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The Atomic Masses of the Heavy Elements*

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Comparisons have been made between a series of different atomic masses by means of a double-focusing mass spectrograph. The small displacement between the positions of multiply charged ions of one mass and atoms of another mass is measured and gives a value for the difference in the packing fractions of the two atomic masses. The following pairs of ions have been compared: O^+-Ti^{+3}, C^+-Ti^{+4}, N^+-Fe^{+4}, O^+-Cu^{+4}, Al^+-Ag^{+4}, Cu^+-Au^{+3}, Ti^+-Au^{+4}, Cu^+-Pt^{+3}, Sn^+-Th^{+2}, Sn^+-U^{+2}, Sn^+-AcU^{+2}, Zr^+-W^{+2}(91, 92), Mo^+-Pt^{+2}(96, 97, 98), Mo^+-Ir^{+2}, Pd^+-Pb^{+2}(102, 104), Rh^+-Pb^{+2}, Pd^+-Tl^{+2}, Pd^+-Bi^{+2}, Ru^+-Os^{+2}(96), Ru^+-Pt^{+2}(99), Pd-Ga^+. Less exact comparisons have also been made between the following pairs: Mo^+-Os^{+2}(94, 95, 96), Ag^{+5}-Zn^{+3}, Na^+-Zn^{+3}, Sn^+-Ta^{+3}, K^{+2}-Ru^{+5}, Ni^{+2}-Ru^{+5}, Al^+-Pd^{+4}, Fe^+-Ag^{+2}. The values deduced for the packing fractions of titanium, iron, and copper, and the probable values for zinc, silver, gold, and platinum are higher than those to be expected from Dr. Aston's packing fraction curve by about 2 parts in 10,000.

DURING the last year, several redeterminations of the masses of the light elements have been made by Aston[1] and by Bainbridge and Jordan.[2] These now give excellent agreement with the masses deduced from nuclear disintegration experiments.[3] In the present paper, some comparisons of the atomic masses of heavier elements not previously measured will be presented. These have been made possible by the development of the new source of ions referred to in the following section.

Apparatus and Method

In the mass spectrograph used, the rays after passing a narrow slit are deviated through 90° in a cylindrical condenser. A divergent bundle of rays of one velocity is brought to a focus by the electric field at the entrance to a magnetic field in which the rays are then deviated through 180° and brought to a focus on a photographic plate. The velocity dispersion produced by the electrostatic field is compensated by the velocity dispersion in the magnetic field, so that the original divergent bundle may contain rays of slightly different energies. The theory of this type of double-focusing mass spectrograph has been given in a previous paper.[4] A general description with a photograph of the instrument showing the method of mounting the various parts was given in a paper in the *Proceedings of the American Philosophical Society*.[5] The electrostatic stray field at the beginning and end of the cylindrical condenser was computed, and the extra deviation of the ions that would have occurred in these stray fields was avoided by shortening the outer charged cylindrical plate at each end by about 2 mm.

The source of ions was a high frequency spark between solid electrodes as previously described.[5, 6] A study of the types of ions obtainable in this manner has recently been made by Sheng-Lin Ch'u.[7] The ions were accelerated by a potential of 3000 to 10,000 volts obtained from a transformer and rectified by a kenotron and condenser. The electrostatic deflecting field was obtained either from a battery of storage cells or from a transformer and two kenotrons with large condensers, followed by a stabilizing circuit as described by Evans.[8] For

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[1] F. W. Aston, Nature **137**, 357, 613 (1936).

[2] K. T. Bainbridge and E. B. Jordan, Phys. Rev. **49**, 883 (1936); **51**, 384 (1937).

[3] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937).

[4] A. J. Dempster, Phys. Rev. **51**, 67 (1937). Two typographical errors should be corrected. At the bottom of the first column, p. 67, the symbol C is an abbreviation for $V \log_e r_2/r_1$, and in the eighth line from the bottom of the second column, p. 67, k^2 is an abbreviation for $e/mC = e/m\ V \log_e r_2/r_1$.

[5] A. J. Dempster, Proc. Am. Phil. Soc. **75**, 762 (1935).

[6] A. J. Dempster, Rev. Sci. Inst. **7**, 46 (1936).

[7] Sheng-Lin Ch'u, Phys. Rev. **50**, 212 (1936).

[8] R. Evans, Rev. Sci. Inst. **5**, 371 (1934).

several months this circuit proved quite satisfactory but was finally discarded on account of irregularities.

Method

It has been found that the spark sources give a considerable proportion of multiply charged atoms. This makes possible the extension of the "doublet" and "bracket" methods of mass comparison to many elements not hitherto studied by ions from a gas discharge. Because of the small divergence of the masses of the elements from exactly integral values, narrow "doublets" are formed when a multiply charged heavy atom is brought into approximate coincidence with a lighter atom having a smaller charge in the ratio of the masses. If the atomic mass (oxygen $16=16.000$) of one type of atoms is $I_1(1+f_1)$ where f_1 is the packing fraction, and I_1 an integer, and that of the other is $I_2(1+f_2)$, and if the charge on the first is n_1e and that on the second n_2e, then the two atoms appear on the plate as though they were singly charged atoms of masses $(I_1/n_1)(1+f_1)$ and $(I_2/n_2)(1+f_2)$. We pick cases where $I_1/n_1=I_2/n_2=m$. Then a doublet appears with the mass difference $m(f_2-f_1)$ and from this, f_2-f_1 may be deduced. The same relation is found when we allow for the mass decrease of the ions due to the loss of n_1 electrons from the first and n_2 from the second type of atoms. To calculate the mass difference from the observed spacing on the plate, we must know the separation due to a known mass difference. The accuracy with which this mass scale need be found is usually small. In this paper we wish the error due to the mass scale to be less than $0.1\times10^{-4}\ m$, in measuring a mass difference $(f_2-f_1)m$. In nearly all cases of the doublets measured (see Table II), this latter mass difference is less than 10×10^{-4} m. The maximum permissible error due to the mass scale is thus one percent or more of the measured difference. The accuracy of the mass scale need not then be greater than one percent. This large tolerance makes it permissible to assume integral spacing between isotopes of the heavy elements for the purpose of calibration. Direct measurement of the mass difference between successive isotopes has been carried out as yet only for the lighter elements, and for bromine for which Aston determined a difference of 1.9983 mass units,[9] with a possible error of 0.0015. The divergence from 2.000 is thus only of 0.08 percent of the mass difference, and the difference in the packing fractions is only 0.04×10^{-4}. Between other pairs of light isotopes, Ne(20, 22); Mg(24, 26); Si(28, 30); S(30, 32); Cl(35, 37), the mass difference differs from 2.000 by much less than one percent, and the difference in the packing fractions is less than 0.2×10^{-4}. In the series of radioactive elements where the mass differences may be accurately computed, the difference from integral spacing is always less than one percent. In cases of neutron absorption leading to a new isotope, the mass added (1.009) might possibly differ from unity by as much as 0.9 percent, but in these cases γ-ray emission is observed, resulting in a much smaller difference from unity. In the elements between mass number 100 and 200, the added mass is approximately 100.1 giving an average mass difference of 0.1 percent more than unity between successive atomic masses. The packing fraction increases on the average over this range by 0.16×10^{-4} for masses separated by two units. The small mass differences observed in this paper will be computed by assuming integral spacing between the isotopes, usually of heavy elements, used as the mass scale. The error in the mass scale required to give an error of 0.1×10^{-4} in the differences of the packing fractions will be computed in many cases, and if later observations should show an unexpected large divergence (amounting to several percent) from integral spacing in any case used, the results reported can be readily corrected.

The theoretical connection between mass and distance on the plate is given by the proportionality of the radius of curvature in the magnetic field to the square root of the mass of the ion. That is $M^{\frac{1}{2}}=a+cx$ where x is the distance measured on the plate and a and c are constants. From the masses used to give the mass scale, c is computed and the unknown mass M at x is then found from $M^{\frac{1}{2}}-(M_1)^{\frac{1}{2}}=c(x-x_1)$. The accuracy of this relation between mass and position on the plate was tested very carefully with several photographs of the series of molyb-

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[9] F. W Aston, Nature **137**, 357 (1936).

denum isotopes 92 to 100 at different positions, and no deviation could be found as large as the experimental error. In case the masses used to give the scale are two units apart, c may be found from $((M+2)^{\frac{1}{2}}-M^{\frac{1}{2}})=c(x'-x)$. As the packing fractions for the masses used are always less than 10^{-3}, we may replace this by $(I+2)^{\frac{1}{2}}-I^{\frac{1}{2}}=c(x'-x)$, and determine c with more than the one percent accuracy desired. The small separation x_2-x_1 between the components of a doublet then gives the difference in the packing fractions by the relation

$$c(x_2-x_1)=m^{\frac{1}{2}}(1+\tfrac{1}{2}f_2)-m^{\frac{1}{2}}(1+\tfrac{1}{2}f_1)=\tfrac{1}{2}m^{\frac{1}{2}}(f_2-f_1).$$

In cases of "bracketing" two isotopes of one element with masses $ni_1(1+f_1)$ and $ni_2(1+f_2)$ with n charges give lines at the masses $i_1(1+f_1)$ and $i_2(1+f_2)$ on either side of an isotope of another element at $i(1+f)$. As we can make only two accurate independent measurements x_2-x_1 and $x-x_1$, it is not possible to determine the three f's involved. However if we calculate

$$a=(x-x_1)/(x_2-x_1)[i_2^{\frac{1}{2}}-i_1^{\frac{1}{2}}]$$

and compute $\Delta M=[i_1^{\frac{1}{2}}+a]^2-i$, we may easily show that

$$\frac{\Delta M}{i}=f-\frac{i^{\frac{1}{2}}-i_1^{\frac{1}{2}}}{i_2^{\frac{1}{2}}-i_1^{\frac{1}{2}}}f_2-\frac{i_2^{\frac{1}{2}}-i^{\frac{1}{2}}}{i_2^{\frac{1}{2}}-i_1^{\frac{1}{2}}}f_1 \qquad (1)$$

to an accuracy much greater than that attained in the measurements.[10] In most of the cases discussed in this paper $i_2^{\frac{1}{2}}-i^{\frac{1}{2}}$ is very nearly equal to $i^{\frac{1}{2}}-i_1^{\frac{1}{2}}$ so that the value of $\Delta M/i$ as computed is $f-\frac{1}{2}(f_1+f_2)$, that is the difference between the packing fraction f of the one element and the arithmetic mean of the fractions for the two isotopes of the other. As discussed above, it is unlikely that the packing fractions f_1 and f_2 of two isotopes differing by two units should differ by more than 0.2×10^{-4}.

TECHNIQUE OF MASS COMPARISONS

It has been emphasized by Aston that the reliability of the measurements of doublets on the photographic plate is much increased when the doublets are of equal intensity. This is particularly true if the lines to be measured are not perfectly symmetrical or are curved. Some of the difficulties of mass spectroscopy are similar to those met with in the measurement of optical spectrum lines. The theoretical resolving power of the mass spectrograph may however be reduced by a new series of experimental troubles not met with in optical spectroscopy. The electric and magnetic fields may change slightly during an exposure giving rise to unsymmetrically broadened lines. In this case the centers of lines of different intensities may appear displaced by various amounts. For this reason there is a great advantage in a source with which exposures may be made in a few seconds. Aston has noticed that comparisons of molecule ions and atom ions are often unsatisfactory. If a source is intermittent or periodic it is possible that the ions to be compared are formed most strongly at different parts of the cycle. A periodic alteration of gas pressure may accompany a periodic gas discharge and may lead to one ion appearing as a slightly broadened line while another formed during an earlier part of the discharge may be sharper. Possibly the passage of the ions into the electric field may give rise to a space charge or surface polarization which reduces the field acting on the ions by various amounts at different times during the discharge. In the present experiments, it was noticed that lines of unequal sharpness were often obtained in comparisons of a metal ion and an ion formed from the gas in the tube, such as copper with oxygen or iron with nitrogen. With sparks between two metals of high melting points, the lines appeared equally sharp and even in many cases of metals with great differences in their boiling points, such as platinum and lead, no difference in sharpness was observed. In these cases both ions probably pass the field simultaneously immediately after the spark has passed. A further cause of error may be the formation of insulating layers on metal surfaces bombarded by the rays[11]

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[10] From the relations above $i^{\frac{1}{2}}=cy(1-\frac{1}{2}f)$ where $y=x+a/c$ with similar expressions for $i_1^{\frac{1}{2}}$ and $i_2^{\frac{1}{2}}$. Substituting these in the expression for a, we find

$$[i_1^{\frac{1}{2}}+a]^2=i+i^{\frac{1}{2}}\left(f-\frac{f_2y_2-f_1y_1}{y_2-y_1}\right)+i_1^{\frac{1}{2}}(f_2-f_1)\frac{y_2}{y_2-y_1}$$

neglecting a^2. Thus

$$\frac{\Delta M}{i}=f-\frac{y-y_1}{y_2-y_1}\cdot\frac{y_2}{y}f_2-\frac{y_2-y}{y_2-y_1}\cdot\frac{y_1}{y}\cdot f_1$$

giving relation (1) as a sufficient approximation by the substitution of $i^{\frac{1}{2}}$ for y.

[11] R. Lariviere Stewart, Phys. Rev. **45**, 488–90 (1934).

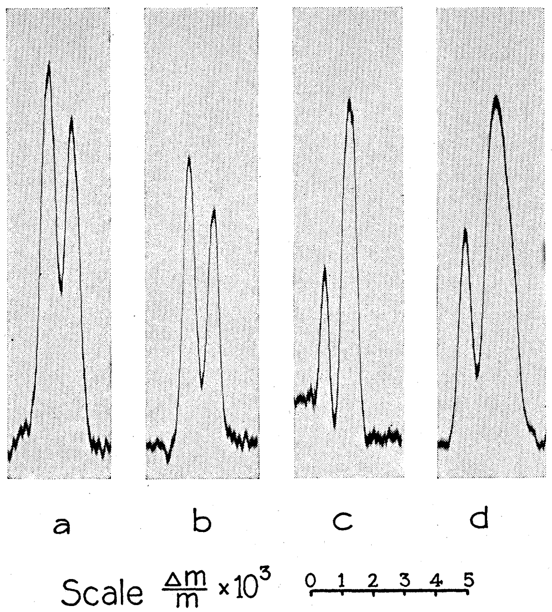

FIG. 1. Microphotometer traces of doublets. (a) Titanium-oxygen at mass 16, (b) rhodium-lead at mass 103, (c) molybdenum-platinum at mass 98, (d) tin-thorium at mass 116. The scale shows the displacements corresponding to mass changes of 1, 2, 3, 4, and 5 parts in 1000.

or the occurrence of insulating dust particles on the surfaces.[12] The formation of insulating patches on metallic surfaces is specially liable to occur when hydrocarbons are present.[11] These surfaces or particles become charged and may cause spurious deflections and curved or sloping lines.[13] Provided both ions pass the electric field and charged surfaces simultaneously and follow almost identical paths it is likely that any variation in the spacing due to surface charges is very small. This is one reason for preferring close doublets to brackets which are more widely spaced.

A difficulty common to mass spectroscopy and to optical spectroscopy is the actual measurement of the separation of the two lines forming a close doublet on the photographic plate. A discussion of the errors that may occur in measuring doublets in the solar spectrum has been given by St. John and Ware.[14] On page 21 of that paper, photometer traces are given of lines reproduced on the plate facing page 20, and errors of 7 to 10 percent were made by trained observers in visual measurements of the separations. However, the doublets used in the present measurements were in nearly all cases much sharper and more completely separated than those shown in St. John and Ware's paper. Microphotometer traces of most of the doublets reported in this paper were made on process films with a Moll recording microphotometer. On the same trace was recorded for calibration the light transmitted through a fifth millimeter scale carefully ruled on a silvered glass plate. The separations computed from the traces were compared with the direct measurements. Examples of photometer traces of doublets are given in Fig. 1, (a) Ti^{+3}-O^{+}, (b) Rh^{+}-Pb^{+2}, (c) Mo^{+}-Pt^{+2} (98), (d) Sn^{+}-Th^{+2}, the larger mass being to the right. The displacements corresponding to a mass change of 1 in 1000 are indicated on the mass scale. The last trace shows a broadening of the over-exposed thorium line. Between positions of half the maximum intensity, the widths of some lines correspond to mass changes as small as 1 in 2500.

The direct visual measurements were first made with a Geneva measuring instrument using two fibers in the eyepiece. The magnification was adjusted so that the part of the line included between the two fibers corresponded roughly to the center half or free portion of the line as recorded on the trace. In this way any residual intensity between the lines would not be expected to affect the setting on one line. All the measurements in this paper were later repeated with a Gaertner measuring instrument, which was tested for absence of error by an accurate scale having twenty rulings to the millimeter. In the eyepiece, a circular opaque diaphragm made of a silvered piece of glass was often used. It had a clear sector across the top and a narrow vertical space 0.2 mm wide, in which the magnified image of the central part of the line appeared. In this way, any lack of symmetry in the field of view due to the second component of the doublet was avoided. The doublets to be measured were usually selected from a larger number;

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[12] A. J. Dempster, Proc. Am. Phil. Soc. **76**, 492 (1936).

[13] F. W. Aston (Nature **138**, 1094 (1936)) points out that his measurement of the CH_4-O doublet gives a value that differs from Bainbridge and Jordan's value by much more than the experimental error. In the reproduction of the doublet given in the Phys. Rev. **50**, 287 (1936), Fig. 9, it is apparent that the two lines forming the doublet are not parallel.

[14] Charles E. St. John and L. W. Ware, "Accuracy in Separation of Close Solar Lines," J. Astr. **44**, 17 (1916).

any doublets with unsymmetrical lines, due to variations in the electric or magnetic field, being discarded. In many cases, doublets with overexposed lines, which may conceal a small dissymmetry, were also discarded. Most of the lines photographed were, however, remarkably straight and symmetrical. With the best lines settings could be reproduced with a probable error of 0.001 mm. This corresponds to a probable error of 0.1×10^{-4} in the packing fraction. However, in most cases the error was greater than this. A slight broadening became noticeable if the pressure in the analyzing chamber was above 2×10^{-5} mm of mercury. The pressure in the spark chamber was usually several times as high due to evolution of gas from the electrodes.

EXPERIMENTAL RESULTS

The masses of many of the light elements have recently been compared with the mass of the lightest oxygen isotope (16.000) with a high degree of accuracy.[15] Also by observing the energy set free in nuclear transformations, the masses of most of the nuclei up to argon may be found with very great accuracy.[16] Among the mass comparisons reported in this paper, there are only a few which have been made directly with these accurately known masses (Ti, Fe, Cu, Pd, Ag). A second group of comparisons have been made, with these latter as secondary standards (Au, Pt, Zn, Ga, Pb, Bi, Tl). A third group includes comparisons of masses of elements neither of which has as yet been compared with known masses. In these cases, the measurements give the difference between the packing fractions of the two elements. As the investigation proceeds, it is expected that many more secondary standards will be established and that it will be possible to refer more and more of these masses back to oxygen as the primary standard. This last group, which includes many of the most accurate mass comparisons, is, however, of immediate interest in connection with the packing fraction curve, as the measurements give a series of differences between pairs of points on this curve. The packing fraction curve that is in best agreement with these observations will be discussed in a later paper. All of the mass comparisons reported in this paper are new. The comparisons are all between atomic masses, since molecules occur very rarely in the spark sources.

OXYGEN-TITANIUM (48)

Triply-charged titanium ions are produced by a spark between titanium electrodes, and the strongest isotope at 48 forms a doublet with singly-charged oxygen atoms which come either from the residual gas or from a layer of titanium oxide on the metal. Nine doublets with exposure times of 3 to 8 seconds gave an average mass difference of 0.01155 ± 0.00015. This gives a packing fraction for titanium of $(-7.22 \pm 0.1) \times 10^{-4}$ and an atomic mass of 47.9651 ± 0.0005. The nine doublets were picked as the best out of a total of nineteen, ten were considered inferior because overexposed, diffuse or very unequal in intensity. Almost the same mass difference however was given by the rejected doublets, as the average of the whole nineteen gave a packing fraction of $(7.09 \pm 0.2) \times 10^{-4}$ only slightly different from the value given by the nine best doublets. In this paper, the errors will be estimated as "probable errors," that is, a value of $x \pm r$ means that the probability of the true value lying in the range $x-r$ to $x+r$ is one-half. A recent paper by R. T. Birge[17] emphasizes the advantages of this method of indicating the uncertainty in a measurement, and points out the relation of this to other methods of estimating errors.

The mass scale used in evaluating the mass difference was the spacing of the titanium isotopes 47, 48, 49 which was assumed as integral. As discussed above, no error as large as 0.1×10^{-4} would occur in the packing fraction in this case unless the mass differences between these isotopes should differ from unity by more than two percent.

CARBON-TITANIUM

Doublets were found at mass 12 with a spark between titanium and gold electrodes. These are almost certainly due to quadruply-charged

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[15] F. W. Aston, Nature **137**, 396, 613 (1936); **139**, 922 (1937); **140**, 149 (1937). Bainbridge and Jordan, Phys. Rev. **51**, 384 (1937).

[16] E. Pollard and E. J. Brasefield, Phys. Rev. **51**, 8 (1937). M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937).

[17] R. T. Birge, Phys. Rev. **52**, 241 (1937).

titanium ions and singly-charged carbon. The carbon is probably an impurity in the titanium although it could also come from the wax used to seal the chamber. Four doublets with exposures of one to one and one-half minutes gave a difference of the packing fractions of carbon and titanium of $(9.8\pm 0.4)\times 10^{-4}$. If the packing fraction of carbon is taken[18] as 2.96×10^{-4}, that of titanium is -6.84×10^{-4}, in satisfactory agreement with the value determined from the oxygen comparisons.

NITROGEN-IRON

With a spark between a titanium and a cast iron electrode, doublets were formed at mass 14, which are almost certainly due to nitrogen and quadruply-charged iron atoms of mass 56. Eight doublets with exposures of 10 to 20 seconds were measured and gave a mass difference of 0.017 using as mass scale the spacing between the titanium isotopes assumed as integral. This gives a difference of 12.3×10^{-4} between the packing fractions of nitrogen and of iron. If the packing fraction of nitrogen is taken as 5.2×10^{-4}, that of iron is -7.1×10^{-4}. The large estimated error was ± 0.4, as the doublets were unequal in intensity and not suitable for measurements of the highest precision.

OXYGEN-COPPER

Quadruply-charged copper ions appear approximately at mass numbers 15.75 and 16.25, nearly equally spaced on either side of the oxygen isotope at 16. As explained above from the positions of the two copper isotopes with masses $15.75\ (1+f_1)$ and $16.25\ (1+f_2)$, the arithmetic mean of the two packing fractions may be calculated. The difference given by three photographs with exposures of 2 minutes for the quantity ΔM was 0.011 mass units, using as mass scale the distance between the lines due to the two copper isotopes (assumed to differ by two units in mass). Thus the mean of the packing fractions of the copper isotopes, $\frac{1}{2}(f_1+f_2)$, is -6.90×10^{-4}. As the lines were not perfectly sharp and only three of the best were used, a relatively large error of $\pm 0.2\times 10^{-4}$ is estimated. A divergence from integral spacing in the copper isotopes amounting to 1.3 percent would be required before the mass scale would introduce an error amounting to 0.1×10^{-4} in the packing fraction.

ALUMINUM-SILVER

Quadruply-charged ions of the silver isotopes at 26.75 and 27.25 may be compared with aluminum ions at mass 27. It was difficult to get suitable lines for comparison as the singly-charged aluminum ions are generally much stronger than the silver ions. This difficulty was overcome by evaporating in vacuum a thin coating of aluminum on to a sheet of silver, and making an electrode by rolling up the sheet into a small pencil. For some of the photographs, the second electrode was palladium, and for others an alloy of silver with ten percent of zinc. The average mass difference ΔM for seven photographs with exposure times of 15 to 20 seconds was 0.0032, giving a difference between the packing fraction of aluminium and the mean of the fractions for the silver isotopes of 1.18×10^{-4} with an estimated probable error of 0.2×10^{-4}. A scale error of 0.1×10^{-4} would result from a difference from integral spacing in the silver isotopes used as the mass scale of eight percent. Aston has recently given -3.4×10^{-4} as a provisional value for the packing fraction of aluminum. It is probable however that the packing fraction for aluminum is slightly greater than Aston's provisional value. From the maximum energy of the electrons emitted by Al^{28}, and the mass of silicon, the mass of Al^{28} may be calculated,[19] and from this the mass of Al^{27} may be computed from the energy of the protons set free by deuteron bombardment.[20] The mass as computed by Livingston and Bethe[21] is 26.9899 ± 0.0008 giving a packing fraction equal to $(3.75\pm 0.3)\times 10^{-4}$. With this value the arithmetic mean of the packing fractions of the two silver isotopes is $(-4.93\pm 0.5)\times 10^{-4}$.

Several photographs were made with one electrode a copper-aluminum alloy and the other a copper-beryllium alloy, and strong doublets were found at atomic mass 9 between triply-

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[18] F. W. Aston, Nature **139**, 922 (1937).

[19] Cork, Richardson and Curie, Phys. Rev. **49**, 208 (1936).

[20] McMillan and Lawrence, Phys. Rev. **47**, 343 (1935).

[21] Livingston and Bethe, Rev. Mod. Phys. **9**, 373 (1937).

charged aluminum ions and singly-charged beryllium atoms. Unfortunately, no reliable measurements could be made due to a lack of a suitable mass scale for the large separation at this small mass. However, it may be possible to superimpose on these doublets lines from known masses to serve as a scale and thus give an independent determination of the mass of aluminum.

COPPER-PLATINUM

With one electrode made of platinum-iridium alloy and the other of copper-beryllium alloy, triply-charged platinum and iridium ions appeared at the masses 64.33···, 64.66···, 65, 65.33···, and 66. The triply-charged atoms at 65 formed a doublet with the singly-charged atoms of the heavier copper isotope. Five good doublets with exposure times of 20 to 60 seconds gave a mass difference of 0.058 with the difference between the lines at 64.66··· and 65.33··· as mass scale. The difference in the packing fraction of copper (65) and platinum (195) is then $(8.93\pm0.1)\times10^{-4}$. The mean of the fraction for the two copper isotopes has been determined as $(-6.9\pm0.2)\times10^{-4}$. It is very probable as discussed above that the two fractions differ by less than 0.2×10^{-4}. If the packing fraction for copper (65) is taken as $(-6.9\pm0.2)\times10^{-4}$, that for platinum 195 is $(2.03\pm0.3)\times10^{-4}$.

COPPER-GOLD

Triply-charged gold atoms from a spark between an 18-carat gold electrode and a platinum-iridium electrode appeared at the mass 65.66··· and were compared with the singly-charged copper atoms at 65 present as an impurity in the gold. The separation between the two copper isotopes was used as the mass scale. It was found that the gold line was displaced from the position it should have occupied if its packing fraction had been the "mean" of the fractions for the copper isotopes. The average of ten photographs with exposure times of one to two minutes gave a value of 0.058 mass units for ΔM. This gives a difference of $(8.90\pm0.2)\times10^{-4}$ between the gold packing fraction and the "mean" of the fractions for the two copper isotopes. The "mean" in this case, as given by (1) above, is quite different from the arithmetic mean. However, if the packing fractions of the two copper isotopes differ by less than 0.2×10^{-4}, no appreciable error is made in using the value previously determined for the arithmetic mean. If this latter is taken as $(-6.9\pm0.2)\times10^{-4}$, the packing fraction of gold is 2.0×10^{-4} with an estimated error of 0.4×10^{-4}. The gold line was much weaker than the copper lines, hence the large estimated error.

TITANIUM-GOLD

With a spark between a gold electrode and a titanium electrode, quadruply-charged gold ions at mass 49.25 appeared between the two titanium isotopes at 49 and 50. Ten photographs made with 30 to 100 seconds exposure were measured and gave a value for ΔM of 0.048 mass units. This gives a difference in packing fractions of $(9.36\pm0.2)\times10^{-4}$ between that for gold and the average given by (1) for the titanium isotopes. If the packing fraction for gold is taken as 2.0×10^{-4}, as suggested by the comparison with copper, the average for the two titanium isotopes at 49 and 50 is -7.36×10^{-4}. This is in close agreement with the directly observed packing fraction -7.22 for the titanium isotope at mass 48.

In addition to the mass comparisons in which the atomic mass of one of the masses has been determined in terms of oxygen, a great many comparisons have been made between masses, neither of which has as yet been referred to the oxygen standard. These comparisons are of significance since it is probable that the reference to oxygen will become possible for one or other of the masses. Also the difference in the packing fractions of two elements allows us to make comparisons directly with any assumed packing fraction curve and to detect any unexpected irregularity in it.

TIN-THORIUM

With a spark between a thorium electrode and one of tin, doubly-charged thorium atoms form a doublet[22] with the singly-charged tin atoms at

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[22] A reproduction of a thorium and a uranium doublet is given in Nature **138**, 120 (1936), also in the Proc. Am. Phil. Soc. **76**, 497 (1936).

mass 116. Sixteen doublets with exposures of 7 to 30 seconds were measured using the separation of the tin isotopes at 116 and 118 to fix the mass scale. An error of one percent in the mass scale leads to an error of less than 0.1×10^{-4} in the difference of the packing fractions. A difference of 0.120 mass units was found giving a difference in the packing fractions of 10.0×10^{-4}. Seven of the sixteen doublets were, however, sharper than the others, and the average value given by these seven was $(10.12 \pm 0.1)\ 10^{-4}$, and is considered more probable than the average of the whole group.

URANIUM-TIN

With a spark between an electrode of uranium metal and a tin electrode, a doublet[22] at mass 119 is formed by the singly-charged tin isotope and doubly-charged ions of the uranium isotope at 238. The best results were obtained after the tin had been worn completely down to the iron holder, so that the spark played between the uranium and the iron, a little tin apparently evaporating into the spark from the hole in the iron where the end of the tin electrode remained. The mass scale was taken from the separation of the two tin isotopes at 118 and 120 assumed as two mass units. The five best doublets made with exposures of one to two minutes gave a mass difference of 0.124 units, giving for the difference in the packing fractions of the tin isotope at 119 and uranium a value of $(10.41 \pm 0.1)\ 10^{-4}$. The position of the uranium line was also compared by the bracket method with the computed position it should have had if its packing fraction had been the average of the fractions for the two tin isotopes at 118 and 120. The difference between the average and the packing fraction of uranium was found from five photographs to be $(10.53 \pm 0.1) \times 10^{-4}$.

ACTINO-URANIUM-TIN

On several photographs the doubly-charged faint actinium isotope at 235, actino-uranium, appeared between the tin isotopes at 117 and 118. The mass difference between this line and a line corresponding to a mass midway between the tin isotopes was 0.123, giving a difference in packing fraction for actino-uranium and the mean of the packing fractions for the two tin isotopes of $(10.5 \pm 0.3) \times 10^{-4}$.

TUNGSTEN-ZIRCONIUM

With a spark between a tungsten and a zirconium electrode, doublets were obtained with exposures of one to two and a half minutes between the doubly-charged tungsten atoms of mass 182 and 184 and the singly-charged zirconium atoms at 91 and 92. Using the distance between the zirconium masses as the mass scale, three doublets at 91 gave a mass difference of 0.0714 units. This gives a difference between the packing fraction of zirconium 91 and tungsten 182 of $(7.85 \pm 0.2) \times 10^{-4}$. Three doublets at 92 gave a mass difference of 0.0740, and a difference in the packing fractions of zirconium 92 and tungsten 184 of $(8.05 \pm 0.2)\ 10^{-4}$.

PLATINUM-MOLYBDENUM

With a spark between a molybdenum electrode and one made of platinum-iridium alloy, doublets were obtained with one minute exposures at atomic masses 96, 97 and 98 between singly-charged molybdenum ions and doubly-charged platinum atoms of mass 192, 194 and 196. The doublets at 96 were not satisfactory. Four were measured, using the two iridium lines as mass scale, and the best two gave $(8.3 \pm 0.4) \times 10^{-4}$ as the difference in packing fractions between molybdenum 96 and platinum 192. At mass 97, three fairly good doublets gave $(7.7 \pm 0.2) \times 10^{-4}$ as the difference between the packing fractions of platinum 194 and molybdenum 97. At mass 98 four doublets gave $(7.68 \pm 0.2) \times 10^{-4}$ for the difference in packing fractions of Mo 98 and Pt 196. Here the mass scale was given by the separation of the two platinum isotopes at 196 and 198.

IRIDIUM-MOLYBDENUM

In the photographs made with the spark between molybdenum and platinum-iridium electrodes, singly-charged molybdenum ions of mass 96 occurred between the two doubly-charged iridium isotopes[23] at 95.5 and 96.5. The measurement on nine photographs of the dis-

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[23] A. J. Dempster, Nature **136**, 909 (1935).

placement of the molybdenum line from the calculated position of a mass midway between the two iridium masses gave a difference of $(7.72 \pm 0.2) \times 10^{-4}$ between the packing fraction of molybdenum 96 and the mean of the packing fractions of the two iridium masses

On the same plates the iridium line at 95.5 was measured with respect to the two molybdenum lines at 95 and 96. The same nine photographs gave $(7.68 \pm 0.2) \times 10^{-4}$ for the difference between the packing fraction of iridium 191, and the mean of the packing fractions of the molybdenum masses at 95 and 96.

PALLADIUM-LEAD

With a spark between a palladium electrode and a lead electrode to which a little thallium and bismuth had been added, doublets were obtained with 30 to 90 seconds exposure at mass 104 between singly-charged palladium[24] and the doubly-charged lead isotope at 208. Five of the best doublets were measured and the mass difference found to be 0.0828 mass units, taking the mass scale from the two lead isotopes at 206 and 208, and 0.0826 mass units, when the mass scale was taken from the two palladium isotopes at 104 and 105. A departure from integral spacing of the isotopes of 1.2 percent would be required before a difference as large as 0.1×10^{-4} would be produced in the packing fractions. Taking the mean of the two mass differences, we find $(7.96 \pm 0.15) \times 10^{-4}$ as the difference between the packing fractions of palladium 104 and lead 208.

Doublets were also formed between the palladium isotope at 102 and the doubly-charged lead atoms of mass 204. Only two obtained with 15 seconds exposure were measured using the difference between the two thallium lines at 101.5 and 102.5 to give the mass scale. A difference of $(8.07 \pm 0.2) \times 10^{-4}$ was found between the packing fraction of the two masses.

PALLADIUM-THALLIUM

In several photographs made with the electrodes used in the last comparison, the palladium isotope at 102 was bracketed by the two doubly-charged thallium isotopes at 101.5 and 102.5. Two photographs with 60 seconds exposure were measured and gave a difference of $(8.03 \pm 0.2) \times 10^{-4}$ between the packing fraction for palladium 102 and the mean of the packing fractions for the thallium isotopes.

RHODIUM-LEAD

With the same lead alloy electrode but with a second one of platinum-rhodium alloy (10 percent rhodium) doublets[24] were obtained at mass 103 with 20 to 40 seconds exposure between the rhodium atoms and the doubly-charged lead isotope at 206. If the distance between the masses 206 and 207 is taken as mass scale, the difference between the packing fraction of lead 206 and rhodium 103 as given by three doublets was found to be $(7.96 \pm 0.15) \times 10^{-4}$.

PALLADIUM-BISMUTH

With the same electrodes doubly-charged bismuth ions appeared with 30 to 90 seconds exposure between the two palladium isotopes at 104 and 105. Five brackets were measured using the unit of mass between the isotopes at 104 and 105 to give the mass scale. The difference between the packing fraction of bismuth and the mean of the fractions for the two palladium isotopes was $(7.84 \pm 0.1) \times 10^{-4}$.

RUTHENIUM-PLATINUM

With electrodes made of an alloy of platinum, gold, osmium and ruthenium, a doublet of doubly-charged platinum (198) and singly-charged ruthenium (99) was obtained with one to two minutes exposure. By using the spacing between the gold line 197 and the platinum line at 198 for the mass scale, an average mass difference for three doublets of 0.082 was found. This gives a difference between the packing fractions of platinum 198 and ruthenium 99 of $(8.26 \pm 0.2)\ 10^{-4}$.

RUTHENIUM-OSMIUM

With the same electrodes, a doublet was found with singly-charged ruthenium atoms at 96 and doubly-charged osmium atoms at 192. By using the osmium lines at 190 and 192 as

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[24] A reproduction showing doublets at 102, 103 and 104 is given in the Proc. Am. Phil. Soc. **74**, 497 (1936).

mass scale, an average mass difference for three doublets of 0.0815 units was obtained, giving a difference between the packing fractions of ruthenium 96 and osmium 192 of $(7.9 \pm 0.2)\ 10^{-4}$.

PALLADIUM-GALLIUM

With an alloy of lead, gallium and zinc (85 : 10 : 5) as one electrode and a palladium rod as the other, the two gallium isotopes at 69 and 71 appeared with 15 to 120 seconds exposure between the sequence of palladium isotopes at 68, 69.33···, 70, 70.66···, 72, 73.33···, that is, at two-thirds the value of the palladium masses. These lines may be attributed to palladium ions that passed the electric field with six charges and then picked up three electrons before passing the magnetic field. If the palladium isotopes at 106 and 108 are taken to give the mass scale, the gallium mass at 71 was found displaced from the computed position by an amount which gave a difference in packing fraction between the gallium 71 mass and the mean of the two palladium masses of $(1.46 \pm 0.2)\ 10^{-4}$. Similarly the isotope at 69 was compared with the palladium isotopes at 102 and 104 and a difference of $(1.55 \pm 0.2) \times 10^{-4}$ was found.

In addition to the mass comparisons reported above, several provisional comparisons were made where there was a greater probable error, due to the lines not being sharp, or due to the fact that only a few doublets were obtained. They are reported here as they serve to confirm some of the other measurements and indicate comparisons that may be made with greater precision in the future.

SILVER-IRON

With a spark between an iron and an eighteen carat gold electrode, doubly-charged silver atoms appeared at masses 53.5 and 54.5 bracketing the iron isotope at 54. Two photographs were measured by using the silver isotopes as mass scale. The mass difference between the iron mass and the calculated position of a mass midway between the silver masses was 0.0166 mass units. This gives a difference between the packing fraction of iron (54) and the average of the silver fractions of $(2.55 \pm 0.3) \times 10^{-4}$. If we take the average of the silver fractions to be -4.95×10^{-4} as determined above by comparison with aluminum, we find the fraction for iron 54 to be -7.4×10^{-4}. The errors in the aluminum (0.3) and the two comparisons (0.2 and 0.3) are however so large that this value can be regarded as only approximate.

SILVER-ZINC

With electrodes made from an alloy of silver (90 percent) and zinc (10 percent), triply-charged zinc ions occurred at 21.33··· and 22 close to the silver ions with five charges at 21.4 and 21.9. By using the separation of the silver ions as mass scale, the difference between the packing fraction of zinc 64 and the mean of the fractions for the silver isotopes was $(2.0 \pm 0.3)\ 10^{-4}$ while the difference for the zinc isotope at 66 was $(2.5 \pm 0.3)\ 10^{-4}$. The arithmetic mean of the fractions for the silver isotopes was determined above as $(-4.95 \pm 0.5) \times 10^{-4}$. The "means" in the present comparisons given by (1) probably do not differ from this value by more than the estimated error. We can thus deduce an approximate value -6.9×10^{-4} for zinc 64 and -7.4×10^{-4} for zinc 66.

OSMIUM-MOLYBDENUM

With a spark between an osmium and a molybdenum electrode doublets were found at masses 94, 95 and 96 between singly-charged molybdenum ions and doubly-charged osmium ions of masses 188, 190, and 192. Only one doublet was measured for each mass and the difference in the packing fractions of the three molybdenum and three osmium isotopes were found to be $(7.78 \pm 0.3)\ 10^{-4}$ at 94, $(7.76 \pm 0.3) \times 10^{-4}$ at 95, and $(7.58 \pm 0.3) \times 10^{-4}$ at 96.

ZINC-SODIUM

In the comparison of triply-charged zinc atoms and silver atoms with five charges, singly-charged sodium atoms appeared on two photographs and could be compared with triply-charged zinc ions at 22.66··· and 23.33···. By using the separation of the two zinc isotopes to give the mass scale, the difference between the packing fraction of sodium and the mean of the fractions for zinc was found to be (4.9±0.5)×10⁻⁴. If we take the packing fraction of sodium to be (1.7±0.15) ×10⁻⁴ as deduced from the energy set free in the disintegration by deuterons and the mass of neon 21, then the mean of the packing fractions for zinc 68 and 70 is (−6.6±0.6)×10⁻⁴.

NICKEL-RUTHENIUM

With an electrode made by packing a nickel tube with ruthenium powder, strong triply-charged nickel ions at mass 20 were bracketed with fainter ruthenium atoms with five charges at 19.8 and 20.2. By using the ruthenium atoms to give the mass scale, the difference between the packing fraction for the nickel isotope and the mean of the fractions for the two ruthenium isotopes was found to be (1.1±0.3)×10⁻⁴.

POTASSIUM-RUTHENIUM

With the same electrode doubly charged potassium ions appeared at mass 19.5. The packing fraction difference was calculated to be (0.4±0.3)×10⁻⁴.

ALUMINUM-PALLADIUM

With an electrode of copper-aluminum alloy and another of palladium, quadruply charged palladium ions appeared at 26, 26.25, 26.5 and 27.5 superimposed on a strong aluminum line at 27. The palladium line which should also appear near 27 was concealed by the stronger aluminum line, and could not be resolved. By using the separation of the palladium isotopes as mass scale the difference in packing fraction was computed to be (1.6±0.4)×10⁻⁴.

SUMMARY

A summary of the measurements reported in this paper are given in Table I and Table II. The first gives the difference in packing fractions in cases where one atomic mass is known, so that a value may be deduced for the packing fraction of the second. The values for the heavy element all lie above Aston's packing fraction curve by about 2×10⁻⁴. This curve however did not claim to give the values for the heavy elements with any great accuracy. The value found for gold by the copper comparison is confirmed to a

TABLE I. *Differences in packing fractions. $f=(M-I)/I$ observed, and values deduced for different elements, m = mass number near which the measurement was made, n = number of photographs measured. A bar over some of the f's indicates a mean value.*

m	IONS	n	$(f_2-f_1)10^4$	ASSUME	DEDUCE
16	O-Ti	9	−7.22±0.1	O, $f_1\times10^4=0.0$	Ti(48), $f_2\times10^4=-7.22\pm0.1$
12	C-Ti	3	−9.8 ±0.4	C, $f_1\times10^4=2.96$	Ti(48), $f_2\times10^4=-6.8\pm0.4$
14	N-Fe	8	−12.3 ±0.4	N, $f_1\times10^4=5.3$	Fe(56), $f_2\times10^4=-7.0\pm0.4$
16	O-Cu	3	−6.9 ±0.2	O, $f_1\times10^4=0.0$	Cu(63–.65), $\bar{f}_2\times10^4=-6.9\pm0.2$
27	Al-Ag	7	−1.2 ±0.2	Al, $f_1\times10^4=-3.75\pm0.3$	Ag(107–109), $\bar{f}_2\times10^4=-4.95\pm0.5$
65	Cu-Pt	5	8.93±0.1	Cu, $\bar{f}_1\times10^4=-6.9\pm0.2$	Pt(195), $f_2\times10^4=2.03\pm0.3$
65	Cu-Au	10	8.90±0.2	Cu, $\bar{f}_1\times10^4=-6.9\pm0.2$	Au(197), $f_2\times10^4=2.0\pm0.4$
49	Au-Ti	10	9.36±0.2	Au, $f_1\times10^4=2.0\pm0.4$	Ti(49–50), $\bar{f}_2\times10^4=-7.36\pm0.6$
54	Ag-Fe	2	2.55±0.3	Ag, $\bar{f}_1\times10^4=-4.95\pm0.5$	Fe(54), $f_2\times10^4=-7.4\pm0.8$
21.3	Ag-Zn	5	2.0 ±0.3	Ag, $\bar{f}_1\times10^4=-4.95\pm0.5$	Zn(64), $f_2\times10^4=-6.9\pm0.8$
22	Ag-Zn	6	2.5 ±0.3	Ag, $\bar{f}_1\times10^4=-4.95\pm0.5$	Zn(66), $f_2\times10^4=-7.4\pm0.8$
23	Na-Zn	2	4.9 ±0.5	Na, $f_1\times10^4=-1.7\pm0.15$	Zn(68–70), $\bar{f}_2\times10^4=-6.6\pm0.6$

TABLE II. *Differences in packing fractions observed for various pairs of isotopes.*

m	IONS	n	$(f_2-f_1)10^4$	m	IONS	n	$(f_2-f_1)10^4$	m	IONS	n	$(f_2-f_1)10^4$
116	Sn-Th	7	10.14±0.1	102	Pd-Pb	2	8.07±0.2	94	Mo-Os	1	7.78±0.3
119	Sn-U	5	10.41±0.1	103	Rh-Pb	3	7.96±0.15	95	Mo-Os	1	7.76±0.3
91	Zr-W	3	7.85±0.2	102	Pd-Tl	2	8.03±0.2	96	Mo-Os	1	7.58±0.3
92	Zr-W	3	8.05±0.2	104.5	Pd-Bi	5	7.84±0.1	19.5	K-Ru	1	0.4 ±0.3
97	Mo-Pt	3	7.7 ±0.2	96	Ru-Os	3	7.91±0.2	20	Ni-Ru	1	1.1 ±0.3
98	Mo-Pt	4	7.68±0.2	99	Ru-Pt	3	8.26±0.2	27	Al-Pd	3	1.6 ±0.3
96	Mo-Ir	9	7.72±0.2	69	Pd-Ga	7	1.29±0.3	117.5	Sn-AcU	2	10.5 ±0.3
95.5	Mo-Ir	9	7.68±0.2	71	Pd-Ga	7	1.37±0.3	96	Mo-Pt	4	8.3 ±0.3
104	Pd-Pb	5	7.96±0.15								

certain extent by the fact that it gives a value for titanium (49) which is close to the values for titanium (48) found by direct comparisons with oxygen and carbon. The values for iron 54 and 56 deduced by different methods are close together as are also the values for zinc.

In Table II mass comparisons are given between atoms for which neither mass is known accurately at the present time. As soon as further observations give a value for one of the masses, the comparison may be used to deduce the other. The values are also of immediate interest in connection with the packing fraction curve. Theoretical curves may be tested and a probable curve drawn in which the masses agree with all the comparisons in Table II as well as with the values in Table I. A discussion of this curve will be given in a later paper.

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The Recombination of Ions in Pure Oxygen as a Function of Pressure and Temperature

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All previous investigations of the coefficient of recombination in pure gases have employed the older technique which did not allow the use of an outgassed chamber and made no corrections for initial recombination, diffusion, etc. This work was undertaken in pure oxygen in order to compare the results with existing theories. Aside from the initial drop in the curves of the recombination coefficient plotted against time due to preferential and initial recombination, the value of the coefficient of recombination in oxygen was found to be constant at a given pressure over extended intervals of time. It was, accordingly, possible to obtain a definite and probably correct value for the coefficient of recombination in pure oxygen at 76 cm pressure and 25°C. This value is $\alpha=(2.08\pm0.05)\times10^{-6}$. Comparison of the variation with pressure in the range 10 cm to 76 cm pressure was approximately in good agreement with the theory of J. J. Thomson assuming the ion to have a mass of $M=64$ and a mean free path of that given by mobility measurements. The temperature variation between the limits of -78°C to $+105$°C verified the Thomson equation quite accurately using the same data concerning the ion. At the lowest temperature a deviation was observed, indicating a possible increase of ionic mass to 96. While these results are a good confirmation of the Thomson theory they cannot be reconciled with the Langevin theory, although the Langevin theory probably holds beyond 10 atmospheres. Loeb has indicated the character of the transition between the two theories. The outstanding difficulty introduced by the change in the coefficient with time, due presumably to initial recombination, which is impossible of analysis in the less pure gases of the previous workers, is now somewhat more amenable to treatment. It is shown that if one includes the retarded diffusion of the ions created within ten times the radius of the sphere of active attraction, the time intervals involved in the x-ray flash periods, and the gradual formation of ions of mass $M=64$ from the initially ionized particles which may be accelerated by x-ray irradiation, the rough theory of initial recombination given by Loeb will account for the behavior.

INTRODUCTION

When equal numbers of positive and negative ions in a gas are left in a field free space far from the walls of a container they recombine at the rate,

$$dn/dt=-\alpha n^2 \tag{1}$$

where n is the density of ions of either sign and α is the coefficient of recombination.[1] Now experiments evaluating α have shown that under varying conditions ranging from 100 atmospheres of pressure to pressures in discharge tubes the processes giving rise to an α are of diverse types.[2]

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[1] L. B. Loeb, *Kinetic Theory of Gases*, second edition, pp. 583–600. J. J. Thomson, *Conduction of Electricity through Gases*, third edition, Vol. 1, pp. 20–57.

[2] W. R. Harper, Proc. Camb. Phil. Soc. **28**, (Part II) 219 (1932); I. S. Bowen and E. F. Cox, Phys. Rev. **51**, 232 (1937).

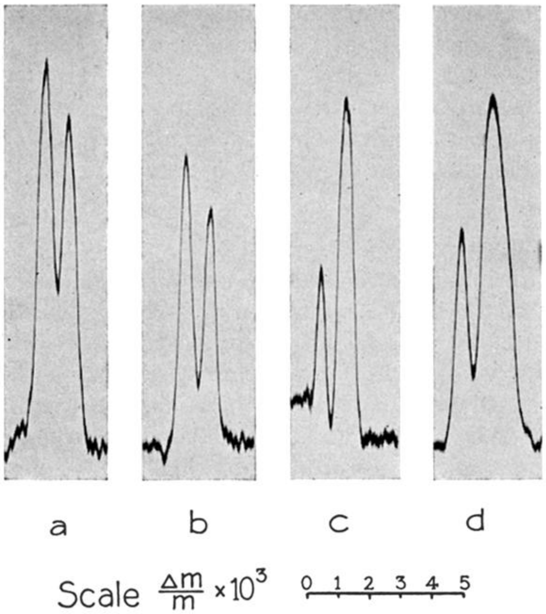

FIG. 1. Microphotometer traces of doublets. (a) Titanium-oxygen at mass 16, (b) rhodium-lead at mass 103, (c) molybdenum-platinum at mass 98, (d) tin-thorium at mass 116. The scale shows the displacements corresponding to mass changes of 1, 2, 3, 4, and 5 parts in 1000.