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A SEARCH FOR ELEMENT 87 BY ANALYSIS OF POSITIVE RAYS

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Abstract

The methods used in previous attempts to discover eka-caesium are briefly examined and their limitations pointed out. *Estimates are given for the sensitivity of detection and identification of element 87* by atomic weight determinations, radioactive means, physiological effects, x-ray and optical spectrum analysis. *Predictions of spectral values* by Moseley's Law and an empirical relation give: $V_i = 4.05 \pm 0.05$ volts, $7^2P_{\frac{1}{2}} = 21340 \pm 200$ cm^{-1}, $7^2P_{3/2} = 19670 \pm 200$ cm^{-1}, $\Delta\nu$ separately determined 1675 ± 50 cm^{-1}, principal series resonance lines 8720 ± 200A and 7600 ± 200A. The large uncertainty is due to uncertainty in the iso-electronic Ra II spectrum. No absorption lines were found in the sun's spot spectrum, although possible, as element 87 should be less highly ionized than Cs. A tungsten filament heated to 1200°–1300°K converts into ions all caesium atoms which strike the tungsten surface and eka-caesium should behave the same way. By this means, first investigated by Langmuir and Kingdon, and Ives, an intense homogeneous source of positive ions is secured. This positive ion source was incorporated into a tube similar to Dempster's mass spectrograph in method of focussing and ray analysis, and positive ions were looked for of mass number 223 or 224. *Chemical separation* of caesium and any admixed eka-caesium was made from pollucite and lepidolite ores from Oxford County, Maine. Eka-caesium was not existent to an extent greater than 3.5×10^{-7} part of the caesium from pollucite or greater than 7.3×10^{-6} part of the caesium from lepidolite.

Vapor Pressure of K, Rb, Cs.—Na_2 was detected, but no K_2, Rb_2, Cs_2 or any intermetallic alkali compounds or doubly charged atomic ions were found. From this it is concluded that the vapor pressure determinations of Cs, Rb, and K by Langmuir, Kingdon, and Killian are the most accurate available. Attention is called to possible uses of a positive ion source of the type utilized in the present investigation, for separation of isotopes and determinations of isotope intensity ratios.

Introductory Review

A CRITICAL survey of the attempts to discover eka-caesium showed that the sensitivity of detection and quantitative estimation by previous methods could be greatly improved by a modified method of positive ray analysis. Following chemical fractionation to increase the concentration of eka-caesium, if existent in the preparations used, the final fractions have been compared by previous investigators and tested for the presence of element 87 by atomic weight determinations,[1,2] radioactive [2,7,8,9] methods, by observa-

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[1] T. W. Richards and E. H. Archibald, Proc. Am. Acad. **38,** 443 (1903).

[2] G. P. Baxter, J. Am. Chem. Soc. **37,** 286 (1915).

[3] L. M. Dennis and R. W. G. Wyckoff, J. Am. Chem. Soc. **42,** 985 (1920).

[4] H. Zwaardemaker, W. E. Ringer and E. Smits, K. Akad. Amsterdam Proc. **26,** 575 (1923).

[5] J. G. F. Druce, Chem. News **131,** 273 (1925); F. H. Loring and J. G. F. Druce, Chem. News **131,** 289, 305, 337, (1925); F. H. Loring, Chem. News **131,** 338, 371, (1925) **132,** 101, (1926).

tion of physiological effects,[4] x-ray spectra,[5,6,10] flame, [1,2] spark,[2] and arc[3] spectra.

The concentration of eka-caesium may be increased in any chemical preparation by proper manipulation. Chemical means of separation can therefore be considered as a common factor to increase the sensitivity for all methods of identification. Atomic weight determinations of caesium from the final fractions of a caesium preparation believed to contain eka-caesium can not detect the presence of element 87 if it is present to less than one ten thousandth, assuming that its atomic weight is 223, and that 132.81 for caesium can be definitely distinguished from 132.82 for a caesium and eka-caesium mixture.

The existence of eka-caesium is, of course, dependent on its nuclear conformation and radioactive characteristics. Fajans[11] has pointed out that isotopes of atomic weight 4*n* and odd nuclear charge are very unstable, and in some cases non-existent within the limits of observation. Th D 208, Z 81, Th C 212, Z 83, and Ms Th_2 228, Z 89, are very unstable short-lived β radiators. The possibility exists that eka-caesium, Z 87, and eka-iodine, Z 85, may come under this grouping. The predictions of the atomic weight of eka-caesium do not confirm this hypothesis. The atomic weight has been variously given as 224[12] and 223[13] on the basis of empirical relationships between atomic number and atomic weight, 221[14] has been proposed after consideration of the known isotopes and radioactive disintegration series. The speculative and unconfirmed nature of the many theories of nuclear structure does not allow a confident prediction of the radioactive characteristics of eka-caesium. However, Hahn and Erbacher[8] determined from a Ms Th and Ms Th_2 preparation the non-existence of more than 10^{-7} admixed eka-caesium if the half life period lies between ten minutes and ten years. Hevesy[7] examined Ms Th_2 and decided less than 5×10^{-6} disintegrated to give 87.

The occurrence of physiological effects agreeing with the behavior predicted for eka-caesium might enable a competent investigator to detect the presence of element 87, but confirmatory identification would always have to be referred to one of the other methods.

Hevesy[15] has given a very excellent discussion of chemical Röntgen spectroscopy and agrees with Thomassen[16] that an element must be present at

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[6] J. N. Friend, Nature **117,** 789 (1926).

[7] G. Hevesy, Danske Videnskab Selskab. **7,** 1 (1926).

[8] O. Hahn and O. Erbacher, Phys. Zeits. **27,** 531 (1926).

[9] O. Hahn, Naturwiss. **14,** 158 (1926).

[10] Herzfinkiel, Comptes Rendus **184,** 968 (1927).

[11] K. Fajans, Composition of Atom Nuclei, Chap. X, Radioactivity (1923).

[12] F. Loewinson-Lessing, Comptes Rendus **176,** 307 (1923).

[13] E. W. Washburn, J. Am. Chem. Soc. **48,** 2351 (1926).

[14] A. S. Russell, Phil. Mag. **47,** 1121 (1924); W. P. Widdowson and A. S. Russell, Phil. Mag. **48,** 293 (1924).

[15] G. Hevesy, Chem. Reviews **3,** 321 (1927).

[16] L. Thomassen, Kgl. Dept. Handel, Sjofart, Ind. og Friskeri Statens Raastoffkomite Publ. **21,** 108 (1925).

the anode at least to 0.1 percent, or better 1 percent, for positive identification.

In the case of the alkali metals spectroscopic methods of analysis are not the most sensitive due to the band and continuous spectra accompanying the line emission and absorption spectra.[17] Walter and Barratt observed that rubidium and caesium both have bands in the far red and that most of the alkali intermetallic compounds possess a diffuse band with no fine structure, probably a true continuous spectrum. It is this continuous background that renders difficult the identification of an alkali metal present in a small quantity when admixed with one or more of the alkalis. Gooch and Hart[18] found that one hundred parts of sodium were sufficient to mask one part of potassium in the flame spectrum. Gooch and Phinney[19] determined that for rubidium in the presence of sodium, the glare due to the band and continuous spectra made the rubidium lines invisible for a ratio as low as one part rubidium to ten parts sodium. Only one part rubidium in fifty parts potassium could be detected. Band spectra accompany the line emission spectra of the alkalis for all modes of excitation except the undamped electrodeless discharge.[20] Spectroscopic identification of eka-caesium has not been tried by this method.

Spectroscopic identification also has disadvantages in that the ultimate lines of eka-caesium would lie in the infra-red in a region of low photographic sensibility.

Ionization potential and resonance lines of eka-caesium: The ultimate and persistent lines of the alkali metals are the first doublet lines of the principal series. Radium II provides an iso-electronic system which, by application of Moseley's law, allows a prediction of the ionization potential and the term values for the first doublet of the principal series of eka-caesium. A great uncertainty is introduced due to the uncertainty of the Ra II spectrum. The term values for Ra II were taken as selected in Fowler's Report. The ionization potential of Ra II is greater than that of Ba II, consequently for Eka-Cs I, V_i is probably greater than for Cs I. The $(\nu/R)^{1/2}$ was plotted against an arbitrary abscissa length for all the alkalis and their iso-electronic counterparts in the alkaline earth metals. This was done to obtain a satisfactory value for the slope to be used for the Eka-Cs I, Ra II plot. A more satisfactory relation, without a simple theoretical basis however, was supplied by plotting as ordinates the ratio ν alkaline earth/ν alkali, for all iso-electronic systems, against a constant abscissa separation, while progressing from one ratio to the next for the successive elements. This method was also extended to the doublet separation ratios in order to get $\Delta\nu$ for eka-caesium. A smooth curve of decreasing slope resulted in every case which could be extrapolated with confidence to νRa II/νEka-Cs I. The weighted spectroscopic values

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[17] J. M. Walter and S. Barratt, Prcc. Roy. Soc. **119A,** 257 (1928).

[18] F. A. Gooch and T. S. Hart, Am. J. Sci. **42,** 3rd series, 448, (1891).

[19] F. A. Gooch and J. I. Phinney, Am. J. Sci. **44,** 3rd series, 392 (1892).

[20] G. Balasse, Comptes Rendus **184,** 1002 (1927).

for eka-caesium obtained by these means are: $V_i = 4.05 \pm 0.05$ volts, $7^2P_{\frac{1}{2}} = 21340 \pm 200$ cm^{-1}, $7^2P_{\frac{3}{2}} = 19670 \pm 200$ cm^{-1}, $\Delta\nu$ separately determined was 1675 ± 50 cm^{-1}, $\lambda 7^2S_{\frac{1}{2}} - 7^2P_{\frac{3}{2}} = 8720 \pm 200$A, $\lambda 7^2S_{\frac{1}{2}} - 7^2P_{\frac{3}{2}} = 7600 \pm 200$A. If the ionization potential value for Ra II is correct, then the ionization potential of eka-caesium being greater than that of caesium, element 87 would not be as highly ionized as caesium near the sun's surface[21] and the absorption lines of the first doublet of the principal series might appear in the sun's spot spectrum.[22] A search was made from 7000A to 9000A[23] for two lines with the proper intensity ratio and wave number separation, but no lines were found that could not be properly assigned to some other element. The wave-number separation is more reliable than the wave-lengths predicted, as the latter of course depend on two extrapolations introducing large uncertainties.

Positive ray analysis method. Positive ion source. Preliminary calculations of the sensitivity possible by a method of positive ray analysis showed that this method would exceed in sensitivity all but the radioactive system of identification and detection of eka-caesium, provided an efficient method of production of ions could be secured. Positive ray analysis of a likely source of eka-caesium would be independent of the radioactive properties (if the half life period were great enough to allow a concentration of eka-caesium within the limit of detection of the method), and would give definite identification from measurement of the e/M ratio. Moreover, a quantitative estimate could be made of the amount present. An efficient method of producing positive ions has been investigated by Langmuir and Kingdon,[24] and Ives.[25] Langmuir and Kingdon have shown that a tungsten filament heated to 1200°K or more converts into ions all caesium atoms which strike the tungsten surface. Together with Killian[26] they have utilized this phenomenon to determine the vapor pressure of caesium, rubidium and potassium, and have shown experimentally that ionization occurs in accord with Saha's equation. The equilibrium constant $K_n = n_e n_p / n_a$, where n_e, n_p, and n_a denote the number of electrons, positive ions, and atoms per cm^3 respectively, is given by Saha's equation,

$$\log_{10} K_n = 15.368 + \frac{3}{2} \log_{10} T - \frac{5040 V_i}{T},$$

T is expressed in degrees Kelvin and V_i is the ionization potential of the vapor. Langmuir and Kingdon pointed out that in the case of thermal ionization on the surface of a filament there is no necessary relation between n_e and n_p as occurs when the ionization of the vapor is not influenced by the

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[21] M. N. Saha, Phil. Mag. **40,** 472, 809 (1920).

[22] H. N. Russell, Astrophys. J. **55,** 119 (1922).

[23] Solar spectrum wave-lengths, Carnegie Inst. Publ. **396,** (1928).

[24] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **107A,** 61 (1925).

[25] H. E. Ives, Frank. Inst. J. **201,** 47 (1926).

[26] T. J. Killian, Phys. Rev. **27,** 578 (1926).

enclosure walls or other surfaces. n_e is dependent on the temperature and filament characteristics as given by Richardson's equation $I = AT^2\epsilon^{-b/T}$. The electron density is obtained from the relation

$$n_e = \left(\frac{2\pi m}{e^2 kT}\right)^{1/2} I = 4.034 \times 10^{13} \frac{I}{T^{1/2}},$$

I being expressed in amperes per cm^2. n_e, obtained by the elimination of I in the second and third equations, when substituted in the first equation yields the simple expression

$$\frac{n_p}{n_a} = \frac{57.93}{A} \times 10^{(b-11{,}600V_i)/2.3T}$$

for the ratio of the number of positive ions to the number of neutral atoms per unit volume. The most useful and stable thermionic surfaces have the following values for A and b: thorium on tungsten,[27] $A = 7$, $b = 31{,}200°$; tungsten,[28] $A = 60.2$, $b = 52{,}600°$; oxygen on tungsten,[28] $A = 5 \times 10^{11}$, $b = 107{,}000°$. A has the dimensions amp cm^{-2}deg^{-2}. In the present experiment the positive ions were produced thermally at the surface of a tungsten strip by this very efficient method. For eka-caesium with an ionization potential of 4.05 volts and tungsten filament at 1300°K, n_p/n_a is 71 or practically complete ionization of the incident atoms occurs. No two stage ionization can occur as the removal of the outer electron leaves a rare gas shell whose ionization potential is too great to permit ionization on the filament surface.

Apparatus design. This positive ion source was incorporated into a tube, Fig. 1, similar to Dempster's[29] mass spectrograph as regards focussing, but differing in the method of production of the ions, and in one arrangement used differing in the method of their measurement. A is the positive ion source and at the same time acts as a collimating slit as all the ions originate on the surface of A and so the beam is defined by the field distribution between A and B. With the design used, the field distribution approximated the uniform distribution between two parallel planes. For the potential differences used, the beam spread due to non-uniformity of the field was negligible and is smaller the greater the atomic weight.[30] A was a tungsten strip rolled 0.01 cm thick from a 0.051 cm diameter filament. This was heated by a ten volt secondary, center tap transformer. Connections to this filament were made to the center tap thereby eliminating lead potential differences to a large extent and acting in effect as if the connection had been made directly to the center of the strip filament. The temperature of the strip was measured by a L and N optical pyrometer. The "brightness

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[27] S. Dushman, H. N. Rowe, Jessie Ewald and C. A. Kidner, Phys. Rev. **25**, 338 (1925).

[28] K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

[29] A. J. Dempster, Phys. Rev. **11**, 316 (1918).

[30] L. Tonks, H. M. Mott-Smith Jr., I. Langmuir, Phys. Rev. **28**, 104 (1926)

temperature" measured this way was corrected using Forsythe and Worthing's[31] data. Due to the cooling effect of the leads there was a considerable temperature gradient This is not important as the percentage ionization at the surface of the filament does not appreciably differ from 100 percent over the range 1200° – 1300°K. Only the center half centimeter was actually utilized. A strip of large cross section was used so as to minimize the voltage gradient along the filament for a given temperature. The increased surface area of the strip above a cylindrical filament of the same cross section and the cooling effect of the leads necessitated a current of 9 amperes for a temperature of 1300°K at the center of the strip. The voltage gradient was then approximately 0.14 volts per cm which was not enough to interfere with the definition of the ion beam. The transmitting slit in *B* was 0.071 cm wide and 0.54 cm long,. the receiving slit at *D* being 0.64 cm long and 0.075 cm wide cut in 0.011 cm thick sheet molybdenum. The radius of curvature of the beam path was about 3.2 cm. The surface of *F* was silvered chemically and then coated with a crystalline electrolytic deposit of copper by slow deposition from an acid bath. By this means specular reflection of the beam from the walls is reduced and consequently no collimating baffles were placed in *F*. The small amount of reflection still remaining could be minimized by "spraying" the walls with the ion beam before taking readings. Evidently the walls were then covered with a film of the same metal as the vapor and instead of reflection condensation with loss of charge and re-evaporation occurred. Connection to *F* was made from a side tube not shown in Fig. 1. *D* is a thoriated tungsten filament 0.005 cm radius totally enclosed by a nickel cylinder of 1 cm radius and 2 cm long. The slit in *D* placed above the slit *C* was 0.75 cm long and 0.12 cm wide approximately.

When all the electrodes had been incorporated the preparation to be tested for the presence of eka-caesium was enclosed in the appendix connected by *H* to *G*. Caesium chloride was used prepared from two sources, as will be described later, and was mixed with calcium filings. This mixture was placed in a small vacuum fired nickel cylindrical container. The tube was evacuated by a Langmuir condensation pump backed by a Cenco Hyvac, with a liquid air trap interposed between the tube and the mercury pump. Exhaust was continued for four hours with the tube enclosed in a furnace at 260°C, higher temperatures being prohibited by the tendency of the silver copper coating to leave the walls of *F*. The bake out temperature was higher than any subsequent temperature. The pellet containing the caesium chloride and calcium was then heated inductively by a high frequency coil, the caesium distilling to the walls and then later was redistilled into appendix *G*. The tube was sealed off at a pressure less than 0.001 barye, the limit of the McLeod gauge and was then ready for test.

Chemical preparation of material. Two series of tests were made. The first trial was made using caesium chloride supplied and prepared through the courtesy of the General Electric Company. The method of separation

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[31] W F. Forsythe and A. G. Worthing, Astrophys. J. **61,** 146 (1925)

from pollucite from Oxford County, Maine, followed Browning essentially.[32] The finely powdered mineral was decomposed with strong hydrochloric acid. The acid solution was then treated with antimonous trichloride which precipitates the double chloride of antimony and caesium. This precipitate is filtered out and then hydrolyzed, the antimonous oxide precipitates leaving caesium chloride in solution, the dissolved antimony being separated with hydrogen sulphide. From the predicted chemical solubilities the eka-caesium salts should accompany the caesium salts throughout this process. No further concentration was essayed. The caesium chloride obtained in this way from pollucite was used for the first test.

Dobroserov[33] has suggested that the radioactivity of potassium is due to admixed eka-caesium. Kracke[34] doubts the existence of any potassium radiation. Although these suppositions are hardly tenable in view of the careful work of Campbell and Wood[35] Hoffman,[36] and Ringer,[37] a potassium and caesium ore was sought. All five known alkalis occur together in lepidolite, the usual ore containing 10 to 12 percent K, 1 to 3 percent Na, 1 to 2 percent Li., 0.5 to 1 percent Rb., 0.2 to 3 percent Cs. This ore then constitutes a likely source for eka-caesium. The method of separation differed slightly from that for pollucite. The powdered mineral, also from Oxford

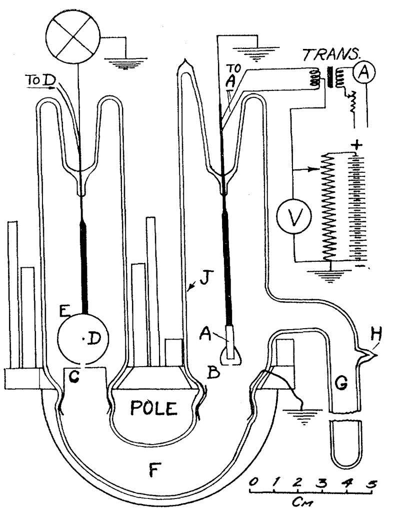

Fig. 1. Mass spectrograph.

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[32] P. E. Browning, Introduction to the Rarer Elements, 9, (1917).

[33] D. Dobroserov, Ukrainskii Khem. Zhurnal **1,** 491 (1925); Chem. Zentr. *II,* 162 (1926).

[34] B. Kracke, Phys. Zeits. **27,** 290 (1926).

[35] N. Campbell and A. Wood, Proc. Camb. Phil. Soc. **14,** 15 (1907); N. Campbell **14,** 211, 557 (1907); **15,** 11 (1909).

[36] G. Hoffman, Phys. Zeits. **24,** 475 (1923).

[37] W. E. Ringer, Onderz. physiol. Scheikunde **1,** 23 (1921).

County, Maine, was heated with a mixture of calcium carbonate and ammonium chloride, and the chlorides resulting from treatment were distilled onto a cool iron pipe and the hard chloride cake chipped off. The material was received in this form from the General Electric Company. The mixed chlorides were dissolved in a minimum quantity of water and treated with antimonous chloride as before. Only a few grams were treated at a time so that the antimonous oxide resulting from hydrolysis could be reconverted to antimonous chloride by solution in hydrochloric acid. In this way if the eka-caesium chloride should be partially adsorbed on the antimonous oxide it would go back into solution and eventually most of it would appear with the caesium chloride in the final solution. This was merely a precautionary measure, no trouble from adsorption was expected as eka-caesium chloride from its predicted solubility, hardly admitting of error, should fulfill the radioactive precipitation[38] rules, and should accompany caesium salts in solution or crystallization. The final preparation was not completely purified but intentionally included Li, Na, K, and Rb to the extent of about 25 percent. In both cases no concentration was attempted beyond the separation of caesium and eka-caesium from the ores.

Procedure and results. After the tube had been prepared it was placed between the poles of the DuBois magnet and adjusted to secure the optimum focus and connected as in Fig. I. The magnetic field was maintained constant while the accelerating voltage was varied to bring the ion beams of different e/M ratios to the receiving cylinder. The positive ion current may be limited by space charge[39] or by the rate of arrival of atoms at the filament surface. The current limited by space charge for parallel planes and singly charged ions is given by $I_s = 5.43 \times 10^{-8}\ (1/M^{1/2})\ (V^{3/2}/x^2)$, where I is the maximum current density in amp. cm^{-2}, V the potential difference in volts, x the distance of separation of the planes and M is the atomic weight of the ions. The current limited by vapor pressure is given by kinetic theory as $I_p = 10ep/(2\pi m_H MkT^{1/2})$ where e is the electronic charge, p the pressure in baryes, m_H the mass of the hydrogen atom, k the Boltzman constant, and T is the absolute temperature of the vapor. For caesium at 20°C, $p = 1.07 \times 10^{-3}$ baryes[24] and $I_p = 21.8 \times 10^{-6}$ amp. cm^{-2}. The transmitter slit, area 0.038 cm^2, allows a current of 83×10^{-8} amp., if the currents were not limited by space charge. The radius of curvature of the ion beam is

$$R = 1/H(2Mm_H V/e)^{1/2} \text{ cm.}^{29}$$

The allowable accelerating potential and so the space charge current for any ion is limited by the magnetic field strength and radius of curvature. R was 3.2 cm, so the present apparatus with a slit width of 0.075 cm had a resolution of 1/42 approximately. The magnetic field was held constant for any one run but different runs were taken with H from 3000 to 5000 gauss. MV is then constant for any run with R and H

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[38] O. Hahn, Ber. **59B,** 2014 (1926).

[39] I. Langmuir, Phys. Rev. **2,** 450 (1913).

constant and the quantitative sensitivity of detection of any ion may be calculated if it is known whether or not the ion current is limited by space charge or by the rate of arrival of the atoms at the filament surface. For a magnetic field of 3050 gauss an accelerating potential of 60 volts brings the caesium beam to a focus at the receiving slit. At this accelerating potential for caesium the received current, if limited only by space charge, should be 209×10^{-8} amp. The current actually obtained at the receiving slit for caesium was 6.25×10^{-8} amperes. By varying the magnetic field and thereby the potential required to bring caesium into position, $V^{3/2}/I_{Cs}$ was found to be constant. So under the conditions obtaining in the tube the current was limited by space charge and was only 3.3 percent of the theoretical. This was not due to poor definition of the beam as the peaks observed, plotting current against accelerating potential or atomic weight, were very close to the ideal that would be obtained if the positive ion beam were defined by the first slit and perfect focussing occured. As the current was space charge limited the quantitive estimation of the sensitivity of the apparatus for detecting eka-caesium was made on this basis.

$$V_{Eka-Cs}=\frac{M_{Cs}}{M_{Eka-Cs}}\times V_{Cs}$$

for constant magnetic field strength. From space charge considerations I is proportional to $V^{3/2}/M^{1/2}$. From kinetic theory considerations the rate of arrival of atoms at the source surface is proportional to $1/M^{1/2}$. By combination of these controlling factors, the fraction of eka-caesium present in the vapor state admixed with caesium is equal to $(I_{Eka-Cs}/I_{Cs})\times(M_{Eka-Cs}/M_{Cs})^{5/2}$ I in this case referring to the received currents at D. Currents were measured with a Compton electrometer of sensitivity 10,900 mm per volt, and a L and N galvanometer. The minimum current that could be read with the electrometer by observing the rate of deflection was 5×10^{-15} amp.

In one run E was made several volts electropositive with respect to C, with D ten or twelve volts negative. The field distribution was such that positive ions could enter the slit in E. The current from the filament D was limited by space charge which was partially neutralized by the incoming positive ion beam resulting in a great increase in current through a galvanometer in the circuit D to E, the normal emission current being balanced out in the local galvanometer circuit. To permit the electrons from D to reach E[40] the tube was shielded from the magnetic field by two concentric soft iron pipes as shown in Fig. 1. The neutralization of space charge[41] occasioned by the entering positive ions resulted in an increase of current in the case of caesium which was 5,700 times greater than the positive ion beam current. The ultimate sensitivity of this arrangement was less than could be obtained with the electrometer so that this method of amplification of the received beam was abandoned.

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[40] A. W. Hull, Phys. Rev. **18**, 31 (1921).

[41] K. H. Kingdon, Phys. Rev. **21**, 408 (1923).

Six trials were made to detect eka-caesium in the caesium prepared from the pollucite ore. A globule of molten caesium was held on the walls of *J* by cooling with an air blast and the potential was varied over the range required to bring ions between 200 to 250 mass units into focus as the globule was evaporating. Readings were made until the globule had completely evaporated so that the determination would be independent of the vapor pressure of the eka-caesium. No eka-caesium was present to an amount greater than 3.5×10^{-7} of the caesium metal from the pollucite ore. With the lepidolite caesium two runs were made and no eka-caesium was present to an amount greater than 7.3×10^{-6}. The temperature of the molten caesium was approximately 40°C in these trials. At this temperature peaks were observed for Ca, K and Rb. At higher temperatures Na and Na_2 occured in almost equal amount, but to a very small extent when using the pollucite caesium. There was no evidence of any Cs^{+}_2 present to more than 10^{-6}. The only molecular beam detected was Na_2. Any other molecular configurations or intermetallic compounds were dissociated if present at all. This appears anomalous in view of the fact that Na_2 has the smallest heat of dissociation[17] of any of the alkalis or their intermetallic compounds. No satisfactory explanation has yet been formulated.

Discussion. The sensitivity of the method described is of the same order as the radioactive test results obtained by examining Ms Th and Ms Th_2. The positive ray analysis method is based on a more secure foundation being dependent chiefly on eka-caesium having a low ionization potential and being independent of its radioactive characteristics providing the half-life period is great enough to allow a small concentration of the element. In view of the uncertain knowledge of nuclear structure this method appears to be superior to any system of detection depending on highly speculative predictions of the radioactive properties of eka-caesium or possible parent elements, and at least provides a new and sensitive mode of attack in seeking for the interesting element 87. If eka-caesium is found to be present to a small extent in any preparation tested by this means, a quantitative estimate is easily made which can direct the amount of fractionation required to provide a quantity of this element sufficient for confirmatory identification by methods allowing a permanent and incontestable record.

No doubly charged alkali ions were detected at all. The measurements of the vapor pressures of the alkali metals by Langmuir and Kingdon,[24] and Killian[26] by measurement of the positive ion current thermally produced from tungsten filaments in the vapor of the elements K, Rb, and Cs have been criticised by Rowe[42] on the grounds that multiple ionization did occur. From the present examination of the products of ionization this criticism is unfounded in fact and it is believed that the above vapor pressure determinations are the most accurate available. Disagreement is found with Ives'[25] results who reported molecular ions of K, Rb and Cs, besides

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[42] H. Rowe, Phil. Mag. **3**, 534 (1927).

Na. Ives' results were probably due to the filament not being coaxial with the cylinder.

A new apparatus is being constructed that will be able to separate completely ions differing in mass by 1/250. The ion source in this case is an oxygen coated filament which Kingdon[43] has shown can ionize Ca, Cu, and Bi ($V_i=8$). On this surface many of the metallic elements which are difficult to deal with by the usual methods of positive ion production can be ionized and examined for isotopes and the isotope intensity ratios can be obtained. Particularly those elements of very low vapor pressures, even at temperatures of 2000°K, are amenable to this method if their ionization potentials are not greater than eight volts. An attempt is also being made to use an apparatus essentially like the present one in principle to separate the isotopes of Li and K.

In conclusion I wish to thank Professor H. D. Smyth for valuable criticisms and suggestions, and the General Electric Company for the materials and ores supplied.

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[43] K. H. Kingdon, Phys. Rev. **23**. 778 (1924).