POSITIVE-RAY ANALYSIS OF POTASSIUM, CALCIUM AND ZINC.

By A. J. Dempster.

Synopsis.

Isotopes of potassium, calcium and zinc have been determined by positive-ray analysis, using the apparatus and method previously described in which the charge deflected by a constant magnetic field through a fixed slit into a Faraday cylinder is measured as a function of the voltage accelerating the rays. Curves showing maxima corresponding to the various isotopes are reproduced. With potassium, isotopes with atomic weights 39 and 41 were found as previously observed by Aston. With pure calcium isotopes at 40 and 44, and with zinc isotopes at 64, 66, 68, and 70 were observed. After a disturbing effect of the electric field was eliminated, the ratio of the intensities obtained, 18 to 1 for the two isotopes of potassium and 70 to 1 for those of calcium, gave average atomic weights agreeing well with accepted values, 39.10 and 40.07 respectively. It is pointed out that when the determination of the relative proportions of all the isotopes of an element is made sufficiently accurate and reliable, a comparison between calculated and observed average atomic weights would give a measure of the packing effect or divergence of the weights of the isotopes from integral values. If the width of the slit used in limiting the beam of canal rays were reduced from 0.37 to .07 mm., isotopes of elements of atomic weight 100 or more should be resolved with the present apparatus.

In the following paper the method of positive-ray analysis previously described is extended to the elements potassium, calcium and zinc. The analyzing apparatus is shown in Fig. 1 and is described in detail in two previous papers.[1] The charged atoms are formed at the right and the masses for different elements may be compared by observing the total potentials applied when they are bent so as to fall on the second slit S_2. The only alteration made in the apparatus has been to cover both sides of the slit in P with fine wires a short distance apart in order to insure that the discharge is not influenced when the electric field between P and S_1 is changed.

Experiments with Potassium (Atomic Weight 39.10).

Rays of potassium were observed from two sources. They were first found associated with sodium in some preliminary attempts to obtain rays from metals with high melting points, probably from the decomposition of water glass used in the cement on the hot anode. Two components, one much stronger than the other, were readily observed

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[1] A. J. Dempster, Physical Review, 11, p. 316, 1918; Phys. Rev., 18, p. 415, 1921.

two units apart in atomic weight. A comparison with sodium located the main potassium component as close to 39. The curve in Fig. 2 shows the intensity of the rays observed as the accelerating potential was altered to bring the various parts of the bundle on to the second slit.

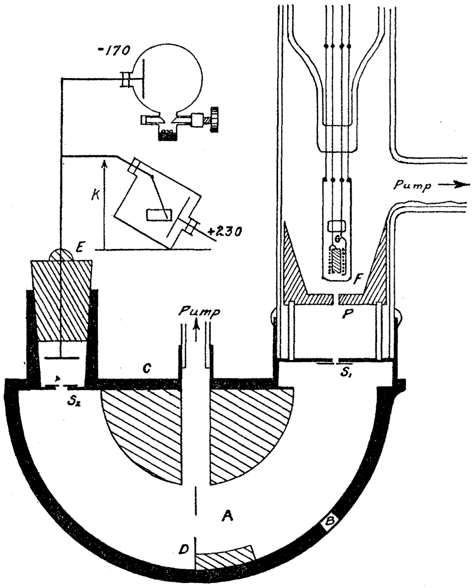

Fig. 1.

The maximum of the strong component is placed exactly at 39, and the atomic weight abscissæ are obtained by dividing 39 times 911 by the potential in volts for each measurement. The current scale for the

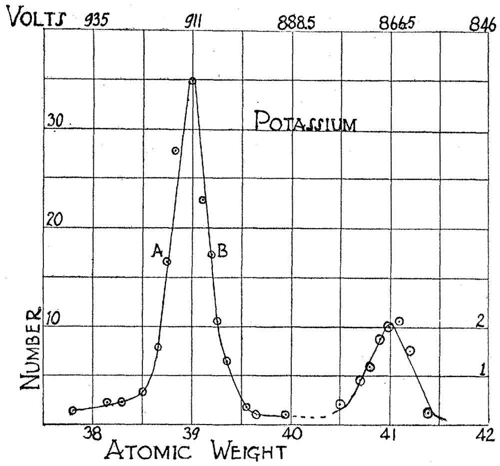

Fig. 2.

fainter isotope in the figure is made five times that for the stronger. The intensity ratio is approximately 18 to 1, giving a mean atomic mass of 39.10 in agreement with the chemical atomic weight. A possible significance of this agreement will be discussed below in connection with the measurements with calcium. Potassium rays were also measured from an anode of lithium, containing potassium as an impurity, which was heated in an iron capsule. The same two components were observed as in the case described above. The experiments thus confirm the existence of the two isotopes in potassium found by Aston with his method of analysis.[1]

Experiments with Calcium (Atomic Weight 40.07).

Calcium metal was found to be very suitable for use in this method of analysis. It was heated in an iron container and evaporated readily at a red heat. A strong line appeared suddenly as the evaporation commenced and was always accompanied by a faint line four units greater in atomic weight. The atomic weight 40 for the strong component was confirmed to 0.3 per cent. by comparison with a potassium line at 39 which appeared for a short time during the heating. Complete curves were drawn for the calcium lines, but as they are practically identical in form and sharpness with those in Fig. 2, they are not reproduced. The atomic masses of the two lines from calcium were compared by observing the potentials for the maxima. In Fig. 3 is shown the accuracy with which the observations of the maxima may be made. The center of each short line indicates the value taken as the maximum and the length of the line indicates on the atomic weight scale the estimated possible error in the setting (corresponding usually to ± 2 volts). The first two lines show the comparison with the potassium line at 39. It is seen that to the accuracy obtained the atomic weights agree with 40 and 44. With the parabola method of analysis, G. P. Thomson[2] has examined calcium rays from calcium fluoride and detected

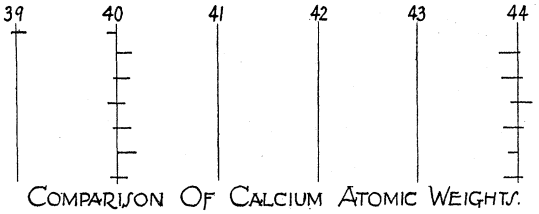

Fig. 3.

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[1] Phil. Mag., 42, p. 857, 1921.

[2] Phil. Mag., 42, p. 857, 1921.

a rather broad line around 40 in atomic weight. No isotope at 44 was observed.

The calcium used was, however, found to contain traces of calcium carbonate as an impurity, so that the rays with mass 44 might be due to carbon dioxide liberated by the decomposition of the carbonate. To avoid this uncertainty a sample of calcium was prepared by distillation in a high vacuum. Considerable quantities of gas were set free during the evaporation and continually removed by a mercury vapor pump. The calcium was condensed directly in the anode and this was then transferred to the analyzing apparatus as rapidly as possible. With the calcium thus prepared it was found that the component at 44 was still present, and was approximately 1/70 as strong as the main component. We may therefore conclude that calcium consists of two isotopes with atomic weights 40 and 44.

With the crude metal several measurements at low temperatures gave about 70 to 1 for the intensity ratio of the components, the same as found for the distilled calcium, but on increasing the temperature of the anode the component at 44 became much stronger than at low temperatures, probably due to carbon dioxide being evolved at the higher temperatures. The ratio 70 to 1 gives a mean atomic weight of 40.055, whereas the chemical atomic weight is given as 40.07. Further experiments will be necessary to obtain a more accurate value of the ratio and to examine the possibility of still fainter isotopes with other atomic weights. Accurate intensity measurements may be expected to involve considerable difficulty, since, if they are to indicate the relative proportions of the isotopes in the element, several conditions must be fulfilled; the faint background of scattered and reflected rays must be considered or suppressed, the intensity ratios must be independent of the particular experimental conditions used, the primary ionization must be unaffected by the alterations in the electric or magnetic fields used to bring a new component onto the slit, and the possibility must be considered that, as appears to hold in the case of lithium, the different components may have different rates of evaporation at different temperatures and with different surface conditions.

RATIOS OF COMPONENTS AND ATOMIC WEIGHTS.

It may be pointed out, however, that a reliable determination of the proportions of all the isotopes in an element by positive-ray measurements would allow conclusions to be drawn as to the existence or absence of a "packing effect" or a slight divergence of the atomic weight from an integral value. If the mean atomic weight calculated from the positive-ray ratios, on the assumption of integral values for the components, is lower than the chemical atomic weight, we must conclude that the components have atomic weights greater than exact integers by an amount sufficient to make up the difference. Thus the agreement of the mean atomic weight obtained for potassium with the chemical atomic weight, might be used as an argument that the atomic weight of the strong potassium component is exactly 39.00 to within one integer in the second decimal place. In the case of calcium we might use the low computed atomic weight 40.055 to deduce the value 40.07 − 0.055 = 40.015 as the correct atomic weight of the heavier component. More careful measurements of the intensity ratios will however be necessary before conclusions of this nature can have much weight.

Experiments with Zinc (Atomic Weight 65.38).

Strong rays were obtained from a zinc anode when heated to a very dull red temperature. Three strong and one faint maxima were observed, separated by two units on the atomic weight scale. It was found that the zinc lines were also obtained from a calcium anode to which a little zinc had been added. Probably due to the higher temperature the rays were then usually sharper than with pure zinc. The curve in Fig. 4 shows the different components observed with this anode. The first experiments with a zinc anode were made before those with calcium and

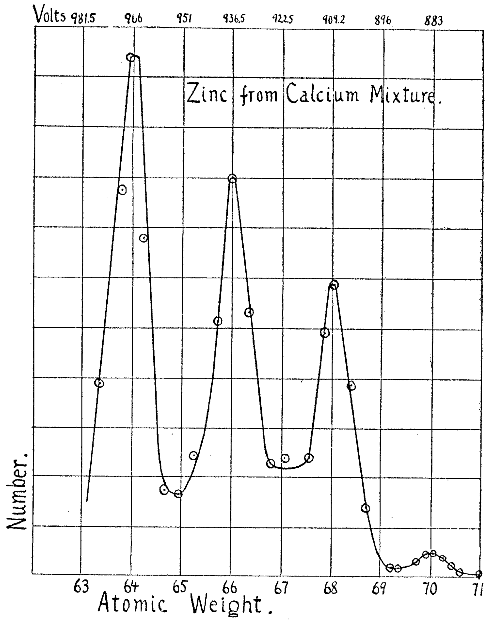

Fig. 4.

potassium, and before the two gauzes had been placed on each side of the slit in P (Fig. 1). These first experiments gave quite different intensity ratios for the components from that shown in Fig. 4, and a mean atomic weight almost a unit higher. An early curve is reproduced in Dr. Aston's book on Isotopes, p. 147. Later, with two different anodes containing mixtures of calcium and zinc, and with one containing very pure zinc, intensity ratios similar to that shown in Fig. 4 were obtained. The mean atomic weight from curve 4 is approximately 65.5.

It was suspected that the changes in the field between P and S_1, used to bring the different components on to the second slit, might have influenced the total intensity of the rays in the first experiments by means of the stray field through the slit in P. Two gauzes were therefore introduced as mentioned in the first paragraph. Intensity ratios similar to that shown in the curve were then always obtained from anodes of both pure and commercial zinc, and the total positive-ray current as indicated by a galvanometer was found independent of the field.

The accuracy with which the maxima of the three strong zinc components agreed with integral atomic weights is shown in Fig. 5. The center of each short line indicates the value taken as the maximum and the length of the line indicates the estimated error in the setting (usually ± 2 volts). It is seen that to the accuracy obtained the atomic weights are two integers apart.

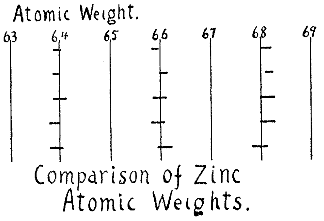

Fig. 5.

It was at first assumed that the atomic weights of the components were 63, 65, 67 and 69, since, with the intensities first observed, a mean atomic weight was obtained which agreed with the chemical atomic weight 65.38.[1] This reasoning was invalidated by the different intensity ratios obtained with the improved shielding, and a direct comparison with the calcium component at 40 showed the atomic weights to be near the integers 64, 66, 68, and 70. With a calcium anode to which a little zinc had been added rays of both elements were obtained, and the atomic weights could be compared by observing the potentials required to

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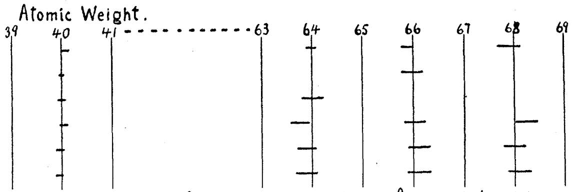
[1] Science, Vol. 54, p. 516, 1921.

bring the different maxima on to the second slit, while the magnetic field was kept constant. The settings could usually be made with an uncertainty of 2 volts or less, and are illustrated in Fig. 6. The center of the short line represents, as before, the value taken for the maximum and the length of the line represents the estimated error. Thus the potentials in volts used in the first plot were 974 ± 2; 610 ± 1; 592.6 ± 1; 575.1 ± 2. The first three comparisons were made with one anode and the last three with a new filling and adjustment. It is seen that within the experimental error the atomic weights of the three zinc components are 64, 66, and 68. The faint isotope at 70 was not used in the comparisons with calcium since much more time and care is required in setting on it than on the stronger components.



Comparison of Calcium and Zinc Atomic Weights.

Fig. 6.

In all the curves drawn for the zinc rays the intensity at atomic weight 67 is greater than at 65, although the neighboring lines at 66 and 68 are weaker than 64 and 66. This is probably due to the existence of an unresolved isotope at 67, and in two curves a slight maximum was also indicated at this atomic weight. Experiments with sharper bundles will be necessary to decide definitely if a fifth isotope exists at 67 or not.

Resolving Power of the Apparatus.

The sharpness of the curves and the dependence on the slit width and other factors is of interest in connection with the possibility of improving the resolution sufficiently to analyze heavier elements. The slit widths used in all the experiments described in this paper were 0.37 mm. for the first, and 0.42 mm. for the second. If the focusing were perfect the width of the bundle at S_2 would be 0.37 mm. The curve in Fig. 2 is obtained as this bundle is moved from one edge of the slit S_2 across to the other, the displacement of the bundle in moving between the positions which give the currents A and B half way to the maximum being exactly the width of the bundle. From the relation M.V. = const. d^2, as discussed in the first paper,[1] we see that the beam must have had a width of 0.55 mm. in order to give the curve for potassium. The beam originally 0.37 mm. wide has thus increased in width by 0.18 mm. in

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[1] A. J. Dempster, Phys. Rev., 11, p. 320, 1918.

going a distance of 17 cm. This extra width is probably due entirely to a lack of homogeneity in the velocity of the rays since a dispersion of only 3 volts in the 900 used would account for the extra width of the image. The sharpest curves observed with zinc indicate a width of 0.68 mm. at the second slit, and some experiments showed that the sharpness was affected to a considerable extent by the adjustment of the potentials between the plate *P*, the cathode and the anode.

If as great a uniformity in velocity can be obtained with heavier elements, as in the case of calcium or potassium, a considerable increase in resolution should be secured with narrower slits. Thus with $S_1 = 0.07$ mm. the beam should be 0.25 mm. wide at S_2 and the separation of the points *AB* on the atomic weight scale would be half a unit for an atomic weight of 100, so that all integral components less than this should be sharply separated. If the total potential were increased to 2,000 volts, elements as high as 200 in atomic weight should be similarly separated, provided the necessary magnetic field of 18,000 gauss could be secured.

Should it prove necessary to deal with a greater velocity dispersion than that found in the case of potassium and calcium, an electric field may be added to focus rays with slightly different velocities as in the apparatus designed by Dr. Aston. With slow rays it is also possible to combine the velocity focusing, for a single mass, with the direction focusing as used in these experiments. Figs. 7 and 8, in which *A* and *B* represent two rays diverging in direction, and *C* a ray of the same mass and smaller velocity, illustrate diagrammatically two arrangements of the magnetic and electric fields. In Fig. 7 the fields act simultaneously, and it may be readily shown that a small range of velocities is focused at S_2 when the electric force is half the magnetic and opposite in direction. In Fig. 8 the magnetic and electric fields, *M* and *E*, act separately, the velocity focusing occurring when the electric force is twice the magnetic.

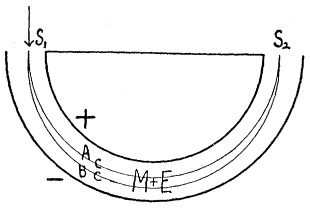

Fig. 7.

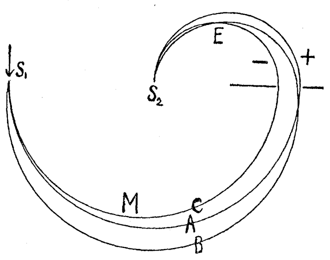

Fig. 8.

The author's thanks are due to Mr. F. B. Haynes for the use of the apparatus and method he developed for distilling calcium in vacuo, and to Mr. J. K. Morse for testing the calcium chemically for carbon dioxide.

RYERSON PHYSICAL LABORATORY,
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