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THE DISSOCIATION OF WATER IN THE GLOW DISCHARGE

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Abstract

The theory that ionization in the dark space increases exponentially with distance from the cathode, is applied to the dissociation of water vapor. Experimental results are given, which it is shown can be explained quantitatively if the total energy of the electrons generated in the dark space is taken to be

$$\int_0^S e(V_1-V)dn$$

where S is the width of the dark space, V_1 is the total cathode potential drop, V is the space potential, and n is the number of electrons per element of volume, the exponential increase of which is given by Townsend's equation. The experimental data include measurements of the rate of dissociation for currents from 1 to 28 ma, electrode spacings from 1 to 9.75 cm, and a pressure of 0.75 mm of mercury, also measurements of the cathode potential drop and the width of the Crookes dark space. Possible reaction mechanisms are discussed. The net energy per dissociation has an almost constant value of 11 volts, whereas the amount of dissociation ranges from 4.78 to 5.90 molecules per electron in the dark space and negative glow, depending upon the magnitude of the cathode drop. Probe measurements in the positive column give an electron density of 7.95×10^7 electrons per cm^3, and an average energy of 3.71 volts per electron. The probability of dissociation by an electron in the positive column having an energy greater than 7.6 volts, is computed to be 0.00115.

I. Introduction

THEORIES of the cathode fall of potential and the Crookes dark space, based on the idea of ionization increasing exponentially with distance from the cathode within the dark space, have been developed by H. A. Wilson,[1] Güntherschulze,[2] Compton and Morse,[3] and Morse,[4] and have been found generally to give fair agreement with the principal electrical phenomena. The work described here shows that the same idea can also be applied so as to lead to a fair quantitative interpretation of cases in which chemical action occurs in the discharge.

Lack of sufficient knowledge of conditions in electrical discharge has long been a serious obstacle in the study of their chemical effects. In particular, no satisfactory comparison of the chemical yield with amount of ionization has been possible, because of the absence of a suitable method of determining the amount of ionization or even the total energy expended by the electrons. The theory presented here offers a means of determining this latter quantity, and its application to the dissociation of water vapor is shown to result in fair quantitative agreement.

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[1] H. A. Wilson, Phys. Rev. **8**, 227 (1928).

[2] A. Güntherschulze, Zeits. f. Physik **33**, 810 (1925).

[3] K. T. Compton and P. M. Morse, Phys. Rev. **30**, 305 (1928).

[4] P. M. Morse, Phys. Rev. **31**, 1003 (1928).

II. Apparatus

The apparatus is shown in Fig. 1. It consisted essentially of a discharge tube so arranged that water vapor could be passed through it at a suitable rate and pressure, and the decomposition products collected and measured. In the figure the tube is shown in detail, while the trap, pump, and storage bottle are illustrated schematically and on a smaller scale. The bulb *B* contained ice, which was used as the source of water vapor. The rate of evaporation was controlled by surrounding *B* with a water bath. In the work described here, this bath was always held at a temperature of 10°C.

The discharge tube was made of Pyrex glass, and was about 6 cm in diameter and 17 cm in length. It contained two aluminum disk electrodes, E_1 and E_2, about 0.3 cm thick and 3 cm in diameter, which were used as cathode and anode. The distance between these could be varied by sliding the tube *a* through the tube *b*. A wax seal was made at *W*. Tubes *a* and *b* were close-fitting, and *b* was made 10 cm long to diminish the possibility of wax vapors entering the discharge tube.

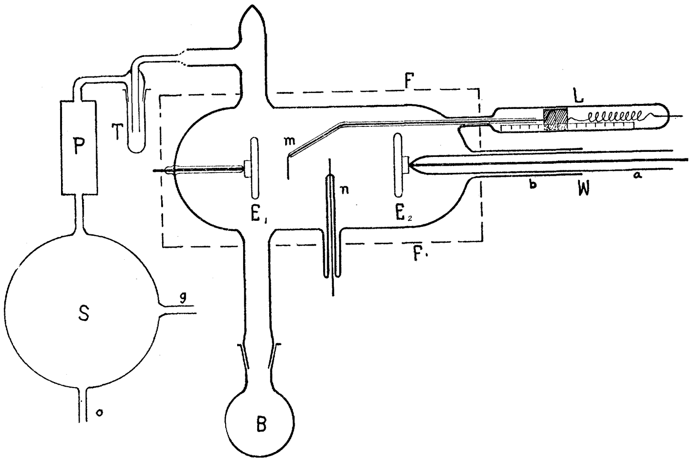

Fig. 1. Glow discharge tube and auxiliary apparatus.

Besides the aluminum electrodes, there were two probe electrodes, *m* and *n*, which were made of 25 mil tungsten wire. Electrode *n* was used for making measurements of the electron density and energy by the Langmuir—Mott-Smith method. Electrode *m* was used for measuring space potentials in the dark space and negative glow. Its position could be varied by moving the iron block in the side-tube *L* with a magnet, and its distance from the cathode, could be read on the scale along *L* shown in the figure.

The discharge tube was surrounded by an electric furance *F*, with which it was baked out for about thirty minutes at 350°C before each run. This was found to lead to better reproducibility of the data. *P* was a two-stage mercury pump, and *S* a ten-liter storage bottle in which the gases produced by the dissociation of the water were collected. A McLeod gauge, connected at *g* was used to measure the pressure.

III. Data

Runs to measure the amount of dissociation were made with discharge currents from 1 to 28 m.a., electrode spacings from 1 to 9.75 cm, pressure at 0.75 mm, and temperatures, as measured by a thermometer inside the furnace, from 25 to 50°C. Under these conditions the discharge was abnormal. The negative glow was rose-colored, while the positive column and anode glow were not visible.

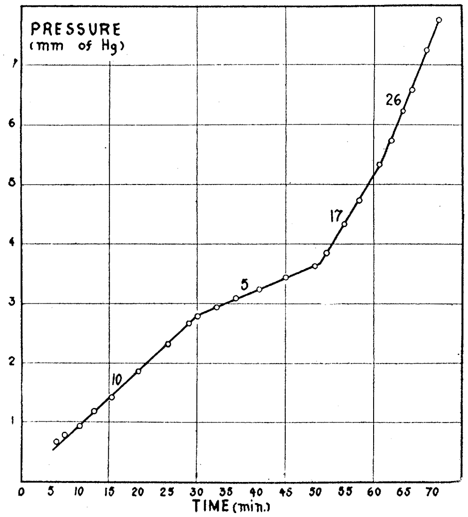

Fig. 2. Typical curve showing increase of pressure with time for various discharge currents.

Readings of the gas pressure in S were taken at intervals of a few minutes. Typical data of this sort are shown in the graph of Fig. 2, where pressure in S is plotted against time, for discharge currents of 10, 5, 17, and 26 m.a., and

Table I. *Rates of gas production.* ($cm^3/sec. \times 10^6$).

I m.a.	d cm					
	1.0	1.9	3.0	4.3	7.75	9.75
1.0	239	159	166	150	173	
1.5						239
2.0						343
3.0	465	531	520	510	531	571
5.0	717	822	916	862	929	909
10.0	1430	1725	1900	1860	2020 1925	2230
15.0	2585	2880	3030	2980		3340
17.0					3610	
20.0	3420	3935	4140	4150		4640 4360
25.0	4420	4770	4870	5000		5970 5710
26.0					5530	
28.0				5620		

an electrode spacing of 7.75 cm. The slopes of the various sections of this graph give the rates of dissociation for the corresponding currents. A complete list of such rates is given in Table I.

Fig. 3 shows these rates plotted against discharge current. These curves all pass through the origin, but are shifted to the right for clarity. The slight curvature of these graphs indicates that the relation between the rate of reaction dq/dt and the current can not be linear as was reported by the writer previously[5] for measurements over a smaller current range on the decomposition of normal paraffins in the glow discharge. It will be shown later on that this upward curvature can be interpreted as due to the increase in the cathode potential drop with increase in discharge current.

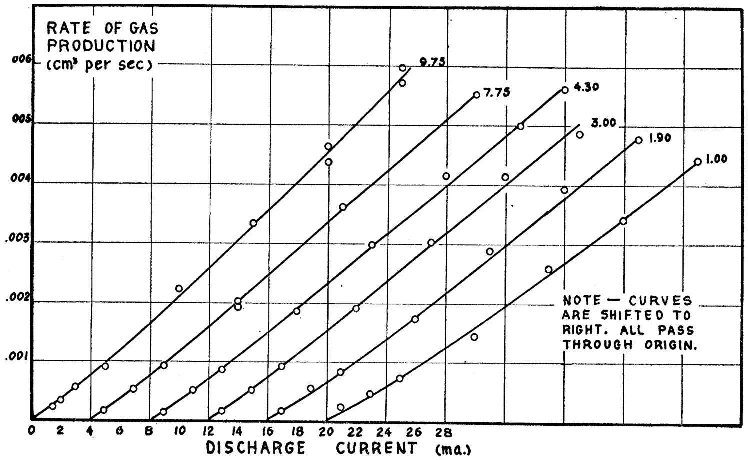

Fig. 3. Rate of dissociation for various discharge currents and electrode spacings.

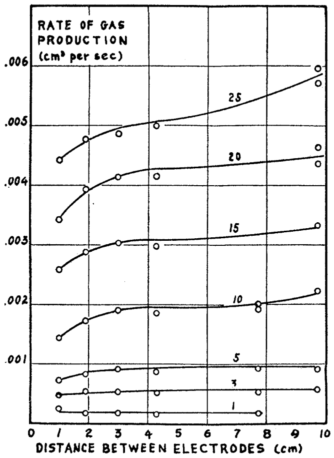

Fig. 4. Variation of rate of gas production with electrode spacing.

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[5] Ernest G. Linder, Phys. Rev. **36**, 1375 (1930).

If the rate of dissociation, i.e., the rate of production of gas, is plotted against electrode spacing, the curves of Fig. 4 are obtained. From these it may be seen that separating the electrodes from 1 cm to 9.75 cm produces but a comparatively small increase in the amount of reaction. In fact, for currents up to 5 ma., such increase in separation produces almost no detectable change. Hence the conclusion may be drawn that the greater part of the dissociation occurs in a region close to the cathode, probably the Crookes dark space or the negative glow, or both. This same conclusion was reached by A. K. Brewer and his coworkers,[6] who synthesized a number of compounds in a glow discharge tube immersed in liquid air and found that the products froze out in a sharp band on the walls near the negative glow.

The writer's method of determining the locus of the reaction is valid only if the amount of dissociation occurring behind the anode is negligible. That this is true will be shown in a later paragraph describing the probe measurements.

Two analyses[7] of the gas collected in the storage bottle gave the following results:

	I	II
Oxygen	30.0 percent	30.4 percent
Hydrogen	70.0	69.6

There is obviously a small deficiency of oxygen, which may be due to the possible formation of small amounts of O_3, which could not be distinguished from O_2 by the method of analysis used. Tests for H_2O_2 in the water in the trap showed only a trace, an amount far too small to account for the missing O_2. A similar deficiency of oxygen has been found by Bates and Taylor,[8] and also Urey and Lavin,[9] who dissociated water by photochemical and electrical discharge methods, respectively.

Because of this uncertainty in the nature of the oxygen compounds present, the quantity of hydrogen was taken as the measure of the amount of dissociation, it being assumed that each H_2 molecule represented one dissociated H_2O molecule.

On the above basis, the number of molecules dissociated per electron of current has been calculated for different values of discharge current. To get the dissociation occurring only in the dark space and negative glow, the rates used in the computations were those for an electrode spacing of 3.5 cm, which corresponds to a fairly flat region of the rate vs. separation curves of Fig. 4, and probably represents closely the rate of dissociation in the region mentioned. The quantities N_{H_2} thus obtained, are given in column eight of Table III.

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[6] A. K. Brewer and J. W. Westhaver, Jour. of Phys. Chem. **34,** 153 (1930); **34,** 2343 (1930); A. K. Brewer and P. D. Kueck, Jour. of Phys. Chem. **35,** 1281 (1931); **35,** 1293 (1931).

[7] The writer is indebted to Mr. Ardith P. Davis of the Cornell Department of Chemistry for making these analyses.

[8] J. R. Bates and H. S. Taylor, J.A.C.S. **49,** 2438 (1927).

[9] H. C. Urey and G. I. Lavin, J.A.C.S. **51,** 3290 (1929).

IV. CALCULATION OF THE AVERAGE ENERGY EXPENDED BY THE ELECTRONS GENERATED IN THE DARK SPACE

In attempting to interpret the data presented above, or chemical action in glow discharges in general, it is desirable to know the energy of the electrons which are either produced at the cathode surface and traverse the entire dark space,[10] or are generated at some point in the dark space and travel therefore only the distance between that point and the edge of the field-free region in the negative glow (e.g., such a path as *ab* in Fig. 5) before ceasing to gain energy from the field.

Obviously the energy gained by each electron will be $e(V_1 - V)$, where e is the electronic charge, V_1 is the total cathode potential drop, and V is the potential of the point at which the electron is produced. In general each electron will also receive some energy from the impacting electron which ejects it from its parent atom. However, in calculating the total energy of the electrons, the initial energies will cancel out, since the energy thus gained by one electron is lost by another. Hence only the quantity $e(V_1 - V)$ need be considered.

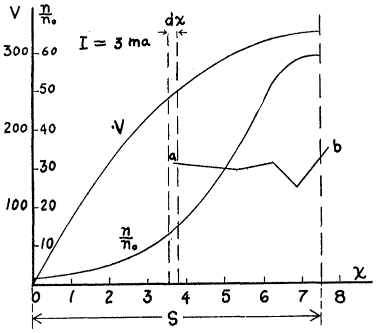

Fig. 5.

It is clear also that some of the energy $e(V_1 - V)$ will in general be lost before all of it has been gained, due to impacts of various kinds made by the electron before it reaches the edge of the field-free region. But for the moment all methods of expenditure of energy shall be disregarded, and only the average energy gained by each electron computed.

If n_0 electrons leave the cathode surface, the total energy gained by these and the n_s secondary electrons produced by them in the dark space, will be

$$W = W_1 n_1 = n_0 e V_1 + \int_{n_0}^{n_1} e(V_1 - V) dn \tag{1}$$

where $n_1(= n_0 + n_s)$ is the total number of electrons which enter the field-free region of the negative glow, and W_1 is the average energy per electron.

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[10] In this article the term "dark space" is used to designate the space between the cathode surface and the edge of the field-free region in the negative glow, but not the visible edge of the glow, as is sometimes the case.

Now consider an element of volume such as is indicated by the dashed lines in Fig. 5. Let it be of width dx, and let it be at the position $x=x$, where the cathode surface is given by $x=0$, and the edge of the field-free region by $x=S$. The number of electrons generated in this element is

$$dn = n\alpha dx \tag{2}$$

where n is the total number of electrons which cross the inner boundary of the element, and α is the number of ionizing collisions made by an electron in one centimeter of advance. By integrating, we get,

$$\log (n/n_0) = \int_0^S \alpha dx. \tag{3}$$

To express α in terms of x, we make use of Townsend's equation[11] as modified by Compton and Morse,[12]

$$\alpha = pC \exp\left[\frac{-pCD}{X - X'/2pC}\right], \tag{4}$$

where p is the pressure, X is the field strength, X' its space derivative, and C and D are semi-empirical constants which have been determined by Townsend[14] for a number of gases including water vapor. This modified equation applies to nonuniform fields, whereas the original equation applied only to uniform ones.

Substituting Eq. (4) in Eq. (3) yields

$$n/n_0 = \exp\left[pC \int_0^x \exp\left(\frac{-pCD}{X - X'/2pC}\right)dx\right]. \tag{5}$$

Now from Aston's work[13] we have

$$X = C_1(S - x)$$

so that by integration,

$$V = -C_1(Sx - x^2/2) + C_2.$$

Since $V=0$ when $x=0$, and $V=V_1$ when $x=S$, the two constants C_1 and C_2 can be evaluated, we get

$$V = (2V_1/S^2)(Sx - x^2/2), \tag{6}$$

and

$$X = -(2V_1/S^2)(S - x). \tag{7}$$

By substituting Eq. (7) in Eq. (5) we get an expression for n/n_0 in terms of x and the constants C, D and p. If we call X positive when it accelerates electrons away from the cathode, and put

$$z = \frac{2Dp^2C^2S^2}{4pCV_1(x - S - 1)},$$

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[11] J. S. Townsend, The Theory of Ionization of Gases by Collision, Chap. I.

[12] K. T. Compton and P. M. Morse, Phys. Rev. **30**, 305 (1928).

[13] F. W. Aston, Proc. Roy. Soc. **84**, 526 (1911).

and integrate, we obtain,

$$\log (n/n_0) = \frac{Dp^2S^2C^2}{2V_1}\left[\frac{e^z}{z} - \log z - F(z)\right]_{z(x=0)}^{z(x=x)}, \tag{8}$$

where

$$F(z) = z + \frac{z^2}{2 \cdot 2!} + \frac{z^3}{3 \cdot 3!} + \cdots .$$

Eq. (8) permits the calculation of n/n_0 at any point in the dark space from Townsend's constants C and D, and the experimentally measurable quantities, p, S and V_1. A graph of n/n_0 computed in this manner from data presented in this paper is given in Fig. 5. For this case, the discharge current is 3 m.a., $p = 0.75$ mm of Hg, $S = 0.75$ cm, $V_1 = 325$ volts, $C = 12.9$ and $D = 22.4$.[14] A graph of the potential distribution computed by means of Eq. (6) for the same case, is also given in Fig. 5. These curves are typical of all the other cases, the data for which are given in Table II.

TABLE II. *Values of n/n_0 at various positions in the dark space for different discharge currents.*

x \ I	1 m.a.	3	5	10	15	20	25
0.1 cm	1.96	2.07	2.26	2.22	2.43	2.25	2.34
0.2	3.77	4.39	4.39	4.86	5.42	5.21	5.50
0.3	6.82	8.42	9.35	10.50	11.80	11.30	12.60
0.4	12.30	16.00	18.60	20.00	23.70	24.00	27.10
0.5	20.70	28.00	31.00	35.50	43.30	45.00	51.50
0.53							57.00
0.56							63.50
0.585						65.20	
0.595					63.30		
0.600	32.80	45.00	49.00	52.00			
0.610				53.00			
0.650			56.00				
0.690			60.00				
0.700	51.00	59.00					
0.750		59.00					
0.800	68.80						
0.900	79.00						
0.960	72.00						

The integral of Eq. (1) can now be evaluated graphically by plotting n (obtained from Eq. (8)) against $V_1 - V$ (obtained from Eq. (6)). Values of the integral thus computed, are listed in Table III, column six. To obtain W_1, divide the total energy W, (obtained from Eq. (1)) by n_1 (computed from Eq. (8)). Values of W_1, found in this manner, are given in column seven of Table III.

It should be noted that the above method of computing electron energies permits the calculation of the average energy only, and not the energy distribution, due to the fact that an electron is in general ejected from its parent atom with an energy which may be any fraction of the excess over the ionization energy possessed by the impacting electron. Knowledge of how the en-

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[14] J. S. Townsend, The Theory of Ionization of Gases by Collision, p. 26.

TABLE III. *Summary of results.*

I (m.a.)	S (cm)	V_1 (volts)	$\log n_1/n_0$	n_1/n_0	$\int(V_1-V)dn$ (volts)	W_1 (volts)	N_{H_2}	k (volts)	$\frac{V_1-W_1}{V_1}$
1	0.96	302	4.28	72	49.8	53.8	4.78	11.2	82.2%
3	0.75	325	4.08	59	50.0	55.5	5.18	10.7	82.8
5	0.69	343	4.09	60	51.1	56.8	5.30	10.7	83.1
10	0.61	385	3.97	53	56.0	63.3	5.67	11.2	83.6
15	0.595	435	4.15	63	57.8	64.7	6.03	10.7	85.2
20	0.585	500	4.18	65	62.8	70.5	6.22	11.3	85.9
25	0.560	554	4.15	64	70.5	79.2	5.90	13.4	85.7

ergies of the impacting electron and the ejected electron are related is too incomplete at present to permit a calculation of the energy distribution by a method such as the above.

If the reaction only in the neighborhood of the cathode is considered, we can write,

$$ND_1 = pW = pn_1W_1, \tag{9}$$

where N is the total number of H_2O molecules dissociated per n_1 electrons, D_1 is the net energy per dissociation, and p is the fraction of the total electron energy expended in producing dissociation. Differentiating this, we have,

$$\frac{dN}{dt} = \frac{p}{D_1} W_1 \frac{dn_1}{dt},$$

or

$$\frac{dN}{dt} = \frac{p}{D_1} W_1 I. \tag{10}$$

Thus the rate of dissociation is proportional to both the discharge current and the average energy of the electrons. Experimental values of dp/dt, which is proportional to dN/dt, are plotted against I in Fig. 3. The upward curvature of these graphs may be accounted for by the increase in the cathode drop and hence the increase of W_1 with increase of the current in the abnormal discharge. A quantitative check of this interpretation can be obtained from Eq. (9), for the quantity

$$\frac{W_1 n_1}{N} = \frac{D_1}{p} = k,$$

should be a constant independent of current if dN/dt is proportional to the product $W_1 I$. Values of k are given in Table III column nine, and are constant within the experimental error.

It can also be shown that the calculated energy W_1 is ample to produce the observed amount of dissociation, for although there are intermediate reactions, the net reaction is $H_2O \rightarrow H_2 + O_2/2$, which requires 2.48 volts[15], whereas it has been shown that the available energy is $W_1 n_1/N$ or about 11 volts.

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[15] R. Mecke, Zeits. f. phys. Chem. **B7,** 108 (1930).

Thus the fraction of the total electron energy expended in producing dissociation is found to be,

$$p = D_1/k = 2.48/11 = 0.226. \qquad (11)$$

The average energy per electron W_1 is only about fifteen percent of the total cathode drop energy V_1. This is in marked contrast with theories such as that of Ryde,[16] in which the assumption is made that all electrons traverse the entire dark space without making collisions, and for which we should therefore have $W_1 = V_1$. The present theory yields an energy of only about $0.15\,V_1$ because the electrons on the average are generated in the dark space at a position so near to the boundary of the field-free region that they fall through only about fifteen percent of the total cathode drop V_1. This may be seen clearly by referring to Fig. 5.

An experimental check on the accuracy of the calculated value of W_1 is given by the work of Güntherschulze[17] on the energy of the positive ions generated in the dark space. In work on water vapor he obtained the result that for a current of 50 m.a., the energy absorbed by the cathode was 84.8 percent and 85.7 percent of the total cathode drop energies for pressures of 1.83 mm and 5.03 mm, respectively. These data are in good agreement with the figures given in the last column of Table III, which represent the percentages of the total cathode drop energies not absorbed by the electrons according to the theory presented here.

V. Discussion of Possible Reaction Mechanisms

Barton and Bartlett[18] have shown in their work with the mass spectrograph, that the primary product resulting from ionizing impacts in water, is H_2O^+, and that H and OH^+ are probably the immediate secondary products. Hence it appears that some dissociation results from the ionization process. However, in view of the results presented here, it does not seem likely that in the glow discharge all of it can be attributed to ionization, since that would require an excessive total ionizing power, the number of ions produced per electron of W_1 volts energy being then equal to N_1, the number of molecules dissociated per electron, Thus, according to the data in Table III, the total ionizing power would have to be about three or four times that usually observed.[19] It seems more probable that some excited molecules dissociate, either spontaneously or upon subsequent impacts with other molecules.

Foote and Mohler[20] have reported an excitation potential for water at 7.6 volts. Such an energy would be sufficient to produce either of the following reactions:

$$(1)\quad H_2O \rightarrow H + OH \quad 4.83 \text{ volts}^{21}$$

$$(2)\quad H_2O \rightarrow H_2 + O \quad 5.26 \text{ volts}^{21}.$$

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[16] J. W. Ryde, Phil. Mag. **45**, 1149 (1923).

[17] A. Güntherschulze, Zeits. f. Physik **23**, 334 (1924).

[18] H. A. Barton and J. H. Bartlett, Jr., Phys. Rev. **31**, 822 (1928).

[19] K. T. Compton and I. Langmuir, Reviews of Modern Physics **2**, 127 (1930).

[20] Bull. N. R. C., **9**, Critical Potentials, p. 124 (1924).

[21] R. Mecke, Zeits. f. phys. Chem. **B7**, 108 (1930).

Of these, (1) seems most likely, since the spectrum of the discharge in water[22] shows the Balmer lines and the OH bands strongly, but no spectrum due to the H_2 molecule. Reaction (1) is also analogous to that due to ionization suggested by the work of Barton and Bartlett.

The negative ions H^- and OH^- are apparently not present in the discharge in important amounts. There is no spectroscopic evidence for their existence, nor did the work of Barton and Bartlett indicate their presence. Hence it is not likely that reactions such as

$$H_2O \rightarrow H^+ + OH^-$$

or

$$H_2O \rightarrow H^- + OH^+$$

occur to any great extent. This is fortunate since the presence of such ions of opposite sign would lead to recombinations producing neutral H_2O again, so the hydrogen and oxygen reaching the storage bottle would be only a net result of an unknown amount of dissociation and recombination, and it would be impossible to compute the actual dissociation per electron as was done above.

It seems that the only negatively charged particles present in the gas in a great amount are the electrons. Recombinations of H_2O^+ and an electron are of small probability. Furthermore the density of neutral molecules under the experimental conditions was about 10^6 times that of the electrons in the negative glow, so that impacts with neutral molecules would likely cause the dissociation of the H_2O^+ ion, as was demonstrated by Barton and Bartlett, before it could pick up an electron. Negative ions on the walls might lead to recombinations producing water, if the H_2O^+ ions reached there before dissociating, but this is unlikely on account of the large number of collisions that most such ions make with neutral molecules before reaching the walls (about 10^4 per centimeter).

VI. PROBE MEASUREMENTS

Electrode *m*, Fig. 1, was used for making measurements of the space potential in the dark space and negative glow. These were not made by the Langmuir—Mott–Smith method[23] since this was found to be beset with difficulties, to be described later, due to the presence of chemically active gases. Instead, the space potential was taken as that of the probe when it collected zero current. This procedure is known to give erroneous results due to the high velocity electrons present. Later some successful runs by the Langmuir—Mott-Smith method were made which showed the error to be about eight volts in the positive column and negative glow. This is about two percent of the total cathode drop, hence no correction was made for it, since it is but slightly larger than the error in measuring the cathode drop.

The length *S* of the Crookes dark space was taken as the distance from

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[22] W. Watson, Astrophys. J. **60**, 145 (1924).

[23] H. M. Mott-Smith and I. Langmuir, Phys. Rev. **28**, 727 (1926); I. Langmuir, Gen. Elec. Rev. **27**, 449, 538, 616, 762, 810 (1924).

the cathode to the point where the potential became constant. This point could be determined to within about 0.5 mm. Values of S, so measured, are listed in column two of Table III. The cathode potential drops are given in column three.

Electrode n was used for making probe runs by the Langmuir—Mott-Smith method,[23] and thus determining the electron densities and energies. As has been stated, difficulties were encountered due to the chemical activity of the gases present. At first tungsten electrodes were tried, but these were found soon to become coated with a layer of oxide, which seemed to interfere with the collection of electrons, so that the values of electron density obtained were far too small (about 1/100 th of the values eventually found). Nevertheless, such an oxide-coated probe was used as electrode m, and functioned satisfactorily since a null method was employed for the measurements with it.

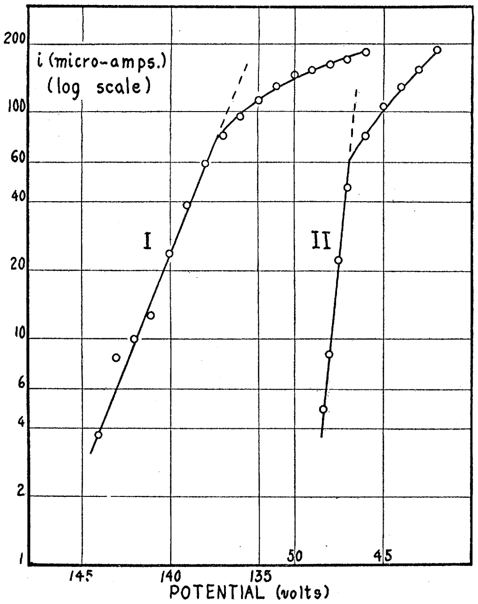

Fig. 6. Typical probe runs by the Langmuir—Mott-Smith method. I. In the center of the positive column, 5.5 cm from the cathode. II. Back of the anode 3 cm; ordinates multiplied by 100.

Platinum was then substituted for the tungsten, but this too was found to oxidize. A light amber color could be observed, and the currents collected decreased with use of the probe.

Tungsten was then returned to, and the procedure adopted of cleaning off the probe by positive ion bombardment before the runs, by using the probe as a cathode for two or three minutes with a discharge current of a few milliamperes. This process produced a bright metallic surface, with which reproducible results could be obtained in the positive column, and which were not altered even after additional cleanings of the same sort. Upon standing for a day or two with either air or water vapor in the tube, the readings then obtained were found to have only about half their former value, but when the probe was again cleaned the previously found data could be reproduced.

If electrode E_2 was used as cathode and moved close to n so that n was in the negative glow, n was found to oxidize so rapidly that it became medium brown colored in about ten minutes. Hence it was not found possible to make runs by the Langmuir—Mott-Smith method in the negative glow, even by use of this cleaning procedure.

Curve I in Fig. 6 is a graph of run 31, which is typical of the measurements taken in the positive column. The points do not lie on as smooth a curve as might be desired because of the difficulty inherent to such conditions as a flowing stream of gas, of obtaining a steady state in the discharge. The accuracy, however, is ample for determining satisfactory values of electron density and energy.

In the upper part of Table IV, data from five probe runs are given, for which n was 5.5 cm from the cathode, the electrode separation was 9.95 cm, the discharge current 10 m.a., and the pressure 0.75 mm. $\overline{V}$ is the mean energy of the electrons and T their temperature, I_e the electron current density, and N_e the electron density. No corrections were made for the positive ion current, since it was negligibly small.

TABLE IV. *Probe measurements data.*

Run No.	$\overline{V}$ (volts)	T (°C)	I_e (Amps./cm^2)	N_e (el/cm^3)
31	3.51	27,100	380 (10^{-6})	9.30 (10^7)
32	3.67	28,400	334	7.93
33	3.93	30,400	303	7.02
36	3.51	27,100	326	7.95
37	3.93	30,400	326	7.55
Av.	3.71	28,680		7.95
42	1.06	8,170	13.9	0.143
43	1.06	8,170	16.2	.167
Av.	1.06	8,170	15.1	0.155

A value for the probability of dissociation by electron impact in the positive column was obtained by computing the number of impacts made by electrons having energy in excess of 7.6 volts, the excitation potential, and comparing it with the experimentally observed amount of dissociation in the positive column. The volume of the positive column was taken as 250 cm^3, the dissociation there was computed from the data shown in Fig. 4. The value of the probability was found to be 0.00115. This is of the order of magnitude usually found for the probabilities of excitation by electron impact.

In the lower part of Table IV are given data from runs made 3 cm back of the anode, with discharge conditions the same as above, except that the electrode separation was only 2 cm. Here the electron density was found to be only about 0.02 of its value in the positive column, and the energy about 0.33. As above, the number of electrons having energies in excess of 7.6 volts may be calculated, and it is thus found that the amount of reaction in this region back of the anode is only 1/6650th of that in the positive column. Curve II of Fig. 6 represents data taken in this region. It is a graph of run 43 of Table IV. The ordinates are multiplied by 100.

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