surface with various ledges here and there. The presence of such a structure along with the possibility of arrival of echoes from angles other than the vertical can easily account for the complex echoes. If this view of the production of the complex echoes is accepted, we have to search for the agency which can cause such a structure of the ionosphere."

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Nuclear Isomerism in Selenium and Krypton

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A study has been made of the radioactive chain

$$Se^{83} \rightarrow Br^{83} \rightarrow Kr^{*83}.$$

The last member is an isomer of the stable krypton of mass 83. An isomeric pair $Se^{79 \text{ or } 81}$ has been found and the two genetically related nuclear isomers have been separated chemically. Kr^{83} and Br^{83} are produced by the fission of uranium and thorium as well as by the bombardment of selenium with deuterons and slow neutrons.

IN the course of an investigation of radioactive products of thorium and uranium fission, we observed a radioactive krypton growing out of a radioactive bromine with a period of 2.4 hours. This bromine period coincides with that assigned by Snell[1] to Br^{83}, which he found to be the product of the decay of Se^{83} produced by deuteron bombardment of selenium. He did not, however, observe radioactive krypton growing out of the bromine. We therefore repeated this deuteron bombardment of selenium and were able to extract from the products a radioactive isotope of krypton having the same period as the fission product, and emitting the same type of radiation. Since the radioactivities of selenium and bromine appeared rather complicated, we thought it desirable to go over the different points in detail.

The main results of our investigation are the identification of an excited state of the stable Kr^{83}, the identification and chemical separation of an isomeric pair in $Se^{79 \text{ or } 81}$, and confirmation of the identification of Se^{83}. Although discovered by Snell, there had been some uncertainty as to the true half-life of Se^{83}.

[1] A. H. Snell, Phys. Rev. **52**, 1007 (1937).

THE CHAIN $Se^{83} \rightarrow Br^{83} \rightarrow Kr^{*83} \rightarrow Kr^{83}$

We have produced Se^{83} by means of slow neutrons with the reaction Se^{82} (n,γ) Se^{83} and by deuterons with the reaction Se^{82} (d,p) Se^{83}. The latter reaction of course gives much more concentrated samples and has been used for all the chemical separations. In order to determine the period of Se^{83}, repeated extractions of Br^{83} are necessary to identify its parent in the complex of selenium activities. The Br^{83} can be recognized easily from the fact that it is the only bromine isotope giving rise to an active krypton.

In order to make repeated extractions of bromine, the bombarded selenium was converted to selenic acid free of the primary 34-hour bromine activity produced by the reaction Se^{82} $(d,2n)$ Br^{82}. Preliminary experiments with the more rapidly prepared selenious acid had shown serious difficulties as a result of the apparent impossibility of achieving a complete extraction of bromine from this material, so that the longer chemical preparation of selenic acid was found to be necessary. To the selenic acid solution we added periodically five milligrams each of potassium bromide and iodide, and precipitated them with silver sulphate solution. Decay curves of the bromine activities thus

extracted are shown in Fig. 1, curves I–VII. Curves I–V all indicate a half-life of 140 minutes which is assigned to Br^{83}. In each of these curves the point marked with a cross represents the bromine activity extrapolated back to the time of extraction. Curve VIII, drawn through these crossed points, indicates that the period of the parent Se^{83} is about 30 minutes.

The absorption curve of the Br^{83} beta-rays gives an end-point of 1.05 Mev by Feather's method.[2]

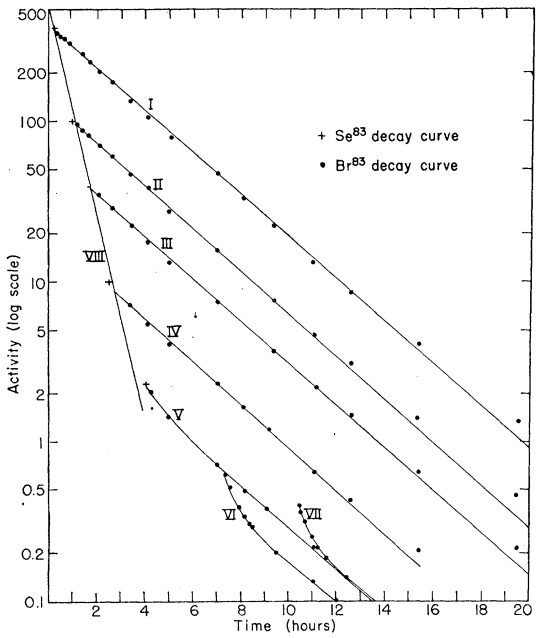


FIG. 1. Decay curves of successive bromine extracts from deuteron-bombarded selenium. The crosses represent the bromine activity extrapolated back to the time of extraction. The curve VIII through the crosses represents the decay curve of the parent selenium 83.

Decay curves of the last two extracts of bromine from the active selenic acid are shown in curves VI and VII of Fig. 1. They are distinctly anomalous in intensity and slope. Although we have not investigated this anomaly, it might be due to a short-lived bromine activity which grows out of a selenium activity with a period longer than that of Se^{83}. Since the curves of Fig. 1 are compounded of the decay curves of Br^{83} and another unknown activity, there is some uncertainty in the assignments of

[2] N. Feather, Proc. Camb. Phil. Soc. 34, 599 (1938).

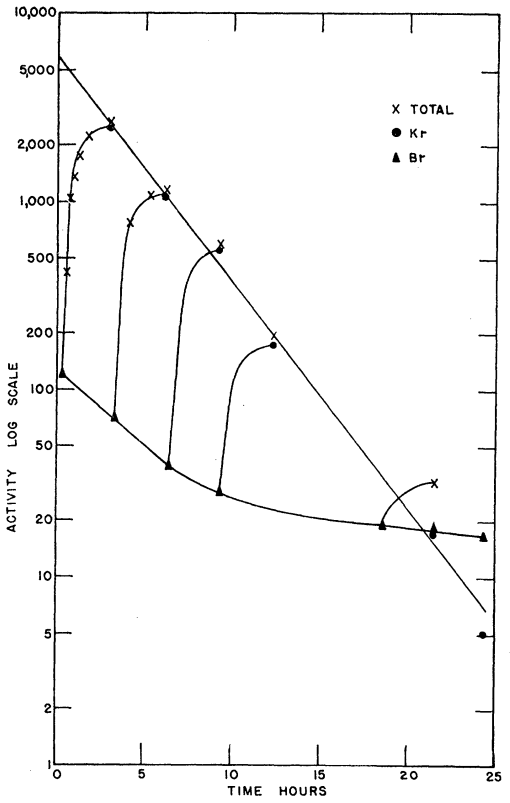


FIG. 2. Activity of an emanating bromine sample inside an ionization chamber. Triangles represent activity due to bromine; crosses represent total activity. The growth of activity is all due to accumulation of krypton. The dots give the activity due to krypton alone after 3.5 hours of growth. The line through the dots gives the period of the bromine parent of the krypton activity.

the periods of Se^{82} and Br^{83} from the data of this figure. We have, therefore, made use of the simple activity of Kr^{83} to confirm the above assignments of periods to the Br^{83} and Se^{83}.

Radioactive krypton can be extracted from a solution containing Br^{83} simply by boiling the solution. However, rather prolonged boiling combined with bubbling of a gas stream through the solution is required for a quantitative extraction. Although we have used this technique, we found it more convenient to use emanating solid samples when we wanted to make repeated extractions or when krypton was wanted with but little air admixture. We will describe later how to prepare emanating samples.

The decay curve of krypton is a perfect exponential; we followed it over a factor of ten

thousand, and the half-value period is 113 minutes.

The relation of Kr^{83} to Br^{83} has been shown by the following experiment. An emanating sample of radioactive bromine was suspended inside an ionization chamber which measured the sum of the bromine and krypton activities. The air was pumped out and replaced by fresh air at equal time intervals, so that each exhaustion was an extraction of krypton. The decrease of activity due to this extraction is, therefore, a direct measure of the krypton activity, and the residual activity immediately after letting in fresh air is bromine activity. In Fig. 2 the crosses represent the total activity, the triangles show the bromine activity, and the circles represent the krypton activity. Since the times of extraction of krypton were uniformly spaced, the curve of krypton activity is simply the decay curve of its parent substance. It will be seen that the period of the bromine so obtained agrees with that of the Br^{83} found directly.

As indicated before, we found it desirable to check the period of the Se^{83} by the Kr^{83} activity because we were not sure that the bromine decay curve was simple. This was done by extracting bromine periodically from active selenic acid with carbon tetrachloride. Half of the extracted bromine was converted into an emanating sample and half was measured directly. All the emanating samples were allowed to accumulate krypton for 3.5 hours so that the activity due to krypton after this interval of time was proportional to the amount of parent bromine initially present. Fig. 3 shows the results of measurements of the krypton and bromine activities. The initial bromine and krypton activities for different extractions are in a constant ratio. This shows that practically all of the bromine activity in our extracts is due to Br^{83} and affords also an independent check on the half-life of Se^{83}.

Krypton 83 emits a particularly soft radiation. We have been able to detect it only by introducing the gas into an ionization chamber. In order to have an estimate of the energy of the electrons emitted, the active krypton was admitted into a spherical ionization chamber of 12.6 cm diameter, which had previously been evacuated. Air was then admitted and Fig. 4 shows the ionization as a function of pressure. Similar curves have been obtained in x-ray work, and a discussion of their shape as a function of the absorption coefficient of the electrons is to be found in Bothe's article.[3] His discussion refers to a plane condenser, whereas our experimental arrangement corresponded to a spherical condenser, which introduces some uncertainty in the determination of the dimension of the vessel to be considered as corresponding to the plate

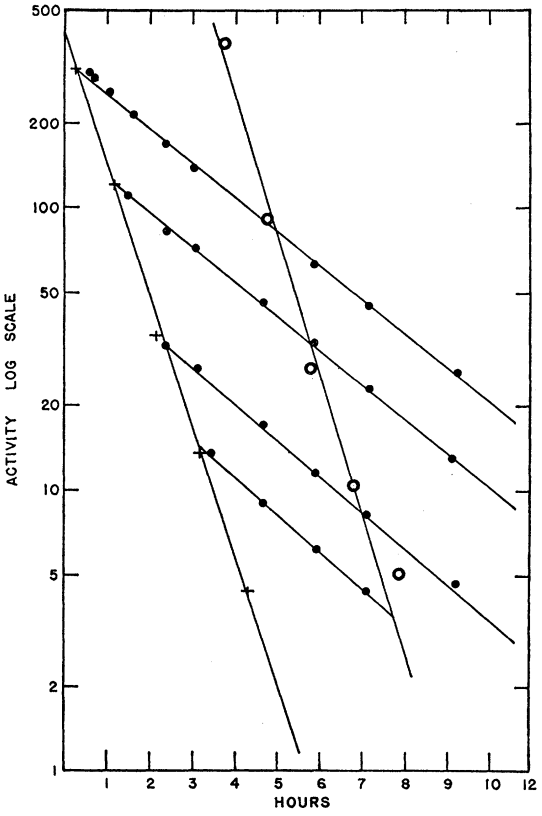


FIG. 3. Successive extractions of bromine from selenium. Dots and crosses same as in Fig. 1. Circles represent krypton activity which grows out of bromine extracts in 3.5 hours.

separation of the plane condenser. Nevertheless, the absorption coefficient varies so rapidly in the region concerned that a considerable error in the estimation of the absorption coefficient makes only a small error in the estimation of the energy. From Fig. 4 the absorption coefficient

[3] W. Bothe, Geiger, Scheel, *Handbuch der Physik* (Berlin, 1933), **23/2**, 26.

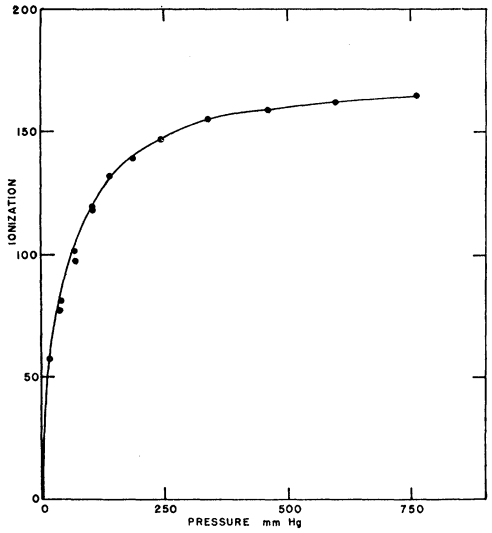


FIG. 4. Ionization due to krypton electrons as a function of the air pressure in the spherical ionization chamber of diameter 12.6 cm.

is about 1630 cm²/g, and the practical range is about 4.2 mg/cm². Both these results give an energy of about 35 kev for the electrons.

The natural interpretation of the observations is that the electrons are conversion electrons of a 49-kev gamma-ray. This energy is obtained by adding to the observed electron energy the binding energy of the K level in krypton. This interpretation is further confirmed by the detection of the characteristic x-radiation of krypton by absorption measurements on a gas sample. X-rays were detected with a "freon" chamber. We found that arsenic absorbs the x-rays more strongly than selenium. Since the energy of the characteristic K radiation of krypton lies between the absorption edges of arsenic and selenium, this experiment shows conclusively that the x-rays are characteristic of krypton.

Since there is no doubt that the parent of this radioactive krypton is the bromine isotope of atomic weight 83 (i.e., Br^{83}), we must conclude that this krypton is a metastable excited isomer of stable Kr^{83}.

In this connection, we want to point out that Kr^{83} is known to have a nuclear spin of 9/2.[4] According to the computations of H. Hebb and G. E. Uhlenbeck,[5] the observed energy and half-life indicates a change of spin of four, so that the excited state probably has a spin of $\frac{1}{2}$.

We think it is within the possibilities of the cyclotron to prepare enough excited Kr^{83} to observe the hyperfine structure in its spectrum and its change when Kr^{83} reverts to the ground state. This would permit a direct test of the Weizsäcker theory of nuclear isomerism.

SELENIUM 79 OR 81

The selenium activity is so complex that we thought it worth while to look for isomers, as a means of furthering the analysis, especially since we know that the chemical method of separation of nuclear isomers[6] is applicable in the case of tellurium[7] which is chemically similar to selenium.

Radioactive selenic acid and hydrochloric acid were mixed so that the final solution was four

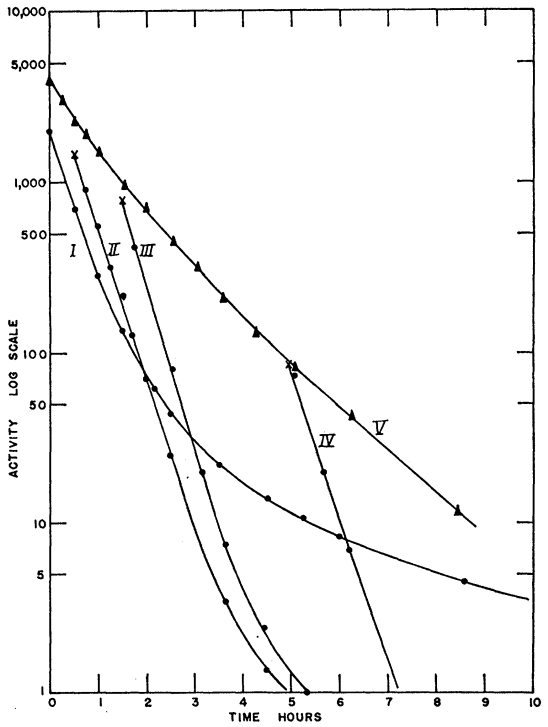


FIG. 5. Successive extractions of the lower isomeric state of $Se^{79, 81}$ from the total selenium activity. Dots for separated isomer activities; crosses for the initial activity give the period of the parent isomeric state approximately. Total selenium activity (triangles) is on a different scale.

[4] H. Korsching, Zeits. f. Physik **109**, 349 (1938).
[5] H. Hebb, G. E. Uhlenbeck, Physica **5**, 605 (1938).
[6] E. Segrè, R. S. Halford and G. T. Seaborg, Phys. Rev. **55**, 321 (1938).
[7] G. T. Seaborg, J. J. Livingood and J. W. Kennedy, Phys. Rev. **55**, 794 (1939).

normal with respect to hydrochloric acid. The solution was then saturated with sulphur dioxide. Under such conditions selenic acid is reduced very slowly whereas selenious acid is reduced rapidly to selenium which can be filtered out of the solution. To this selenic acid solution we added at intervals of time selenious acid and separated the elementary selenium. Fig. 5 shows a decay curve of the parent selenium and of the extracts. The extracts show a half-life of 19 minutes, whereas the parent selenium has a half-life very close to one hour.

The assignment of this isomeric pair to $Se^{79 \text{ or } 81}$ is based upon the observation that it can be obtained also by neutron bombardment of bromine, which has only two stable isotopes, Br^{79} and Br^{81} in equal amounts. The activity of selenium obtained from bromine by the (n,p) reaction is much less complex than the activity which one obtains by deuteron bombardment of selenium. Using this latter method of preparation of $Se^{79 \text{ or } 81}$, we could directly measure the half-life of the upper isomeric state with good accuracy. It is very close to one hour, in agreement with an observation of Snell.[1]

We also checked that this isomeric pair of selenium activities does not decay into any active product, a result that is to be expected.

These observations explain the discrepancy between the results of Snell,[1] and Bothe and Gentner.[8] The latter probably observed the lower isomeric state of $Se^{81 \text{ or } 79}$ which they obtained by gamma-ray bombardment; Snell, on the other hand, had not distinguished Se^{83} from the lower isomer of Se^{79-81}.

By the chemical method we extracted the 20-minute lower isomeric state of $Se^{79, 81}$ produced by bombardment of bromine and found thereby that we had extracted at least one-half of the beta-ray activity of the parent selenium. It must, however, be borne in mind that the yield of our separation, due to its chemical features, may be rather low. It is quite possible, therefore, that all of the beta-ray activity of $Se^{79, 81}$ is due to the lower isomeric state. The absorption curve in aluminum of the beta-rays of both activities is the same and gives by Feather's method[2] an upper limit of the energy of about

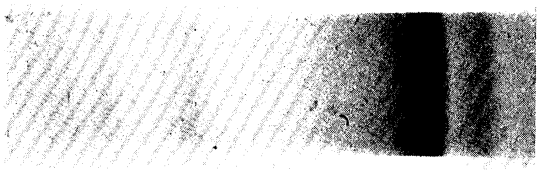


FIG. 6. Beta-spectrogram of Se bombarded with deuterons showing K- and L-conversion electrons ejected in the isomeric transitions of $Se^{79 \text{ or } 81}$ and Kr^{83}.

1.5 Mev. These results indicate that the upper state decays to the lower one, which in turn disintegrates to bromine. The conversion electrons which correspond to the transition from the upper to the lower state have been observed as a very soft component in the absorption curve of the electrons emitted by the one-hour activity and have been detected in a magnetic spectrogram. Both K- and L-conversion lines, are illustrated in Fig. 6. The energy of the K-conversion electrons is about 85 kev, corresponding to an energy difference between the isomeric states of 98 kev. The same value has been found by absorption measurements on the electrons.[9]

CHEMICAL PREPARATIONS

Selenic acid

The bombarded selenium was dissolved in nitric acid containing some bromide ion, then evaporated to dryness to eliminate most of the strong primary bromine activities, redissolved and boiled with sodium hydroxide, then filtered to remove metallic contaminations such as copper from the target plate. The solution was acidified with nitric acid and treated with an excess of normal silver nitrate to precipitate silver selenite. This compound was washed, suspended in water, and the selenite was oxidized to selenate by treatment with bromine, of which the excess was removed by boiling. The filtered solution contained selenic acid free of primary radioactive bromine.

Separation of bromine

As an alternative method to the precipitation of silver bromide out of selenic acid solution as already described, we have added equivalent

[8] W. Bothe and W. Gentner, Zeits. f. Physik **112**, 45 (1939).

[9] We thank Mr. A. C. Helmholz for photographing the line spectrum of electrons.

quantities of sodium bromide and sodium bromate in order to liberate bromine, which was then extracted with carbon tetrachloride. This method, while not so efficient as the former precipitation technique, has the advantage of giving the bromine in a form well suited to the preparation of emanating samples.

Emanating samples

We prepared silica gel impregnated with silver nitrate by immersing the granular silica gel (8 to 16 mesh) in 0.1 *N* silver nitrate solution for about 15 minutes. The gel was then drained and dried for several hours on a hot-plate at about 70°C. The radioactive bromine was prepared in the form of free bromine with several milligrams of bromine carrier, dissolved in about 5 cc of carbon tetrachloride (free of any visible water layer but not specially dried). Several cubic centimeters of the silver nitrate-impregnated silica gel were added to this solution and shaken with it until the bromine color had completely disappeared. This usually took about 15 minutes. The silica gel was drained and dried on the hot-plate for about one-half hour. It was then ready to be placed in a vessel for collection of the emanating krypton. This method of preparing an emanating solid has been found to be equally applicable in the case of radioactive xenons which are produced by decay of iodine extracted from thorium and uranium fission products.

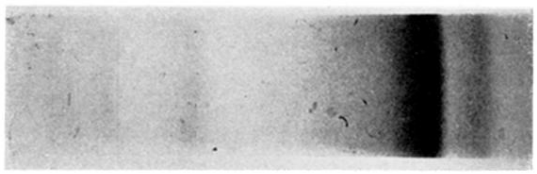
Other observations

The preceding work is not a complete investigation of the radioactivities produced by bombardments of selenium. Our work indicates there are several points requiring further study. Perhaps there is a radioactive bromine with a half-life less than one-half hour which grows from a radioactive selenium with a half-life considerably longer than that of Se^{83}. This unidentified activity has already been discussed in connection with Fig. 1, curves VI and VII.

We have also observed an activity in selenium bombarded with deuterons with a half-life of more than a day. Since this longer-lived activity tends to be selectively extracted from the parent selenate solution when making the first isomeric separation, for $Se^{79 \text{ or } 81}$, it may be that this longer-lived activity is itself the lower isomeric state of another as yet unknown selenium. Fig. 5 shows evidence on which these conclusions are based. Curve I, Fig. 5, shows a strong long-lived tail in the first isomeric extract. This tail is much less pronounced in later extracts. It cannot be due to an imperfect isomeric separation, because the tail actually shows a longer period than is shown by the *total* selenium activity in curve V of Fig. 5. However, the possibilities of the presence of impurities in the selenium and of the formation of arsenic during the bombardment have to be borne in mind in appraising the results reported in this paragraph.

Since Br^{83} and Kr^{83} are observed in the fission of thorium and uranium, it is probable that Se^{83} is also a product of the fission. It has not, however, been observed directly. An extract of selenium from neutron irradiated uranium showed the presence of several different activities, which prevented a simple confirmation of the presence of the Se^{83} activity.

Our thanks are due to Professor E. O. Lawrence for his interest in this work. The financial support of the Research Corporation and of the Rockefeller Foundation is gratefully acknowledged.



? Kr Se

FIG. 6. Beta-spectrogram of Se bombarded with deuterons showing K- and L-conversion electrons ejected in the isomeric transitions of $Se^{79\ or\ 81}$ and Kr^{83}.