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THE EFFECT OF CHANGES IN THE PRESSURE AND TEMPERATURE OF GASES UPON THE MOBILITY OF THE NEGATIVE IONS PRODUCED BY ULTRA-VIOLET LIGHT.

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§ 1. INTRODUCTION.

THE experiments to be described in this paper had for their object the investigation of the changes produced in the ionic velocity by variations in the pressure and temperature of the gas. The ions used were the negative ones which are produced by ultra-violet light falling upon a negatively charged metal surface.

It is known that at very low pressures these ions are corpuscular in size, and if, when the gas is at atmospheric pressure, they consist of clusters of molecules about charged nuclei, as is generally believed, then evidently as the pressure is reduced the cluster must eventually fail to form. A study of the ionic velocity at different pressures should reveal whether a change in the size of the ion actually takes place, and if it does, whether the cluster gets smaller gradually as the pressure is diminished or whether the change in size is more or less abrupt.

Again, the size of the ion may depend upon the temperature, and a determination of the ionic velocity at different temperatures should throw some light upon this point.

In the present investigation the ionic velocity was determined in air and carbon dioxid for pressures between 8.8 mm. and 760 mm. of mercury, and in air at atmospheric pressure for temperatures between 84.5 and 698 degrees absolute.

Some results[1] on the effects of pressure and temperature upon the ionic velocity had been published already when these experiments were begun two years ago, and other papers[2] have appeared since, but the present results extend the ranges of the variations heretofore published and are not in complete agreement with some of the previous observations.

The subject matter will be treated under the following headings:

§ 2. Method.
§ 3. Pressure apparatus.
§ 4. Precautions aad corrections observed in the experiments.
§ 5. First pressure experiments in dry air and in dry carbon dioxid.
§ 6. Final experiments in dry air and in dry carbon dioxid.
§ 7. Temperature experiments.
§ 8. Summary and conclusion.

§ 2. Method.

The method used for determining the mobility of the ions is a modification of that used by Rutherford.[3] One of two parallel plates is illuminated by the ultra-violet light and charged with an alternating potential, and the electrical charge carried by the ions to the second plate is observed for different values of the alternating potential.

Let t be the half-period of the alternating field, u the mobility of the ions (*i. e.*, their velocity in a field of one volt per centimeter), P the potential difference between the plates, and d their distance apart. Then the space the ions will travel from the illuminated plate in the time t is

$$s = \frac{P}{d} ut.$$

While P is so small that s is less than d, no ions starting from the illuminated plate can get to the second plate before their motion is reversed by the reversal of the field. It is only after the potential

[1] Rutherford, E., Proc. Camb. Phil. Soc., Vol. 9. p. 401, 1898. Langevin, P., Ann. de Chimie et de Physique, 28, p. 289, 1903. Phillips, P., Proc. Roy. Soc., A, p. 167, 1906.

[2] Blanc, A., J. de Phys. (4), 7, p. 825, 1908. Wellisch, E. M., Proc. Camb. Phil. Soc., Vol. 15, p. 1, 1908; Phil. Trans., A, Vol. 209, pp. 249–279, 1909.

[3] Loc. cit.

has reached some value P_0, which makes s equal to d, that some of the ions which were produced at the beginning of an alternation can get across to the second plate before the field is reversed. As the potential is increased further, the quantity of electricity reaching the second plate should for a time increase regularly with the increase of potential, and finally when practically all of the ions produced by the light are carried to the second plate, any further increase in the potential should not alter the charge received.

If, therefore, values proportional to the charge received are plotted against the corresponding values of P, the curve should start as a straight line from the point P_0 on the axis of P and finally become horizontal. The experimental curve does not actually start as a straight line from P_0, for reasons given later, but it has a well defined straight portion which produced intersects the axis of potentials at P_0.

Knowing the value of P_0, the rate of alternation and the distance between the plates, the value of the mobility can be obtained from the relation

$$u = \frac{d^2}{P_0 t} = \frac{2nd^2}{P_0},$$

where n represents the number of alternations of the field per second.

§ 3. Pressure Apparatus.

The vessel in which the ionic velocity was measured at different pressures (see Fig. 1.) was made of a brass tube 10 cm. long and 10 cm. in diameter. The rear of the vessel was permanently closed by a heavy brass plate P having in its center an ebonite plug E forced into a brass collar. A brass rod R, holding the illuminated plate and strong enough not to bend appreciably when in a horizontal position, was screwed into the ebonite plug and had a wire leading to the source of potential. The zinc plate Z exposed to the light was 8 cm. in diameter, turned to a true plane and polished with a buffer and vienna lime. It had a ball and socket arrangement which permitted its plane to be adjusted by means of three srcews whose points rested against its rear face and passed through another plate rigidly fixed to a strong brass tube T which fitted over the rod R

to which it was firmly screwed when the zinc plate was set for any required distance from the opposite parallel plate. The fore part of the vessel was closed by a removable heavy brass plate having a circular groove cut in it to fit the cylinder. This cover could be brought tight against the cylinder by means of thumb screws *SS* fitted to four rods passing through the cover and extending to the rear plate on the outside of the vessel. The second of the parallel plates was a gauze *G* placed flush with the inner surface of the cover and had a ring of air one millimeter wide around it. The cover thus served as a guard ring. The gauze was made of No. 40 brass wire, two wires to a millimeter running in one direction only. It was held in position by a screw passing through an ebonite plug which was forced into a brass collar in the cover. A wire soldered to the screw led to the electroscope. A window 3.6 cm. in diameter was cut centrally with respect to the parallel plates and was closed by a quartz plate *Q* held in position by paraffin. The groove and all points of juncture were paraffined.

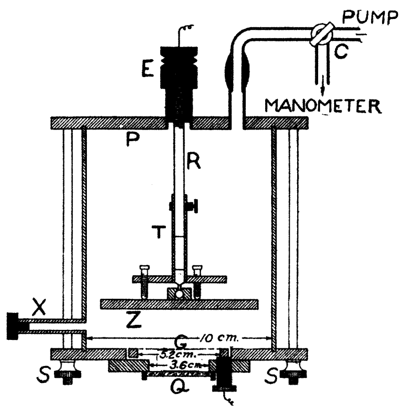

Fig 1.

A three-way stop-cock *C* was sealed with wax into the rear plate. One of its arms led to the manometers and another to the pump and source of supply of gases. An exit tube *X* was also provided in the fore part of the vessel. A diagram of the various connections is given in Fig. 2.

The mercury manometers used were the open air manometer *A* and the baromanometer *B*, the latter being used for pressures less than 150 millimeters. Readings were made by means of a cathetometer.

A C. T. R. Wilson's inclined electroscope *W* was used for the measurement of electric charges. An electroscope was chosen in preference to a quadrant electrometer because the inappreciable inertia of the leaf permits quick repetition of observations. The plate of the electroscope was connected to a series of 91 small lead accumulators *D*, the other pole of the series being connected to a slide movable over a high resistance *R* through which a current was continually flowing from a large chloride accumulator *F*, the positive pole of which was earthed. In this manner the zero could

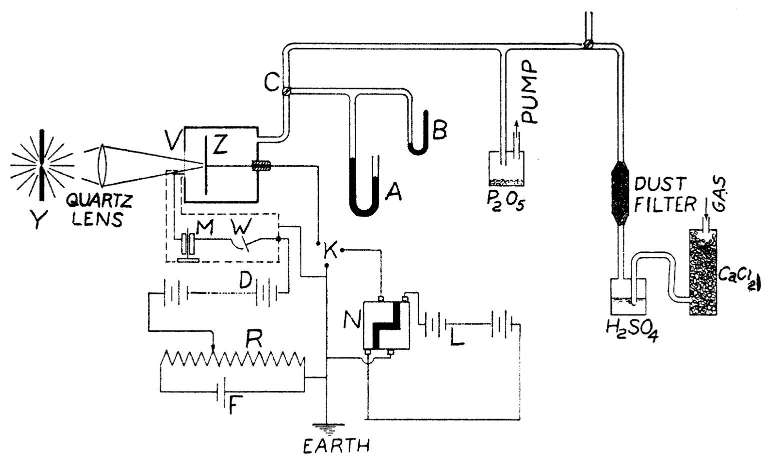

Fig. 2.

be easily kept fixed if for any reason the potential of the plate changed. The leaf was connected through a McLennan key *M* to the gauze of the testing vessel *V*. The sensitiveness of the electroscope was 17.5 divisions in the eye-piece for one volt, but only 5 divisions, corresponding to 0.35 volt, were used, as the sensitiveness over this distance was found convenient and also uniform.

The source of potential was a series of small lead accumulators *L*. The alternation of the field was brought about by a secohmmeter *N*. A triple key *K* was placed between the secohmmeter and the zinc plate, the third connection being to earth.

In the first experiments, the source of light *Y* was a spark between two zinc electrodes connected to the terminals of an induction coil. In the course of the investigation it was found that when synchronism existed between the alternation of the field and the intermittence of the light, the observations could not be depended upon. An arc between iron electrodes was consequently substituted for the spark. The light from the arc was generally not as steady as from the spark, but by giving it sufficient attention it could be kept fairly constant.

§ 4. Precautions and Corrections Observed in the Experiments.

1. A small portion of the light incident on the zinc plate strikes the walls of the vessel which are charged alternately positively and negatively by induction. Some of the ions thus produced reach the gauze. Again a certain number of the ions produced at the zinc diffuse toward the gauze. In both of these cases, the gauze will receive a charge even when the potential difference between the parallel plates is less than P_0. Evidently, the experimental curve showing the relation between the current and the potentials will begin with values of P smaller than P_0. The quantity of electricity due to these ions is generally very small compared with that due to the ions coming directly from the zinc plate and for this reason the straight line portion of the experimental curve obtained with potentials immediately above P_0 is readily separated from the curve below P_0.

It was also observed that when the zinc plate became coated with a film of oxide or of moisture, the gold leaf showed a charge opposite in sign to that which it received when the zinc plate acted photoelectrically. This is due to the production of negative ions at the surface of the gauze by the light reflected from the zinc plate and also by that directly incident upon it, thus charging the gauze to a positive potential. When the zinc is polished, the effect of the gauze in sending out ions toward the zinc on alternate intervals is to decrease the effect of the zinc by a certain per cent. The effect of this in the curve is to decrease each ordinate by a fixed per cent. of itself, which alters the slope of the straight line portion of the curve without altering the intersection with the axis of potentials, *i. e.*, P_0 is unaffected by this phenomenon. This point was carefully tested by coating the gauze and the interior of the vessel with lamp black.

2. It was observed that with a slow rate of alternation of the field — *i. e.*, when the time required by the ions to pass between the plates was large — the velocity obtained was smaller than with a

high rate of alternation. At atmospheric pressure the difference between the values obtained is quite small but at low pressures it is very pronounced. This behavior is probably due to the diffusion of the ions to the sides.[1] It is however possible that if the ions are complex, they require a time comparable to that used in the experiments to grow to the final size, in which case also the value of the velocity with the long time of passage between the plates should be smaller than with the short time. When the values of the velocity were plotted against the time required for the ions to cross the field, the distribution was found to be linear and by producing the straight line thus obtained until it intersected the ordinate at the time $T = 0$, a value of the velocity was found which in each case was used as the desired velocity. It was therefore necessary to obtain values for the mobility using different rates of alternation and hence different values of T.

3. The use of a guard ring, small distances between the plates and a large zinc plate insured a uniform field. The ions were made to move, in most of the experiments, in the central portion, by having only a small central area of the zinc illuminated. This was brought about by a quartz lens in front of the apparatus.

No tests were made on the non-uniformity of the distribution of potential between the plates.[2] Experiments were, however, performed with different intensities of light but the value of the velocity was found to be unaffected by such changes. No correction was, therefore, made in the calculation.

4. The source of light is, of course, subject to changes in intensity but these changes were greatly obviated by proper attention. However, the readings were taken in such a manner as to minimize any errors arising from any changes in the intensity occurring during an experiment. Sometimes readings were taken with increasing potentials and then decreasing, the mean for any potential being used as the final value. Generally, however, some high potential was chosen and readings taken for this potential were considered as control readings. The control readings preceded and followed

[1] See also J. Zeleny, Phil. Trans., A, 195, p. 193, 1900.

[2] Zeleny, J., Phil. Mag., 46, p. 120, 1898. Childs, Wied. Ann., 65, p. 152, 1898. Schweidler, quoted by Prof. Thomson, Cond. of Elect., p. 260. Buisson, H., C. R., CXXVII., p. 224, 1898.

each individual reading for any potential. Then by interpolation all the readings were reduced to some uniform value of the control reading. In this manner any gradual changes in the intensity of the light during any one reading could be readily corrected. This plan of taking readings also corrects for the photo-electric fatigue when this is small; and it was found to be small, after the plate had been exposed to the light for some time. Tests on this point were made in air and in carbon dioxid, at atmospheric pressure and at low pressure.

5. On account of electrostatic induction the potential difference between the parallel plates is less than the potential of the zinc plate. The amount of the diminution can be readily found experimentally. This it shown by a specific example. The gauze at zero potential was insulated from the earth. The zinc plate then received a charge from 8 cells equivalent to 16.6 volts, and the leaf of the electroscope became deflected 8.8 divisions equivalent to 0.558 volt. The induction was, therefore, $0.558/16.6 = 3.37$ per cent. Using 22 cells $= 45.6$ volts, the deflection was 32 divisions $= 1.55$ volts, and the induction was $1.55/45.6 = 3.4$ per cent. Consequently, the value of P_0 obtained from the curve had to be diminished by 3.4 per cent., the distance between the plates in this case being 19.34 mm.

It is evident that on account of this induction the leaf will vibrate with the alternation of the field. The amount of this vibration depends on the induction, rate of alternation and the inertia of the leaf. In the present investigation it was found that for the potentials and the rate of alternation used, the vibration of the leaf could hardly be noticed. Exceptions noted are the ones with a very low rate of alternation and when the plates were very close together; but even in these cases, readings were easily taken as the vibration of the leaf did not exceed one half of a scale division. In these cases the mean position of the leaf had to be estimated.

6. The method used demands an equality of time for the opposite directions of the field. This depends on the secohmmeter itself and on the uniformity in the rate of rotation. If the brushes were not placed correctly or if they formed a poor contact with the segments, the leaf of the electroscope showed a "kick" to one side at the

moment when the zinc received the alternating charge. The "kick" is due to unequal induction. It was also noticed at times that the contact of the brushes with the segments produced a difference of potential which was also registered by a "kick" of the leaf. The former was remedied by careful adjustment of the brushes and the latter by cleaning the brushes and the segments, and rubbing both with paraffin oil,[1] carefully removing all excess.

It is here supposed that the field was fully established as soon as the brush came in contact with the segment of the secohmmeter. A water resistance always kept between the brush and the zinc plate was taken out and no difference was observed in the values of the mobility. Presumably then, the field establishes itself practically instantly through the resistance.

The alternating potential through the brushes was taken on a static voltmeter on different occasions and was found to correspond to the reading from a current voltmeter applied directly to the cells.

7. When there is an excess of ions of one kind in a gas, a force is exerted on the gas in these regions, which will produce a motion of the gas when the ions are in motion. A current of gas of this kind has been observed by Zeleny.[2] The motion of the gas is, however, very small in comparison with the velocity of the ions and the correction for it may be left out of account.

Convection currents due to difference of temperature in various parts of the field undoubtedly existed in a few of the temperature experiments. These will be noted in their proper place.

8. The reliability of the method used was tested by varying the distance between the plates, by varying the intensity of the incident light, and by changing the apparatus itself. In view of the fact that the values of the mobility of the ions in air at atmospheric pressure were all concordant under these various changes, it is believed that the method used is accurate.

9. In the experiments with dry gases the air was slowly passed into the exhausted vessel through a series of purifying and drying agents arranged as follows: potassium permanganate with dilute sulphuric acid, concentrated potassium hydroxid, calcium chloride,

[1] Allen, H. N., The Electrician (London), Vol. XXXIX., p. 379, 1897.

[2] Zeleny, J., Proc. Camb. Phil. Soc., X., p. 14, 1898.

concentrated sulphuric acid, and cotton; the carbon dioxid passed through the same series with the hydroxid omitted. The vessel was refilled with the gas 5 to 10 times before readings were taken at any pressure.

10. It hardly seems necessary to remark that due precautions were taken to carefully screen those portions of the apparatus requiring shielding from outside electrostatic disturbances.

§ 5. First Pressure Experiments.

Dry Air. — In the first experiments a spark was used as the source of light, the intensity of which varied very little. Only one set of readings was taken to obtain the value of the mobility. A set illustrating the readings and the calculation is given below.

Table I.

Pressure = Barometric reading = 734.0 mm.
Temperature = Room temperature = 24°.0 C.
5,000 alternations of the field in 139.0 sec. (beginning), 139.2 sec. (end), 139.1 sec. (mean),
or 35.95 alternations per second.
100 cells = 215.8 volts.
Distance between the parallel plates = 19.34 mm.

Potential of the Plate.	Time to Deflect Leaf 25th to 30th Division.		Reciprocal of the Time × 10^4.
60 cells	485.0	485.0 sec.	21
70	90.0		
	90.0	90.0	111
80	44.2		
	42.8		
	45.0	44.0	227
90	29.4		
	31.6		
	30.8	30.6	327
100	24.0		
	24.0		
	24.0	24.0	417
95	27.0		
	27.0		
	27.0	27.0	370
85	36.2		
	37.2	36.7	272
75	60.4		
	60.4	64.0	165
65	166.2	166.2	60

The reciprocal of the time is plotted against the potential in Fig. 3. The straight line portion of the curve intersects the axis of the

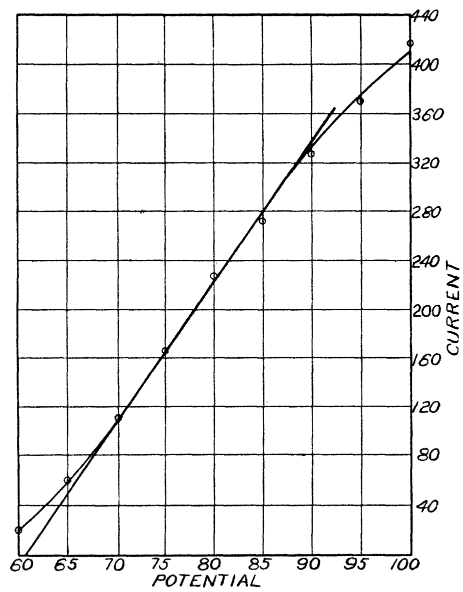

Fig. 3.

potentials at $P_0 = 60.7$ cells $= 131.0$ volts. The correction for the induction, as explained in § 4, 5, is 3.4 per cent. when $d = 19.34$ mm. and is, therefore, 4.5 volts. Hence,

$$P_0 = 131.0 - 4.5 = 126.5 \text{ volts.}$$

Substituting in the equation

$$u = \frac{2nd^2}{P_0},$$

we get

$$u = \frac{2 \times 35.95 \times 1.934 \times 1.934}{126.5}$$

$$= 2.13 \text{ cm. per sec. per volt per centimeter.}$$

The mobility will in each case be reduced to what it would be at a pressure of 760 mm., on the supposition that the mobilities at two pressures are inversely proportional to the pressures. The mobility at 760 mm. pressure thus obtained will be designated by v. In the above example

$$v = \frac{u \times p}{760} = \frac{2.13 \times 734}{760} = 2.06 \text{ cm. per sec.}$$

Table II. gives the collected data for various pressures for dry air when $d = 19.25$ mm.

Table II.

Dry Air. Light from Spark Used. $d = 19.25$ *mm.*

p	t	T	n	P_0	u	v
746.0	20.0° C.	0.0129	38.7	133.4	2.15	2.11
743.4	19.0	.0100	49.5	180.4	2.03	1.98
735.0	20.0	.0078	64.0	224.0	2.12	2.05
736.0	20.0	.0125	40.2	143.5	2.06	2.00
734.0	24.0	.0139	35.95	123.7	2.16	2.08
510.5	20.0	.0080	62.5	146.6	3.16	2.12
408.1	19.0	.0080	62.0	121.3	3.78	2.03
268.5	20.0	.0079	63.5	78.4	6.00	2.12
207.9	20.0	.0083	60.6	61.0	7.35	2.01
180.4	24.0	.0079	63.7	48.3	9.75	2.31
169.3	19.0	.0081	61.9	45.0	10.4	2.32
166.0	25.0	.0079	63.5	45.6	10.3	2.25
140.2	20.0	.0079	62.8	36.3	12.8	2.36
90.3	20.0	.0084	59.3	20.34	21.6	2.57
64.0	20.0	.0104	48.0	10.88	32.7	2.76
53.9	21.0	.0080	62.3	9.64	48.0	3.40
36.0	19.5	.0079	63.5	4.59	102.4	4.85
27.7	21.0	.0080	62.3	3.47	133.0	4.84
11.4	20.0	.0079	63.3	1.16	404.0	6.07

The results of this table are shown graphically in Fig. 4. The curve shows that v is independent of p between the pressures 760 mm. and about 200 mm. At 200 mm. the curve rises somewhat, and at 100 mm. it passes through a pronounced bend. This rather sudden change in the mobility v indicates that near this pressure there is a rapid change in the mass of the ion, *i. e.*, the number of molecules which are supposed to be gathered about a central charge to form the ion rapidly diminishes on the average ion as the pressure is reduced below 100 mm.

Carbon Dioxid. — Readings similar to those for air were also taken for carbon dioxid. A set of these is given in Table III.

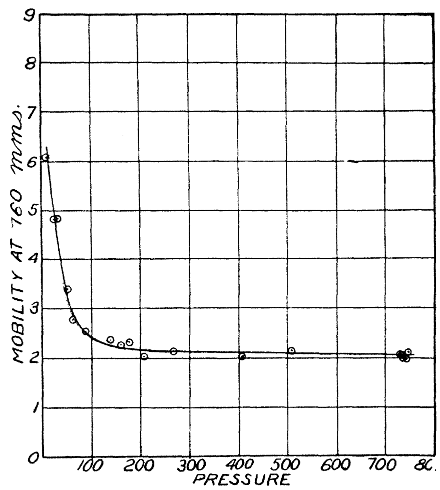

Fig. 4.

TABLE III.

Dry Carbon Dioxid. Light from Spark Used. $d = 19.25$ *mm.*

p	t	n	P_0	u	v
739.0	20.0°	18.3	148.2	0.91	0.88
755.0	21.0	19.0	149.0	0.94	0.93
755.0	20.0	19.0	144.0	0.98	0.97
754.0	20.0	23.2	188.0	0.91	0.90
748.0	20.0	18.8	144.0	0.97	0.95
748.0	21.0	32.3	253.6	0.95	0.93
447.6	21.0	23.4	121.2	1.43	0.84
402.0	20.0	49.1	177.0	2.05	1.09
323.0	21.0	35.2	115.6	2.26	0.96
299.7	20.0	49.0	128.6	2.82	1.11
266.6	22.0	47.9	132.7	2.67	0.94
187.0	21.0	35.3	53.4	4.90	1.21
150.0	22.0	47.8	54.8	6.45	1.27
118.0	20.0	61.7	50.8	9.00	1.40
102.1	22.0	47.7	32.4	10.9	1.46
77.1	19.0	47.7	22.5	20.7	2.10
62.5	22.0	62.9	11.92	29.6	2.43
58.2	20.0	63.0	12.55	37.2	2.85
38.2	20.0	62.9	4.06	114.2	5.75
25.4	22.0	47.7	1.34	264.0	8.80

The values of v are plotted against p in Fig. 5. It will be noticed that here also there is a sudden change in the mobility v.

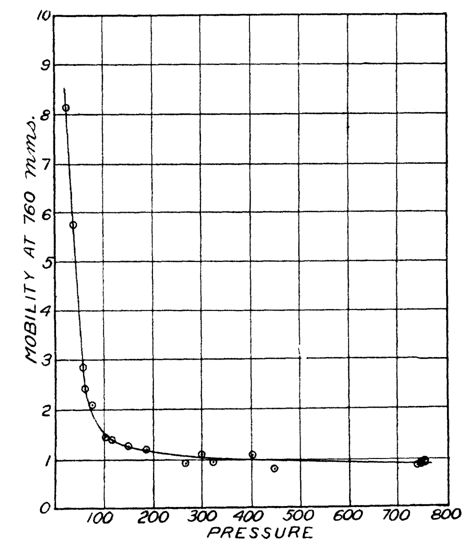

Fig. 5.

§ 6. Final Pressure Experiments.

Dry Air. — In the final experiments all the precautions noted in § 4 were carefully observed. An arc between iron electrodes was used as the source of light in all of these experiments. The rate of alternation of the field was changed a sufficient number of times in each pressure experiment to permit the determination of the value of the mobility at $T = 0$, vide § 4, 2. An illustration of the general method of taking the readings with the arc as the source of light is given in Table IV(a).

The readings in Table IV(a) were next reduced and corrected for the changes in the intensity of the arc, vide § 4, 4. These results are tabulated in Table IV(b), 2,400 being taken as the current corresponding to the highest potential, namely 15 cells.

The curve showing the relation between the potential and the current is given in Fig. 6. The straight line portion of the curve produced intersects the axis of the potentials at 8.68 cells. The correction for induction is 3.4 per cent. The value of P_0 is therefore 8.38 cells or 17.27 volts.

Table IV(*a*).

Dry Air. Fe Arc Light. $d = 19.34$ *mm.*

Baromanometer reading = 97.8 mm.
20 cells = 41.2 volts. Temperature = 24°.0 C.
5000 alternations of the field in 104.4 sec. (beginning),
104.4 sec. (end),
104.4 sec. (mean),
or $n = 47.8$ per second.

Potential of the Plate.	Time to Deflect Leaf 25th to 30th Division.		Reciprocal of the Time $\times 10^4$.
15 cells	4.4		
	4.6		
	4.6		
	4.6		
	4.4		
	4.2	4.47	2,237
10	20.2		
	18.6		
	18.0		
	20.4	19.3	518
15	4.4		
	4.0		
	4.4		
	4.2	4.25	2,353
12	9.4		
	9.2		
	8.0		
	7.4	8.50	1,176
12	6.6		
	6.8		
	6.8	6.73	1,486
15	3.8		
	3.8	3.8	2,632
8	44.6		
	42.4	43.5	230
15	3.8		
	4.0		
	3.6	3.8	2,632
7	98.0	98.0	102
15	3.8		
	3.8	3.8	2,632
9	24.6		
	23.8	24.2	413
15	3.6		
	3.6		
	3.6	3.6	2,778
11	8.8		
	9.2		
	9.4		
	10.0	9.35	1,070
15	4.2		
	4.0		
	3.8		
	3.8		
	4.0	3.96	2,525
13	5.8		
	5.6		
	5.6	5.67	1,764
15	4.0		
	4.0		
	4.0	4.0	2,500
10	18.0		
	16.8		
	17.0	17.3	578
15	4.0		
	4.0	4.0	2,500
8	53.0		
	59.0	56.0	179
15	4.4		
	4.4	4.4	2,273
12	8.4		
	8.0		
	7.8	8.07	1,239
15	4.4		
	4.4	4.4	2,273
14	5.0		
	5.0	5.0	2,000
15	4.6		
	4.6		
	4.4		
	4.6	4.55	2,198

Table IV(*b*).

Alternating Potential.		Current in Arbitrary Units.
15 cells.		2,400
10		542
12	1,132	1,281
12	1,430	
8		210
7		93
9		362
11		969
13		1,688
10		555
8		180
12		1,309
14		2,146

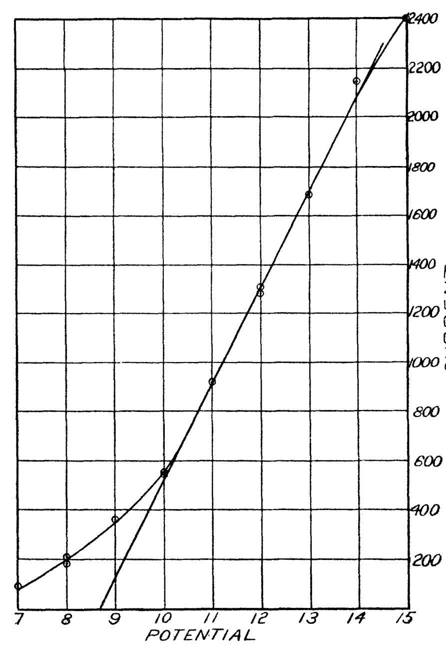

Fig. 6.

Now,

$$u = \frac{2nd^2}{P_0}$$
$$= 20.7 \text{ cm. per sec.,}$$

and

$$v = \frac{u \times p}{760}$$

$$= \frac{20.7 \times 97.8}{760},$$

$$= 2.67 \text{ cm. per sec.}$$

The time for the ions to cross the field is

$$T = \frac{1}{2} \times \frac{1}{5,000} \times 104.4$$

$$= 0.01044 \text{ second.}$$

In a similar manner, the values of the mobility for other rates of alternation of the field were obtained using the same air pressure; and these are given in Table V.

Table V.

Dry Air. $p = 97.8$ *mm.* $t = 24°.0$ *C.* *Arc*

T	u	v
0.0076	22.4	2.88
.0104	20.8	2.68
.0148	19.2	2.47
.0209	17.3	2.23
.0266	16.4	2.11

A set of results for dry air at atmospheric pressure and room temperature is given in Table VI.

Table VI.

Dry Air. $d = 19.235$ *mm.* *Arc Light.*

T	n	p	t	P_0	u	v
0.0077	64.5	739.0	19°.0	229.0	2.08	2.02
.0077	64.5	754.0	22.5	230.8	2.08	2.06
.0104	47.9	739.0	19.0	174.0	2.04	1.98
.0126	39.56	739.0	23.0	134.0	2.18	2.12
.0130	38.5	738.0	23.0	140.0	2.04	1.98
.0149	33.67	739.0	24.0	116.4	2.12	2.06
.0183	27.3	739.0	25.0	97.0	2.08	2.02
.0275	18.2	742.2	22.0	65.4	2.06	2.01
.0282	17.76	739.0	25.0	63.0	2.08	2.02
.0294	17.01	739.0	25.0	60.7	2.07	2.02
.0328	15.30	742.0	23.0	52.3	2.16	2.10
.0354	14.12	754.0	22.0	54.0	1.94	1.92
.0401	12.47	742.2	23.0	43.7	2.11	2.06
.0459	10.92	742.0	23.0	39.3	2.06	2.01

The graphical representation of the values of v for the various values of T is shown in Fig. 7. The curve in this case is a horizontal

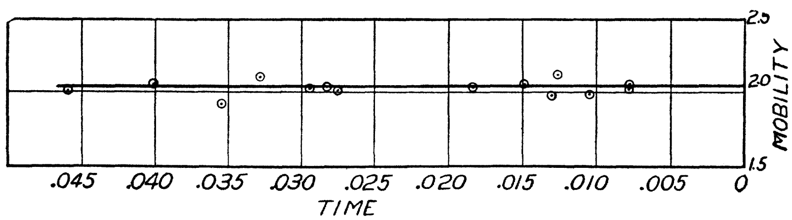

Fig. 7.

straight line which intersects the ordinate for $T = 0$ at a point $v = 2.04$, which is the value taken for the mobility.

A similar set of readings at atmospheric pressure was taken when the distance between the plates was 6.854 mm. In this set the illuminated area of the zinc plate was nearly the size of the gauze This may account for the greater slope of the curve on account of diffusion to the sides, vide § 4, 2. The readings are given in Table VII. and the corresponding curve is given in Fig. 8. The value of the mobility obtained from this set is 2.05 cm. per second.

TABLE VII.

Dry Air. $d = 6.854$ *mm.* *Arc Light.*

T	n	p	t	P_0	u	v
0.00776	64.4	738.0	23.0	28.28	2.14	2.07
.00795	62.8	725.0	22.0	27.2	2.16	2.07
.00795	62.9	722.0	24.0	27.7	2.13	2.02
.0090	55.56	738.0	23.5	24.8	2.10	2.05
.0103	48.5	722.0	24.0	21.7	2.10	2.00
.0117	44.7	722.0	24.0	20.2	2.08	1.98
.0135	37.1	722.0	25.0	16.37	2.13	2.03
.0146	34.13	738.0	23.5	15.67	2.05	1.99
.0172	29.0	735.0	24.0	14.09	1.94	1.88
.0188	26.6	738.0	23.0	12.76	1.96	1.90
.0203	24.63	738.0	23.0	11.70	1.98	1.92
.0230	21.7	738.0	23.0	10.44	1.95	1.90
.0233	21.46	738.0	23.0	10.30	1.96	1.90
.0266	18.8	738.0	23.5	9.21	1.92	1.86
.0253	19.76	735.0	24.0	9.23	2.01	1.94
.0280	17.83	738.0	23.0	7.66	2.18	2.12
.0343	14.58	722.0	24.0	7.16	1.92	1.82
.0362	13.8	735.0	24.0	6.88	1.89	1.82
.0404	21.39	738.0	23.0	5.77	2.02	1.95

Table VIII. gives the collected values of the mobility at atmospheric pressure, reduced to 760.0 mm., obtained under various conditions. In numbers 1 and 2 the apparatus used was that employed in the pressure experiments while in the numbers 3, 4 and 5, the apparatus used was the one constructed for the temperature experiments. In number 3 the gauze and the interior of the vessel were covered with lamp black whereby the effect of the reflected light

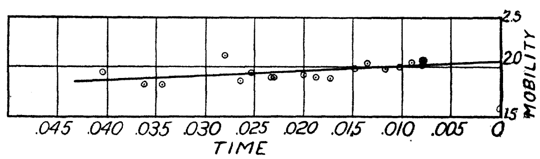

Fig. 8.

was reduced to a minimum. Zinc, platinum and brass were used as metals for the illuminated plate. It will be noticed from the table that the change of metal had no effect on the velocity. This was observed by Rutherford.[1] The agreement in the values of the mobility for the different distances between the parallel plates adds weight to the accuracy of the method.

Table VIII.

Dry Air. Atmospheric Pressure. Room Temperature.

No.	d	Metal.	v at 760 mm.	t	Remarks.
1	19.34 mm.	Zinc	2.04	20.0°	Pressure apparatus.
2	6.854	Zinc	2.05	23.5	
3	18.70	Platinum	2.05	21.0	Temperature apparatus.
4	18.70	Brass	2.05	24.0	
5	9.93	Brass	2.02	20.0	
			2.04 = mean		

The experiments with the variation of the intensity of light were performed with a fixed distance of 19.24 mm. between the plates and a fixed rate of alternation of 64.5 per second. The intensity of the light was changed in two ways, namely, either by screening off some of the light incident on the quartz lens or by changing the position of the arc relative to the apparatus. With weak intensities,

[1] Rutherford, E., Proc. Camb. Phil. Soc., IX., p. 401, 1898.

the motion of the gold-leaf of the electroscope was slow and fewer divisions on the scale were taken than generally (the scale divisions having a uniform value in the portion of the scale used), and with strong intensities an air condenser was put in parallel with the gauze to decrease the motion of the leaf. The intensity was calculated from the effect it produced and the one with the smallest effect was taken as unity. In order to compare the intensities, readings in each case were taken for a potential difference of 160 cells. Table IX. gives the results of the experiments. It will be noticed that the variation of the intensity has no effect on the value of the mobility. In numbers 6 and 7 the arc was close to the apparatus and the whole of the quartz plate was illuminated.

TABLE IX.

Dry Air. $d = 19.24$ *mm.* $n = 64.5$ *Alternations per Second.* *Potential* = 160 *Cells.* *Arc Used.* $p = 730.0$ *mm.* $t = 22°.0$ *C.*

No.	Deflection.	Time for the Deflection.	Capacity in E.S. Units.	Intensity of Light.	Mobility at 760 mm.
1	25–28 div.	34.0 sec.	30	1.00	2.05
2	25–27	17.1	30	1.30	2.05
3	25–28	19.0	30	1.79	2.04
4	25–27	10.0	30	2.27	2.05
5	25–30	25.9	68	4.96	2.04
6	25–30	11.55	57	9.30	2.02
7	25–30	11.7	295	47.5	2.02

The intensity generally used corresponds to that in number 4.

Change of Pressure in Air. — The values of the mobility at different pressures were obtained in the same manner as those obtained at atmospheric pressure.

The set of results given in Table X. is one of a number of such sets that were obtained and it was chosen because in this set the conditions of illumination were uniform, for which reason a comparison of the inclination curves for the different pressures can be made (vide Fig. 10). The column designated "tan a" represents the inclination of the straight line which determined the value of v at $T = 0$, and is the ratio of the increase of the mobility divided by the change of time to cross the field.

TABLE X.

Dry Air. $d = 19.34$ *mm.* *Arc Light.*

p	t	u	v	tan a
750.0 mm.	23.0° C.	2.07	2.04	1.0
547.4	21.5	2.79	2.01	2.0
316.0	22.0	4.93	2.05	2.8
215.3	24.0	7.49	2.12	11.8
160.0	19.5	10.9	2.30	19.6
125.0	23.0	15.2	2.50	27.1
97.8	24.0	24.6	3.16	37.6
77.0	23.0	42.9	4.34	62.5
51.8	21.0	90.0	6.14	116
34.0	24.0	180.0	8.05	178
16.0	24.0	470.0	9.90	230
8.8	26.5	1,800.0	20.8	614

The relation between the reduced mobility v and the pressure is shown in Fig. 9. From 760 mm. to 200 mm. the curve is linear

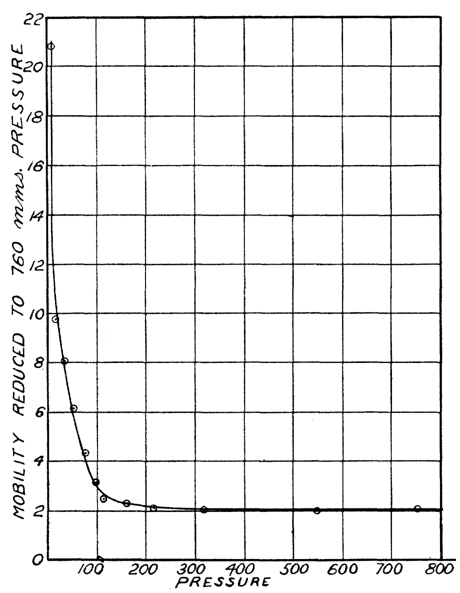

Fig. 9.

and nearly parallel to the axis of pressures, which indicates that the mobility u varies inversely with the pressure. At 160 mm. the value v is 12 per cent. higher than at atmospheric pressure, at 125 mm. it is 22 per cent. higher, at 100 mm. it is 55 per cent. higher, at 77 mm. it is more than double the value at atmospheric pressure, and at 8.8 mm. it is ten times that value. The curve shows a marked bend at a pressure of about 110 mm. and below this pressure it rises rapidly. The mobility below this pressure changes far more rapidly than the inverse-pressure law indicates. The comparatively sudden change in the velocity at 110 mm. pressure is very suggestive of a sudden change in the constitution of the ion, as if, at this pressure, the complex structure suddenly disintegrated. As there is a sudden change in the mobility of the ions there should be a sudden change in their coefficient of diffusion. This phase of the problem was not studied, but the curve of Fig. 11, in which "tan a" is plotted against the pressure, may point in that direction.

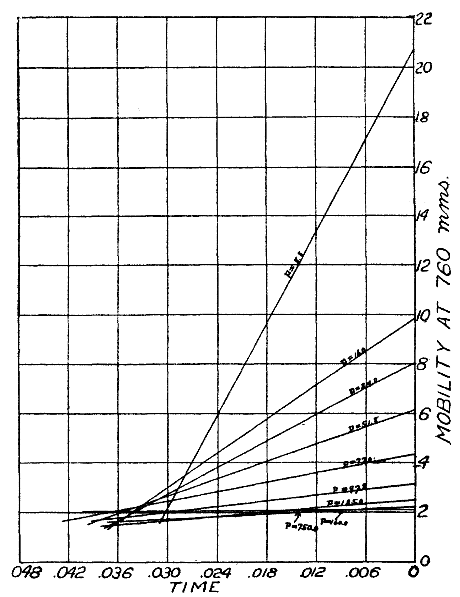

Fig. 10.

Dry Carbon Dioxid. — Experiments on the velocity of the negative ions in carbon dioxid at various pressures were performed in the same manner as the experiments on the velocity in air. Ordinary liquid carbon dioxid was used and on testing it by the absorption method, it was found to be 99.6 per cent. pure . Several curves were obtained for the relation between the mobility reduced to 760 mm. and the pressure, all having the characteristic bend at low pressures noticed in the curves for air. All but one of the curves were like the one shown as curve *I* in Fig. 12, having the bend at about 150 mm. and rising much more suddenly than was the case with air. In the exceptional case noted, shown as curve *II*, Fig.

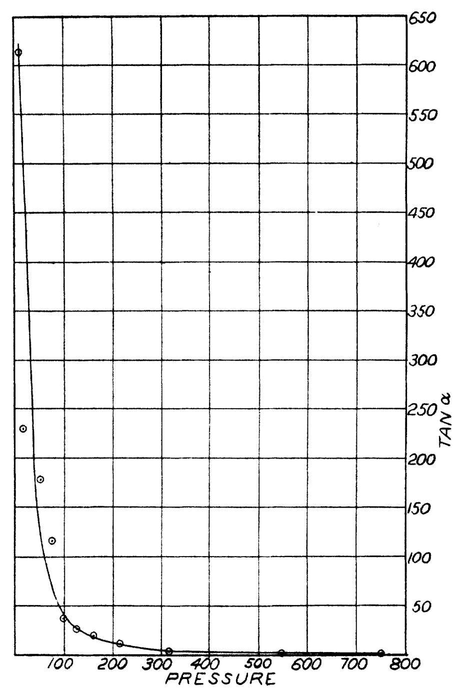

Fig. 11.

12, the bend is at a much lower pressure and the curve otherwise also resembles more closely the one for air. The reason for this is not known unless it be due to some impurities, for the gas used in this set was the last supply in the tank and its purity was unfortunately not tested. The results corresponding to the curves *I* and *II*, Fig. 12, are given in the table below.

For the curve *I* the per cent. of increase above that at atmospheric pressure is 80 per cent. at 154 mm., 170 per cent. at 118 mm.

and 600 per cent. at 88 mm., while for the curve *II* it is 24 per cent. at 176.6 mm., 50 per cent. at 87 mm. and 700 per cent. at 17 mm. The per cent. of increase in the value of v with the diminution of pressure over the value at atmospheric pressure is greater throughout in the case of carbon dioxid than in the case of air.

Table XI.

Dry Carbon Dioxid. Arc Light. $d = 19.34$ *mm.*

Curve I.

p	t	u	v
738.0 mm.	22°.0 C.	1.04	1.01
362.0	21 5	2.22	1.06
257.0	22.5	3.72	1.26
197.3	21.0	4.65	1.20
154.0	23.0	8.93	1.81
118.0	23.0	17.7	2.74
118.0	23.0	17.4	2.69
88.5	24.0	57.5	6.70
66.9	24.0	222.0	19.6

Curve II.

738.0	22.0	1.04	1.01
501.2	20.5	1.66	1.09
362.0	20.0	2.20	1.05
176.6	21.0	5.37	1.25
139.0	21.0	7.43	1.36
109.5	21.0	9.56	1.38
87.0	21.0	13.2	1.51
52.4	20.0	33.5	2.31
20.0	21.0	100.5	3.70
17.1	21.0	366.0	8.24

Experiments with Moist Gases. — It was observed by Zeleny [1] that the presence of moisture in gases decreases the mobility of the negative ions. Professor Zeleny in his paper expresses the view that the molecules of aqueous vapor collect upon the negative ion which, thus loaded, necessarily moves slower. Similar observations on the decrease of the mobility of the ions in vapors of ether and alcohol

[1] Zeleny, J., Phil. Trans., A, 195, p. 193, 1900.

were made by Rutherford,[1] and recently Blanc[2] reported similar results.

Experiments with moist gases were performed at atmospheric pressure and room temperature. The gases, air and carbon dioxid, were saturated with aqueous vapor by passing them through a flask containing boiling water and then through a flask containing water at room temperature. A difficulty in carrying out the experiments

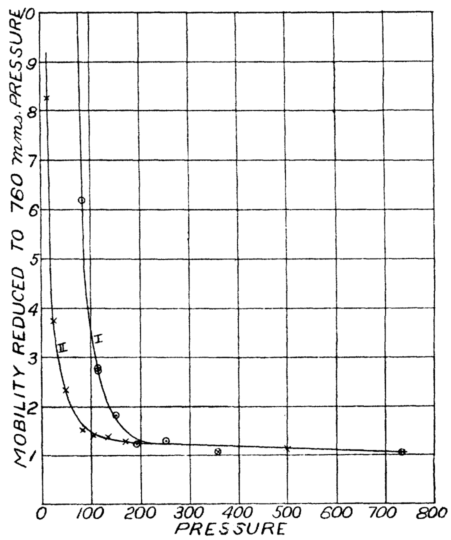

Fig. 12.

was at first encountered for zinc covered with a layer of moisture will not act photo-electrically. By increasing the intensity of the light, it was noticed that the gauze produced enough photo-electric effect (vide § 4, 1) to make it possible to take readings. The leaf of the electroscope became in these cases, of course, charged positively. This action of the brass wire gauze seemed strange in view of the fact that metals covered with moisture are reported to cease acting photo-electrically, as indeed zinc does. It may, therefore, be of interest to note that by covering the zinc with a sheet of brass, the photo-electric effect in gases saturated with water vapor appeared the same as in dry gases. The readings, however, were taken by

[1] Rutherford, E., Phil. Mag., VI., 2, p. 210, 1901.
[2] Blanc, A., J. de Physique, 4, 7, p. 825, 1908.

utilizing the effect from the gauze. The results for moist air are given in Table XII. and for moist carbon dioxid in Table XIII. The linear distribution of the mobilities gives a horizontal line, which in the case of moist air intersects the ordinate for $T = 0$ at $v = 1.64$ cm. per sec. and in the case of moist carbon dioxid at $v = 0.806$ cm. per sec. It will thus be noticed that the velocity of the negative ions both in moist air and in moist carbon dioxid is 20 per cent. below the value in dry air and in dry carbon dioxid, respectively.

TABLE XII.

Moist Air. Arc Light. Gauze = Source of Negative Ions. Pressure = 745.4 mm. Temperature = 26°.0 C.

T	u	v
0.0076	1.66	1.63
.0098	1.60	1.57
.0139	1.72	1.68
.0173	1.72	1.68
.0212	1.77	1.74
.0267	1.55	1.52

TABLE XIII.

Moist Carbon Dioxid. Arc Light. Gauze = Source of Negative Ions. Pressure = 740.0 mm. Temperature = 25°.0 C.

T	u	v
0.0270	0.824	0.802
.0218	.832	.800
.0175	.816	.795
.0138	.850	.828

§ 7. CHANGE OF TEMPERATURE EXPERIMENTS.

High Temperature. — The apparatus used in the final temperature experiments, both at high and low temperatures, is shown in Fig. 13. The gauze G was fastened by its wires to a piece of tubing T, 3 cm. in diameter, which was held in position by 3 quartz rods Q from brass blocks adjustable on the front face plate of the apparatus. The gauze was set so as to be in the plane of the inner surface of the plate, and it had a ring of air 1 mm. wide around it. The plate to be illuminated P was held in position by 3 glass rods R passing through cleaved collars. The front plate screwed into a brass cylinder B. The whole apparatus could be readily placed in position in the oven by an iron rod A screwed into the front plate. The heating electric oven had a porcelain cylinder 600 mm. long and 80 mm. in diameter. The heating current was generally an alternating current. The interior of the porcelain cylinder was lined with a sheet of brass connected to earth so as to avoid induction effects from the heating current which were very marked when the screen was omitted.

The apparatus was placed in the middle of the oven. Several centrally perforated discs of asbestos were placed inside the oven at both ends of the apparatus and at some distance from each other, so as to break up any air currents inside the oven and to prevent changes of temperature.

The ends of the porcelain cylinder were closed quite tightly by means of brass covers, allowing only a small leak for the equalization of the pressure with the outside. One of these covers was provided with a quartz plate to allow transmission of the light, and an ebonite plug (quartz and glass tubes were also used instead of the ebonite plug in some experiments) for the wire leading to the electroscope; the other cover had a glass window (used for viewing the interior) and two tubes used respectively for a wire leading to the secohmmeter and for a clay tube containing the thermo-couple used for measuring the temperature. The junction was placed in contact with the rear central portion of the illuminated plate.

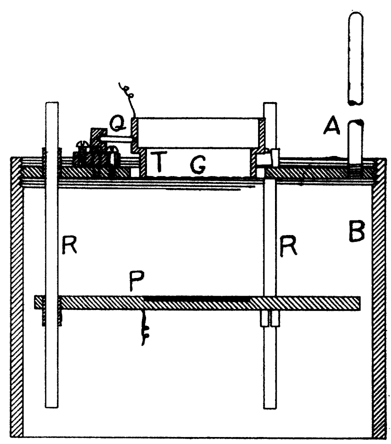

Fig. 13.

Observations were not carried above 425° C. because of a leak through the quartz rods at higher temperatures. The leak of an electric charge from the electroscope through the quartz rods was studied and found to increase with the increase of temperature, becoming very fast indeed at about 425° C. It was found to obey an exponential law, and for this reason it was utilized in taking a few readings at high temperatures by the constant deflection method.

The readings so taken give the values in numbers 1, 2 and 9, Table XIV. The remaining readings were taken by the rate method, as before.

Low Temperatures. — The apparatus was placed in a tin can through whose cover all the wires passed out. Between the apparatus and the cover were several discs of paper to break up currents of air. Phosphoric anhydride was placed at the bottom of the can and also in a ring at about the middle portion of the can. A tube through the cover and leading to the bottom of the can was also provided for passing dry air into the can previous to any experiment. The quartz plate in the cover of the can was kept dry by blowing dry air over it continually during an experiment.

The low temperatures were obtained in no. 18 (Table XIV.) by packing the can in a freezing mixture of ice and salt; in no. 23 by immersion into liquid air; in nos. 19–22 by lowering the liquid air flask so that the apparatus was above the liquid air but the bottom of the can still remained in the liquid air.[1] The lowering or raising of the liquid air flask could be done by very small amounts and the temperature could be kept constant within 5° C. However, the temperature at the upper plate differed from the temperature at the lower plate by as much as 12° C. and it is possible that some convection currents existed in these experiments. Such currents would move upwards in the center of the apparatus and would bring the ions to the gauze sooner than would otherwise be the case. This was somewhat apparent from a small downward slope in the curve for the different values of T in the experiments given by nos. 19–22. The temperature was measured by two thermo-junctions of iron and nickel wires; one of them rested on the top of the upper portion of the apparatus while the other rested against the side of the apparatus at about the position of the illuminated plate. The mean value of the two temperature readings was used as the temperature of the gas in the experiment. The calibration at low temperatures was done by means of liquid air, the liquid air temperature was obtained by the density method[2] which gave $-193°.4$ C., while a pentane thermometer read in the same air $-193°.0$ C.; intermediate calibration

[1] Compare Zeleny, J., PHYS. REV., XXIV., p. 42.

[2] U. Behn und F. Kiebitz, Ann. d. Phys., 4 S., 12, p. 421, 1903.

points were obtained by placing the pentane thermometer and the junction in a tube of pentane and raising the tube out of the liquid air to different points, the pentane being constantly stirred.

The illumination was brought about by reflecting the light by means of a polished brass plate downward into the apparatus. The results for all the temperatures tried are given in Table XIV.

Table XIV.

Dry Air.

No.	Absolute Temperature.	p	u	v	V	d	Plate.
1	698°	744.0	5.72	5.60	2.19	18.70 mm.	Brass.
2	648	745.0	5.60	5.50	2.32	"	Brass.
3	570	746.0	4.57	4.48	2.15	"	Platinum.
4	540	746.0	4.43	4.35	2.20	"	Platinum.
5	503	741.0	4.12	4.02	2.18	"	Platinum.
6	468	732.0	4.08	3.94	2.30	"	Brass.
7	463	746.0	3.80	3.73	2.20	"	Platinum.
8	428	734.0	3.82	3.68	2.35	"	Brass.
9	416	742.0	3.46	3.38	2.27	"	Brass.
10	409	738.4	3.42	3.32	2.22	"	Platinum.
11	388	733.0	3.02	2.92	2.05	"	Platinum.
12	378.	742.0	2.84	2.77	2.00	"	Platinum.
13	360	744.0	2.69	2.64	2.00	"	Platinum.
14	340	731.0	2.72	2.62	2.10	"	Brass.
15	335	737.0	2.58	2.50	2.04	"	Platinum.
16	300	732.6	2.18	2.10	1.91	"	Brass.
17	296	738.0	2.10	2.05	1.88	"	Brass.
18	268	738.0	1.853	1.80	1.83	9.93	Brass.
19	237	738.0	1.588	1.54	1.77	"	Brass.
20	202	740.2	1.160	1.13	1.53	"	Brass.
21	180	738.0	0.896	0.87	1.32	"	Brass.
22	149	741.2	0.638	0.622	1.14	"	Brass.
23	84.5	746.0	0.226	0.222	0.717	"	Brass.

The mobility reduced to normal pressure is plotted against the temperature in Fig. 14. It will be noticed that the points are very nearly on a straight line which intersects the temperature axis at about 80° absolute. Phillips (loc. cit.) using a shorter range, obtained a less inclined straight line.

The above curve does not give direct information about any changes that may take place in the ion with change of temperature, for, although the values were all obtained at atmospheric pressure, the density of the gas was markedly different at the different temperatures. The mobility v for each temperature was reduced therefore to the

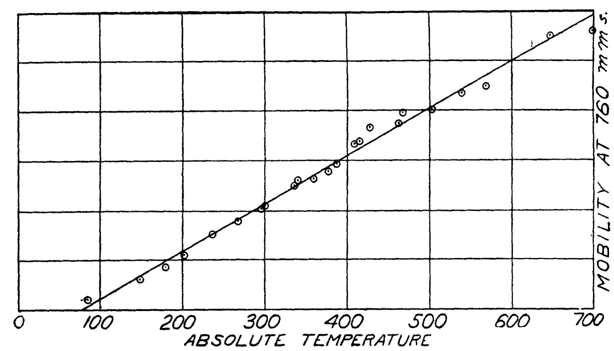

Fig. 14.

density at 0° C., on the supposition that the mobility varies inversely as the density of the gas. The values thus obtained are given in the above table in the column marked V, and they are plotted against their temperatures in Fig. 15. From 700 down to 400 degrees absolute there is no change in the value of V, but below 400 it diminishes until at 84.5 degrees absolute it is only one third of the value at the higher temperatures. This decrease in the

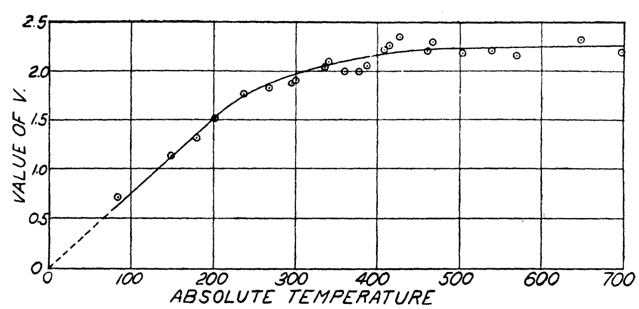

Fig. 15.

mobility of the ions indicates that at the lower temperatures the cluster of molecules about the ion becomes larger on the average as the temperature is lowered.

§ 8. Summary and Conclusion.

1. At atmospheric pressure and room temperature the mobility of the ions produced by ultra-violet light, when reduced to 760

mm. pressure, was found to be 2.04 cm. per sec. per volt per cm. for dry air, and 1.01 cm. per sec. for dry carbon dioxid. In air saturated with water vapor at 26°.0 C. the reduced value was 1.64 cm. per sec. and in carbon dioxid saturated with water vapor at 25°.0 C. the reduced value was 0.806 cm. per sec.

2. The mobility of the negative ions in air at ordinary room conditions is the same whether the metal illuminated by the ultra-violet light is zinc, platinum or brass.

3. With changing pressure the mobility of the ions, in both dry air and dry carbon dioxid, varies inversely with the pressure from 760 mm. down to about 200 mm., so that the product of the mobility by the pressure is constant.

4. In dry air below 200 mm. the product of the mobility by the pressure increases as the pressure is reduced, the increase being slow at first but very sudden at about 100 mm. so that at 8.8 mm. the product was found to be ten times as great as that at atmospheric pressure. This result indicates that below 200 mm. the size of the ion is increasingly smaller as the pressure is reduced.

5. In dry carbon dioxid below 200 mm. there is likewise a sudden increase in the product of the mobility by the pressure, but this occurs at a somewhat higher pressure than in air.

6. With a change of temperature from 84.5 to 698.0 degrees absolute, the mobility of the negative ions in dry air at atmospheric pressure was found to increase uniformly with rise of temperature. When reduced to a common gas density, the value obtained for the mobility remains unchanged from 700° to 400° absolute, but below that temperature it diminishes until at the temperature of liquid air it is only about one third of its value at the higher temperatures. In this region the cluster of molecules forming the ion increases in size, therefore, as the temperature is lowered.

In conclusion, I desire to express my deep gratitude to Professor John Zeleny, who suggested this investigation and under whose supervision these experiments were carried out, for the valuable advice from him, and to Dean Frederick S. Jones for the kindly interest he has shown in my work.

Physical Laboratory,
University of Minnesota,
August 23, 1909.