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POSITIVE RAY ANALYSIS OF LITHIUM AND MAGNESIUM.

By A. J. Dempster.

Synopsis.

Isotopes of lithium and magnesium have been *determined by positive ray analysis*, using the apparatus and method previously described in which the positive ray spectrum is determined by measuring the charge passing through a fixed slit into a Faraday cylinder as a function of the accelerating difference of potential keeping the deflecting magnetic field constant. The source of the rays was a small cylindrical anode containing the metal to be studied, which was heated by a concentric coil and bombarded by electrons. It was found that there are two isotopes of lithium with atomic weights 6 and 7, while magnesium has three isotopes with atomic weights 24, 25 and 26. The relative proportions of the isotopes of lithium varied with the conditions. For magnesium the relative numbers were 7 : 1 : 1.

Compensation Method of Measuring Small Currents.—The current to be measured is balanced by the current through an ionization chamber, which is adjusted to equality by varying the width of the slit through which the ionizing beta rays pass.

Introduction.

THIS paper discusses further experiments with the apparatus for positive ray analysis which was described in the Physical Review for April, 1918. In that paper the method of analysis was found to have a comparatively high power of separating elements with slight differences in their atomic weights, provided a steady source of positive atoms of the elements could be devised.

The positively charged atoms are allowed to fall through a definite potential difference; a narrow bundle is separated out and bent into a semicircle by a strong magnetic field. By varying the magnetic field or the accelerating potential, the beam of rays may be made to fall on a second slit and give up their charge to an electroscope. From the equation for the velocity v acquired by a particle of mass m and charge e, in falling through a potential difference V, the equation and for the radius of curvature r in which the rays are bent by a magnetic field H;

$$\tfrac{1}{2}mv^2 = eV \qquad \text{and} \qquad \frac{mv^2}{r} = Hev,$$

the mass of the particle is found to be given by $m = eH^2r^2/2V$, and the molecular weight may be calculated if H, r, and V are known.

The ratio of different atomic weights may be found more simply by keeping the magnetic field constant and finding the ratio of the potentials for which the rays have the same radius of curvature. This potential is inversely proportional to the atomic weight, and having identified any element such as sodium, nitrogen, or hydrogen, other atomic weights may be found by comparing the potentials necessary to bring the different atoms on to the second slit. In the previous paper this relation was shown to still hold when the deviations in the stray magnetic field before the slit are taken into account.

SOURCE OF THE RAYS.

The chief difficulty in applying the method to new elements is in obtaining steady sources of the rays desired. The arrangement illustrated in Fig. 1 has been found to work well with lithium and magnesium.

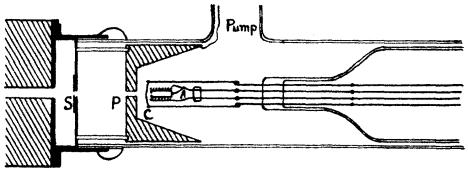

Fig. 1.

The shaded portion to the left represents the iron plates between which the strong magnetic field is produced, S is the first slit, and P is a cylindrical iron shield. The main variable accelerating field, usually 800 to 1,000 volts, acts between P and S. The charged atoms come from the anode A which is heated by a coil of wire and bombarded with electrons that have fallen through 30 to 160 volts from the coated platinum cathode C. In general P and C are at the same potential. The anode is a small iron cylinder filled with the metal; in several cases it was 6 mm. long, 3 mm. in diameter, and closed by a cap with a hole which was varied in size in different experiments. The cylinder was coated with an insulating cement, the heating coil of iron-alloy wire was slipped on, and the outside again coated. The four leads to the hot cathode and anode are brought through seals in a glass inner tube as shown. The inner tube is sealed to the outer with sealing wax and can be easily removed for renewing the anode and cathode. The figure is about one third the actual size, and in the experiments the rays travelled vertically downward into the magnetic field. Even under the best conditions it has not been found possible to keep the strength of the rays absolutely constant over more than two or three minutes.

Many preliminary experiments using ribbons and rods of magnesium showed that if the anode is too much exposed to the electron bombard-

ment, localized arcs form which are very irregular. It was also found to be unwise to depend on electron bombardment to heat the anode, as the discharge tends to become unstable. The converging electron current and the diverging vapor stream would concentrate the ionization at the anode, but it may be that under electron bombardment the positive atoms are detached from the hot surface itself in the ionized condition. The tube was exhausted with a mercury vapor pump and the pressures were lower than could be read on a McLeod gauge. It was found that no special precautions were necessary to keep mercury vapor away from the apparatus when the vapor pump was not in use, the difficulties previously attributed to mercury vapor probably being due to the warming of wax joints.

CURRENT MEASUREMENTS.

The quadrant electrometer used in the previous experiments to detect the rays was replaced by a Wilson tilted electroscope and the compensating arrangement illustrated in Fig. 2. After being deflected magnetically, the positive rays fall on the electrode through the second slit S, and their charge is balanced by an equal negative ionization current driven to the electrode in the ionization chamber at the right. The electroscope indicates quickly when the two currents exactly balance. K is a grounding key. The novel feature of the arrangement is the method used for adjusting the ionization current to balance the positive ray current. The ionizing agent is a group of a dozen old radium emanation tubes that had been discarded for medical work and emit strong β rays from RaE. They are placed in a side tube as shown, and cut off from the ionization chamber by an adjustable graduated slit, which was made from a micrometer eyepiece by replacing the cross hairs by the two halves of a slit. A calibration curve was drawn connecting the ionization current and the slit width and was found to be approximately a straight line over a considerable range. The slit scale is graduated in half millimeter divisions up to 10 mm. width and one hundredth of a division can be read on a drum attached to the screw. A slit width of one millimeter gives an ionization current of approximately 6×10^{-12} amperes. Settings for balance can be made in about 5 seconds to within 1/40 mm. Apart from the great range, convenience and rapidity of the measurement, the arrangement has the advantage of an almost continuous control of the steadiness of the positive ray current during the measurements.

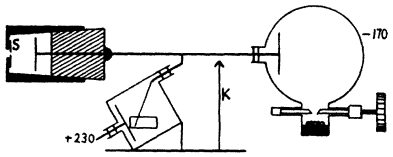

Fig. 2.

POTENTIAL MEASUREMENTS.

The potential through which the charged atoms fall was obtained from small lead cells. It was measured for groups of the cells with a high resistance voltmeter and occasionally checked by a standard voltmeter connected in a potentiometer arrangement as shown in Fig. 3. A and B are two slide wire resistances connected in series to a large storage battery of about 180 volts. The double pole switch S is thrown to the left and the sliders adjusted for zero voltmeter reading. The switch is then thrown to the right and the voltmeter indicates the potential of the cells on open circuit. R is a resistance equal to that of the voltmeter; it is connected in parallel with the main current when no current flows in the voltmeter. It was found that the readings with the high resistance voltmeter were low by about 1.3 per cent. even when the cells were fully charged.

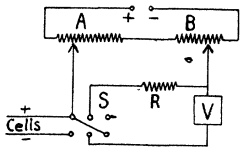

Fig. 3.

As discussed in the previous paper the potential through which the charged atoms fall is, with high vacua, equal to the total potential applied between the anode and the slit. While the rays all fall through the main accelerating field between P and S, it might be thought that the charged atoms could be formed at various points of the auxiliary field CA. When the pressure was not very low broad gas lines were observed, possibly partly due to this cause, but when the vacuum was good the sharpness of the curves obtained shows that the atoms have all fallen through the same potential. That this potential is the total applied, indicating that the rays are formed at the surface of the anode, is shown by the fact that the total potential required for the maximum in the curves is independent of the part used as auxiliary potential between cathode and anode, and also by the fact that the ratio of the atomic weights of known lines agrees with the ratio of the total potentials applied to make the bundles fall on the second slit.

EXPERIMENTS WITH LITHIUM.

Strong lithium rays appeared when the anode was heated to a dull red temperature. On all occasions two atomic weights appeared simultaneously, the lighter much weaker than the other. The values of the atomic weights were calculated from the magnetic field determinations to be in the neighborhood of 6 and 7, and these values were verified by comparison with hydrogen atoms, the voltage ratios for the maximum currents being, $968/138 = 7.02$, and $968/162 = 5.98$, with a possible error of 1 per cent. It is possible that this ratio may be obtained accu-

rately enough to distinguish, as already done by Aston, between an atomic weight of 1,000 and 1,008 for hydrogen on the assumption of 6 and 7 for lithium. In a letter to Nature of Feb. 24, 1921, G. P. Thomson and F. W. Aston state that they obtained two isotopes using anodes of heated lithium salts, with the method of analysis developed by F. W. Aston. In the Proceedings of the Cambridge Philosophical Society, Vol. 20, p. 210, 1920, G. W. Thomson describes experiments with the method of Sir J. J. Thomson designed to detect any isotopes of lithium.

A curve giving the positive ray current in terms of atomic weights is given in Fig. 4. Keeping the magnetic field constant at a certain value, a potential of 969 volts between the anode and the slit gave a maximum for the element of atomic weight 6, and the abscissæ in the curve plotted as atomic weights are obtained by dividing 6 x 969 by the potential through which the rays fall in each case. The potential between the

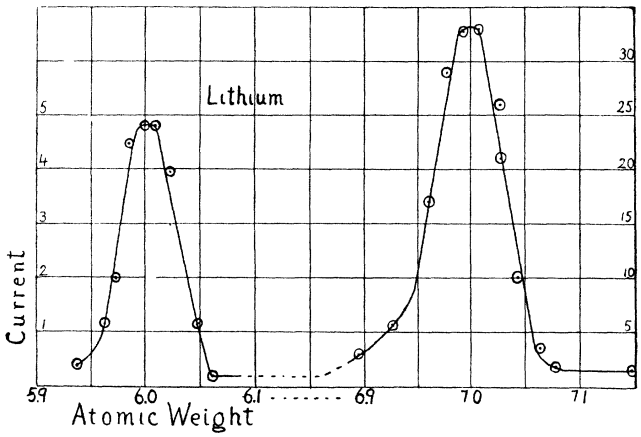

Fig. 4.

cathode and the anode was 96 volts and between the iron screen and the anode was 128 volts. The ordinates of the element at 6 are multiplied by 5 in plotting, so that in this case the ratio of the amount of the two was about 7 to 1. The width of the curves may be attributed entirely to the slits (which were .58 mms. and .75 mms. wide). In the previous paper it was shown that (with slits of equal width) the curve to be expected as the rays are moved over the second slit by increasing the potential is a linear increase to a maximum and then a linear decrease. The width of the curve half way to the maximum is given by $(M \cdot S)/r$ where M is the atomic weight, S the slit width and r the radius of curvature (= 5 cm.). A slit width of 0.6 mm. would thus account for the width found. The difference in the two slits would lead to a slight broadening of the maximum.

That the two components both belong to lithium is shown by the fact that they always appear together and change in intensity in the same way. No other components were found, and at 5, 8 and 9, the intensity was certainly less than 2 per cent. of that at 7. No line at 12 was observed that might suggest that 6 was due to doubly charged carbon.

Many observations were made of the voltages required for the maxima of the two lithium lines. These could be obtained within one or two volts without measuring the complete curves. Assuming the maximum of the curve to represent the position of the atomic weight, and the lighter component to have an atomic weight of exactly 6, the atomic weight of the heavier component was 7.00 within two, or under good conditions, within one unit in the second decimal place. These observations show that to this accuracy the two elements are one unit apart in atomic weight.

PROPORTION OF THE TWO COMPONENTS OF LITHIUM.

If we assume the chemical atomic weight of lithium 6.94 to be the mean of the atomic weights of the two components, we should expect the number of atoms of the heavier component to be 16 times as great as the number of the lighter, and it is of interest to see if the ratio of the strengths of the positive rays agrees with the ratio of the two components in the metal. It has been found that this is in general not the case. Observations were made by comparing the intensities of the maxima of the two components under steady conditions. With one anode a ratio was found at first of 37 to 1, much greater than that to be expected. (In a letter to Science for April 15, 1921, it was overlooked that in a few cases a ratio greater than that to be expected had been obtained.) Later the ratio was 18 to 1, with a variation in several readings of less than 10 per cent. Three days later the ratio was 7.5 to 1 with a variation in six readings of less than 10 per cent. With a new anode, the ratio was at first 4.8 to 1 much less than with the other anode, and increased after a few minutes to 7 and 8 to 1. The next day the ratio was between 7 and 10 to 1. No dependence of the ratio on the strength of the rays could be observed over a small range of variation. A possible explanation is that the rates of evaporation of the two isotopes vary differently with the surface conditions of the metal. An assumption on theoretical grounds[1] of a difference in the vapor pressure curve for the two isotopes would still require an explanation of the relative variations in the amounts evaporating on different occasions. Surface films on the molten metal are possible causes of these differences; also the evaporation in these experiments occurred under electron bombardment,

[1] F. A. Lindemann and F. W. Aston, Phil. Mag., 37, p. 23, 1919. F. A. Lindemann, Phil. Mag., 38, p. 173, 1919.

and it may be that this influenced the conditions of evaporation. This variability makes impossible at present any determination of the chemical atomic weight of lithium from positive ray analysis.

It was observed that strong hydrogen rays were obtained from the lithium while it was being heated. It is of interest that the hydrogen all appeared in the form of atoms. No H_2, H_3 or helium rays as strong as 1 per cent. of the H_1 rays could be detected. The hydrogen atoms were obtained from new anodes on their first heating, and also from anodes, from which all the occluded gases had been driven off, if they had been allowed to stand in air for a day, the fresh hydrogen probably having been formed from traces of moisture.

EXPERIMENTS WITH MAGNESIUM.

Magnesium rays were obtained with anodes of two types. In the first experiments the heating coil was wound directly on a rod of mag-

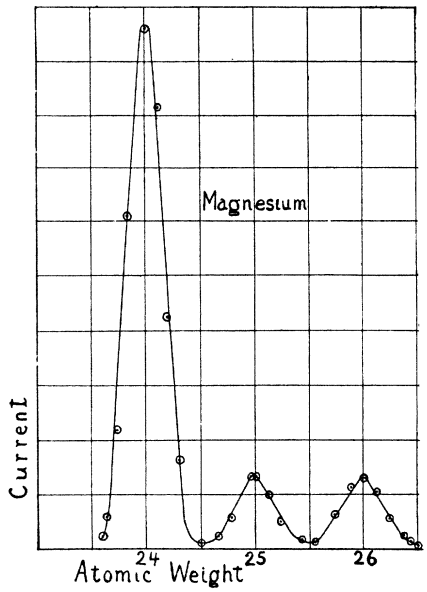

Fig. 5.

nesium, and the whole covered with a glass tube having a hole 3 mm. in diameter between the magnesium and the cathode to restrict the electron bombardment. Later an anode as shown in Fig. 1 was used. With both types three components with atomic weights 24, 25 and 26 were found. They appeared together as the magnesium was heated so as to vaporize slightly, and their atomic weights could be checked by com-

parison with rays at 28, probably due to occluded nitrogen, which is driven off before the magnesium rays appear. Two curves made with the first type of anode are given in a paper in the Proceedings of the National Academy of Sciences for February, 1921. They show that the lighter of the three components has an atomic weight 24, within one tenth of a unit, and that the other components have atomic weights 25 and 26. The curve in Fig. 5 was made from observations with the second type of anode and shows the ionization current corresponding to different atomic weights. It is drawn with the maximum of the lighter component exactly at 24, although its position was not compared in this case with the gas line at 28 with the accuracy indicated in the curve. The auxiliary potential between cathode and anode was 46 volts and between the screen and cathode 6 volts. The atomic weight abscissae are obtained by dividing 22440 by the total potential in each case. A slit width of 0.8 mm. would account for the width of the curves.

The ratios of the components shown in the curve were observed in several measurements under steady conditions. The component at 24 is about 6.7 times as strong as the one at 25, while the latter is about 1.04 as strong as the one at 26. These ratios give a mean atomic weight of times 24.336 which agrees well with the chemical atomic weight of 24.36. Although no such variations as in the case of lithium have been observed in the proportions of the magnesium components, yet several reliable comparisons have given slightly different ratios from that shown; in some cases the component at 24 was even ten times as strong as that at 25. Thus no great reliance can be placed as yet on determinations of the ratios of the various kinds of magnesium present in the metal, from observations of the ratios of the evaporating ionized atoms.

In preliminary experiments, rays of boron, aluminium and silicon have been obtained, and it is hoped that they may be made suitable for measurement. The bea-ing of these and other experimental results on general theories and speculations as to the atomatic structure is not entered into here, as the matter has been discussed at length by other authors in several recent papers.[1]

The writer wishes to express his thanks to Miss A. Hepburn for the radium emanation tubes used in the measurements, and to Mr. N. Y. Priessman for assistance in calibrating the ionization chamber.

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June 2, 1921.

[1]Especially by W. D. Harkins, PHYSICAL REVIEW, Feb., 1920, Phil. Mag., Sept., 1921.