} . Attempts to find the half-lives of Br^{89} and Br^{91} by extraction of the Sr were unsuccessful. Extractions of the Xe and Cs from AgI pre-

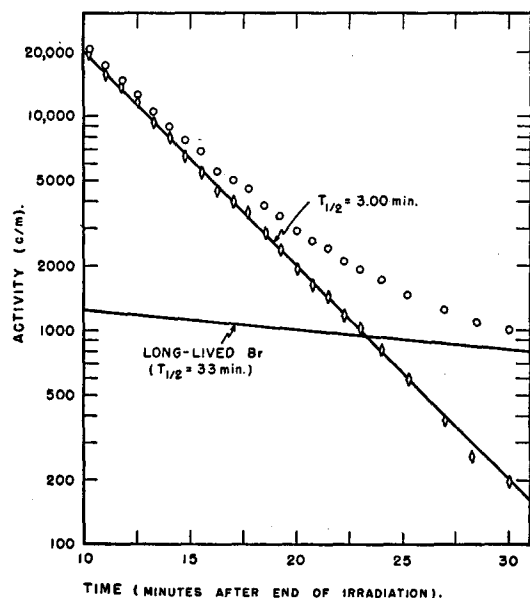


FIG. 1. Decay curve of Br isolated from irradiated uranyl nitrate solution. Counted through 211 mg Al/cm². ○ original points; ◇ subtracted curve, activities of 30-min. Br^{84} and 2.4-hr. Br^{88} determined from later part of curve (average $T_{1/2} = 33$ min.).

² International Critical Tables, 7, 149 (1930).

precipitates determined the half-lives of I^{137} and I^{138} . The half-life of I^{139} was determined by analyzing for Ba^{139} , and no activity of Ba^{140} was observed from AgI precipitates.

2. CHARACTERISTICS OF Br^{85} ; HALF-LIFE AND RADIATIONS

Strassmann and Hahn³ found two short-lived Br activities of 50 ± 10 sec. and 3.0 ± 0.5 min. half-life in fission by chemically separating Br soon after irradiation. Seelmann-Eggebert and Born⁴ have shown that the 75-min. Kr and 4.5-hr Kr could be extracted from the short-lived Br fraction and that the variation of their intensities with time related the 75-min. Kr to the 50-sec. Br and the 4.5-hr. Kr to the 3-min. Br provided no other short-lived Br activities were present. Later, cross-bombardments led to mass assignments of 85 to the 3-min. Br and 87 to the 50-sec. Br.⁵

The use of Br^{85} as a normalizing activity in experiments on the half-life of Br^{87} and Br^{88} (Sections 3 and 4), made it necessary to determine its half-life more precisely. Because of the greater neutron fluxes available it was possible to separate quickly sufficient activity for measurement after short irradiations of small amounts of uranium. These conditions enhance the activity of the Br^{85} relative to the longer-lived isotopes, 30-min. Br^{84} and 2.4-hr. Br^{83} because of the hold-up in growth from their Se ancestors, ~ 2 -min. Se^{84} , 67-sec. Se^{83} and 25-min. Se^{83} .¹

The active Br was isolated from a uranyl nitrate solution irradiated for 10 sec. in the pneumatic tube of the Argonne heavy water pile. The chemical procedure was modified from that of Glendenin, Edwards, and Gest.⁶ Carriers of Br^- and I^- are added to the irradiated solution which is then transferred to a separatory funnel containing CCl_4 and $KMnO_4$ acidified with HNO_3 . The liberated Br is transferred to the CCl_4 layer. This Br extraction is performed within 30 sec. from the end of irradiation. The CCl_4 extract is added to a funnel containing H_2O and $NH_2OH \cdot HCl$. The Br is transferred to the

H_2O layer. Two oxidation-reduction cycles with $KMnO_4$ as oxidant and $NaHSO_3$ as reductant are then performed. The last aqueous $NaHSO_3$ layer is acidified with HNO_3 , the solution is boiled to expel SO_2 , and $AgBr$ is precipitated. The precipitate is filtered on a filter paper disk and mounted for counting. In general, radioactivity measurements began within 7 min. after the end of irradiation. Aqueous samples used for half-life determination were washed with extra CCl_4 to remove suspended material and insure purity. These samples were counted within 10 min. from the end of irradiation.

Decay curves were obtained through various Al absorbers. The ratio of the activity of Br^{85} to the 55.6-sec. Br^{87} , 30-min. Br^{84} , and 2.4-hr. Br^{83} decreased with increasing absorber weight beyond 325 mg Al/cm². The optimum absorber weight for determination of the half-life of Br^{85} was found to be in the range 100 to 325 mg Al/cm². Ten decay curves taken through 101, 211, and 311 mg Al/cm² yielded a half-life for Br^{85} of 3.00 ± 0.05 min. A typical decay curve through 211 mg Al/cm² is given in Fig. 1.

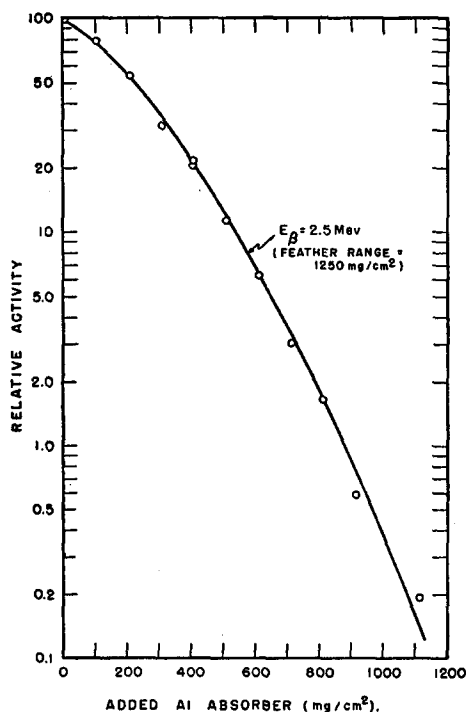


FIG. 2. Aluminum absorption curve of 3.00-min. Br^{85} . Absorber thickness at zero added Al estimated at 35 mg/cm².

³ F. Strassmann and O. Hahn, *Naturwiss.* **28**, 817 (1940).

⁴ W. Seelmann-Eggebert and H. J. Born, *Naturwiss.* **31**, 59 (1943).

⁵ H. J. Born and W. Seelmann-Eggebert, *Naturwiss.* **31**, 86 (1943).

⁶ L. E. Glendenin, R. R. Edwards, and H. Gest, *Plutonium Project Record*, Vol. 9B, 8.4.2 (1946).

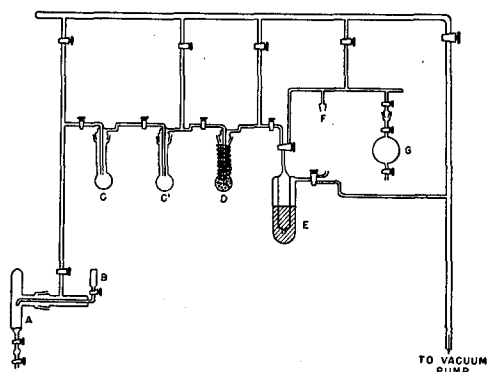


FIG. 3. Vacuum line for removing active gases from dissolved AgBr(I) precipitates. A. Dissolver; B. Port for introducing NaCN; C, C'. Traps (surrounded by liquid nitrogen or filled with Drierite); D. Charcoal trap; E. Toepler pump; F. Lead to gas cell; G. Bulb for removing aliquot of gas for Rb or Cs analysis.

The absorption characteristics of Br^{85} were determined by following the decay of active 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 3.00-min. Br^{85} is given in Fig. 2. The β -energy was found to be 2.5 Mev by a Feather comparison method⁷ of the absorption curve of Br^{85} with that of the 1.5 Mev β -particles of the 17-min. Se^{81} .¹ It is apparent from Fig. 2 that γ -radiation is not present in a high counting rate.

3. HALF-LIFE OF Br^{87}

The 55.6-sec. delayed neutron emitter* identified as an isotope of Br by Snell and co-workers⁸ was tentatively assigned by them to Br^{87} and

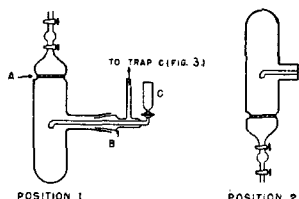


FIG. 4. Details of dissolver. Position 1—for dissolving of AgBr(I) precipitates; Position 2—for sweeping active gases from solutions of dissolved AgBr(I) precipitates. A. Sintered glass plate (fine); B. Ground joint; C. Solution port.

⁷ N. Feather, Proc. Camb. Phil. Soc. **34**, 599 (1938).

* The half-lives of the delayed neutron emitters adopted in this paper are those of D. J. Hughes, J. Dabbs, A. Cahn, and D. Hall, Phys. Rev. **73**, 111 (1948). (Also reference 1.)

⁸ A. H. Snell, J. S. Levinger, E. P. Meiners, Jr., M. B. Sampson, and R. G. Wilkinson, Phys. Rev. **72**, 545 (1947).

was thought to be the 50-sec. Br referred to earlier.³ Glendenin, Coryell and Edwards⁹ in their discussion of the variation in yield as a function of charge found it difficult to correlate the variation in yield of the 55.6-sec. delayed neutron emitter in the thermal neutron fission of U^{233} , U^{235} , and Pu^{239} with their postulate of "equal chain length" and a mass of 87. They suggested that the mass of the delayed neutron emitter might be 89 or 90 and that therefore there might be two Br activities with half-lives of ~ 50 sec. The experiments reported here establish the half-life of Br^{87} as 56.1 sec., identical within experimental error with the 55.6-sec. Br delayed neutron emitter, and suggest the improbability of another Br activity of the same half-life at mass 89 or 90.

The half-life of Br^{87} was determined by measuring the variation in intensity of the 75-min. Kr^{87} in the active AgBr samples precipitated from irradiated uranyl nitrate solutions at various times after short irradiations. The solution of uranyl nitrate containing Br^- carrier was irradiated for 10 sec. At the desired time after irradiation the active material was poured into a heated solution of AgNO_3 acidified with HNO_3 . The solution was allowed to stand for about 20 min. and was then filtered through a filter paper disk and the precipitate washed with water and dried with alcohol and ether. The precipitate on the filter disk was transferred to a dissolver on a vacuum line (Fig. 3) and after evacuation was dissolved in NaCN. The dissolver was made from a 30-ml fine sintered glass funnel sealed off at the top, with a ground joint side arm attached to the vacuum line for evacuation, gas flow, and introduction of solutions under vacuum (see Fig. 4). During the solution process the dissolver was in the position in which the precipitate and NaCN solution were off the sintered glass plate (position 1, Fig. 4). The dissolver was then rotated so that the solution rested on the sintered plate and introduction of air from the bottom resulted in efficient sweeping of the solution (position 2, Fig. 4). This apparatus was used earlier by Hoagland and Sugarman¹⁰ in their study of Xe^{135}

⁹ L. E. Glendenin, C. D. Coryell, and R. R. Edwards, Clinton Laboratory Memo CL-LEG No. 1, July 25, 1946.

¹⁰ E. J. Hoagland and N. Sugarman, Metallurgical Laboratory Report, CC-3007, April 5, 1945; Plutonium Project Record, Vol. 9B, 7.37.3 (1946).

and was adapted from the techniques developed by Turkevich and co-workers¹¹ in investigating the short-lived Kr and Xe activities in fission.

The active gases were swept from the solution containing the dissolved precipitate and passed successively through two traps cooled with liquid nitrogen and a charcoal trap at room temperature. Desorption of the gases from the charcoal at room temperature by a Toepler pump yielded an active gas fraction containing Kr nearly free of Xe. The gas was transferred to a glass counting cell with a mica window and counted with a standard Eck-Krebs counter of 30 mg/cm² wall thickness. The decay of the gas activity showed the presence of two major components, the 4.5-hr. Kr⁸⁵ and the 75-min. Kr⁸⁷. The 75-min. Kr activity was determined more easily by counting through 405 mg Al/cm² which absorbed the β -activity of the 4.5-hr. Kr. After the decay of the 75-min. Kr, the 4.5-hr. Kr activity was determined by counting without absorber. In the experiments in which precipitations were performed within two minutes after the end of irradiation the gas activity contained some contribution from the 2.8-hr. Kr⁸⁸ arising from its Br⁸⁸ parent. Since the fission yields of the neighboring Br isotopes vary by only a factor of 4, and since Br⁸⁸ has a much shorter half-life than Br⁸⁷ or Br⁸⁵, the 2.8-hr. Kr⁸⁸ activity grown from it was negligibly small relative to the activities of the 75-min. Kr and 4.5-hr. Kr for later precipitations (cf. Section 4).

Intercomparison of the activities of the 75-min. Kr⁸⁷ and the 4.5-hr. Kr⁸⁵ in samples obtained from AgBr precipitated at various times after irradiation permit determination of the half-lives of the Br ancestors provided operations are quantitative or at least chemical yields are constant. Since it proved difficult to maintain a constant yield for the gas sweeping and desorption process the 4.5-hr. Kr activity was used as a monitor for the over-all chemical yield. A 3-min. Br parent was used. The activity of the 75-min. Kr was then normalized for changes in irradiation conditions and loss in activity by correcting the 4.5-hr. Kr activity to a 3-min. decay curve and normalizing the 75-min. Kr activity by this

¹¹ C. Dillard, R. M. Adams, H. Finston, and A. Turkevich, Metallurgical Laboratory Reports, CC-1805, July 14, 1944, CC-2310, Jan. 1, 1945; Plutonium Project Record, Vol. 9B, 7.5.3, 7.5.5, (1946).

TABLE II. Activities of 4.5-hr. Kr⁸⁵ and 75-min. Kr⁸⁷ extracted from AgBr precipitates.

Time of precipitation of AgBr	4.5-hr. Kr ⁸⁵			75-min. Kr ⁸⁷	
	Activity at AgBr precipitation (no Al absorber) (c/m)	Activity from arbitrary 3-min. decay curve (c/m)	Normalization factor	Activity at AgBr precipitation (405 mg Al/cm ²) (c/m)	Normalized activity (c/m)
8 sec.	12400	6100	0.492	25400	12500
15 sec.	27000	5900	0.219	48250	10550
25 sec.	23300	5700	0.245	45500	11150
41 sec.	25300	5400	0.213	42000	8950
55 sec.	11650	5100	0.438	17600	7700
70 sec.	15400	4800	0.312	18600	5800
85 sec.	11500	4550	0.396	12700	5030
90 sec.	21800	4450	0.204	24000	4900
100 sec.	16000	4300	0.269	15800	4250
115 sec.	17600	4050	0.230	15800	3630
2.5 min.	13800	3530	0.256	8000	2050
3.07 min.	3020	3100	1.026	1390	1430
3.5 min.	33200	2800	0.0843	13100	1100
4.0 min.	21900	2500	0.114	6825	780
4.5 min.	6600	2220	0.336	1585	530
5.0 min.	10900	1990	0.183	2000	365
5.5 min.	8800	1780	0.202	1260	255
6.0 min.	5500	1580	0.287	520	149

factor. The variation of the normalized 75-min. Kr activity as a function of time of precipitation yielded the half-life of the Br⁸⁷ parent (Fig. 5). The data for the gas activities from the various experiments are given in Table II.

The half-life of Br⁸⁷ is found to be 56.1 ± 0.6

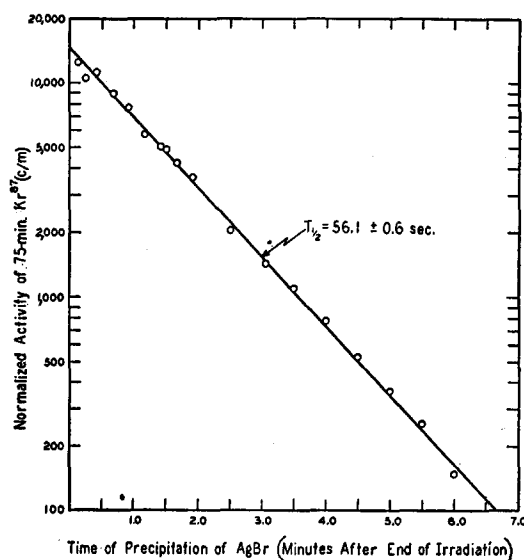


Fig. 5. Decay curve of Br⁸⁷ from 75-min. Kr⁸⁷ activities extracted from AgBr precipitates. Activities of 75-min. Kr⁸⁷ multiplied by normalization factors of 4.5-hr. Kr⁸⁵ obtained by correcting to arbitrary 3-min. Br⁸⁵ decay curve (data of Table II).

sec. by least squares analysis of the normalized activity data of Table II. Including the error in the half-life of Br^{85} , one finds the error in the half-life of Br^{87} to be 0.7 sec. The good fit of the data by an exponential decay curve suggests that, if Kr is lost from the AgBr precipitate between the time of precipitation of AgBr and the introduction of the precipitate into the dissolver about 30 minutes later, the loss occurs either very soon after precipitation or very slowly relative to 3 minutes. This condition must hold to preserve the activity ratio of 75-min. Kr and 4.5-hr. Kr generated by parents whose half-lives are quite different, 56.1 sec. and 3 min., respectively. A more complete discussion of this question is given later (cf. Section 12).

4. HALF-LIFE OF Br^{88}

The half-life of Br^{88} was determined in a manner similar to that of Br^{87} except that the activity of Kr^{88} could not be measured directly in the gas because of the interference of Kr^{85} and Kr^{87} . Instead, the activity of the Kr^{88} was measured by analyzing for the 17.8-min. Rb^{88} activity in the gas. An aliquot of each gas sample counted was transferred to a bulb, and a wash solution of Rb carrier acidified with HAc was added. The Rb activity was allowed to grow for 1 hour during which time the bulb was shaken periodically to effect interchange between the Rb activity and carrier. The wash solution was then

removed, the solution boiled to expel the active gases, the Rb precipitated as the cobaltinitrite by adding 15 ml of sodium cobaltinitrite reagent solution according to the procedure of Treadwell and Hall,¹² and the solution allowed to stand for 3 min. after filtration. Rubidium analysis as a measure of Kr activity was tested by determining the apparent half-life of Kr^{88} through successive Rb extractions of a single gas sample. A value of 2.8 hr. was found, in good agreement with published values.¹³ The Rb samples were counted without absorber, and the decay curves were followed to check the radio-chemical purity. After corrections were made for the chemical yield of Rb, for decay of the 2.8-hr. Kr before growth of 17.8-min. Rb started, and for growth of 17.8-min. Rb during the standing period (1 hour), the Kr activities so derived were extrapolated to the time of AgBr precipitation and normalized by the 4.5-hr. Kr normalization factors of Table II. Least squares analysis of the normalized activities *versus* the time of precipitation (Table III) yielded a half-life of 15.5 ± 0.3 sec. for Br^{88} . The error in the half-life of Br^{85} does not appreciably affect this result. A graphical representation of the data of Table III is given in Fig. 6.

5. SEARCH FOR Br^{89} AND Br^{91}

A search was made for Br^{89} through its active descendants 2.6-min. Kr^{89} , 15.4-min. Rb^{89} , and 53-da. Sr^{89} . In the first experiments the active Kr

TABLE III. Activity of 2.8-hr. Kr^{88} from analysis for 17.8-min. Rb^{88} in gas samples extracted from AgBr precipitates.

Time of precipitation of AgBr	Activity of 17.8-min. Rb^{88} at time of separation from Kr^{88} (c/m)	Milli-grams Rb precipitate	Activity of 17.8-min. Rb^{88} corrected to 50 mg Rb precipitate (c/m)	Decay factor for Kr^{88} from time of AgBr precipitation to Rb growth	Rb growth factor (1 hr. growth)	Activity of 2.8-hr. Kr^{88} at time of AgBr precipitation (Rb counting geometry) (c/m)	Normalization factor, 4.5-hr. Kr^{85} (Table II)	Normalized activity (c/m)
8 sec.	19000	52.5	18100	1.368	1.30	32100	0.492	15800
15 sec.	28000	49.8	28100	1.302	1.30	47600	0.219	10400
25 sec.	18200	50.0	18200	1.255	1.30	29700	0.245	7250
41 sec.	8900	40.3	11040	1.255	1.30	18000	0.213	3830
55 sec.	2080	35.8	2905	1.247	1.30	4710	0.438	2060
70 sec.	880	28.5	1544	1.371	1.30	2750	0.312	860
85 sec.	790	46.4	851	1.270	1.30	1405	0.396	555
90 sec.	960	33.5	1433	1.224	1.30	2280	0.204	465
100 sec.	600	48.8	615	1.286	1.30	1030	0.269	275
115 sec.	225	38.8	290	1.281	1.30	483	0.230	110

¹² F. P. Treadwell and W. T. Hall, *Analytical Chemistry* (John Wiley & Sons, Inc., New York, 1942), Vol. II, p. 275.

¹³ J. C. Jacobsen and O. Kofoed-Hansen ($T_{1/2}=2.7$ hr.), D. Kgl. Danske Vidensk. Selskab Mat.-fys. Medd., **23**, No. 12 (1945); G. N. Glasoe and J. Steigman ($T_{1/2}=2.8$ hr.), Phys. Rev. **58**, 1 (1940); A. Langsdorf ($T_{1/2}=3$ hr.), Phys. Rev. **56**, 205 (1939).

fraction from AgBr precipitated at 8 sec. after a 10-sec. irradiation was examined for a short-lived component by performing the operations quickly enough to start the counting 10 min. after the end of irradiation. No short-lived activity was observed. An effort was then made to isolate the 15.4-min. Rb^{89} . Active AgBr samples precipitated from a AgNO_3 solution containing Rb carrier 6 to 9 sec. after the end of 10-sec. irradiations were examined. The variation in this activity might be used to measure the half-life of Br^{89} . This procedure was unsuccessful, however. The 17.8-min. Rb^{88} interfered with the measurement of the 15.4-min. Rb^{89} present even when Rb was removed from the dissolved AgBr precipitate within 10 min. after the end of irradiation. At this time the 2.6-min. Kr^{89} has almost completely decayed to 15.4-min. Rb^{89} whereas the 17.8-min. Rb^{88} is only at ~ 30 percent of its equilibrium value. From the ratio in half-lives of 15.4-min. Rb^{89} and 2.8-hr. Kr^{88} and the relative growth factors for Rb^{89} and Rb^{88} which should emphasize Rb^{89} relative to Rb^{88} , one concludes that Br^{89} , if it exists, is present in low yield and/or its half-life is much shorter than 16 sec., the half-life of Br^{88} . Still another attempt was made to identify Br^{89} by isolation of Sr from the AgBr precipitated at 7 sec. after a 10-sec. irradiation from a AgNO_3 solution containing Rb, Cs, Ba and Sr carriers. No activity of 53-da. Sr^{89} in the precipitate was observed. If the activity of Sr^{89} in the Sr fraction isolated from the AgBr precipitate is < 4 c/m, the ratio of Sr^{89} activity in the precipitate to Sr^{89} in the uranyl nitrate supernate is < 0.001 . This suggests that Br^{89} has either a very low yield in fission and/or its half-life is short. The short half-life of the halogen would lead to low activity of decay products both because of radioactive decay before precipitation and because of the marked loss of Kr from the precipitate during coagulation (cf. Section 12).

Experiments on the half-life of Br^{91} yielded similar results. The Sr samples isolated for the study of Br^{89} were isolated early enough to detect any 9.7-hr. Sr^{91} if present. A negligibly small activity was observed in the precipitate samples (~ 10 c/m) giving a ratio of Sr^{91} activity in the AgBr precipitate to the supernate of

$< 2 \times 10^{-5}$, leading to the same conclusion on half-life and yield of Br^{91} as for Br^{89} .

6. MASS ASSIGNMENTS OF THE 55.6-SEC. Br AND 4.51-SEC. Br DELAYED NEUTRON EMITTERS

The determination of the half-life of Br^{87} for β^- -emission to be 56.1 ± 0.7 sec., identical within experimental error with the 56.6-sec. half-life for the Br delayed neutron emitter and the unsuccessful attempts to detect Br^{89} and Br^{91} , make it probable that the mass number of the delayed neutron emitter is 87. If the assignment of the mass to 89 or 90 suggested by Glendenin *et al.*⁹ were correct, on the basis of the fission yields expected for Br^{89} or Br^{90} from their postulate, one should have found activity in later members of these chains. No effort was made to study Br^{90} because of the inconveniently short half-life of Kr^{90} (~ 33 sec.) and long half-life of Sr^{90} (25 yr.). However, Sr^{89} would have been detected if the 55.6-sec. Br were of mass 90, because of the change in mass following the delayed neutron emission.

The assignment of the mass number of the 4.51-sec. Br delayed neutron emitter to masses

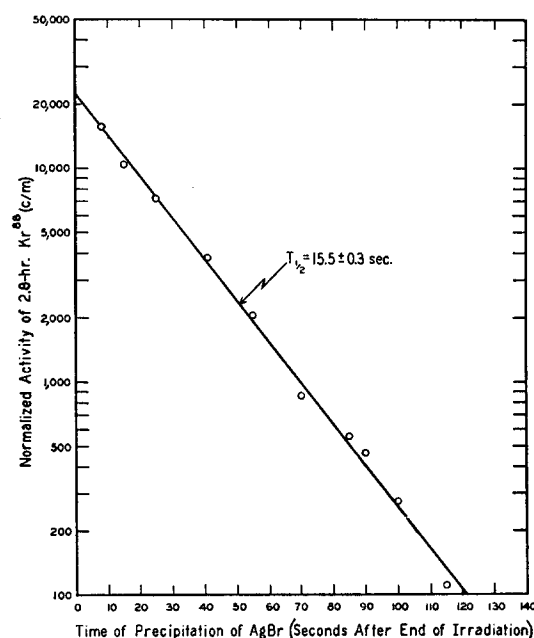


FIG. 6. Decay curve of Br^{88} from 2.8-hr. Kr^{88} activities extracted from AgBr precipitates. Activities of 2.8-hr. Kr^{88} multiplied by normalization factors of 4.5-hr. Kr^{88} obtained by correcting to arbitrary 3-min. Br^{88} decay curve (data of Table III).

87 to 88^{14} was based on mass 87 for the 55.6-sec. Br. Now that the half-lives of Br^{87} and Br^{88} are established, the 4.51-sec. Br must be of mass higher than 88 unless it is an isomer of Br^{87} or Br^{88} and was not observed in these studies because of the adverse conditions of the experiment, namely, the long irradiation time of 10 sec., the time elapsed before precipitation of 7 to 8 seconds, and the loss of Kr from the precipitate during coagulation (cf. Section 12). Each of these factors would reduce the production of daughter activity from the 4.51-sec. Br relative to that grown from a longer-lived isomeric state. Although loss of 4.51-sec. Br from the first two

TABLE IV. Activity of 3.8-min. Xe^{137} extracted from AgI precipitates.

Time of precipitation of AgI	Activity of 3.8-min. Xe^{137} observed at 15 min. after precipitation of AgI (c/m)	Pile power (kw)	Milliliters $\text{UO}_2(\text{NO}_3)_2$ solution irradiated	Normalization factor to 300 kw and 10 ml U solution	Activity of 3.8-min. Xe^{137} normalized (c/m)
8 sec.	23300	200	5	3.0	69900
9 sec.	32000	300	5	2.0	64000
12 sec.	38200	300	5	2.0	76400
15 sec.	23800	250	5	2.4	57120
17 sec.	22900	300	5	2.0	45800
20 sec.	28000	300	5	2.0	56000
20 sec.	14800	200	5	3.0	44400
25 sec.	35000	300	10	1.0	35000
27 sec.	32000	300	10	1.0	32000
30 sec.	32000	300	10	1.0	32000
32 sec.	30000	300	10	1.0	30000
35 sec.	25700	300	10	1.0	25700
40 sec.	22000	250	10	1.2	26400
45 sec.	19000	300	15	0.667	12670
50 sec.	20700	300	15	0.667	13800
1.5 min.	3800	250	15	0.80	3040
2.0 min.	1350	250	15	0.80	1080
2.5 min.	680	250	15	0.80	545

factors would be decreased by shorter irradiations and quicker precipitations, the loss of activity from the precipitate would seriously hamper observation of a short-lived isomeric state. Assignment of the 4.51-sec. Br to mass 89 or 90 does not conflict with the failure to detect Sr^{89} in AgBr precipitates (Section 5) since it is expected that most of the Kr^{89} would leave the precipitate during coagulation.

7. HALF-LIFE OF I^{137}

Strassmann and Hahn³ chemically separated two short-lived I activities of 30 ± 6 -sec. and

1.8 ± 0.4 -min. half-life in fission. Seelmann-Eggebert and Born⁴ isolated the short-lived I fraction from irradiated uranium solutions, and extracting the gas activity found that a 3.8-min. Xe activity could be related to the 30-sec. I, and that no active gas grew from the 1.8-min. I. Irradiation of Xe with neutrons¹⁵ led to the formation of 3.4-min. Xe^{137} and a mass assignment of 137 to the 30-sec. I. The agreement in half-lives of the 30-sec. I^{137} and the 22.0-sec. I delayed neutron emitter led Snell *et al.*⁸ to assign mass 137 to the 22.0-sec. I activity. Glendenin and co-workers⁹ suggested the possibility of 138 or 139 as the mass assignment of the 22.0-sec. delayed neutron emitter on the basis of a comparison of the variation of the yields of this activity among the fissionable isotopes with those predicted by their postulate of "equal chain length." The experiments reported here show that the 22.0-sec. I delayed neutron emitter is probably of mass 137, and cannot be of mass 138, 139, or 140.

The half-life of I^{137} was studied via the activity of its Xe daughter. The experiments were performed in a manner similar to that used for Br^{87} and Br^{88} . The irradiated uranyl nitrate solution contained both Br^- and I^- carriers since it proved difficult to filter the solution containing AgI alone. The presence of AgBr enhanced the coagulation of the precipitate and did not interfere with subsequent operations. The AgI precipitate was transferred to the vacuum line (Figs. 3 and 4) and dissolved in NaCN. The active gases were passed successively through two drying traps filled with Drierite and a charcoal trap at room temperature. The Xe activity was enriched in the gas fraction relative to Kr by discarding the gas removed from the charcoal at room temperature, and the first gas fraction from the charcoal after heating it to $\sim 100^\circ\text{C}$. Later gas samples from the heated charcoal showed a Xe enrichment of about 15-fold. The time elapsed between the AgI precipitation and filling of the gas cell was about 15 minutes.

The variation of Xe^{137} activity with time of precipitation can be used to find the half-life of I^{137} in two ways. First, the chemical yield of Xe extracted from the AgI precipitates can be

¹⁴ N. Sugarman, J. Chem. Phys. **15**, 544 (1947).

¹⁵ W. Riezler, Naturwiss. **31**, 326 (1943).

assumed to be constant in the various experiments and the activity then plotted *versus* time of precipitation. Secondly, another I activity can be used as the monitor of the chemical yield by measuring the activity of its Xe daughter and correcting this Xe activity to the half-life of the I parent. The difficulty in this procedure is that the only I activity which can be used, I^{138} , has a half-life of about 6 sec. (see Section 8), so that a relatively small error (10 percent) in the half-life of the normalizing activity causes a considerably larger error in the half-life of I^{137} .

The half-life found for I^{137} via its Xe daughter (3.8-min. half-life observed) assuming constant chemical yield in the Xe extraction is 19.3 ± 0.5 sec. by least squares analysis of the normalized activities of Table IV. The marked deviation of the points from an exponential curve (Fig. 7) is not surprising in view of the large differences in chemical yield which can occur.

Lower neutron fluxes in the larger samples used for later precipitations arising from the neutron absorption of the uranyl nitrate solution may explain the shorter half-life found for I^{137} than that expected of 22 sec.

The discrepancy in the half-life values of Xe^{137} of 3.4 min. found by Riezler¹⁵ by (n, γ) activation of Xe and 3.8 min. observed by Seelmann-Eggebert and Born⁴ and in this work when extracted from I, has been resolved. Activation of spectroscopically pure Xe with neutrons led to a half-life determination of 3.9 ± 0.1 min. in good agreement with the value found for Xe^{137} from fission.

8. HALF-LIFE OF I^{138}

The half-life of I^{138} was determined in a manner similar to that used for Br^{88} (cf. Section 4). The activity used for normalization of the irradiations was Xe^{137} on the basis of a 22.0-sec. half-life for its parent activity, I^{137} . A fraction of the gas separated in the manner described in Section 7 is counted to determine the 3.8-min. Xe^{137} activity, and an aliquot transferred to a bulb for determination of the 17-min. Xe^{138} activity via its 32-min. Cs daughter after a 30 min. growth period of Cs from Xe. The gas and bulb are washed with a solution containing Cs and Rb carriers and the wash solution is analyzed for Cs. In this analysis the only separation neces-

sary is that of the 32-min. Cs from the 17.8-min. Rb (grown from the 2.8-hr. Kr^{88} in the gas). The separation is effected through the use of BiI_3 in HI as a specific precipitating reagent for Cs.

The procedure used is a modification of one devised by Evans.¹⁶ The Cs is precipitated from the wash solution containing 40 mg Cs and 10 mg Rb carriers, 10 ml H_2O , and 1 ml. 6M HAC by adding 3 ml BiI_3 -HI reagent (10 g BiI_3 in 50 ml 55 percent HI). The solution is cooled in an ice bath and centrifuged. The precipitate is washed twice with 5 ml H_2O containing 3 drops

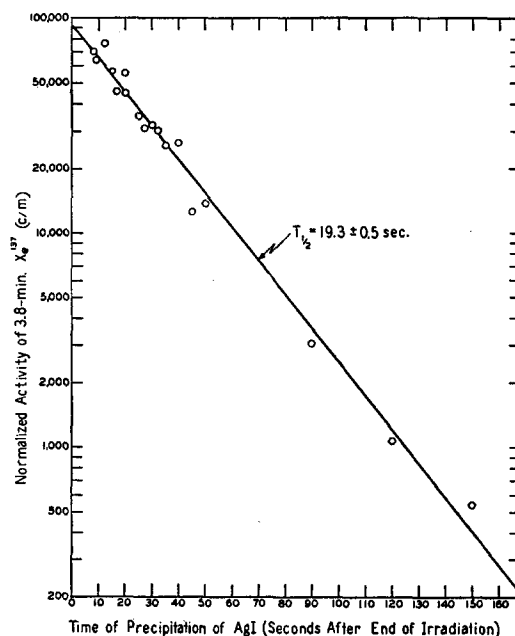


FIG. 7. Decay curve of I^{137} from 3.8-min. Xe^{137} activities extracted from AgI precipitates. Activities of 3.8-min. Xe^{137} multiplied by normalization factors for pile power and milliliters of solution irradiated on the assumption of constant chemical yield (data of Table IV).

6N HCl and 0.5 ml BiI_3 -HI reagent, and cooled before centrifugation. The precipitate is then dissolved by adding 10 ml H_2O , 10 mg Rb carrier, and 7 drops conc. HCl, and heating. After cooling, the Cs is reprecipitated and washed twice. The precipitate is dissolved by boiling out the I_2 after adding 3 ml 6M HNO_3 and 2 ml Fe^{+++} carrier solution (~ 10 mg Fe^{+++} /ml). The solution is diluted to 10 ml and the Fe and Bi are precipitated as hydroxides with NaOH. After

¹⁶ H. B. Evans, Plutonium Project Record, Vol. 9B, 8.22.2 (1946).

TABLE V. Activities of 3.8-min. Xe^{137} and 32-min. Cs^{138} in gas samples extracted from AgI precipitates.

Time of precipitation of AgI	3.8-min. Xe^{137}			32-min Cs^{138}				Normalized activity (c/m)
	Activity at 15 min. after AgI precipitation (c/m)	Activity from arbitrary 22-sec. decay curve (c/m)	Normalization factor	Activity at time of separation from Xe after 30 min. growth of Cs from Xe (c/m)	Correction factor for decay of Xe to bulb filling time of 15 min.	Milligrams Cs precipitate	Activity corrected for Xe decay to bulb filling time of 15 min. and to 50 mg Cs precipitate (c/m)	
8 sec.	23300	47000	2.015	9050	0.98	38.7	11450	23100
9 sec.	32000	45500	1.420	5500	1.02	19.8	14150	20100
12 sec.	38200	41500	1.085	6100	1.01	19.8	15550	16900
15 sec.	23800	37800	1.590	1820	1.02	17.4	5330	8450
17 sec.	22900	35200	1.535	2140	1.02	19.4	5630	8650
20 sec.	28000	32000	1.145	2290	0.98	23.3	4820	5520
20 sec.	14800	32000	2.160	2000	0.98	38.2	2570	5550
25 sec.	35000	27300	0.780	1400	1.01	17.2	4110	3210
27 sec.	32000	25800	0.805	1390	1.02	22.4	3160	2540
32 sec.	30000	22000	0.735	618	1.04	17.6	1825	1340
35 sec.	25700	20000	0.780	500	1.02	22.6	1130	880
40 sec.	22000	17000	0.775	110	1.02	9.4	597	465
45 sec.	19000	14700	0.775	108	1.02	19.2	287	220
50 sec.	20700	12400	0.600	71	1.06	18.1	208	125

acidification with HAc, the Cs is precipitated as the cobaltinitrite by adding 15 ml of the sodium cobaltinitrite reagent. The chemical yield of Cs is ~ 50 percent and the time of analysis about 1

hr. The Cs is freed from the Rb contamination very effectively by this procedure as is evidenced by the decay curves of Cs obtained from samples where the Rb activity was many times that of the Cs.

After correcting the Cs activities for chemical yield, decay of Xe, etc., one can normalize these activities by the factor found for Xe^{137} on the basis of a 22.0-sec. half-life for I^{137} . The normalized activities of the 32-min. Cs^{138} (Table V) as a function of the time of AgI precipitation give a half-life for I^{138} of 5.6 ± 0.1 sec. (Fig. 8) as determined by least squares analysis.

Another measurement of the half-life of I^{138} was made by analyzing the AgI precipitates for 32-min. Cs^{138} and comparing this activity as a function of time of precipitation of AgI with the 32-min. Cs activity in the supernates. Since it was shown that most of the activity of the 32-min. Cs (> 99.5 percent) is in the supernate, its activity should not be affected by time of precipitation and can be used as a monitor of the irradiations. In these experiments the AgI was precipitated from a solution containing Rb and Cs carriers to minimize the adsorption of Cs activity on the AgI precipitate. The solution was allowed to stand for 1 hr. before filtration to permit growth of the 32-min. Cs from its 17-min. Xe parent. The precipitate on the filter disk was washed thoroughly with H_2O , alcohol, and ether,

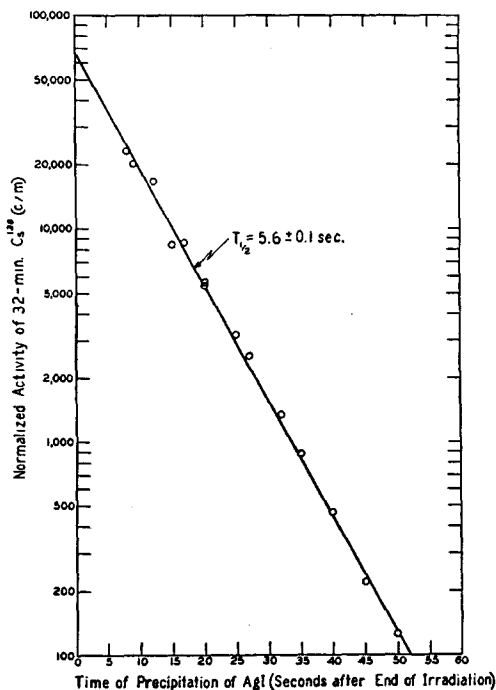


FIG. 8. Decay curve of I^{138} from 32-min. Cs^{138} activities separated from the gas fractions extracted from AgI precipitates. Activities of 32-min. Cs^{138} multiplied by normalization factors of 3.8-min. Xe^{137} obtained by correcting to arbitrary 22.0-sec. I^{137} decay curve (data of Table V).

transferred to a centrifuge tube containing Rb and Cs carriers, and dissolved in NaCN. The NaCN solution was analyzed for 32-min. Cs along with an aliquot of the supernate.

In the first experiments the analytical procedure used was modified from that of Glendenin and Nelson¹⁷ in which Rb and Cs are separated by precipitation of Cs as silicotungstate. The procedure consists of a cobaltinitrite precipitation, solution of the precipitate in HCl, a silicotungstate precipitation, two HCl washings of the silicotungstate, solution in NaOH, fuming with HClO₄ to precipitate SiO₂ and WO₃, a CsClO₄ precipitation, two Fe(OH)₃ scavengings and a final cobaltinitrite precipitation. The Cs samples from the supernate solutions decayed with a 32- to 33-min. half-life, but those of the precipitate samples of precipitations later than 25 sec. decayed with somewhat shorter half-lives (27 to 30 min.). In the latter samples the 17.8-min. Rb⁸⁸ activity grown from the 15.5-sec. Br⁸⁸ is considerably greater than that of the 32-min. Cs and must be removed efficiently to determine the 32-min. Cs activity. The activities so determined led to a 7-sec. half-life for I¹³⁸. However, since the weakly active samples of later precipitations are contaminated with some 17.8-min. Rb activity, the true half-life is expected to be somewhat shorter than that measured.

The half-life of I¹³⁸ was redetermined after a desirable chemical procedure was devised for the separation of Cs in the precipitate from Rb and the other fission products. The Cs is precipitated from the NaCN and supernate solutions as the cobaltinitrite. The precipitate is washed once with 10 ml 10-percent HAC. The precipitate is then dissolved in 1 ml 6N HCl by heating, 8 ml 70-percent HClO₄ is added, and the solution heated until dense fuming occurs. The solution is cooled and CsClO₄ is precipitated by addition of 15 ml absolute ethyl alcohol. The precipitate is washed once with 10 ml absolute ethyl alcohol. The precipitate is dissolved in 10 ml H₂O, and 3 ml BiI₃-HI reagent added to precipitate the Cs. Following the procedure given earlier in this section, the precipitate is washed twice, the I₂ expelled, two hydroxide precipitations are performed and the Cs is precipitated as the covalti-

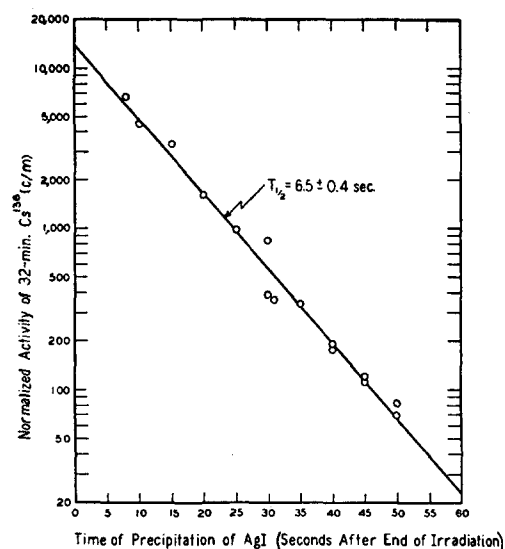


FIG. 9. Decay curve of I¹³⁸ from 32-min. Cs¹³⁸ activities extracted from AgI precipitates. Activities of 32-min. Cs¹³⁸ in precipitates multiplied by normalization factors obtained by correcting Cs activities in supernates to 10⁶ c/m (data of Table VI).

nitrite. The chemical yield is ~60 percent and the time for analysis of two samples about 1½ hrs. The Cs is freed from contamination by Rb and the other fission products very effectively by this procedure as is evidenced by the decay curves of Cs obtained from samples of later precipitations where the Cs activity was much lower than that of Rb or the other fission products.

The measured activities of the Cs samples of the precipitate and supernate from a given experiment are corrected for chemical yield and aliquot of solution taken. Since the Cs activity is predominately in the supernate, this activity is used for monitoring the irradiations by normalizing the activity to a constant level, 10⁶ c/m. The half-life found for I¹³⁸ by least squares analysis is 6.5±0.4 sec. (Fig. 9) using the normalized activity data of Table VI.

The half-lives found for I¹³⁸ by the two methods, 5.6±0.1 sec. and 6.5±0.4 sec., differ by more than the estimated errors of the determination. Such a discrepancy would result if Cs activity coseparated with Ag(Br, I) to the extent of one part in 5×10⁴. This possibility was tested under conditions identical with those of the experiments already reported. Approximately one part in 5×10⁵ of the Cs activity was found

¹⁷ L. E. Glendenin and C. M. Nelson, Plutonium Project Record, Vol. 9B, 8.22.1 (1946).

with the precipitate when the former was present at time of precipitation. When Cs activity was added one minute after precipitation, only one part in 10^6 coseparated. Thus the source of the discrepancy lies elsewhere. Coseparation of the Xe activity will lengthen the apparent half-lives in both procedures although the error in the first case should be smaller since the Xe^{137} used for normalization will also coseparate. If other fission products are not removed to the required degree by the isolation procedure used for radio-Cs, the apparent half-life of I^{138} will be longer in the second method. In the first method Xe^{138} was separated from the precipitate and non-volatile radioactive contaminants before analysis for Cs.

The average half-life by weighting the first determination twofold relative to the second is 5.9 ± 0.4 sec.

9. HALF-LIFE OF I^{139}

The half-life of I^{139} was determined by analyzing the AgI precipitate and supernatant solution containing Rb, Cs, Sr, and Ba carriers for 85-min. Ba^{139} . After thorough washing of the precipitate on the filter disk, it was dissolved in NaCN solution containing Ba carrier and analysis for Ba was performed on this solution and an aliquot of the supernatant solution. The Ba was precipitated as BaCO_3 about 1 hr. after the end of irradiation. At this time the 7-min. Cs^{139} has completely decayed to the 85-min. Ba^{139} . After dissolving this precipitate in acid the Ba was separated by the procedure of Glendenin¹⁸ which includes two precipitations of Ba as $\text{Ba}(\text{NO}_3)_2$ from fuming HNO_3 solution, a $\text{Fe}(\text{OH})_3$ scavenging, and two precipitations of BaCl_2 using conc. HCl—ether reagent. The Ba was then converted to BaCrO_4 and counted. The 85-min. Ba^{139}

TABLE VI. Activity of 32-min. Cs^{138} extracted from AgI precipitates and supernatant solutions.

Time of precipitation of AgI	Sample	Activity of 32-min. Cs at 3 hrs. after AgI precipitation (c/m)	Milligrams Cs precipitate	Aliquot	Activity of 32-min. Cs corrected to 25 mg precipitate* and for aliquot	Normalization factor for supernate activities (corrected to 10^6 c/m)	Activity of Cs in precipitate (normalized) (c/m)
8 sec.	precipitate	4150	24.4	1.0	4250	—	6720
	supernate	13300	25.8	0.02	0.630×10^6	1.58	—
10 sec.	precipitate	1720	14.9	1.0	2885	—	4500
	supernate	13100	26.1	0.02	0.640×10^6	1.56	—
15 sec.	precipitate	2910	24.9	1.0	2920	—	3360
	supernate	17200	25.2	0.02	0.870×10^6	1.15	—
20 sec.	precipitate	1310	24.7	1.0	1325	—	1615
	supernate	13900	21.6	0.02	0.820×10^6	1.22	—
25 sec.	precipitate	371	22.5	1.0	412	—	985
	supernate	9100	27.7	0.02	0.420×10^6	2.39	—
30 sec.	precipitate	388	26.0	1.0	373	—	388
	supernate	19200	25.4	0.02	0.965×10^6	1.04	—
30 sec.	precipitate	435	21.4	1.0	508	—	845
	supernate	12200	25.8	0.02	0.605×10^6	1.66	—
31 sec.	precipitate	280	25.1	1.0	279	—	360
	supernate	14500	23.8	0.02	0.775×10^6	1.29	—
35 sec.	precipitate	148	25.3	1.0	146	—	340
	supernate	8550	25.5	0.02	0.430×10^6	2.33	—
40 sec.	precipitate	88	17.7	1.0	124	—	192
	supernate	12250	24.2	0.02	0.645×10^6	1.55	—
40 sec.	precipitate	152	24.8	1.0	153	—	177
	supernate	16200	24.0	0.02	0.860×10^6	1.16	—
45 sec.	precipitate	88	23.0	1.0	92	—	111
	supernate	17200	26.6	0.02	0.825×10^6	1.21	—
45 sec.	precipitate	68	25.7	1.0	66	—	120
	supernate	10800	25.0	0.02	0.550×10^6	1.82	—
50 sec.	precipitate	31	13.0	1.0	60	—	70
	supernate	17600	26.3	0.02	0.855×10^6	1.17	—
50 sec.	precipitate	61	26.4	1.0	58	—	83
	supernate	13800	25.1	0.02	0.700×10^6	1.43	—

* Supernate activities multiplied by another factor of 1.02 to correct for Cs carrier originally present in solution at AgI precipitation.

¹⁸ L. E. Glendenin, Plutonium Project Record, Vol. 9B, 8.23.1 (1946).

activity is predominately in the supernate (>99.98 percent) so that the supernate activity can be used for monitoring the irradiations. The half-life found for I^{139} by least squares analysis was 2.7 ± 0.1 sec. (Fig. 10) using the normalized activity data of Table VII.

The half-life found for I^{139} is quite sensitive to the coseparation of Ba^{139} activity or its antecedents since so small a fraction of the total Ba activity is in the precipitate. For the coseparated activity to be less than 10 percent of the total activity of the samples from later precipitations (17 sec.), the coseparation factor must be less than 10^{-6} . Coseparation tests with Cs and Ba yielded factors of this magnitude, $\sim 1 \times 10^{-6}$ for Cs and $< 2 \times 10^{-6}$ for Ba. Since the factor for Xe and the fate of the Cs and Ba decay products of coseparated Xe are unknown, the half-life found for I^{139} may be somewhat higher than the true value.

10. SEARCH FOR I^{140}

Two of the Ba samples isolated for the study of I^{139} (Section 9) were followed long enough to detect any activity of 12.8-days Ba^{140} , if present. None was observed in the AgI samples precipitated at 7 and 10 sec., and on the assumption that an activity of 4 c/m would have been detected, a ratio of $< 5 \times 10^{-5}$ for the 12.8-days Ba^{140} activity in the precipitate to that in the supernate was obtained. The conclusion from this is that the half-life of I^{140} is short and/or the isotope is formed in low yield.

11. MASS ASSIGNMENT OF THE 22.0-SEC. I DELAYED NEUTRON EMITTER

The half-life of I^{137} has been determined on the assumption of constant chemical yield of Xe extraction to be 19.3 ± 0.5 sec. (Section 7). It seems probable that I^{137} and the 22.0-sec. I delayed neutron emitter are identical. This result and the half-lives found for I^{138} and I^{139} eliminate the possibility of the assignment of the mass of the 22.0-sec. I to 138 or 139.⁹

Another uncertainty introduced into the assignment of the 22.0-sec. I delayed neutron emitter to mass 137 by the relatively lower yield of the stable isotope Xe^{136} compared to Xe^{134} found in fission by Thode and Graham,¹⁹ has been

¹⁹ H. G. Thode and R. L. Graham, Can. J. Research 25, 1 (1947).

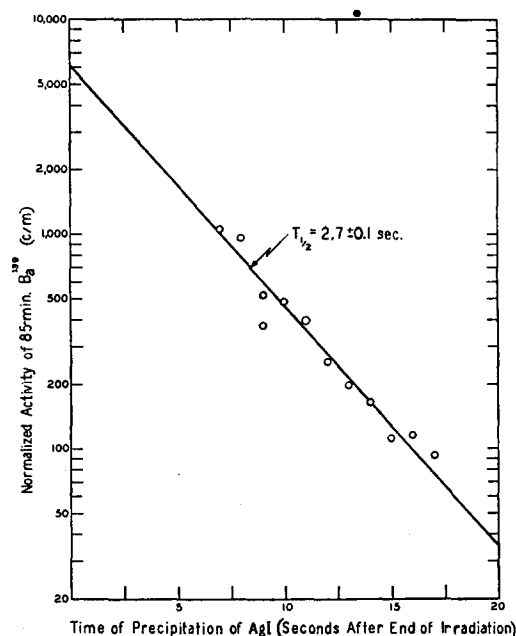


Fig. 10. Decay curve of I^{139} from 85-min. Ba^{139} activities extracted from AgI precipitates. Activities of 85-min. Ba^{139} in precipitates multiplied by normalization factors obtained by correcting Ba activities in supernates to 10^7 c/m (data for Table VII).

removed. An assignment of the delayed neutron emitter to I^{136} was proposed¹⁴ to explain the lower yield of Xe^{136} and the fission yield of 9.2-hr. Xe^{135} formed independently of the 6.7-hr. I^{135} . On the basis of a mass of 136, the 9.2-hr. Xe activity in a AgI precipitate should arise from two sources, the 22.0-sec. I decaying to the 9.2-hr. Xe^{135} by a process of β^- -decay followed by

TABLE VII. Activity of 85-min. Ba^{139} extracted from AgI precipitates and supernatant solutions.

Time of precipitation of AgI	Activity of 85-min. Ba in precipitate at time of AgI precipitation (c/m)	Activity of 85-min. Ba in supernate at time of AgI precipitation (c/m)	Normalization factor for supernate activities (corrected to 10^7 c/m)	Activity of Ba in precipitate (normalized) (c/m)
7 sec.	1025	0.975×10^7	1.025	1050
8 sec.	389	0.405×10^7	2.470	960
9 sec.	340	0.905×10^7	1.105	376
9 sec.	630	1.200×10^7	0.835	525
10 sec.	1015	2.085×10^7	0.480	485
11 sec.	650	1.655×10^7	0.605	393
12 sec.	410	1.605×10^7	0.625	256
13 sec.	342	1.725×10^7	0.580	198
14 sec.	110	0.675×10^7	1.480	163
15 sec.	117	1.045×10^7	0.955	112
16 sec.	173	1.475×10^7	0.680	118
17 sec.	138	1.485×10^7	0.675	93

neutron emission, and the 6.7-hr. I^{135} decay during the time interval of about 6 min. between the AgI precipitation and the sweeping of the active gases from the NaCN solution of the dissolved precipitate.

This hypothesis can be tested. The activity of the 9.2-hr. Xe should show variation with time of precipitation of AgI leading to a resolution of the composite decay curve into two periods, 22 sec. and 6.7 hr. Some of the Xe samples used for the study of the half-life of I^{137} (Section 7) were followed long enough to measure the 9.2-hr Xe activities in them. It was found that the ratio of the activity of 9.2-hr. Xe to 3.8-min. Xe increased 70-fold for AgI precipitations in the time interval 15 sec. to 2.5 min., showing a much

TABLE VIII. Activity of 9.2-hr. Xe^{135} extracted from AgI precipitates.

Time of precipitation of AgI	3.8-min. Xe^{137}			9.2-hr. Xe^{135}	
	Activity of 3.8-min. Xe^{137} at 15 min. after AgI precipitation (c/m)	Activity from arbitrary 22-sec. decay curve (c/m)	Normalization factor	Activity of 9.2-hr. Xe^{135} at 24 hr. after AgI precipitation (c/m)	Normalized activity (c/m)
15 sec.	23800	62500	2.62	39	102
30 sec.	32000	39000	1.22	108	132
35 sec.	25700	33500	1.30	92	119
40 sec.	22000	28500	1.29	98	127
50 sec.	20700	21000	1.01	143	144
1.5 min.	3800	6000	1.58	72	114
2.0 min.	1350	2300	1.71	72	123
2.5 min.	680	900	1.32	74	98

slower decrease of the 9.2-hr. Xe activity relative to the 3.8-min. Xe activity as a function of time of AgI precipitation. Normalizing the 3.8-min. Xe^{137} activities to a 22-sec. half-life for I^{137} and multiplying the 9.2-hr. Xe^{135} activities by these normalization factors, one finds that the 9.2-hr. Xe activity is roughly constant for AgI precipitations from 15 sec. to 2.5 min. (last column of Table VIII). These results show that the delayed neutron emitter cannot be I^{136} since the contribution of 9.2-hr. Xe from this species would have resulted in a considerably higher activity in the 15 sec. AgI precipitate relative to the 2.5-min. sample. The lower yield of Xe^{136} relative to Xe^{134} observed by Thode and Graham¹⁹ must, therefore, arise from some other source.

12. LOSS OF ACTIVITY FROM SILVER HALIDE PRECIPITATES

In the course of this work some semi-quantitative information was obtained on the loss of the active decay products from AgBr(I) precipitates. A comparison of the activity in the precipitate with that in the supernate yields the composite value of the fraction of the halogen activity precipitated and the fraction of the activity of the decay products retained by the precipitate. The fraction of the halogen activity precipitated with AgBr may be expected to be less than unity since activity present chemically in oxidized states of the halogens will not precipitate unless the carrier species (Br^- or I^-) reacts fast enough to reduce them to states exchangeable with I^- or Br^- before precipitation. The retention factor expresses the loss of activity from the precipitate by the diffusion of Kr or Xe which may be expected to occur rapidly during coagulation while considerable surface is exposed, and more slowly afterward. This factor will be approximately the exponential decay of the halogen activity during the time of rapid diffusion.

The ratio of the Ba^{139} activity in the AgI precipitate to the activity in the supernate at the end of a 10-sec. irradiation is 6.2×10^{-4} (see Fig. 10). After correcting for the saturation of the 2.7-sec. I^{139} during irradiation, and assuming the fission yield of I^{139} to be about 0.3 that of Ba^{139} ,⁹ one finds the product of the fraction of the I activity precipitated as AgI and the fraction of the decay products retained by the precipitate is 0.006. Similarly, this value for the 5.9-sec. I^{138} is 0.05. A rough value of ~ 0.25 is found for the 15.5-sec. Br^{88} by comparing the 17.8-min. Rb^{88} activity with that of the 32-min. Cs^{138} activity in a mixed Ag(Br+I) precipitate where no separation of Rb from Cs is made in the analysis for Cs. From these results there is found a marked variation in the fraction of the decay products found in the precipitate as a function of the half-life of the halogen ancestor. Assuming the fraction of Br or I activity exchanged with Br^- or I^- carriers is about 0.5, one can correlate the derived retention factors with a time required for retention of about 20 sec.

The precision of the half-life determination of the halogen by the method employed here will

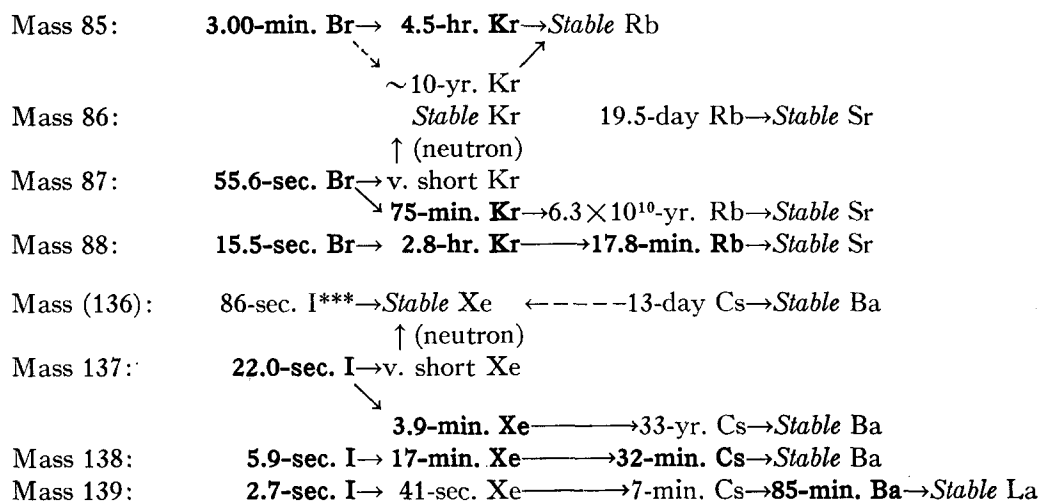
be affected by the difference in time required for "setting" of the precipitate from experiment to experiment. In those cases where the half-life of the halogen is long relative to ~ 20 sec., e.g., Br^{85} and Br^{87} , the loss of activity during "setting" will not be significant and the scattering of the data from time variations in "setting" will be small. This result is borne out by the good precision of the determination of the half-life of Br^{87} based on normalization values of Br^{85} (cf. Section 3 and Fig. 5). On the other hand, where the half-life of the halogen is short relative to ~ 20 sec., e.g., I^{138} , I^{139} , there is considerable loss of activity during the "setting" process and greater scatter of the points due to differences in "setting" time (see Fig. 10). It should be noted, however, that the variation in "setting" time is probably small relative to 2.7 sec. or considerably more scattering would have resulted.

The considerations above offer an explanation

for the absence of 53-day Sr^{89} in AgBr precipitates if the mass assignment of the 4.51-sec. delayed neutron emitter is 89 or 90 (cf. Section 6). Little activity would be retained by the precipitate because of the short-half-life of the halogen, leading to difficulty in observing either an increase in Kr^{88} activity above that formed from decay of 15.5-sec. Br^{88} or the Sr^{89} activity if the mass is 89, or Sr^{89} activity formed via neutron emission and subsequent β^- decay if the mass is 90.

13. SUMMARY

The results of these experiments on the half-lives of the halogen fission products clarify some of the ambiguities in mass assignment formerly existing in the table of "Nuclei Formed in Fission."¹ Some new short-lived Br and I activities have also been found. The chain relations as modified in this work are given below:**



ACKNOWLEDGMENT

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** Boldface indicates activities studied in this paper.

*** This value is taken from recent work of S. Katcoff and C. W. Stanley, Los Alamos Report, La-628, March 25, 1947.