Non-Existence of Ion Mobility Spectrum in Air

By ROBERT N. VARNEY
University of California, Berkeley

(Received July 19, 1932)

A modified form of the Rutherford a.c. method of measuring ion speeds, as suggested by Loeb and Bradbury, has been used to investigate the range of speeds with which negative ions in air travel. It differs in that the ions are produced only during a small fraction of the a.c. period, this being accomplished by interrupting the ultraviolet light beam with a rotating shutter. The theoretical curves of $d(i/i_0)/dV$ against V assuming both the presence and the absence of an ion spectrum are given. The experimental curves for ions 0.03 to 0.006 sec. old agree closely with the theoretical curves for a spectrum, but it is shown that on application of a diffusion correction the spectrum in clean dry air reduces to negligible width; the presence of ozone in considerable amounts, however, produces a spectrum extending 10 to 12 percent on each side of the mean mobility.

INTRODUCTION

THE question of whether normal ions in air travel with a unique speed or with speeds spread over a range or spectrum of values has been completely discussed and all experimental evidence to date on both sides has been analyzed in a recent paper by Loeb and Bradbury.[1] They suggested that, if in the Rutherford a.c. method of measuring mobilities a shutter in conjunction with the commutator which produced the square-wave a.c. were used to interrupt periodically the ultraviolet light beam, a higher resolving power might be obtained for the a.c. method. The principle has been used by Fontell[2] and by Bradbury,[3] both, however, using x-ray ionization, and by Hamshere[4] using α-ray ionization. The suggested photoelectric method promised to be an improvement over the first of these because the exact distance travelled by the ions could be more exactly determined; and over the second, because it was hoped that ultraviolet light would produce less active substances in the air than either x-rays or α-rays.

APPARATUS

The apparatus consisted of a metal ionization chamber provided with plane plates, the upper being brass and the lower speculum metal. A quartz window permitted the light from a quartz-mercury arc to fall on the lower plate. The beam of light passed first, however, through a window of the rotating shutter. The air from the room was slowly passed over P_2O_5 and $CaCl_2$, and through a double trap immersed in liquid air.

[1] L. B. Loeb and N. E. Bradbury, Phys. Rev. **38**, 1716 (1931).
[2] N. Fontell, Commen. Physico Mathematicae Soc. Scientiarium Fennica **23**, 7 (1931).
[3] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).
[4] J. L. Hamshere, Proc. Camb. Phil. Soc. **25**, 205 (1929); Proc. Roy. Soc. **A127**, 298 (1930).

The shutter served at the same time as a commutator to provide a square-wave, alternating potential on the lower plate. The shutter, which was variable in size, allowed the speculum plate to be illuminated from the time the negative potential was applied up to any desired time before that at which the potential reversed. Ions thus produced during the negative part of the cycle travelled upward either until they reached the upper plate or until the potential was reversed, when they were drawn back again to the bottom plate. (A slight positive bias insured complete sweeping out of the ions from the field; see Fig. 1).

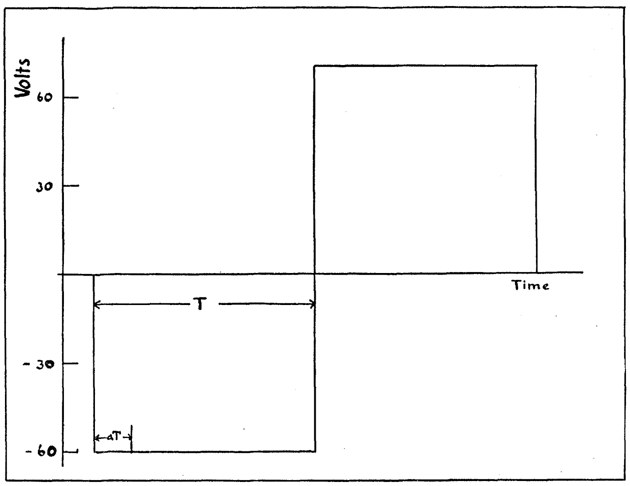

Fig. 1. Diagram showing the characteristics of the square-wave a.c. with the positive bias and the relative magnitudes of T and αT indicated.

Procedure

The following method was used to take and to reduce the results. (1) Electrometer deflections for various voltages applied to the lower plate were taken with the shutter-commutator moving. These deflections are called i. The electrometer could be read to about 0.2 percent of its average deflection, and average reading could be repeated to ± 0.2 percent. The voltmeter could be read to a little better than ± 0.10 volts.

When a smooth curve of i against V was drawn, the curve usually passed directly through all but one or two points. If more than two points deviated noticeably in any one curve, the whole curve was discarded as erratic.

(2) Similar deflections were obtained but with the shutter-commutator stationary, giving the i_0 readings. These gave greater difficulty because of the relatively short time necessary to produce the deflection. A straight line was drawn through the data points and the values of i_0 taken from it. From the work of Bradbury[5] on the photoelectric current in gases, it appears that over ranges of 30 volts or less the use of a straight line is permissible. The probable error on this line was around one-half percent.

[5] N. E. Bradbury, Phys. Rev. **40**, 980 (1932).

(3) The ratio of i to i_0 was then plotted against voltage. Note that i values have not been smoothed. Table I shows a typical set of data. The probable error of points on this curve with respect to the curve lies between ± 0.05 volts and ± 0.02 volts (see Fig. 2).

TABLE I. *Typical set of data for i/i_0.*

V (volts)	i/i_0	V (volts)	i/i_0	V (volts)	i/i_0	V (volts)	i/i_0
150	0.0407	134.5	0.0290	124.84	0.0054	114.9	0.0000
146.75	0.0406	132.2	0.0230	122.8	0.0029	112.9	0.0000
142.75	0.0399	130.5	0.01865	120.8	0.00136		
138.33	0.0363	128.5	0.0128	128.8	0.00039		
136.0	0.0325	126.67	0.00855	116.9	0		

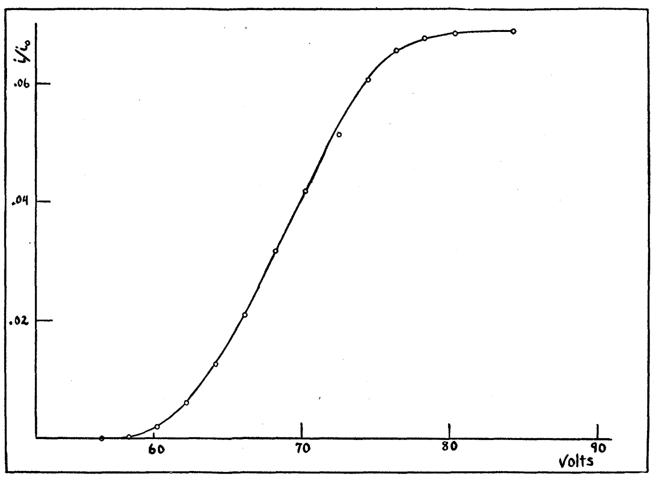

Fig. 2. Experimental curve of i/i_0.

(4) It was desired to plot $d(i/i_0)/dV$ against V, i.e., to plot the derivative curve. It is a well-known fact that integration smooths out while differentiation accentuates discontinuities and irregularities in a curve. In this case, theoretical considerations given below led the writer to believe that the actual discontinuities occurred in the second derivative curve. If so, they would be shown much more sharply in the first derivative curve than in the original curve, a break in the slope appearing in the former case with only an inflexion or hardly noticeable increase in the rate of curvature in the latter case.

Differentiation was performed by taking the slope at various points with a straight edge. An important check was made by placing the straight edge successively through every two adjacent data points and using this for the slope at the mean of the two, i.e., finite differences were used. As a final check, the i/i_0 curve was completely redrawn and redifferentiated in several cases to check against possible personal errors. The deviations were well within the limits claimed for the method.

The probable error in determining the derivative curve is between ± 0.07 volts and ± 0.10 volts. Adding to this the probable errors in reading all instruments, the resulting probable error is between ± 0.15 volts and ± 0.20 volts. The effect of this on the mobilities found is discussed in the conclusion.

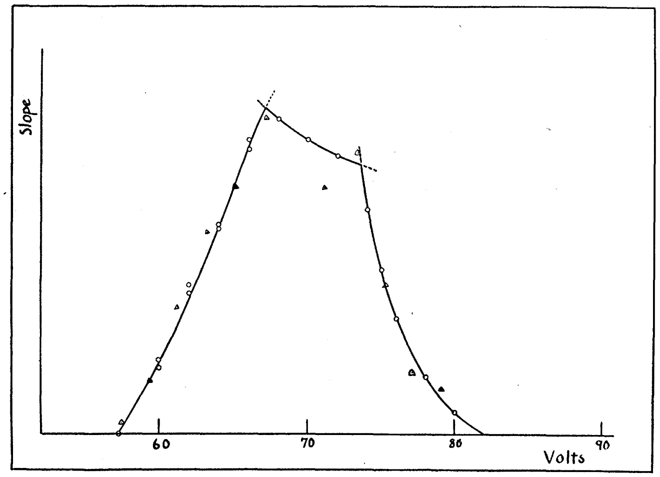

Fig. 3. Curve showing slope of each point of the i/i_0 curve in Fig. 2. This is an experimental result of plotting $d(i/i_0)/dV$ against V and shows the two zeros and the two break points distinctly. The triangles are finite difference points, and the double set of circles come from two different drawings of the i/i_0 curve.

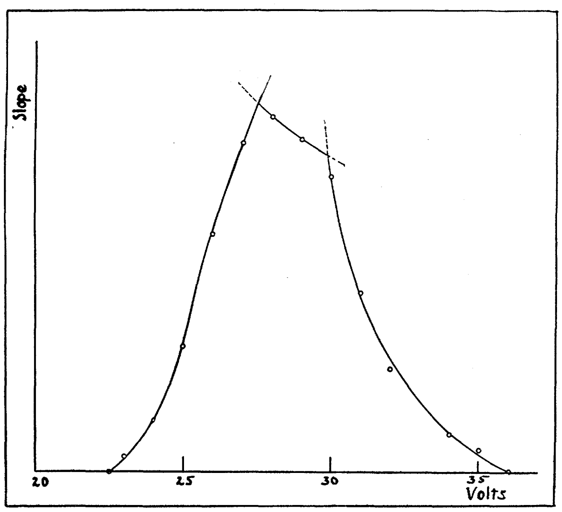

Fig. 4. Another experimental curve of $d(i/i_0)/dV$ against V similar to Fig. 3 but taken with a slower shutter speed.

It is important to notice that while an inflexion point in a curve may only be found by attempting to discover the point at which the curve crosses its tangent, the same point in the first derivative curve may be found as the intersection of two smooth curves, that is, in this case, by the use of five or more ordinary points instead of a single critical point. Since theory indicates a break point and since experiment gives two curves approaching each other at a sharp angle and showing an apparent point of intersection to an accuracy of ± 0.20 volts at worst, the question of whether or not such a single point actually exists in the data becomes of no interest. Just what its disappearance would mean is unknown, but it certainly would not affect the discussion of the existence or non-existence of an ion mobility spectrum.

Two break points were found in each curve, but only the sharper one, occurring at an inflexion point in the i/i_0 curve, was used (see Figs. 3 and 4).

(5) The determination of the limits of the spectrum from the derivative curves and the corrections for diffusion are discussed at a later point.

Significance of the Results

Loeb and Bradbury[1] have worked out the essentials of the theory of the method. What happens when the shutter closes and what the derivative curve would be, was not considered by them.

Taking k_1 and k_2 as the highest and lowest mobilities, respectively, in an assumed ion spectrum; V as the field strength; d as the plate separation; T the half period of the a.c.; and αT the length of time the shutter is open; their work gives directly

$$i/i_0 = [1/V(k_1 - k_2)T](Vk_1T - d - d \log (k_1VT/d)) \tag{1}$$

holding over the region $V = d/k_1T$ to $V = d/[k_2T$ and

$$i/i_0 = 1 - [d/V(k_1 - k_2)T] \log (k_1/k_2) \tag{2}$$

holding from $V = d/k_2T$ on indefinitely.

When the shutter is used, it can be shown that Eq. (2) ceases to hold at $V = [d/k_1(T - \alpha T)]$ and that a new equation

$$\frac{i}{i_0} = 1 - \frac{k_1(T - \alpha T)}{(k_1 - k_2)T} + \frac{d}{V(k_1 - k_2)T}\left(1 + \log \frac{Vk_2[T - \alpha T]}{d}\right) \tag{3}$$

holds over the region $V = d/[k_1(T - \alpha T)]$ to $V = d/[k_2(T - \alpha T)]$.

On differentiating Eqs. (1), (2), and (3) with respect to V, the required result is obtained;

$$\frac{d(i/i_0)}{dV} = \frac{d}{V^2(k_1 - k_2)T} \log \frac{k_1VT}{d} \tag{4}$$

$$\frac{d(i/i_0)}{dV} = \frac{d}{V^2(k_1 - k_2)T} \log \frac{k_1}{k_2} \tag{5}$$

$$\frac{d(i/i_0)}{dV} = -\frac{d}{V^2(k_1 - k_2)T} \log \frac{Vk_2(T - \alpha T)}{d}. \tag{6}$$

Eqs. (4), (5), and (6) hold respectively over the same regions as Eqs. (1), (2), and (3). Fig. 5 represents a theoretical curve for a spectrum of negative ions having mobilities between 1.6 and 2.2 cm/sec. per volt/cm, neglecting any effect of diffusion.

The shape of the curves is not of so much interest as the voltages of the zeros and break points. As the shutter begins to open, the lower zero point at a voltage $V_0 = d/k_1T$, and the first break point at $V_1 = d/k_2T$, are obtained. Similarly, when the shutter closes, the second break point at $V_2 = d/k_1(T - \alpha T)$ and the upper zero at $V_3 = d/k_2(T - \alpha T)$ appear.

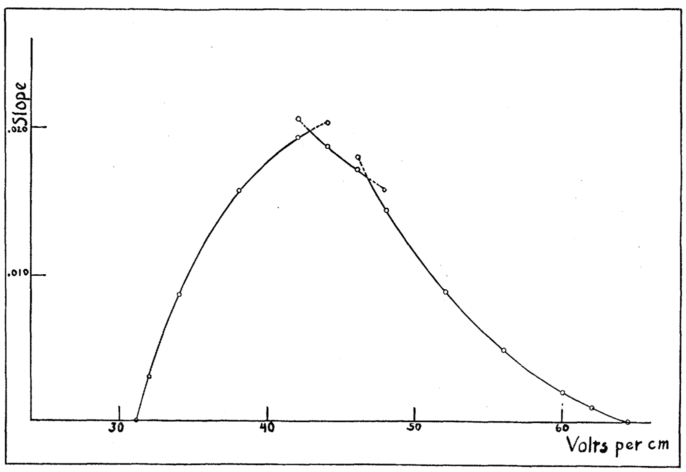

Fig. 5. Graph of the theoretical values of $d(i/i_0)$ with the following assumptions: $k_1 = 2.2$, $k_2 = 1.6$, shutter size, $\alpha T = T/3$, $T = 0.0292$ sec., no diffusion. This is a graph of Eqs. (4), (5), and (6).

In obtaining Eqs. (1), (2), and (3), it was assumed that the mobilities were spread uniformly over the region bounded by k_1 and k_2. The spread in any case would undoubtedly not be uniform, but this would only change the shape of the curves without altering either the positions of the break points or of the zero points. Furthermore, it would alter the equation of the middle curve only by changing its constant coefficient.

Two things are apparent from the curve: (1) If there is a unique mobility, i.e., *no spectrum at all*, the lower break point will occur at the same voltage as the lower zero, and the upper break point will occur at the same voltage as the upper zero. The curves represented by Eqs. (4) and (6) will then become vertical straight lines, (see Fig. 6). This corresponds to saying that the i/i_0 curve will have no asymptotic feet. (2) At any constant speed the smaller the shutter is made the closer together will the two break points lie. Care must be taken not to make the shutter too small for it is possible to eliminate completely the middle curve, represented by Eq. (5), thus giving only one break point which has no significance with respect to the limits of the mobility spectrum.

One further point of great importance is the diffusion of the ions. The effect of diffusion on the curve will be to yield an apparent mobility spectrum, i.e., asymptotic feet on the i/i_0 curve and therefore a derivative curve like Fig. 5 rather than Fig. 6.

The chance that a molecule will move by diffusion in a time t from its position to any point between two parallel planes dx apart and at a normal distance x away, is given by[6,7]

$$[1/(4\pi Dt)^{1/2}]e^{-x^2/4Dt}dx$$

where D is the coefficient of diffusion and is given by $D=0.0236k$.[8]

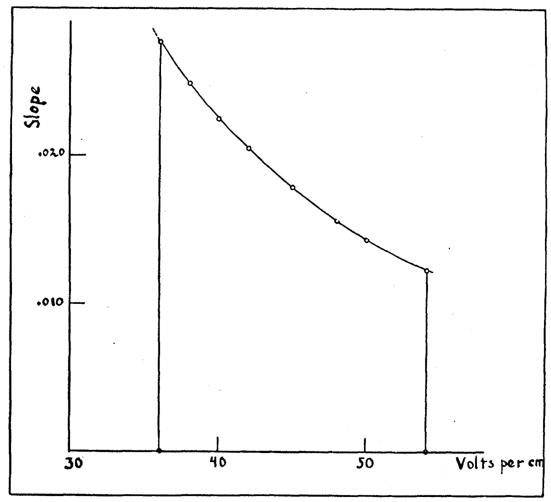

Fig. 6. This curve is represented by the equation $d(i/i_0)/dV = V_0/V^2$, and it is computed on the assumption that there is no mobility spectrum and no diffusion. The other conditions are the same as for Fig. 5.

In order, therefore, to get the number of ions which will diffuse from their non-diffused positions in a band of width αTVk to a distance equal to or greater than the remaining plate distance, the given probability must be integrated with respect to x between the limits $d-Vkt$ and infinity, and with respect to t from $T-\alpha T$ to T. This result must be multiplied by N_0 and divided by the elapsed time αT.

$$N = \frac{N_0}{\alpha T}\int_{T-\alpha T}^{T}\int_{d-Vkt}^{\infty}\frac{1}{(4\pi Dt)^{1/2}}e^{-x^2/4Dt}dxdt.$$

The integrations were performed with the aid of a table of values of the probability integral and by a standard method of approximation (Simpson's rule).

[6] J. Zeleny, Phys. Rev. **34**, 310 (1929).
[7] A. Einstein, Ann. d. Physik **17**, 558 (1905).
[8] L. B. Loeb, *The Kinetic Theory of Gases*, p. 451. McGraw-Hill, N. Y., 1927.

The minimum value of N/N_0, that could be detected by the apparatus was measured, and the value of x, where x is the distance of the upper edge of the undiffused band of ions from the upper plate, was calculated for this N/N_0. In other words, the distance was found to which the minimum detectable number of ions would diffuse. Now ions moved by diffusion as well as by electric forces may be regarded in exactly the same light as ions moving with an extended mobility spectrum. The fastest ions travel a distance $d+x$ while the slowest ions travel a distance $d-x$ under the same voltage. By applying the same method as was used in obtaining the theoretical mobility spectrum curve, it is apparent that under the force of the voltage V_0 the fastest and most diffused ions will travel a distance d, while the undiffused ions of greatest speed will travel a distance $d-x$; likewise, under the voltage V_1, the ions which have been diffusing backward with the greatest speed will have travelled a distance d (forward while the slowest undiffused ions travelled a distance $d+x$.

Therefore, $d-x=V_0k_1T$, and $d+x=V_1k_2T$ where k_1 and k_2 apply as previously defined to the undiffused ions. Thus k_1 and k_2 may be calculated from the voltages of the zeros and the break points (see Figs. 3 and 4).[9]

On applying the diffusion correction the results given in Table II were obtained (results A applying to ions in clean air, and B to ions in old and heavily irradiated air; k_1 and k_2 are in units of cm/sec. per volt/cm).

TABLE II. *Values of highest and lowest mobilities, after correcting for diffusion.*

	k_1	k_2	T	α	k_1-k_2
A	2.22	2.14	0.00580	7/60	0.08
	2.23	2.20	0.00586	7/60	0.03
	2.23	2.13	0.01150	1/6	0.10
	2.22	2.18	0.01150	7/60	0.04
	2.22	2.22	0.0117	7/60	0.00
	2.25	2.20	0.0280	1/6	0.05
	2.27	2.20	0.01148	1/6	0.07
B	2.4	2.0	0.0292	7/30	0.4
	2.4	1.86	0.0292	7/30	0.54

CONCLUSIONS

It is interesting to note that when the air is allowed to remain in the chamber for several sets of readings, a mobility spectrum appears as shown by the results in B above. The spectrum did not appear when air was left in the chamber for several days without exposure to ultraviolet light from the quartz-mercury arc. It was thus shown that ozone and the nitric oxides, which are formed in air in considerable quantity by the light from such an arc, cause a mobility spectrum. The very small residual spectrum that was found in A might be attributed to the inevitable presence of traces of these

[9] A consideration similar to the above applies to the case of the second break point and zero respectively, but these are not used because of the inaccurate knowledge of the exact time at which the shutter closes.

impurities, but it is much more likely due, in large part, to small instrumental irregularities in the measurements.

It is therefore safe to conclude that there was no mobility spectrum in air over the intervals studied, in terms of the magnitude of the spectrum asserted to exist by some writers,[4,10] if the air was relatively clean. An appreciable spectrum did appear after prolonged radiation. The resolving power of the method is excellent and is capable of greater refinement if needed. At the slowest shutter speed, a shift of one volt in the position of one of the critical points shifts the mobility by 0.085 cm/sec. per volt/cm while at the highest speed the mobility is only altered by 0.017 cm/sec. per volt/cm. The probable error in determining the derivative curve is between ± 0.15 volts and ± 0.20 volts, a small figure in consideration of the high resolving power. Whether greater refinement is desirable remains an open question because of the difficulties of accurately correcting for diffusion.

In conclusion, the writer wishes to express his indebtedness to Professor L. B. Loeb under whose direction and continual guidance the experiment was carried out, and to Mr. P. L. Porterfield, who assisted throughout the work. The writer is also grateful to Professor R. T. Birge for his instructions on the method of determining the probable errors and for his critical examination of the work of reduction of the observations.

[10] M. La Porte, Ann. de Physique **8**, 466, 711 (1927).