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Low Mass Francium and Emanation Isotopes of High Alpha-Stability*

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Isotopes of francium with 126 or fewer neutrons have been looked for in bombardments of Th^{232} with 350-Mev protons from the 184-inch cyclotron. Fr^{212}, with an apparent half-life of 19.3 minutes for branching decay by alpha-emission (44 percent) to At^{208} and by orbital electron-capture (56 percent) to Em^{212}, has been found. Em^{212} is shown to be a 23-minute alpha-emitter. At^{208} decays primarily (99.5 percent) by orbital electron-capture to Po^{208}, but shows 0.5 percent alpha-branching. The francium and emanation isotopes have alpha-half-lives completely out of line with the simple predictions based on the previously known isotopes of these elements. Their high alpha-stability is believed to be due to a closed shell of 126 neutrons in analogy to the behavior of elements 83–85. The non-existence of long-lived francium in nature is discussed in the terms of this and other recent work on francium isotopes.

R ECENT work with the 184-inch cyclotron has increased greatly the number of alpha-particle emitting isotopes and stimulated the reexamination of alpha-decay systematics in the heavy region.[1-3] The present paper describes experimental work carried out to get more information concerning the abnormalities in alpha-stability for nuclei in the region of 126 neutrons.

A plot of alpha-particle energy _versus_ mass number for nuclei of elements above atomic number 85 produces a series of nearly parallel curves (see Fig. 1 which is redrawn from the data of Fig. 1, reference 3, using alpha-particle energies instead of alpha-decay energies). The curves for bismuth, polonium, and astatine (elements 83, 84, and 85) differ markedly in showing sharp maxima and minima. It was of interest to know whether those for emanation (element 86) and francium (element 87) show the same behavior. If the emanation and francium curves of Fig. 1 are simply extrapolated back to lower mass numbers, the alpha-particle energies predicted for all low mass isotopes correspond to half-lives of fractions of microseconds. But if the behavior of the astatine, polonium, and bismuth curves is imitated, one might expect that Fr^{213}, Em^{212}, and isotopes of lower mass number would exhibit alpha-half-lives

long enough to permit their chemical isolation from targets bombarded in the 184-inch cyclotron. Should it be possible to do this, it would constitute further evidence for a region of stability at 126 neutrons.[4]

In addition to these considerations, it is of interest to learn-more about element 87. No isotopes of this element were known until Perey's work on the 21-minute β-emitting AcK.[5,6] Since then the five shorter-lived isotopes listed in Table I have been discovered. Any new information concerning the isotopes or the chemical properties of this little known element should be welcome.

Therefore we undertook to prepare new francium isotopes by cyclotron bombardment. Without the aid of the high energy beam of the 184-inch cyclotron it would have been impossible as the closest suitable target material is Th^{232}. However, the use of a high energy proton beam (maximum 350 Mev) on thorium easily effected the preparation of isotopes in the region of interest by spallation reactions. We were able to isolate francium and establish the new family of isotopes shown in Fig. 2. The experimental evidence for this scheme is given now.

In addition evidence was found for Fr^{211} decaying principally by successive orbital electron-captures to At^{211} with a half-life of about 8 minutes. This particular work is not complete.

[1] Perlman, Ghiorso, and Seaborg, Phys. Rev. 74, 1730 (1948).
[2] Perlman, Ghiorso, and Seaborg, Phys. Rev. 75, 1096 (1949).
[3] Perlman, Ghiorso, and Seaborg, Phys. Rev. 77, 26 (1950).
[4] Maria G. Mayer, Phys. Rev. 74, 235 (1949).
[5] M. Perey, Comptes Rendus 208, 97 (1939).
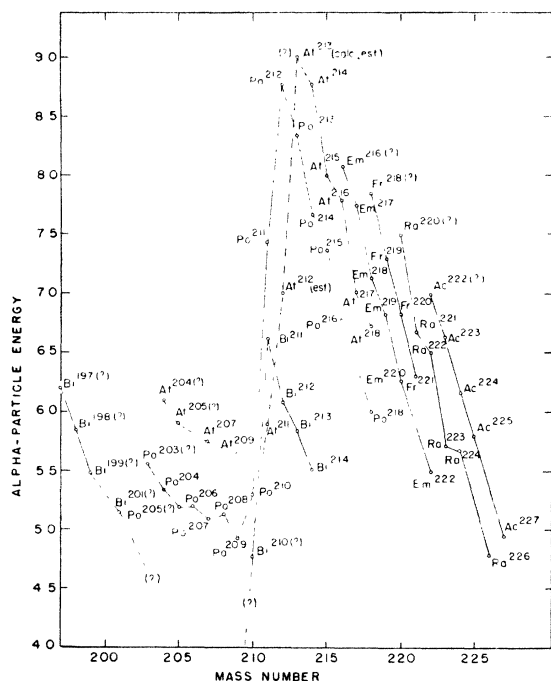[6] M. Perey, J. de phys. et rad. 10, 435 (1939).

FIG. 1. Plot of alpha-particle energy *versus* mass number for isotopes of elements 83–89. Lines join all isotopes of a single element. Redrawn from paper of Perlman, Ghiorso, and Seaborg, reference 3.

It is quite evident then that the emanation and francium curves in Fig. 1 show the same sharp break in the neighborhood of 126 neutrons as do the curves for elements 83–85. One may safely predict that higher elements will show to some degree the same effect, but the possibility of observing it by the method used here for francium and emanation grows slim, because the half-lives for alpha-decay become very short and the region of greater beta-instability is being penetrated. These matters are discussed in much more detail by Perlman, Ghiorso, and Seaborg.[3]

Many writers of the past decade have pointed out the improbability of the natural occurrence of any long-lived isotopes of element 87. It may be well to reiterate this view in the light of the recent increase of the number of known francium isotopes from one to seven. Known isotopes of mass less than 222 are quite short-lived with respect to alpha-emission. Even the stabilization which occurs around 126 neutrons, although it enormously lengthens the expected half-life, is not enough to raise it to as much as an hour. On the other hand, isotopes 222 and 223 are short-lived with respect to beta-emission and those of higher mass are expected to be even more unstable. At this time we can be virtually certain that no very long-lived francium will ever be found. One cannot completely eliminate the possibility of the existence of a long-lived isomer corresponding to a highly forbidden transition.

EXPERIMENTAL SECTION

(1) Bombardment

Thorium foils 0.005 inch in thickness and 0.5 inch wide were bombarded on edge in the 184-inch cyclotron by full energy protons (max. 350 Mev) for periods ranging from 15 to 50 minutes. Numerous bombardments were made to obtain all the data because of the short half-lives involved.

(2) Chemical Isolation of Francium and Proof of Element Assignment

It was necessary to separate francium out of an exceedingly complex mixture of activities produced by (p,xn), (p,pxn), and other spallation and fission reactions.

This was done with cesium carrier, using a procedure based on the fission product assay method for cesium reported by Nelson and Glendenin.[7]

The thorium foil was dissolved in hot $6N$ HCl containing $0.1N$ $(NH_4)_2SiF_6$. After dissolution, 2 mg of cesium carrier was precipitated as cesium silicotungstate from $6N$ HCl, washed in HCl, dissolved in NaOH, scavenged of co-precipitated impurities by means of by-product ferric hydroxide precipitation and finally precipitated as cesium perchlorate from anhydrous alcoholic perchloric acid solution.

The activity listed in Fig. 2 as Fr^{212} was identified as the alkali element, francium, by the facts of its co-precipitation on cesium silicotungstate and cesium perchlorate, and its failure to co-precipitate on ferric hydroxide, thorium fluoride, or barium carbonate. It was possible to partially separate it from cesium by passing a $1N$ HNO_3 solution through a short resin column containing colloidal Dowex 50, the francium coming off last as the results of Cohn and Kohn[8] for the other alkali metals would indicate.

TABLE I. Previously known isotopes of francium.

Isotope	Half-life	Mode of decay	Energy of particle (Mev)	Ref.
Fr^{218}	very short	α	7.85	a
Fr^{219}	0.02 sec.	α	7.30	b
Fr^{220}	27.5 sec.	α	6.69	b
Fr^{221}	4.8 min.	α	6.30	e, d
Fr^{222}	14 min.	β^-		e
Fr^{223} (AcK)	21 min.	β^-, γ	1.20	f

a Ghiorso, Meinke, and Seaborg, Phys. Rev. **74**, 695 (1948).

b Meinke, Ghiorso, and Seaborg, Phys. Rev. **75**, 314 (1949).

c Hagemann, Katzin, Studier, Ghiorso, and Seaborg, Phys. Rev. **72**, 252 (1947); more completely given in U. S. AEC declassified document MDDC 1186 (December 10, 1947).

d English, Cranshaw, Demers, Harvey, Hincks, Jelley, and May, Phys. Rev. **72**, 253 (1947).

e E. K. Hyde and A. Ghiorso, unpublished work (June, 1949).

f See references 5 and 6.

[7] C. M. Nelson and L. E. Glendenin, U. S. AEC declassified document AECD 2556C (March 24, 1949).

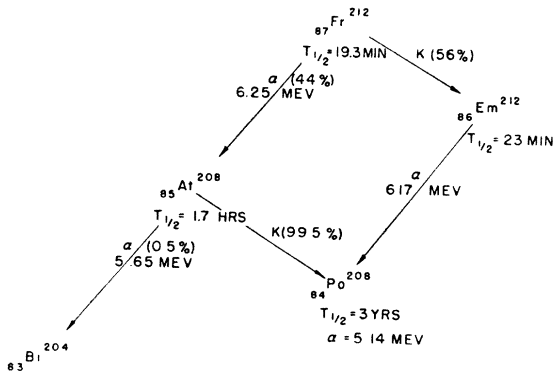[8] W. E. Cohn and H. W. Kohn, J. Am. Chem. Soc. **70**, 1986 (1948).

FIG. 2. Disintegration scheme of Fr^{212}.

In addition, it showed the volatility behavior reported for Fr^{221} [9] and the daughters showed the specific behavior of astatine and emanation. It might also be mentioned that the Fr^{223} (AcK) produced in the bombardment followed the behavior of the 19.3-minute alpha-emitter identically.

(3) Determination of Half-Life of Fr^{212}

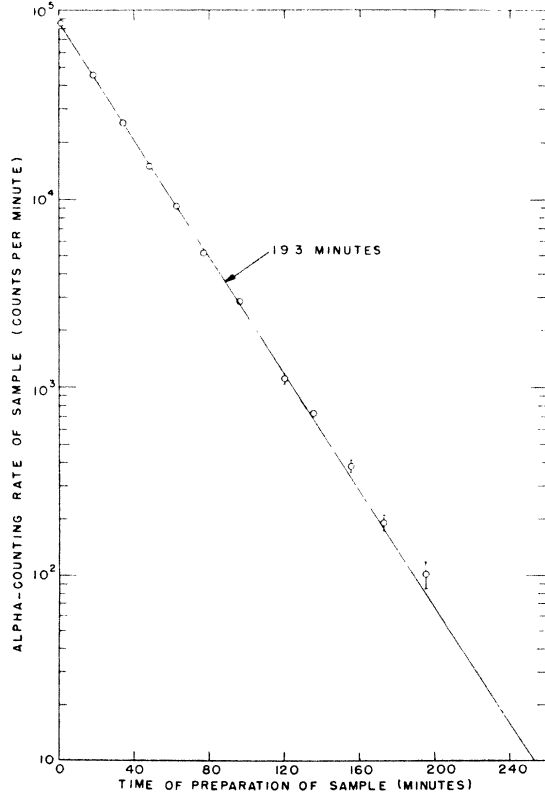The gross alpha-activity of francium samples did not show a straight line decay (see Fig. 8). This curve is a composite of the growth and decay of the alpha-activity of Em^{212} superimposed on the direct alpha-decay of Fr^{212} with small contributions from At^{208} and from the alpha-emitting daughters (AcX chain) of Fr^{223}. Ordinarily such a situation can easily be resolved by frequent differential pulse analyses of the alpha-spectrum by which method the peak due to any isotope can be followed independently of the rest. In our alpha-differential pulse analyzer [9] alpha-pulses from an ionization chamber are passed through a series of 48 electronic channels. Each channel records only the pulses falling within a narrow energy band. By plotting alpha-counts per channel *versus* the channel number, a curve is obtained with peaks which indicate the energy and abundance of each alpha-group.

This powerful method failed in this case because the near identity of the Fr^{212} and Em^{212} alpha-particle energies made it impossible to resolve them accurately.

In the method used, aliquots of a francium solution were taken at intervals of 15–30 minutes and volatilized from one platinum plate heated briefly to red heat to a second cooled plate 2 mm above. This volatilization is believed to be due to the disproportionation of the
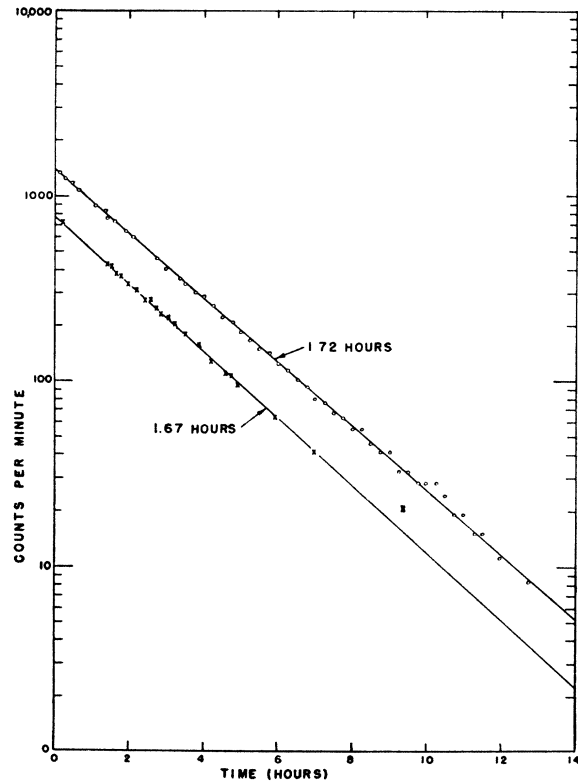

FIG. 3. Determination of half-life of Fr^{212}. Points represent counting rates of equal sized aliquots of a francium solution counted immediately after purification by volatilization.

FIG. 4. Determination of half-life of At^{208} by measurement of decay. Upper curve shows decay of x-ray and γ-activity through 1.87 g/cm^2 beryllium absorber. Lower curve shows alpha-decay.

[9] Ghiorso, Jaffey, Robinson, and Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The transuranium elements: research papers," paper no. 16.8 (1949) (McGraw-Hill Book Company, Inc., New York, 1949); shorter description given in U. S. AEC declassified document MDDC-23 (June 14, 1946).
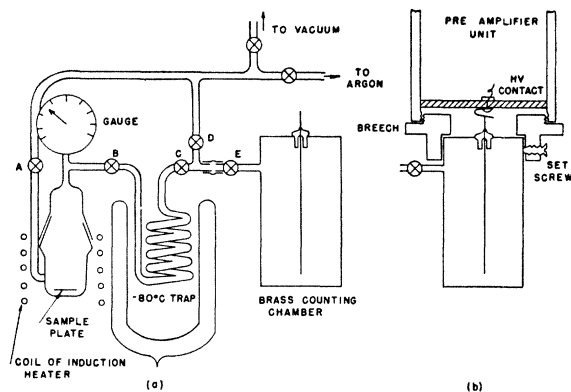
Fig. 5. Apparatus used in the isolation (a) and alpha-counting (b) of Em^{212}.

francium oxide to volatile metal and peroxide coupled with the thermal decomposition of the peroxide in analogy to the behavior of cesium oxide. Thin francium plates could be 99 percent volatilized.

The francium aliquots thus freed of Em^{212} and the Ra^{223} daughter of Fr^{223}, which was also present, were immediately counted before any appreciable re-growth of these had occurred. Corrections were made for an appreciable contribution by At^{208} activity in the later aliquots.

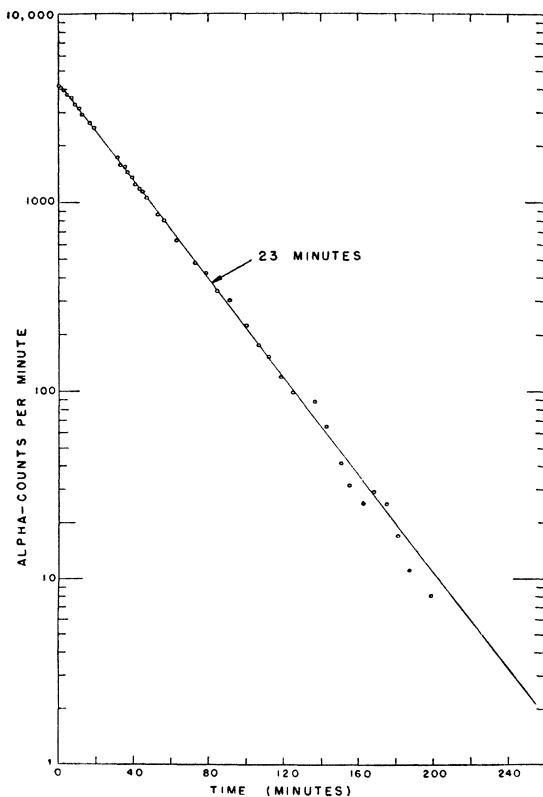Fig. 6. Determination of half-life of Em^{212} by measurement of decay.

A half-life value of 19.3 ± 0.5 minutes is obtained from the data plotted in Fig. 3.

(4) Identification of Astatine Daughter

Alpha-pulse analyses of francium samples after three hours decay clearly showed a new alpha-activity of 5.65 ± 0.02 Mev energy. This activity could be volatilized from one plate to another at temperatures much lower than the francium could be moved.

High volatility is characteristic of astatine,[10] and this 5.65 Mev activity was judged to be the At^{208} daughter of Fr^{212}. Chemical proof involved carrying the activity on tellurium metal precipitated from $2M$ HCl with SO_2 and extraction into benzene from a $2N$ H_2SO_4 solution saturated with SO_2.

Benzene-extracted astatine samples were observed to have a straight line alpha-decay with a half-life of 1.7 hours. These samples emitted x-rays which also decayed with a 1.7-hour half-life. Representative curves are shown in Fig. 4.

By following decay through 2 grams of beryllium absorber with the sample at 10 percent geometry beneath a xenon-alcohol (10-cm pressure) filled end-
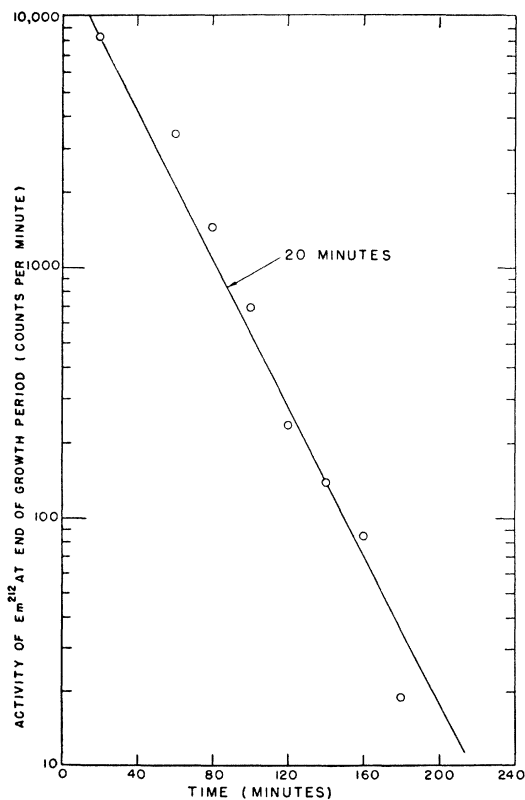

Fig. 7. Determination of half-life of parent of Em^{212}. Points represent counting rate of Em^{212} grown into a sample of Fr^{212} during 20-minute period immediately preceding count.

[10] Johnson, Leininger, and Segrè, J. Chem. Phys. 17, 1 (1949); also published as U. S. AEC declassified document AECD-1952 (May 10, 1948).

window Geiger tube, we observed one Geiger count per two alpha-disintegrations. This Geiger activity is principally K and L x-rays, but includes some γ-rays. A value of 1.1 Mev was determined by lead absorption for the most energetic γ-ray.

A value of the $At^{208}K/\alpha$-branching ratio was obtained by comparing the initial alpha-particle counting rate of a pure sample of At^{208} to the alpha-counting rate of the Po^{208} daughter formed from electron-capture observed on complete decay of the At^{208}. From 7830 alpha-counts per minute At^{208} we obtained 88 counts per minute of 3-year Po^{208} alpha-activity.

From this we obtain 178/1 as the K/α-branching ratio for At^{208}. Duplicate samples gave scattered results, the average value being 180 ± 20. This would make the partial alpha-half-life of At^{208} about 13 days.

It should be pointed out that Barton has found evidence for an isomer of At^{208} in astatine fractions of bismuth targets bombarded with high energy helium ions.[11] This isomer decays by orbital electron-capture to Po^{208} with a half-life of 7 hours.

(5) Identification of Polonium Daughter

The alpha-activity found after complete decay of the 1.7-hour astatine activity in the samples mentioned in Section (4) was shown by pulse analysis to be of 5.15 ± 0.05 Mev energy. Templeton et al.[12] report a

3-year Po^{208} activity emitting alpha-particles of 5.14 Mev energy. Within statistical error our samples have been decaying with a 3-year half-life for a period of more than 6 months. Large samples of initially pure Fr^{212} (10^5–10^6 alpha-counts per minute) were found weeks later to have the amounts of 5.14-Mev alpha-activity consistent with the production of 3-year Po^{208} by the branching scheme of Fig. 2. This evidence plus the isolation of the same polonium activity from an initially pure sample of the 23-minute emanation is the evidence on which the mass assignments of Fig. 2 rest.

(6) The Emanation Isotope

The apparatus shown in Fig. 5 was used in the isolation and identification of Em^{212}.

A platinum plate with a sample of francium on it was placed in the apparatus. After evacuating the entire system, the part between valves A and B was filled with an atmosphere of pure argon. The platinum plate was brought to red heat with the induction heater to volatilize the francium and deposit it as a readily emanating film on the walls of the vessel. By opening valves B, C, and E with D closed and letting argon flow in from A until the pressure reached atmospheric, the greater part of the emanation could be passed through the dry ice-cooled trap into the counting chamber. The trap removed astatine, water vapor, and
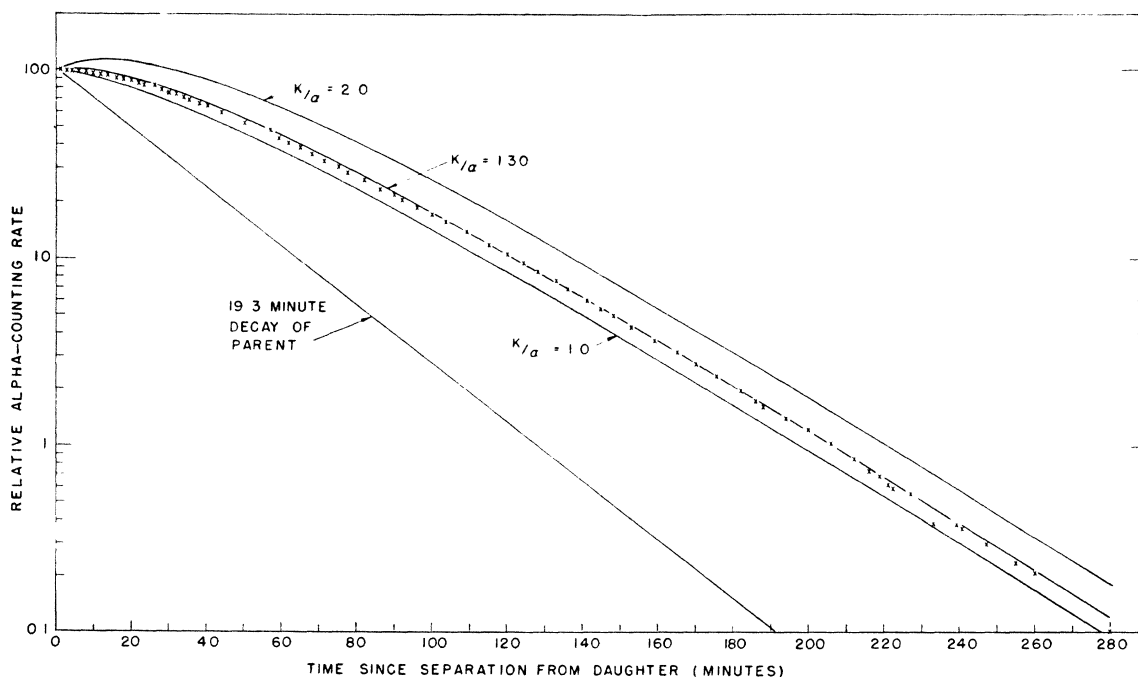

FIG. 8. Determination of the K/α-branching ratio of Fr^{212}. X points are experimental values corrected for small contributions from At^{208} and Ra^{223} and normalized to an initial count of 100. Lines are theoretical curves for the total alpha-counting rate of a 19.3-minute alpha-emitting parent producing a 23-minute alpha-emitting daughter by K-capture with the branching ratio indicated.

[11] Barton, Ghiorso, and Perlman, unpublished work (1949).
[12] Templeton, Howland, and Perlman, Phys. Rev. 72, 758 (1947).

any low volatility impurities. By inserting this chamber into a special breech and setting the pre-amplifier unit of an alpha-counter into the top of the breech, the central wire of the special chamber made contact with the high voltage lead to the counter (Fig. 5 (b)). The unit then functioned as an argon-filled ionization chamber for the collection of alpha-particle pulses. This comparatively crude arrangement was quite adequate for relative measurements and for half-life determinations.

Using this method, an alpha-emitting emanation activity of 23 minutes half-life was discovered (see Fig. 6). This activity, as well as a second alpha-emitting low mass emanation of 2.3 hours half-life, had been previously found in this laboratory.[13] The present work determined its mass assignment and alpha-energy.

To establish that the 23-minute emanation was the daughter of the 19.3-minute francium, the following "milking" experiment was carried out. After flashing an active francium sample into an atmosphere of argon as above, the system was evacuated. Fresh argon was let in to the section of the apparatus between valves A and B and the emanation permitted to grow for exactly 20 minutes. At the end of this time the gas was transferred to the counting chamber and immediately counted. Then the chamber was again placed in the apparatus and pumped out. The emanation which had grown in during a second 20-minute period was transferred to the counting chamber and counted. This procedure was repeated eight times. Results are shown in Fig. 7. The decay line represents the decay of the francium parent. Considering the experimental error, the half-life value is consistent with the assignment of the 19.3-minute francium as the parent of the emanation.

The alpha-particle energy of Em^{212} is established as nearly identical to that of Fr^{212} from the fact that one peak in pulse analysis curves of the francium fraction accounts for the major part of the activity even though the gross alpha-decay is definitely non-linear. More careful work with the energy scale of the pulse analyzer spread out revealed a difference in the two alpha-energies. A difference of about 80 kev was found by pulse analyzing a francium sample freshly freed of Em^{212} by volatilization and continuing to pulse analyze it as the daughter re-grew. Our best energy values are 6.25 ± 0.03 Mev for the Fr^{212} alpha-particle and 6.17 ± 0.03 Mev for the Em^{212} alpha-particle. These values depend on calibration of the instrument with the Ra^{226} series.

The polonium daughter of alpha-emitting Em^{212} was shown to be identical to the orbital electron-capture daughter of At^{208} by pumping an active sample of emanation through two dry ice traps and letting it decay in an isolated glass tube. When the acid used to wash out this glass tube several hours later was evaporated on a platinum plate and pulse analyzed, alpha-activity of 5.15 ± 0.05 Mev energy was found.

[13] Ghiorso, Meinke, and Seaborg, Phys. Rev. 76, 1414 (1949).

This activity, apparently due to Po^{208}, did not decay appreciably in a period of 60 days.

(7) Determination of Fr^{212} K/α-Branching Ratio

In principle, several methods might be used for making this important measurement, but all involve experimental difficulties.

Counting the francium x-rays directly is rendered impossible by the presence of a high background of cesium fission product activity.

Quantitatively isolating and counting the Em^{212} from a measured sample of Fr^{212} would require developing better counting equipment for the gaseous activity.

One could quantitatively determine the amount of Po^{208} produced in an initially pure alpha-counted Fr^{212} sample. The excess of Po^{208} activity over the amount that would be produced if Fr^{212} decayed only by alpha-particle emission would determine the amount of K-branching. This is insensitive because of the long half-life of Po^{208} and the low K/α-branching of Fr^{212}.

The method selected was to determine carefully the shape of the alpha-growth and decay curve for an initially pure francium sample and compare this curve with theoretical curves drawn for various values of the K/α-branching. A sample of francium containing 10^5 alpha-counts per minute was freed of emanation by volatilizing it from one platinum plate to another, quickly sprayed with a zapon solution to insure the complete retention of Em^{212}, and immediately placed in an alpha-counter. This sample was counted continuously for several hours. The experimentally observed decay points were corrected for a background of Ra^{223} (from the decay of AcK present in the initial sample) amounting to 0.2 percent of the initial count. A small contribution to the counting rate due to the growth and decay of the At^{208} daughter was also subtracted. The resulting points were normalized to make the counting rate equal 100 at the time of volatilization and plotted as shown in Fig. 8. The curves shown were derived from the theoretical equation below, using a Fr^{212} half-life of 19.3 minutes and an Em^{212} half-life of 23.0 minutes.

TOTAL ALPHA-COUNTING RATE

$$= -\lambda_1 N_0 e^{-\lambda_1 t} - [\gamma \lambda_2 \lambda_1 N_0 (e^{-\lambda_1 t} - e^{-\lambda_2 t})/(\lambda_2 - \lambda_1)]$$

λ_1 and λ_2 are the disintegration constants of Fr^{212} and Em^{212}, t is the time for Em^{212} growth, γ is the K/α-branching ratio of Fr^{212}, and N_0 is the initial amount of Fr^{212}. $-\lambda_1 N_0$ is arbitrarily set equal to 100. From Fig. 8 we estimate the K/α branching to be 1.3 ± 0.1. This would place the partial alpha-half-life of Fr^{212} at 43 minutes, the partial orbital electron-capture half-life at 34 minutes.

ACKNOWLEDGMENTS