

## Nuclear Isomerism in Element 43

G. T. SEABORG, *Chemistry Department, University of California, Berkeley, California*

AND

E. SEGRÈ, *Radiation Laboratory, Physics Department, University of California, Berkeley, California*

A case of nuclear isomerism in element 43 has been thoroughly studied and is described. An activity of 6.6 hours half-life, which grows from a 67-hour molybdenum activity and has been chemically identified as element 43, decays with the emission of a line spectrum of electrons and no observable nuclear beta-particles. Absorption measurements in aluminum and measurements with a magnetic spectrograph give an energy for the electrons of 116 kev. This line spectrum must be due to the conversion electrons of a highly converted gamma-ray of energy 136 kev and arises as the result of a transition from an excited state of this isotope of element 43. The ground state is

either stable or very long-lived. X-rays are also observed, and critical absorption measurements, as well as observations with a bent crystal spectrograph, show that they are to be ascribed to the  $K\alpha$  line of element 43, as is to be expected from this interpretation. The 6.6-hour activity also emits gamma-rays of about 180 kev energy; the measurements show that these are to be interpreted as following the transition which gives rise to the conversion electrons. A description of the chemical identification of the 6.6-hour activity is given. Other activities of element 43 are mentioned.

### 1. INTRODUCTION

**I**N an investigation of the artificial radio-activities of element 43 we have found some features interesting with respect to the general problem of nuclear isomerism. In a letter<sup>1</sup> to the *Physical Review* we have summarized our main results. In this paper we shall give a detailed account of the investigation.

### 2. APPARATUS

The samples were activated with deuterons or neutrons from the Berkeley cyclotron. For several of the deuteron bombardments inner targets of the type described by Wilson and Kamen<sup>2</sup> were used. The activities were usually measured with ionization chambers connected to a vacuum tube electrometer system of the type described by Hafstad.<sup>3</sup> Two chambers were used, of the type described by Segrè<sup>4</sup> and Amaldi and Fermi.<sup>5</sup> One was made entirely of aluminum and the inner cylinder had a diameter of 10 cm and a height of 10 cm. This chamber was filled with air at atmospheric pressure and the window through which the electrons were admitted had a diameter of six cm and a thickness of 0.16 mg/cm<sup>2</sup>. The outer cylinder of the other chamber

was made of brass, lined on the inside with cardboard, and the inner cylinder was a copper net of nine cm diameter and height. It was filled with methyl bromide slightly above atmospheric pressure. The window was aluminum of 20 mg/cm<sup>2</sup> thickness.

The chemical identifications and separations are described in detail at the end of the paper in Section 8.

### 3. ISOMERISM IN ELEMENT 43

Molybdenum was irradiated with deuterons and neutrons. A strong activity of  $67 \pm 2$  hours half-life was observed and a decay curve of this activity is shown in Fig. 1. This curve starts some days after the end of the bombardment and chemical separation. The most probable identification of this activity is with Mo<sup>99</sup> or Mo<sup>101</sup>. The particles emitted are negative electrons (as determined by magnetic deflection) so that the decay product must be an isotope of element 43. Since, according to current ideas about nuclear stability,<sup>6</sup> this element is unlikely to have any stable isotopes, it is natural to look for a daughter activity. Therefore we looked for the growth of a radioactive isotope of element 43 by successive chemical separations from the active molybdenum. In all of these successive separations we found an electron-emitting activity of  $6.6 \pm 0.4$  hours half-life and this was identified

<sup>1</sup> E. Segrè and G. T. Seaborg, *Phys. Rev.* **54**, 772 (1938).

<sup>2</sup> R. R. Wilson and M. D. Kamen, *Phys. Rev.* **54**, 1031 (1938).

<sup>3</sup> L. R. Hafstad, *Phys. Rev.* **44**, 201 (1933).

<sup>4</sup> E. Segrè, *Nuovo Cimento* **12**, 232 (1935).

<sup>5</sup> E. Amaldi and E. Fermi, *Phys. Rev.* **50**, 899 (1936).

<sup>6</sup> See e.g. H. Jensen, *Naturwiss.* **26**, 381 (1938).

chemically as element 43. A sample decay curve of such an extraction is shown in Fig. 2 and an absorption curve in aluminum of the electrons is shown in Fig. 3, curve (a). This curve was taken on the air chamber with a distance of 1.5 cm between the source and the window and with the aluminum absorbers close to the window. The curve is strikingly different from an ordinary absorption curve of beta-particles having the same half-value thickness, as is shown by comparison with curve (b) of the same figure in which the absorption of the beta-particles of the radioactive isotope of cobalt of 6-8 years period<sup>7</sup> is shown. Moreover, from the end-point of this absorption curve, an energy for the electrons of about 120 kev is obtained and this energy, according to the Sargent relation, could not correspond to a beta-radioactivity of six hours half-life. The form of the curve compared with the results of Varder<sup>8</sup> and Eddy,<sup>9</sup> even taking into account the different geometry, points to monokinetic electrons. That this is the case was

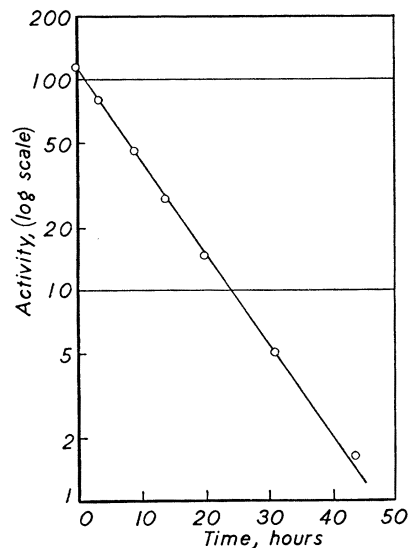


FIG. 2. Decay of radioactive 43. Half-life  $6.6 \pm 0.4$  hours.

confirmed by Mr. D. C. Kalbfell<sup>10</sup> who put a chemically separated sample of the 6.6-hour activity in his magnetic spectrograph and found

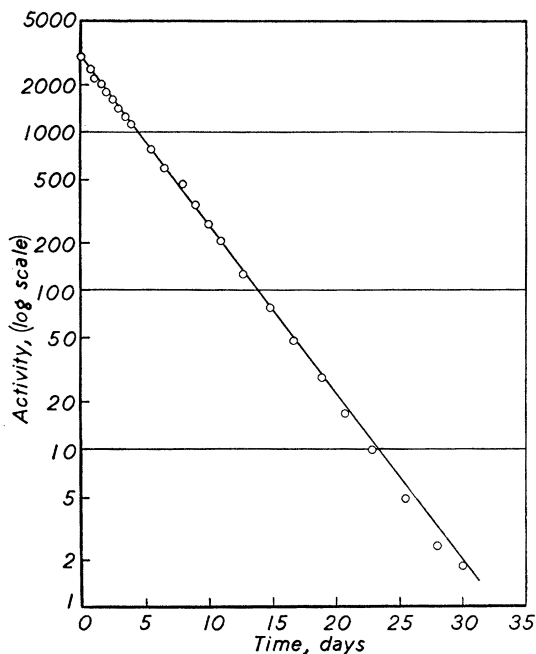


FIG. 1. Decay of radioactive molybdenum. Half-life  $67 \pm 2$  hours.

<sup>7</sup> J. J. Livingood and G. T. Seaborg, Phys. Rev. **53**, 847 (1938). Continued measurements by these authors and G. Barresi have shown that this period is 6-8 years.

<sup>8</sup> R. W. Varder, Phil. Mag. **29**, 726 (1915).

<sup>9</sup> C. E. Eddy, Proc. Camb. Phil. Soc. **25**, 50 (1929).

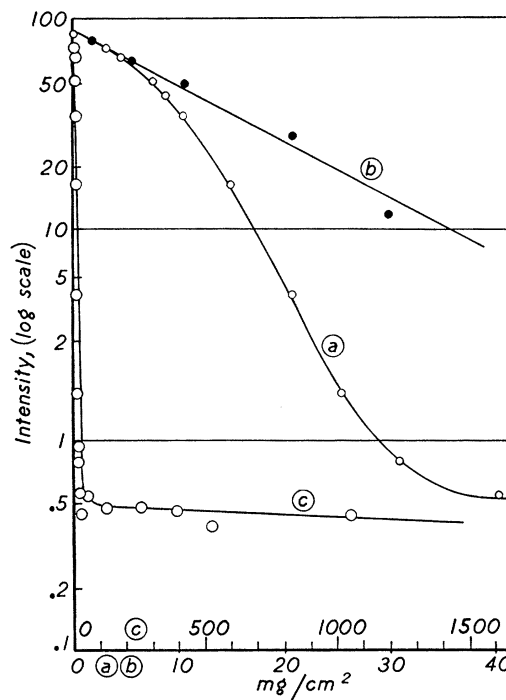


FIG. 3. (a) and (c) Absorption in aluminum of the electrons of 43. (b) Absorption in aluminum of the  $\beta$ -rays of cobalt (6-8-year period).

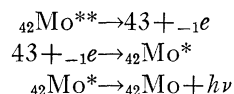
<sup>10</sup> D. C. Kalbfell, Phys. Rev. **54**, 543 (1938).



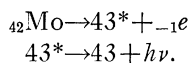
FIG. 4. Electron lines of element 43 (*K* and *L* conversion).

an electron line of 116 kev energy and a weaker one of 133 kev energy, as shown in Fig. 4. These electrons are obviously the *K* and *L* conversion electrons of a gamma-ray of 136 kev energy.

This unusually strong line of electrons immediately suggests that we are dealing with either a case of *K*-electron capture, followed by a gamma-ray which is highly internally converted, or with a transition between isomeric levels of an isotope of element 43 which, according to current ideas about isomerism, should also manifest itself by a gamma-ray of high internal conversion. The process contemplated in the first hypothesis would be of the following type:



in which the nuclei with the asterisks are in excited states. It is seen at once that this explanation is highly artificial. The second alternative would be described thus:



However, to decide experimentally between the two hypotheses it is sufficient to determine the atomic number of the nucleus emitting the converted gamma-ray. One could do this either by measuring the difference in energy of the *K* and *L* conversion electrons or by identifying the characteristic x-radiation which is generated in the rearrangement of the atom after the ejection of the conversion electrons.

We have adopted the latter method, identifying the x-rays by their characteristic absorption. The methyl bromide chamber was used, which enhances the ionization due to the x-rays to a great extent. The aluminum window was of such a thickness (20 mg/cm<sup>2</sup>) as to stop all of the conversion electrons. Fig. 5(a) shows an absorption curve in aluminum. The radiation is obviously composed of at least two parts, a soft and a hard component. The hard component is a gamma-ray and when this is subtracted the

soft component has an absorption coefficient corresponding to the *K* x-radiation of an element in the neighborhood of molybdenum. The exact assignment of the element was obtained by comparison of the absorption of the x-rays in zirconium, columbium and molybdenum. Since sheets of these elements of the proper thickness were not available to us the absorbers were made by filtering fine suspensions of the oxides (ZrO<sub>2</sub>, Cb<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>) through identical filter papers. The layers were fairly homogeneous and for each substance had thicknesses of 5, 10, 20 and 30 mg/cm<sup>2</sup> of the element. The absorption by the oxygen in these substances and by the filter paper was negligible.

The absorption curves for the x-rays (corrected for the gamma-rays) are shown in Fig. 5(b, c, d). It is seen at once that the discontinuity in the absorption coefficient occurs between zirconium and columbium as one would expect for the *K* radiation of element 43, whereas for the *K* radiation of molybdenum the discontinuity would have occurred between zirconium and yttrium. This experiment also rules out the possibility that the x-rays are emitted by ruthenium (discontinuity between columbium

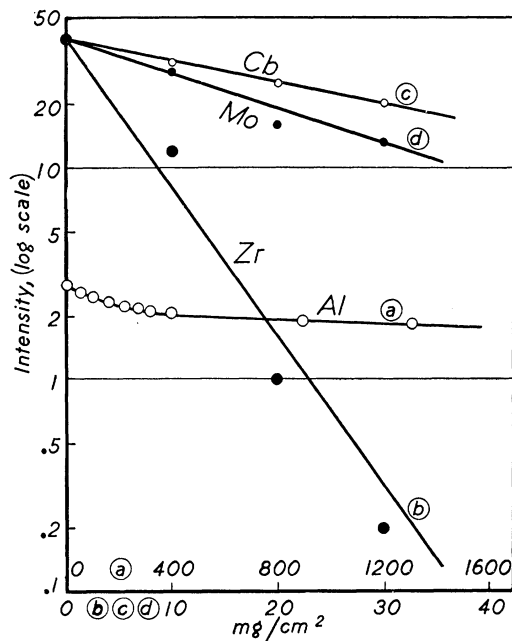


FIG. 5. Absorption curves of x- and  $\gamma$ -rays of element 43. (a) Absorption in aluminum of x- and  $\gamma$ -rays. (b) Absorption of x-rays in Zr. (c) Absorption of x-rays in Cb. (d) Absorption of x-rays in Mo.

and molybdenum) as would be the case if the radioactive element 43 were decaying by the usual type of beta-emission. It is remarkable that in spite of the bad geometry (diameter of source 3 cm; distance between source and absorber 2.5 cm; distance between source and chamber 5 cm) the absolute values of the absorption coefficients are not far from the theoretical ones. The measured values of the high and low mass absorption coefficients are 170 and 35 cm<sup>2</sup>/g, which are to be compared, in the absence of any experimental values for element 43, with the absorption coefficients of 114 and 19 cm<sup>2</sup>/g for the absorption coefficients of the *K* x-rays of molybdenum in yttrium and zirconium.

This result has been confirmed by a direct photograph of the x-ray line with a bent crystal spectrograph taken by Mr. P. Abelson.

4. GAMMA-RAYS AND INTENSITY RELATIONS

In order to get a further insight into the processes involved, an attempt was made to establish the ratio between the number of disintegration electrons of molybdenum and the conversion electrons of the daughter element 43 and to study the gamma-rays emitted by the 6.6-hour activity of element 43. Because of the well-known difficulties in work of this type this part of the investigation is still incomplete, especially with respect to the important point of establishing the conversion coefficient of the gamma-rays corresponding to the conversion electrons of element 43.

a. Intensity ratio between molybdenum beta-rays and electrons of element 43

An extremely thin layer of carefully purified radioactive molybdenum was placed above the

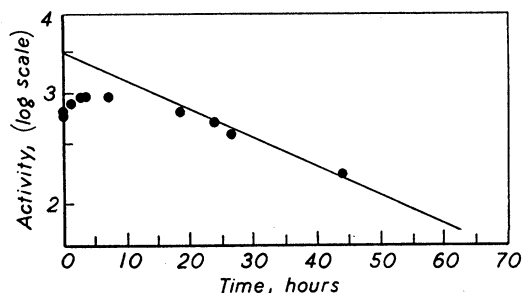


Fig. 6. Curve showing growth of radioactive element 43 in radioactive molybdenum.

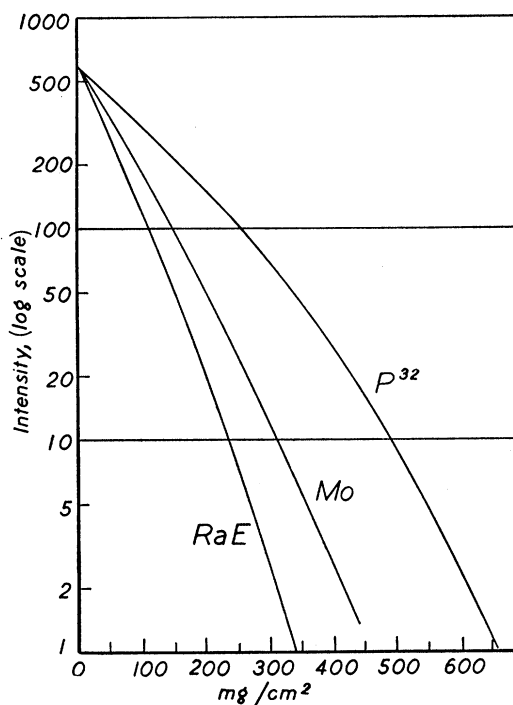


Fig. 7. Absorption curves of electrons of Mo in aluminum. RaE and P<sup>32</sup> as references.

thin window of the air ionization chamber and the decay curve is shown in Fig. 6. This curve shows the growth of the activity of element 43 from the molybdenum and one can find the ratio of the ionization produced by element 43 to the ionization produced by molybdenum when they are at transient equilibrium. This ratio, correcting for the window thickness, is 0.30. Approximately the same value is obtained when the two activities in equilibrium are separated chemically and measured. In order to pass from the ratio of the ionization of the two activities to the ratio of the number of particles from the activities one must estimate from their ionizing powers the relative number of ions produced by the particles, taking into account the fact that the geometry was such that the range of the particles was long compared with their paths in the chamber. In order to measure the average energy of the electrons, which is necessary for estimating their ionizing power, an absorption curve of the molybdenum electrons was taken. The absorption curve of the electrons in aluminum (with the air chamber) is given in Fig. 7 together with the absorption curves of P<sup>32</sup> and

RaE as references. With the method described by Feather<sup>11</sup> we find an end-point for the beta-rays of 0.64 g/cm<sup>2</sup> which corresponds, according to the formula of Feather, to an energy upper limit of 1.5 Mev. This locates the molybdenum activity on the second Sargent curve and, lacking better data, one can assume the average energy of the beta-particles to be about 30 percent of the upper energy as was measured<sup>12</sup> in RaE. This gives a value of 0.45 Mev for the average energy which corresponds to an ionization of 62 ion pairs per cm of path. The line of electrons from element 43 gives an average ionization of about 150 ion pairs per cm and hence the ratio of the number of particles from the parent molybdenum to the number from the element 43 is  $150/(62 \times 0.3) = 8$ .\*

This high ratio between the number of beta-rays of molybdenum and electrons of the daughter substance could be interpreted either by admitting a branching in the primary molybdenum decay, so that the Mo would disintegrate to different 43 levels, or, more unlikely, that the molybdenum decays to a single excited state of the element 43 which reverts to the ground state by the emission of a gamma-ray which has a low internal conversion coefficient. Evidence against the latter of these two alternatives was supplied by a study of the intensity ratio between the gamma-rays and the electrons of the 6.6-hour activity. In fact, in this case one would expect approximately one gamma-quantum for every molybdenum disintegration electron.

#### b. Intensity ratio between gamma-rays and electrons and energy of gamma-rays in element 43

In order to decide the alternative proposed at the end of Part (a) of this section and, more important, to obtain some more experimental data relevant to the general theory of isomerism, an endeavor was made to measure the energy of the gamma-rays and the number of gamma-quanta per electron in this transition. The mass absorption coefficients of the gamma-rays in lead

and copper, with the methyl bromide chamber, were measured. The value of  $\mu/\rho$  for lead is 2.0 g/cm<sup>2</sup> and that for copper is 0.18 g/cm<sup>2</sup> which corresponds in each case to an energy of about 180 kev. The same value is obtained by measuring the absorption coefficient in Cellophane of the electrons ejected from lead and from copper by the gamma-rays and using the data of Vette.<sup>13</sup> This value can be assumed only as a rough indication of the energy of the gamma-rays because of the fundamental uncertainty about the homogeneity of the gamma-rays and because intensity considerations made it necessary to use bad geometry. However, with the same geometry we obtained the correct value for the absorption coefficient for the annihilation radiation of positrons.

The intensity ratio between the electrons and the gamma-rays was determined by using the ionization ratio between the electrons and gamma-rays in the air chamber, where the value 170 was found (as can be seen from Fig. 3(c)). For comparison, the ionization ratio between the positrons and the annihilation radiation of Cu<sup>61</sup> (3.4 hours half-life) was determined under the same conditions and the value 55 was found. For the geometry adopted there are two annihilation gamma-rays per positron which enter the chamber and a special investigation (see appendix) has shown that there are no other gamma-rays of appreciable intensity. Assuming that the gamma-rays from element 43 ionize about the same as the annihilation gamma-rays and taking into account the fact that the electrons from element 43 ionize about 2.5 times as much as the beta-particles of Cu<sup>61</sup> we find that the gamma-rays and electrons from element 43 are, very roughly, equal in number.

These observations are consistent with the assumption that the gamma-ray follows the isomeric transition and that the internal conversion coefficient of the isomeric transition is very high.

#### 5. GAMMA-RAYS FROM MOLYBDENUM

The 67-hour molybdenum activity, freed from the element 43, also shows a gamma-ray activity. The crude half-value thicknesses of this gamma-ray in copper and lead are 5 and 2.5 g/cm<sup>2</sup>. This

<sup>11</sup> N. Feather, Proc. Camb. Phil. Soc. **34**, 599 (1938).

<sup>12</sup> C. D. Ellis and W. A. Wooster, Proc. Roy. Soc. **A117**, 109 (1927).

\* Because of the uncertainty of the method, we think that this estimate may be wrong by a factor 2.

<sup>13</sup> E. Vette, Ann. d. Physik **5**, 929 (1930).

corresponds to an energy definitely larger than the energy of the gamma-ray of element 43 and can be set at about 400 kev. The ratio of the ionization of the beta-particles to that of the gamma-rays in the air chamber is about 500. This indicates that the intensity of the gamma-ray is relatively weak (0.2 quanta per disintegration).

#### 6. THE LOWER ISOMERIC STATE OF ELEMENT 43

It has been pointed out that no stable isotopes of element 43 are expected so that it was of interest to determine whether, after the isomeric transition, there is a further beta-decay to ruthenium. If such a decay of life shorter or comparable to six hours should be present one would have had as many beta-rays as conversion electrons and in case these beta-rays had a normal spectral distribution we would have observed them in the absorption curve in Fig. 3(a). Therefore it seems that the ground state does not decay to ruthenium with a short life. On the other hand, we have prepared samples of element 43 strong enough to follow the decay over a factor of 1000 on the air chamber and no tailing has been observed. This gives a lower limit for the period of the daughter substance of about 6000 hours. Element 43 was also separated and found to be inactive from an old sample of molybdenum which initially contained only the 67-hour activity. The fact that this sample had decayed exponentially by a factor of 60,000 sets a still longer lower limit of 40 years for the period of the element 43 daughter substance (after taking into account the branching ratio of the 67-hour activity). This rules out the possibility that the 6.6-hour activity is isomeric with any of the known radioactive isotopes<sup>14</sup> of element 43. It is still open to question whether the lower state is stable or is radioactive with a very long life or with extremely soft electrons.

#### 7. OTHER ACTIVITIES OF ELEMENT 43

Although no systematic study of the other short-lived activities of element 43 has been made, still in the initial separations of element 43, made in order to separate from molybdenum all of the products formed during the bombardment, we have observed some new activities.

These are reasonably assigned to element 43, though no chemical separations from ruthenium were performed. Provisional values for the half-lives are two hours and two days.

The two-day activity emits strong x-rays, which we have shown by characteristic absorption to be molybdenum  $K\alpha$ . This indicates that this period belongs to an isotope which decays into molybdenum, probably by  $K$ -electron capture. The  $K\alpha$  x-rays of molybdenum were also found to be present in old samples of radioactive element 43, which contained the activities reported by Cacciapuoti.<sup>14</sup>

#### 8. CHEMICAL IDENTIFICATION OF THE ACTIVITY

The chemical identification of the 67-hour activity as molybdenum was performed upon a neutron-activated sample of pure ammonium molybdate by separating columbium by hydrolysis of potassium columbate and by precipitating zirconium as the hydroxide. Both of these fractions were inactive. Molybdenum was then precipitated by the addition of 8-hydroxyquinoline, which does not precipitate element 43 and ruthenium. Rhenium in the form of per-rhenic acid was added as carrier for element 43. The molybdenum contained the 67-hour activity. In order to have this activity radioactively pure in the case of the deuteron bombardment of molybdenum, where other transmutation products are formed, it is necessary to purify further this 8-hydroxyquinoline precipitate. This is done by dissolving the precipitate with concentrated nitric acid, evaporating to dryness, redissolving the residue with water (slightly alkaline with ammonium hydroxide if necessary) and reprecipitating. The fraction of the total activity of element 43 carried down by the 8-hydroxyquinoline molybdenum precipitate is about three percent, so that one reprecipitation reduces this impurity to 0.1 percent.

The 6.6-hour activity is separated from a purified molybdenum fraction, some hours after the purification, by dissolving the 8-hydroxyquinoline precipitate as described above. Rhenium is added as a carrier, the molybdenum is reprecipitated with 8-hydroxyquinoline and filtered off, the filtrate is made strongly acid with hydrochloric acid and the element 43 is precipi-

<sup>14</sup> B. N. Cacciapuoti, Phys. Rev. 55, 110 (1939).

tated with the rhenium as a sulfide by passing in hydrogen sulfide. Since ruthenium, the element above element 43, would also be precipitated with rhenium in this procedure it was decided to make a further separation of element 43 and ruthenium as a check. The rhenium sulfide, containing element 43, was dissolved with a hydrogen peroxide solution. After the addition of ruthenium, as ammonium chlororuthenate, the rhenium and element 43 were precipitated with nitron

(diphenyl-endo-anilo-hydro-triazole). The ruthenium was precipitated from the filtrate with hydrogen sulfide. More than 99 percent of the activity was found in the nitron precipitate.

A complete description of the known chemistry of element 43 and its separation from the neighboring elements is given by Perrier and Segrè.<sup>15</sup>

In conclusion we thank Professor E. O. Lawrence for his interest in this work and the Research Corporation for continued support.

### Appendix on the Calibration of the Ionization Chamber

W. GENTNER AND E. SEGRÈ

*Radiation Laboratory, Physics Department, University of California, Berkeley, California*

(Received March 15, 1939)

We report here some details about the calibration of the ionization chamber which we think might also be of interest to other investigators.

We determined the absorption coefficient of a known radiation (annihilation radiation) and also the ratio between the ionization produced by beta-particles and  $\gamma$ -rays in a simple case, where equal numbers of  $\beta$ - and  $\gamma$ -rays were present, using our standard geometry in order to have a reference for other work.

As a source we used the positron emitter  $\text{Cu}^{61}$  of 3.5 hours half-life, obtained by the deuteron bombardment of nickel. The copper fraction was deposited by reduction on a thin circular Fe sheet (10 mg/cm<sup>2</sup> thickness) of 3.5 cm diameter.

The distance between source and window was 2.5 cm and the absorbers were about 0.6 cm above the window.

The first step was to ascertain that  $\text{Cu}^{61}$  does not emit nuclear  $\gamma$ -rays. This was done by absorbing completely the  $\beta$ -rays, whose absorption curve is practically identical with the absorption curve of Mo (Fig. 7, endpoint at 1.5 Mev), and then placing 1.5 cm of paraffin directly above the source. The residual activity, due to annihilation radiation, was thus multiplied by a factor 1.9. The paraffin absorbs the positrons emitted in the upper solid angle and transforms them into isotropic annihilation radiation. Since the positron absorption occurs in a small region, very close to the source, the whole process is equivalent to doubling the intensity of the annihilation radiation, because without paraffin the greatest part of the positrons emitted in the upper hemi-

sphere are annihilated in air so far from the chamber as to be ineffective.

In an ideal case the ratio between the ionization produced by annihilation radiation with and without upper paraffin should hence be 2. Any nuclear  $\gamma$ -ray would lower this ratio, bringing it to 1.5 if its ionization were comparable to the annihilation radiation. In our case, as was stated above, we found a ratio of 1.9 which, taking into account the thickness of the source itself and the annihilation in the air, seems to be close enough to 2 to rule out a nuclear  $\gamma$ -ray of intensity comparable with the annihilation radiation.<sup>15a</sup>

Another argument for the absence of nuclear gamma-rays is that the half-value thickness for the radiation emitted, in lead, with or without paraffin on top of the source, is constant and equal to 4.0 g/cm<sup>2</sup> for thickness between 2 and 14 g/cm<sup>2</sup>. This absolute value is close to the correct one (4.1 g/cm<sup>2</sup>).<sup>16</sup>

The ratio between the ionization produced by the  $\beta$ -rays and the annihilation radiation, with paraffin above, is 55 and since there are two quanta per positron annihilated, one has 110 in the case of one quantum per electron.

The correct value for the absorption coefficient of the annihilation radiation was also obtained when absorption measurements were made with the methyl bromide chamber.

<sup>15</sup> C. Perrier and E. Segrè, *J. Chem. Phys.* **5**, 715 (1937); **6**, 155 (1939).

<sup>15a</sup> This method has been used by H. R. Crane and C. C. Lauritsen, *Phys. Rev.* **45**, 430 (1934).

<sup>16</sup> W. Gentner, *Physik. Zeits.* **38**, 836 (1937).



FIG. 4. Electron lines of element 43 (*K* and *L* conversion).