

A Mass-Spectrographic Study of the Isotopes of Argon, Potassium, Rubidium, Zinc and Cadmium

ALFRED O. NIER, *Department of Physics, University of Minnesota, Minneapolis, Minnesota*

(Received September 21, 1936)

A mass spectrograph is described with which a study of the isotopic constitution of argon, potassium, rubidium, zinc and cadmium has been made. A calculation is carried out which indicates that the radioactivity of potassium and rubidium can best be explained by assuming that it is K^{40} in the case of potassium and Rb^{87} in the case of rubidium which is undergoing decay.

A PRELIMINARY report of the results to be described here has already been given for potassium¹ and rubidium, zinc and argon.² In addition to including a more detailed discussion of the previous results this paper includes an analysis of cadmium.

APPARATUS

A diagram of the apparatus used for the study of potassium, rubidium, zinc and cadmium is shown in Fig. 1. The apparatus differed from that of Tate and Smith³ in that a much higher magnetic field is employed here as well as a greater radius of curvature for the ions. The resolving power of the present apparatus was thus much higher. The metal parts of the apparatus were constructed entirely of tantalum except for the analyzer *J* which was made of copper. The Pyrex glass housing was entirely free of wax or grease joints. An electric furnace surrounded the main tube which could thus be maintained at any desired temperature. The side arm which contained the analyzer tube was not heated. Consequently any vapor which diffused into this region would condense. The low pressure thus produced in this region greatly reduced the number of collisions suffered by ions on their way around the analyzer; this helped to keep the resolving power of the apparatus at a high value. The substance to be studied was placed in a small side tube not shown in the diagram. By adjusting the temperature of an auxiliary furnace which surrounded this side tube one could adjust the vapor pressure of the substance to be studied. The pressure was always kept below about 10^{-2} mm Hg. A large solenoid whose axis was parallel to the main tube

surrounded the entire apparatus and produced a field of approximately 2000 gauss.

The apparatus used for the study of argon differed only in minor features from that described above.

METHOD

Electrons emitted by the hot tungsten filament *F* are accelerated by a small voltage (about 4 volts) applied between *F* and *A*. In the region between *A* and *B* they are further accelerated to any velocity that one may desire. They are finally collected on a plate *E* in the electron trap *D*. A small voltage is applied between the plates *G* and *M* in such a direction that it draws the positive ions formed by collision of electrons with gas

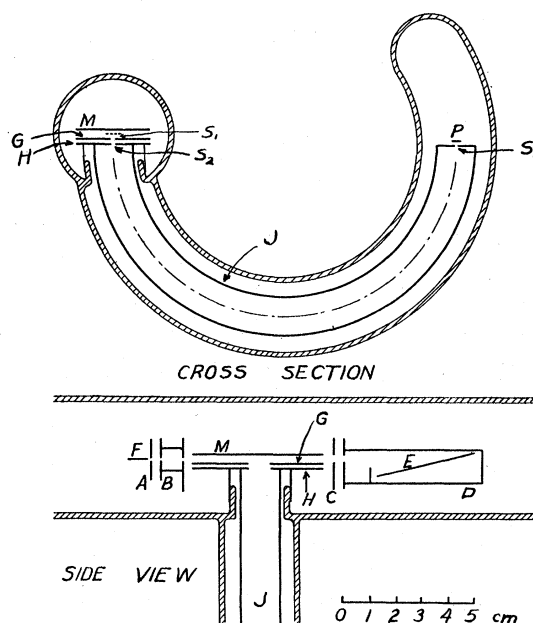


FIG. 1. Diagram of apparatus used for the study of potassium, rubidium, zinc and cadmium. Slit $S_1=0.25$ mm; Slit $S_3=0.15$ mm; Slit $S_2=0.15$ mm for K, 0.07 mm for Rb, Zn and Cd.

¹ A. O. Nier, Phys. Rev. **48**, 283 (1935).

² A. O. Nier, Phys. Rev. **49**, 272 (1936).

³ Tate and Smith, Phys. Rev. **46**, 773 (1934).

molecules or vapor particles toward *G*. Those ions which pass through slit *S*₁ are further accelerated by a potential applied between *G* and *H*. A certain fraction of these then passes through slit *S*₂ into the analyzer. In the analyzer all ions travel in circular paths; those which have the proper ratio of mass to charge will emerge through the slit *S*₃ behind which they are collected by the plate *P* and measured by a vacuum tube amplifier.

By adjusting the difference in potential between *G* and *H* one can sweep over the mass spectrum. The magnetic field is held constant except for unavoidable fluctuations which are compensated for by a special device.⁴

RESULTS

Argon

A typical mass spectrum obtained is shown in Fig. 2. In addition to the isotopes 40 and 36 one can see a very definite peak at 38 corresponding to the very weak isotope reported by Zeeman and de Gier.⁵ From a measure of the peak heights it was found that $A^{40}/A^{36} = 325 \pm 4$ and $A^{36}/A^{38} = 5.10 \pm 0.07$. The A^{40}/A^{36} ratio is in good agreement with the value 304 found by Vaughan, Williams and Tate.⁶ With Aston's values for the packing fraction of argon one calculates from the above ratios an atomic weight for argon of 39.957 in atomic mass units or $39.957/1.000275 = 39.947$ in chemical weight units. The agreement with the International value, 39.944, is within the experimental errors.

The following upper limits can be set for the abundances of hypothetical isotopes relative to A^{40} : A^{41} and A^{39} , 1/10,000; A^{42} and A^{37} , 1/20,000.

Potassium

For potassium besides the isotopes 39 and 41 an isotope of mass 40 was discovered. The K^{39}/K^{41} abundance ratio was found to be 13.96 ± 0.1 and the K^{40}/K^{39} ratio $1/8600 \pm 10$ percent. The presence of K^{40} has since been verified.^{7, 8} The K^{39}/K^{41} ratio has been measured by various individuals in recent years. Brewer and

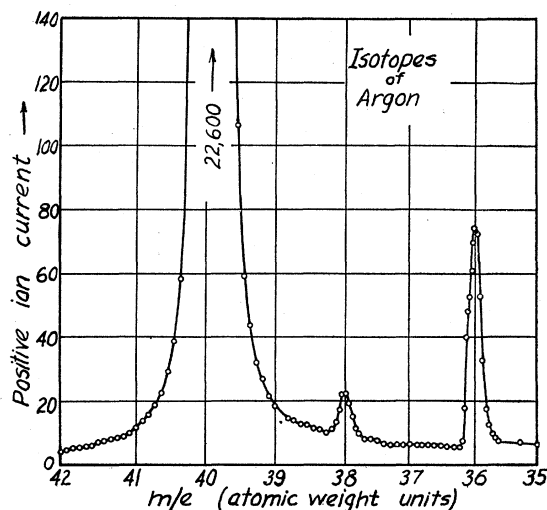


FIG. 2. Mass spectrum showing the isotopes of argon.

Kueck⁹ gave the value 13.88 ± 0.4 . More recently Brewer has given the values 14.25⁷ and 14.20.¹⁰ Bondy, Johannsen and Popper¹¹ gave the value 16.2 ± 2.2 . Manley¹² has given the value 13.4 ± 0.5 . If one assumes the packing fraction of potassium to be the same as that of argon one computes from the abundance ratio, 13.96, a chemical atomic weight 39.096 in exact agreement with the chemical weight measured by Baxter and MacNevin.¹³

Rubidium

For rubidium the previously known isotopes Rb^{85} and Rb^{87} were found. The abundance ratio measured was $Rb^{85}/Rb^{87} = 2.68 \pm 0.02$. Other values which have been given for this ratio are: Aston,¹⁴ 3.0; Brewer and Kueck,⁹ 2.59 ± 0.04 ; Bondy, Johannsen and Popper,¹¹ 2.68; Brewer,¹⁵ 2.59 ± 0.01 . If one assumes the packing fraction of rubidium to be the same as that of krypton one calculates a chemical atomic weight for rubidium of 85.45. The latest determined chemical weight is 85.48.¹⁶

⁹ Brewer and Kueck, *Phys. Rev.* **46**, 894 (1934).

¹⁰ Brewer, *J. Am. Chem. Soc.* **58**, 365 (1936).

¹¹ Bondy, Johannsen and Popper, *Zeits. f. Physik* **95**, 46 (1935).

¹² Manley, *Phys. Rev.* **49**, 921 (1936).

¹³ Baxter and MacNevin, *J. Am. Chem. Soc.* **55**, 3185 (1933).

¹⁴ Aston, *Proc. Roy. Soc.* **A134**, 575 (1932).

¹⁵ Brewer, *Phys. Rev.* **49**, 867 (1936).

¹⁶ Archibald, Hooley and Phillips, *J. Am. Chem. Soc.* **58**, 70 (1936).

⁴ A. O. Nier, *Rev. Sci. Inst.* **6**, 254 (1935).

⁵ Zeeman and de Gier, *Proc. K. Akad. Amsterdam* **37**, 3 (1934).

⁶ Vaughan, Williams and Tate, *Phys. Rev.* **46**, 327 (1934).

⁷ Brewer, *Phys. Rev.* **48**, 640 (1935).

⁸ Sampson and Bleakney, *Phys. Rev.* **50**, 456 (1936).

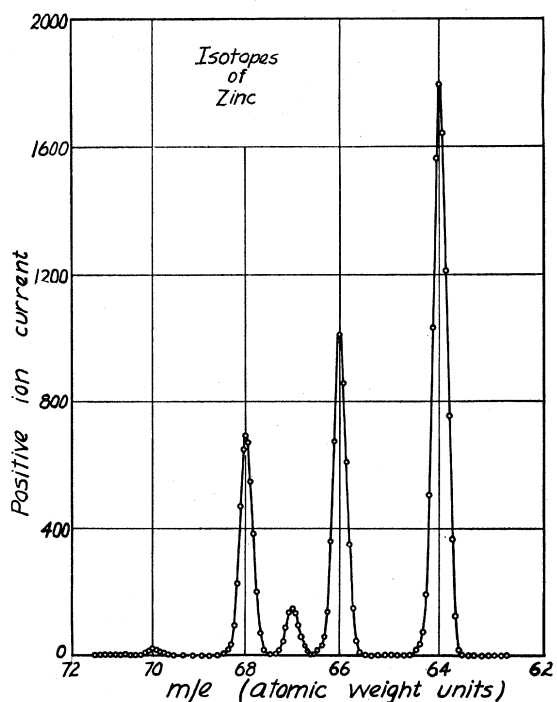


Fig. 3. Mass spectrum showing the isotopes of zinc.

The real reason for undertaking the study of rubidium was to establish the existence or non-existence of other possible isotopes because of the importance of this knowledge in relation to the radioactivity problem of rubidium. No new isotopes were found and it was possible to set the following upper limits for abundances relative to Rb^{85} : Rb^{80} , Rb^{81} , Rb^{82} , Rb^{89} and Rb^{90} , 1/100,000; Rb^{83} , 1/60,000; Rb^{84} , 1/12,000; Rb^{86} , 1/13,000; and Rb^{88} , 1/22,000.

Zinc

Fig. 3 shows a typical mass spectrogram obtained for the isotopes of zinc. It is clearly seen from this that there are present the isotopes 64, 66, 67, 68 and 70 in complete agreement with the results of Bainbridge.¹⁷ Recently Stenvinkel and Svensson¹⁸ claim to have found the isotopes Zn^{63} and Zn^{65} —both more abundant than Zn^{70} . Fig. 4 shows the lower part of Fig. 3 drawn to a greatly magnified scale. It is quite obvious from this that Zn^{65} and Zn^{63} do not exist—at least, not in the magnitude claimed. From a measurement of the background it is concluded that Zn^{65} , Zn^{63} ,

¹⁷ Bainbridge, *Phys. Rev.* **39**, 847 (1932).

¹⁸ Stenvinkel and Svensson, *Nature* **135**, 955 (1935).

and Zn^{69} are present in zinc to less than one part in 40,000, 80,000 and 60,000, respectively. These abundances compared to Zn^{70} would be 1/200, 1/400, and 1/300, respectively.

The following table gives the percentage abundances of the several isotopes. The table also includes the results of Aston as revised by Bainbridge.

Mass number	64	66	67	68	70
Percentage	50.9	27.3	3.9	17.4	0.5
Aston's revised value	50.4	27.2	4.2	17.8	0.4

The agreement is excellent as may be seen.

With a packing fraction of -9.9 for zinc, Aston's figures yield a chemical atomic weight of 65.33. The value obtained from the writer's figures is 65.31. The present International value is 65.38. The writer is unable to explain the large difference between the chemical value and the mass-spectrographic value.

Cadmium

The isotopic constitution of cadmium like that of zinc has been open to question. Aston¹⁹ re-

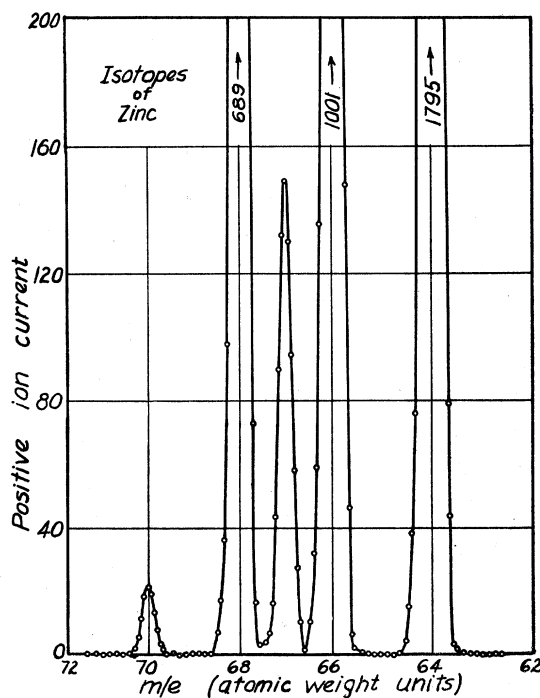


Fig. 4. Lower portion of Fig. 3 drawn to a greatly magnified scale.

¹⁹ Aston, *Proc. Roy. Soc.* **A149**, 396 (1935).

ported the isotopes 106, 108, 110, 111, 112, 113, 114, 115 and 116. Stenvinkel and Svensson¹⁸ from their investigation of the band spectrum of cadmium hydride reported an isotope of mass 118. Recently Bainbridge and Jordan²⁰ showed that Cd¹¹⁵ could not exist in an amount greater than $\frac{1}{8}$ that claimed for it by Aston. They also were unable to find any trace of Cd¹¹⁸. Dempster²¹ could not find Cd¹¹⁵.

Fig. 5 shows a typical mass spectrum obtained. As the mass spectrograph has a greater resolving power for lower masses, doubly charged ions were worked with in this case in preference to the singly charged. The isotopes found and their corresponding percentage abundances are listed below. Aston's values are also listed for comparison.

Mass number	116	115	114	113	112	111	110	108	106
Percentage	7.3	0	28.0	12.3	24.2	13.0	12.8	1.0	1.4
Aston's values	5.9	0.8	23.7	14.9	21.8	15.2	15.2	1.0	1.5

If one assumes a packing fraction for cadmium of -6 one calculates a chemical weight for cadmium of 112.37 from the writer's values. The value calculated from Aston's figures is 112.2 ± 0.1 . The present International value is 112.41.

In addition to the above work it was possible to set the following upper limits for abundances of hypothetical isotopes in cadmium: Cd¹¹⁸, 1/14,700; Cd¹¹⁵, 1/800; Cd¹⁰⁹, 1/2350; Cd¹⁰⁷, 1/2350. The above limit on Cd¹¹⁸ corresponds to 1/200 of Cd¹⁰⁶. Stenvinkel and Svensson in their paper claimed Cd¹¹⁸ to be more abundant than Cd¹⁰⁶. From the present work it is obvious that this is impossible. The above upper limit on Cd¹¹⁵ corresponds to $\frac{1}{8}$ of the abundance claimed for it by Aston. By coincidence this is the same factor by which Bainbridge and Jordan limited Cd¹¹⁵.

THE RADIOACTIVITY PROBLEM OF POTASSIUM AND RUBIDIUM*

Potassium and rubidium have long been known to give off beta-particles spontaneously. The question of which isotope was responsible for this

²⁰ Bainbridge and Jordan, *Phys. Rev.* **50**, 282 (1936).

²¹ Dempster, *Proc. Am. Phil. Soc.* **125**, 755 (1935).

* Hevesy, *Naturwiss.* **23**, 583 (1935), has given an excellent summary of this problem. His paper was written before the writer's analysis of potassium and rubidium had been announced so that it does not include the additional information presented here.

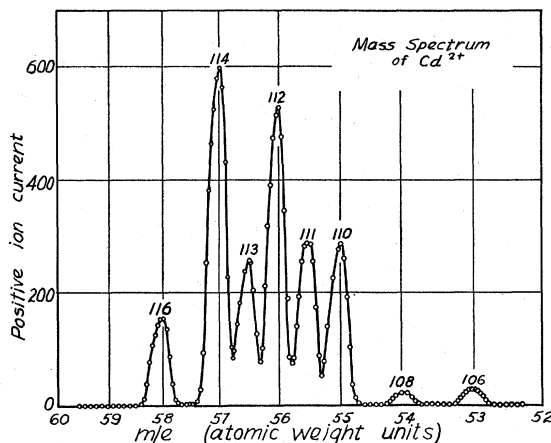


FIG. 5. Mass spectrum showing the isotopes of cadmium.

in each case has for some time been a matter of speculation.

If the calculations of Ruark and Fussler²² on the minimum half-lives of potassium and rubidium are extended to include the writer's present work on the isotopic constitution of potassium and rubidium it is possible to make a calculation which indicates in each case the isotope most likely to be the radioactive one. The method of calculation is as follows: Consider a mineral sample containing N atoms of a radioactive element of which only a fraction, A , are active. Suppose that the age of the mineral is t and that the apparent decay constant of the element is λ' . Then the number of atoms, n , of the decay product which have accumulated in time t is:

$$n = AN(e^{\lambda' t/A} - 1). \quad (1)$$

As some of the end-product atoms may have been present originally in the mineral we may write:

$$N_e \geq AN(e^{\lambda' t/A} - 1), \quad (2)$$

where N_e is the total number of atoms of the end-product type present in the mineral.

For the case of potassium let us now apply Eq. (2) to the hypothetical disintegration: $K^{40} \rightarrow Ca^{40}$, $K^{41} \rightarrow Ca^{41}$ and $K^{42} \rightarrow Ca^{42}$ to see which one or ones will satisfy the equation. We will use Aston's²³ values for the percentage abundances of calcium isotopes in old potassium minerals, namely: Ca^{40} ,

²² Ruark and Fussler, *Phys. Rev.* **48**, 151 (1935).

²³ Aston, *Nature* **133**, 869 (1934).

96.76; Ca^{42} , 0.77; Ca^{43} , 0.17; and Ca^{44} , 2.3. We will also make use of Aston's upper limit for Ca^{41} which was 0.1 percent. The isotopic constitution assumed for potassium is that previously given in this paper. The remainder of the information needed to carry out the calculation is given in Ruark's and Fussler's paper. The results of the calculations show:

- (1) For all three minerals considered the disintegration, $\text{K}^{40} \rightarrow \text{Ca}^{40}$, satisfies the equation.
- (2) For two of the three minerals the hypothetical disintegration, $\text{K}^{41} \rightarrow \text{Ca}^{41}$, will not satisfy the equation. The fact that it does satisfy it in one of the cases is not significant as the disintegration $\text{K}^{40} \rightarrow \text{Ca}^{40}$ also satisfies the equation for this particular mineral.
- (3) For all three minerals the disintegration, $\text{K}^{43} \rightarrow \text{Ca}^{43}$, will not satisfy the equation. This is direct evidence against the speculations of Sitte.²⁴

Additional evidence to support the hypothesis that the radioactivity of potassium is associated with K^{40} comes from the experiments of Klemperer²⁵ and from the distillation experiment of Hevesy and Logstrup,²⁶ when taken together with the new atomic weight determinations of potassium by Baxter and MacNevin¹⁸ and Baxter and Alter.²⁷

K^{42} may be eliminated as the active isotope as it has been produced artificially by three different means²⁸ and found to have a half-life of 16 hours, a value far too low to enable one to assume that the natural activity of potassium is associated with this isotope.

For the case of rubidium let us apply the equation to the following hypothetical disintegrations: (1) $\text{Rb}^{84} \rightarrow \text{Sr}^{84}$; (2) $\text{Rb}^{85} \rightarrow \text{Sr}^{85}$; (3) $\text{Rb}^{86} \rightarrow \text{Sr}^{86}$; (4) $\text{Rb}^{87} \rightarrow \text{Sr}^{87}$; (5) $\text{Rb}^{88} \rightarrow \text{Sr}^{88}$; (6) $\text{Rb}^{89} \rightarrow \text{Sr}^{89}$. The percentage abundances of the strontium isotopes used will be those of Blewett and Sampson²⁹ namely: Sr^{88} , 82.4; Sr^{87} , 7.5; Sr^{86} , 9.6; Sr^{84} , 0.5. Their upper limits on the abundances of Sr^{85} and Sr^{89} will also be used. The isotopic constitution of rubidium used will be that previously given in this paper. In the case of rubidium one does not have definite minerals to consider as in the case of potassium. Consequently, in the absence of any better information one has to use the ratio of the total amount of strontium to the total amount of rubidium in the earth's crust in order to calculate the ratio N_e/N .

Again carrying out the calculations as was done for potassium we find that only the hypothetical disintegrations $\text{Rb}^{85} \rightarrow \text{Sr}^{85}$ and $\text{Rb}^{87} \rightarrow \text{Sr}^{87}$ will satisfy the equation. The latter satisfies the equation very easily whereas the former comes close to not satisfying it. Had the upper limit for Sr^{85} been $\frac{1}{3}$ of that given the disintegration possibility $\text{Rb}^{85} \rightarrow \text{Sr}^{85}$ would have been ruled out by the equation. Thus it seems most reasonable to associate the radioactivity of rubidium with Rb^{87} although it should be remembered that the rough calculation carried out here does not exclude Rb^{85} as the active one. A further search for Sr^{85} should clear up this point.

The writer wishes to express his appreciation to Professor John T. Tate for his constant interest and valuable suggestions in connection with this work.

²⁴ Sitte, *Nature* **136**, 334 (1935).

²⁵ Klemperer, *Proc. Roy. Soc.* **A148**, 638 (1935).

²⁶ Hevesy and Logstrup, *Zeits. anorg. v.a. Chemie* **171**, 1 (1928).

²⁷ Baxter and Alter, *J. Am. Chem. Soc.* **55**, 3270 (1933).

²⁸ Hevesy and Levi, *Nature* **135**, 580 (1935).

²⁹ Blewett and Sampson, *Phys. Rev.* **49**, 778 (1936).