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On the Isotopic Ratio in Oxygen

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A new mass-spectrometer has been constructed along lines previously described in which the defects that appeared in the first apparatus are eliminated. The electrostatic analyzer has been slightly altered to take full advantage of its focussing properties for which a formula is given. Because of the faintness of the scattered background, very weak peaks can be measured precisely. Oxygen, prepared by the decomposition of PbO_2, has been analyzed and the ratio of the amount of O^{16} to O^{18} found to be 503 ±10. It is suggested that the discrepancy between this and previous values may be due to the method of preparation of the oxygen sample.

THE theory of one method of using alternating electric fields to select, from a beam of charged particles, all those having a certain velocity, has been worked out in a previous paper.[1] In this paper it was pointed out that to be passed by the filter the given particle must satisfy two conditions. First, its displacement on leaving the field must be less than the width of the last slit, and, second, its angular deviation must be small enough to enable it to pass through subsequent slits. Two filters, depending chiefly on the first criterion for selectivity have been constructed and described.[2, 3]. Neither of these pieces of apparatus came up to expectations as to resolving power and background and in one case bad "ghosts" rendered the apparatus almost useless. Both used more symmetrical fields than the theory requires and both separated the two halves of the field by a considerable distance, thus, theoretically, greatly increasing the resolving power but involving construction complications. The apparatus described in this paper uses unsymmetrical fields and long collimating sections, thus bringing in the second criterion for selection as well as the first. The two halves of the fields are adjacent, the electrical connections on the second half being reversed to produce the required 180° phase difference. No relative displacement for different velocity ranges is necessary and a more rigid and precise mechanical construction is possible. The theoretical resolving power is about one-seventh that of the original apparatus but is completely attained experimentally.

The theory applicable to the second condition for selection may be obtained quite simply from that originally published.[1] Using Eq. (2) and Eq. (6) of this paper we find that at a distance d beyond the end of the first field the additional displacement of the particle due to its emergent lateral velocity is

$$y' = 2Wn^2\pi^2 d(\Delta v/v_0)^2/a,$$

where W is the total spread of the beam at the center of the fields, $2n$ is the number of oscillations of the electric field during its passage, $4a$ is the total length of the field and Δv is the

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[1] W. R. Smythe, Phys. Rev. **28**, 1275 (1926).

[2] Smythe and Mattauch, Phys. Rev. **40**, 429 (1932).

[3] Mattauch, Phys. Zeits. **33**, 899 (1932).

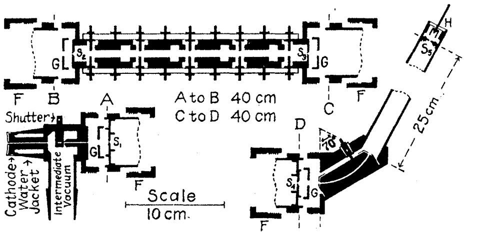

FIG. 1. Section of the new mass-spectrometer showing cathode with canals, collimating slits, S_1 and S_2 for the entering beam and S_3 and S_4 for the emerging beam, condenser section, electrostatic deflecting field and receiving slit, S_5, with Faraday cylinder, H.

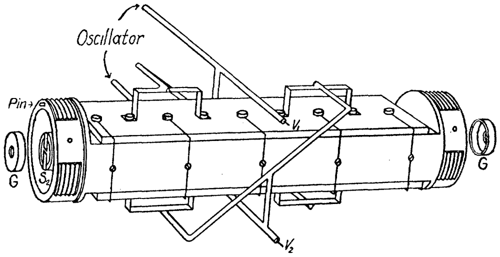

FIG. 2. Condenser section of apparatus showing mounting of slits, electrical connections and "breech block" method of joining sections.

difference between its velocity and v_0, the undeviated velocity. The derivation of the formula indicates that this selection condition is most effective on those phases in which the first is least effective and *vice versa.* It is specially efficient in eliminating large values of Δv since this quantity occurs squared. This is borne out experimentally as the scattered background a short distance away from the peaks in the present apparatus is fifty times smaller than in the first.

The actual construction of the condenser section of the filter is shown in section at the top of Fig. 1. The four upper condenser plates and the five upper diaphragm halves are mounted on a strip of plate glass and carefully adjusted as to spacing and alignment with indicating gauges. The lower system is then similarly assembled and the whole mounted on the brass frame, the two faces of which are accurately parallel. Plate glass strips on the sides of the plates insure permanent alignment. All joints are closed outside with a small fillet of beeswax, which has been boiled under reduced pressure, and then painted with glyptal lacquer. These joints have been permanently tight and give off no detectable amount of vapor. An external view of the condenser mounting, with the electrical connections in place, is shown in Fig. 2. There are four slits to be lined up: S_1, S_2, S_3 and S_4 in Fig. 1. First S_2 and S_3 are set on the axis of the condenser system, then the collimating tubes are attached and S_1 and S_4 are lined up with them. The latter operation is greatly facilitated by the mounting of the slit jaws, shown in Fig. 2, which permits one to see around them during adjustment. When this is finished the perforated cap, G, is placed over the slit permitting the positive rays to pass between the jaws only.

To insure accurately reproducible assembling of the apparatus gaskets were dispensed with. The sections to be joined were fitted together as shown in Fig. 1 and Fig. 2, a pin, not shown, preventing relative rotation. The collars, marked F in Fig. 1, with sectored threads, are then slid over and the joints secured tightly by an eighth turn of the collars. Each end of a collar is rendered vacuum tight by a fillet of beeswax run around it with a hot wire. After such a joint has once been sealed it can be opened in ten seconds and closed, vacuum tight, in five minutes and the alignment is perfect. The water-cooled cathode, the channels separating the discharge tube from the intermediate vacuum and the latter from the high vacuum and a shutter for excluding the positives are shown at the lower left corner of Fig. 1.

The electrostatic analyzing field, shown at the lower right of Fig. 1 has been changed somewhat from that used in previous apparatus[2] to secure better resolution and focussing with approximately the same dimensions as before. Although we were aware that a certain amount of focussing of the beam was present in our original electrostatic analyzer where the receiving slit is some distance beyond the edge of the electric field, it did not occur to us that it might come at the same point as the best angular resolving power until a perusal of the paper by Hughes and Rojansky[4] suggested the possibility. For the voltages, slit widths and resolving power that we need, their arrangement is somewhat cumbersome but a similar analysis may be applied to our case.

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[4] Hughes and Rojansky, Phys. Rev. **34**, 284 (1929).

To compute the arrangement for maximum resolving power we assume that all particles have the same charge and enter the radial cylindrical electric field normal to the lines of force at the point $\theta=0$, $r=r_0$, moving with a velocity v. If the particle of mass m_0 travels in a circular path of radius r_0, then the central force acting on a particle of mass m will be $F=ma=-m_0v^2/r$, and its equations of motion will be

$$\ddot{r}-r\dot{\theta}^2=-m_0v^2/(mr) \qquad (1)$$

and

$$d(r^2\dot{\theta})/dt=0. \qquad (2)$$

Integrating (2) gives $r^2\dot{\theta}=r_0{}^2\dot{\theta}_0=r_0v$, or $\dot{\theta}=vr_0/r^2$. Substituting for d/dt its equivalent $\dot{\theta}d/d\theta$ in Eq. (1) and letting $r=r_0m^{1/2}/(um_0{}^{1/2})$ we obtain the form

$$d^2u/d\theta^2=(1/u)-u.$$

It may be verified that the expression

$$u=1+\epsilon\cos(2^{1/2}\theta)+\epsilon^2(1/4-1/6\cos(2^{1/2}\theta)$$
$$-1/12\cos(2\cdot2^{1/2}\theta))$$

satisfies this equation if we neglect the cube and higher powers of ϵ. This expression, which we owe to Dr. Huff, may be simplified in our case. When $\theta=0$, $r=r_0$ so that $\epsilon=(m/m_0)^{1/2}-1$, which, as we are only interested in values of m close to m_0, is a very small quantity. We shall include only the first power terms in ϵ. Substituting for u and ϵ, multiplying through by $(m_0/m)^{1/2}$ and subtracting both sides from one gives

$$(r-r_0)/r=[1-(m_0/m)^{1/2}][1-\cos(2^{1/2}\theta)].$$

Let x_1 be the amount, $r-r_0$, which the mass m is displaced from the mass m_0 at θ_1, where they emerge from the field. Substitute Δ for $1-(m_0/m)^{1/2}$ giving

$$x_1=r\Delta[1-\cos(2^{1/2}\theta_1)].$$

If ϕ is the angle between the paths of m_0 and m on emerging from the field, then

$$\tan\phi=dx_1/rd\theta=2^{1/2}\Delta\sin(2^{1/2}\theta_1).$$

The total amount that m will be displaced from m_0 at a distance R beyond the edge of the field will be $x=x_1+R\tan\phi$. For best resolving power $dx/d\theta=0$. Thus

$$\tan(2^{1/2}\theta_1)=-2^{1/2}R/r_0 \qquad (3)$$

since $r=r_0$ approximately.

It is not difficult to show, by a method similar to that used by Hughes and Rojansky, that this is also the condition that a homogeneous beam, slightly divergent on entering the field, be brought to a focus at S_5 (Fig. 1), a distance R beyond the edge of the field, after being bent through an angle θ_1, 70° in Fig. 1. If $R=0$ this reduces to their special case.

The oscillator used with this apparatus is the same already described.[2] As Dr. Mattauch pointed out in a letter to the author, one cannot be certain, no matter how symmetrical the system seems to be, that the voltage halfway between the plates will always be zero. Therefore we have now grounded the center of the oscillator coil through a R.F. choke and use a compensator connected across the leads by which earth capacitance can be shifted from one side of the line to the other until $V_1=-V_2$ (Fig. 2). This adjustment is different for 30, 40 and 60 meter wave-lengths. The r.m.s. voltage between V_1 and V_2 is now indicated by a permanently connected, specially constructed, electrostatic voltmeter which can be read to 0.1 percent. Each side of this has an identical capacitance to ground.

Only minor changes have been made in the discharge tube from that previously described.[2] The electrometer system and the scheme of using the electrostatic field as a shutter for positive rays is also the same as before. The pumping system now consists of a two stage glass butyl phthalate diffusion pump backed by a hyvac. One stage pumps from the high vacuum part of the apparatus, which includes the collimating sections, the condenser section, the deflecting field section and the Faraday cylinder. This stage delivers to the other stage which pumps from the region between the channels. Diffusion and creepage of the pump liquid into the apparatus is prevented by charcoal lined tubes. This pumping system is very satisfactory and liquid air is unnecessary.

Naturally, since the whole adjustment was done with oxygen, the first measurements undertaken were on this element. There are now no "ghosts" and the scattered background is very small (see Fig. 3) so that precise measurements of weak peaks are possible. Systematic errors in comparing weak currents with strong currents

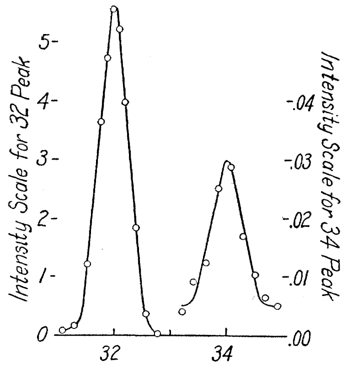

FIG. 3. Oxygen molecule peaks run with low resolving power. Oscillating r.m.s. voltage, $V^{32}=160$ volts, $V^{34}=170$ volts. Wave-length 60 meters.

have been eliminated as already described.[2] The peaks chosen were 32($O^{16}O^{16}$) and 34($O^{18}O^{16}$). To make certain that both molecules travel identical paths in the apparatus the oscillating voltage V^{32} used in measuring the 32 peak and the voltage V^{34} used on the 34 peak were always kept in the ratio $V^{32}/V^{34}=32/34$. The only correction therefore to be applied to the measured peaks is that due to the voltage distribution in the discharge tube. This was determined for each run by shutting off the oscillator and measuring the total positive ion current at the deflecting voltage used for 32 and at that used for 34. This intensity ratio turned out to be surprisingly constant and deviated less than one percent from 1.167 for a variation of 80 percent in the discharge tube current. The actual ratio of the number of $O^{16}O^{16}$ to $O^{18}O^{16}$ molecules is therefore given by $1.167I^{32}/I^{34}$ where I^{32} and I^{34} are the measured intensities of the two peaks.

A typical pair of peaks, obtained with low resolving power in a preliminary run, is shown in Fig. 3. No complete peaks were run with the higher precision used in the final measurements. The curve drawn for the 34 peak is identical in shape with the 32 peak. When the resolving power is increased by raising the oscillator voltage the 33 peak appears. In some cases there is a peak at 31 whose intensity varies independently from that of the oxygen peaks and which is perhaps due to Na_2O^{++}, since the sodium *D* lines frequently appear in the discharge tube. It seems that the increase of the speed of measurement due to the larger intensity at low resolving power is offset by the overlapping of the base of the 33 and 34 peaks. It was finally decided to use higher resolving power and, after locating the top of the 32 peak accurately, measure only four points, the top of the 32 peak and the top and background at each side of the 34 peak. This enables more runs to be made and gives ample time to make the two weak background measurements with precision before the discharge conditions can change.

The oxygen was prepared by the thermal decomposition of PbO_2 at the pressure in the discharge tube, about 0.05 mm Hg. Impurities, chiefly water vapor, were frozen out in a liquid air trap so that the spectrum of the discharge tube showed only oxygen lines and bands and sodium lines. The latter appeared to come from a yellow glow on the surface of the glass. Between atomic weights 10 and 40 no other peaks were found with an intensity as great as five percent of that of the oxygen. In adjusting the apparatus a large charge of PbO_2 was used and the temperature required to maintain the oxygen pressure was constant within a degree or two for weeks. Finally it became necessary to raise the temperature rather rapidly to maintain the pressure and at this point the relative amount of $O^{18}O^{16}$ increased sharply for a short time and then relapsed to its former value. Since no record had been kept of temperature or time of heating, during preliminary adjustments, it was decided to repeat with a smaller amount of PbO_2 to save time. This was a mistake because the effect will be washed out if this phase passes so rapidly that the new composition cannot be established throughout the volume of the apparatus. Furthermore, we were unfortunate in getting no readings at this critical point as we did not recognize it until plotting the data next day. It apparently falls between 4 and 5 in Table I

TABLE I. *Abundance ratio O^{16}/O^{18}.*

No.	Temp. (°C)	Time (hours)	MA Tube current	Ratio O^{16}/O^{18}
1	290°	28	10.0	502
2	292°	34	7.5	499
3	295°	42	7.7	510
4	300°	49	7.0	491
5	310°	57	8.7	(524)
6	318°	63	6.0	512
7	323°	68	7.3	(492)

because the readings in 4 were falling slowly and those in 5 were rising rapidly. For determining the average composition of the oxygen, however, the data are adequate. The apparatus was turned on in the morning and off at night. Each afternoon two or three determinations of the ratio were made. The mean of each set is included in the table and none are omitted. In two cases, 5 and 7, an individual reading deviates more than 10 from the mean of that day and so these sets were discarded in averaging although the result is little changed by including them. The current in the discharge tube is also given. Larger current indicates higher pressure. The r.m.s. oscillating voltages are: $V^{32}=200$ volts, $V^{34}=212.5$ volts.

The mean of these values, excluding 5 and 7, is 503. The maximum deviations are $+9$ and -12 so that it is probably safe to say that this value is correct to ± 10 for our sample of oxygen. It should be noted that this value is considerably lower than any previously given. Aston[5] gives 535, Mecke and Childs (spectroscopic)[6] give 640 and Kallman and Lasareff[7] give 630. Workers at the University of California have found that a partial separation of the oxygen as well as of the hydrogen takes place in electrolysis so that electrolytic oxygen should give too high a value. Most of the oxygen on the earth has been used in oxidizing the earth's crust and only a small fraction of one percent remains in the air. It is possible that some concentration, probably of the O^{16}, has taken place in this process so that the ratio for air is above average. In our sample the method of preparation of the PbO_2 is unknown. It was made by Kahlbaum and is labeled "*zur elem. analyse.*" There may be a certain selectivity in the decomposition of PbO_2 to PbO since only half of the oxygen is released, but, if so, we might expect it to favor the O^{16} and make our ratio too high. Since the chief importance of this ratio lies in the fact that it is used to connect the chemical atomic weight scale with the isotopic scale where O^{16} is taken to be 16.0000, it is important that the sample analyzed contain the same isotopic mixture that is most likely to occur in chemical compounds. We are planning to make other measurements, preparing our oxygen in other ways from different sources. Among these we hope to get a sample from the deep and aged rocks of the earth's crust. We also expect to make determinations of O^{17}.

We believe that in the method described all systematic sources of error have been eliminated except one. There is always the possibility of some unknown ion of mass 34 being present in small amounts. We would expect such an ion, if present, to fluctuate in intensity, relative to oxygen, under different discharge conditions. The fluctuations observed have never exceeded the errors of reading so we think the presence of such an ion improbable.

We wish to thank Mr. Pearson for his advice and to acknowledge the painstaking labor of Mr. Bressler in building this apparatus which was not put into operation until after his death.

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[5] Aston, Nature **130**, 21 (1932).

[6] Mecke and Childs, Zeits. f. Physik **68**, 362 (1931).

[7] H. Kallman and W. Lasareff, Zeits. f. Physik **80**, 237 (1933).