On the Laws Governing Electric Discharges in Gases at Low Pressures

W. R. Carr

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X. *On the Laws Governing Electric Discharges in Gases at Low Pressures.*

By W. R. CARR, *B.A., Post-graduate Student, University of Toronto.*

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I. *Introduction.*

THE researches of recent years have conclusively settled the general connection between the spark potential and the pressure of a gas. It is now well known that as the pressure of a gas diminishes the difference of potential necessary to produce a discharge between electrodes in the gas, a fixed distance apart, also diminishes, until, at a critical pressure, the spark potential reaches a minimum value. It is further established that below the critical pressure the potential difference required to produce discharge rapidly increases as the pressure is lowered.

This connection between the spark potential and the corresponding pressure of a gas has been well illustrated in a series of curves drawn by PEACE,[*] who investigated the sparking potentials between a pair of parallel plates at pressures ranging from one-half an atmosphere down to a little below the critical pressure.

Among others, STRUTT[†] and BOUTY[‡] have carried on the investigation at pressures considerably below the critical point, and their results show that, once the critical pressure has been passed, the rise in potential difference necessary to produce discharge is exceedingly rapid.

The effect of varying the distance between the electrodes was first determined by PASCHEN,[§] who observed the existence of a simple law connecting the pressure at which discharge took place with the corresponding spark potential and the distance between the electrodes.

PASCHEN'S results showed that when a given potential difference was applied to two spherical electrodes, whose distance apart could be varied, the maximum pressure at which discharge occurred varied inversely with the distance between the spheres.

The range of pressures over which he found the law to apply, while considerable, did not extend below 2 centims. of mercury, and his results do not in any case indicate that the critical pressure had been reached. It is evident, then, that PASCHEN'S conclusions are confined to pressures higher than the critical pressures.

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[*] PEACE, 'Roy. Soc. Proc.,' vol. 52, p. 99.

[†] STRUTT, 'Phil. Trans.,' A, vol. 193, p. 377.

[‡] BOUTY, 'Compt. Rend.,' vol. 131 (2), p. 443.

[§] PASCHEN, 'Ann. d. Phys.,' vol. 37, p. 69.

Since the statement of this law by PASCHEN, PEACE* alone seems to have published results which could throw any additional light on the conditions holding for discharge in a gas at very low pressures. PEACE experimented in air, with parallel plates as electrodes, at various distances apart, and found that the value of the critical pressure increased greatly as the distance between the electrodes was lessened, but his results at points below the critical pressure give no evidence of the existence of any such law as had been enunciated by PASCHEN.

This can be readily seen from the numbers recorded in his paper, a few of which, selected from readings taken below the critical pressure, are given in the following table. These results admit of easy comparison, since the potential differences in the cases chosen are very nearly the same. The product of pressure and spark length should be a constant quantity if PASCHEN's law held.

TABLE of PEACE's Results.

Applied potential difference in volts.	Pressures in millims. of mercury.	Distance between electrodes in inches.	Product of pressure and spark length.
649	2·5	·082	·205
660	6	·005	·030
670	5	·021	·105
731	2·5	·030	·075

If we compare the first and second of these results where the difference in spark potentials is only 11 volts, we find the product in the first case nearly seven times that in the second. Again, the product corresponding to the spark potential 660 volts is less than one-third that corresponding to 670 volts, a large difference in the opposite direction. The same irregularity is exhibited by the product corresponding to the spark potential 731 volts, and it seems difficult to understand how experimental errors could be made to explain such a wide divergence of results.

At the critical pressure PEACE's results point to the existence of the law, but, as stated above, it would appear that as soon as lower pressures were approached the indications were uniformly against the existence of the relation which PASCHEN found to hold at high pressures.

Owing to the special precautions taken by PEACE to obtain accurate values for the spark potentials, it is possible to arrive at but one of two conclusions regarding the departure from PASCHEN's law indicated by PEACE's numbers. Judging by the results, either the law ceases to hold when the critical pressure is passed, or else the apparatus used by him in his experiments did not admit of an accurate measurement of the actual spark lengths corresponding to different spark potentials.

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* PEACE, 'Roy. Soc. Proc.,' vol. 52, p. 99.

A short discussion of the apparatus will reveal one considerable defect. The object of the investigations of both Paschen and Peace was to determine the electromotive intensity requisite to cause discharge in a gas. Throughout the range of pressures investigated by Paschen the discharge always took place along the shortest distance between the spherical electrodes, and the electromotive intensity requisite to break down the gas was therefore directly proportional to the spark potentials obtained by him. At points below the critical pressure, as Peace's results indicate, discharge occurs more easily over a longer distance than over a shorter one, and if the values of the electromotive intensities necessary to break down a gas at different pressures are to be compared, it is necessary to know in each case not only the potential difference applied to the electrodes, but also the path between the electrodes along which the initial discharge occurs.

To insure passage of the discharge over the same length of path Peace used plane parallel plates of very large diameter as electrodes, but while in this way he obtained a uniform field of considerable extent, and so was able to obtain an accurate measure of the electromotive intensity between the electrodes, he failed to make certain that the path along which the gas initially broke down was always confined to the uniform part of the field. As mentioned in his paper, there was considerable tendency, at low pressures, to a brush discharge from the edges of the plates, and this indicated a defect in his apparatus, which apparently he did not completely eliminate.

In the present paper an account is given of an investigation on the potentials necessary to produce discharge in a gas, with a form of apparatus which insured the passage of the discharge in a uniform electric field.

With this apparatus the discharge potentials have been determined, for different distances between the electrodes, over a range extending considerably above and below the critical pressure. The results of the investigation not only confirm the truth of the law enunciated by Paschen for discharges at high pressures, but also demonstrate, beyond doubt, the applicability of the same law to the critical pressure and to all pressures below it.

The existence of the same relation has been sought in each of the gases air, hydrogen, and carbon dioxide, and the result of the investigation has been the establishment with equal certainty of the same general law for all pressures, viz., that with a given potential difference, the field being uniform, the product of the pressure at which discharge occurs and the distance between the electrodes is constant.

II. *Description of Apparatus.*

The form of the discharge chamber is shown in fig. 1.

The electrodes consisted of two plane brass plates *a*, *a*, 3·6 centims. in diameter, embedded in ebonite, as shown in the figure, the outer faces of the electrodes being flush with the surface of the ebonite. These pieces of ebonite which carried the electrodes served also to close the glass tube T, T, which thus constituted a discharge chamber. In order to confine the gas in this chamber to the region where the electric field was uniform, a ring of ebonite C, C, which projected over the edges of the brass plates, was inserted. In the construction of the apparatus special precautions were taken to insure that the plugs B, B pressed tightly against the ebonite ring. As a result of this device, that portion of the electric field which was not uniform was entirely confined to the space occupied by ebonite, so that in this way it was rendered impossible for a discharge to occur through the gas in any but a uniform field. The thickness of the ebonite ring, which could be made accurate to $\frac{1}{1000}$ millim., determined the distance between the electrodes and consequently the length of the discharge. The length of the discharge could be varied at will, therefore, by inserting rings of different thicknesses.

The gas was admitted and removed from the chamber by glass tubes sealed into the ebonite plugs, and these tubes were connected with the air-space by two very fine channels leading through the ebonite ring.

Before closing the discharge tube, which was made air-tight with ordinary commercial soft wax, the inner surface of the ebonite ring was carefully rubbed with glass paper to remove any conducting material from its surface.

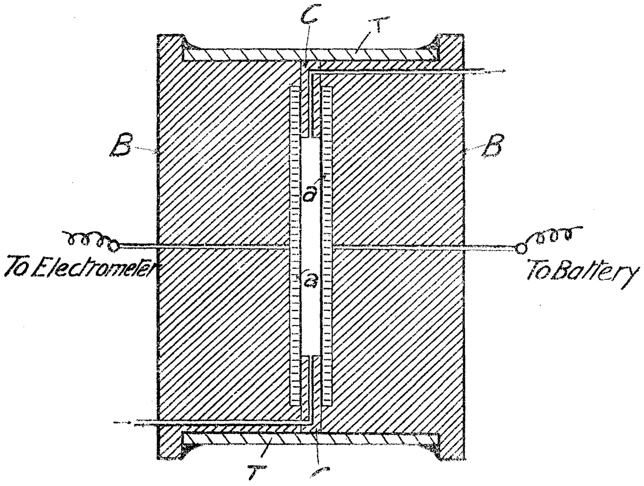

Fig. 1.

The potential differences used in these experiments were obtained from a series of small storage cells, similar to those used in the Reichsanstalt, Berlin. As these cells have a large capacity, their voltage remained constant over long intervals of time, and as a consequence it was possible to make the readings with the greatest accuracy. The potential differences were measured by a Weston voltmeter, which was carefully calibrated by means of a potentiometer furnished with a standard Weston cadmium element.

Throughout the investigation the discharge chamber was connected in series with a drying tube containing phosphoric pentoxide, a glass reservoir about 2 litres in volume, a McLeod pressure gauge giving readings accurate to $\frac{1}{1000}$ of a millimetre, and a mercury pump of small capacity. By using this reservoir and the pump of small capacity it was possible to diminish the pressure in the discharge tube by such exceedingly small amounts that it was easy to obtain a series of discharge potentials over the whole range of pressures investigated without the necessity of admitting fresh gas to the chamber.

In making measurements, one terminal of the battery was joined to earth and the other terminal was connected through a resistance of xylol to one of the electrodes of the discharge tube. The other electrode was permanently joined to one pair of quadrants of a quadrant electrometer, the second pair of which was kept to earth. In determining the potential difference necessary to produce discharge at a given pressure, the electrometer electrode was first earthed, a given potential applied to the battery electrode, and the earth connection of the electrometer electrode then removed.

If after waiting some minutes no discharge passed, the operation was repeated with a slightly higher potential applied to the battery electrode. This procedure was followed until a potential sufficiently high was reached to break down the gas and cause a discharge. The passage of the discharge could be readily noted, as it was accompanied by a violent deflection of the electrometer needle.

The well-known phenomenon of delay in the passing of the discharge, which has been investigated at length by WARBURG,* was observed throughout the experiments. It was especially marked in the neighbourhood of the critical pressure, discharge being frequently obtained ten or even fifteen minutes after the requisite voltage had been applied.

In every case, therefore, as the minimum sparking potential for any pressure was approached, a considerable time was allowed to elapse, with a given applied potential difference, before any increase was made.

III. *Experiments in Air.*

In the experiments on atmospheric air the whole discharge apparatus was first exhausted to a very low pressure and then re-filled by fresh air, which bubbled in very slowly, first through a wash-bottle of sulphuric acid and then through a tube tightly packed with phosphoric pentoxide. The discharge chamber was then exhausted to about 20 millims. of mercury and allowed to stand at this pressure for a period of from eight to twelve hours.

During this time the air was always in contact with phosphoric pentoxide in the drying tube, and was therefore entirely free from moisture when the measurements were taken.

The first measurements were made with the electrodes 3 millims. apart, and the spark potentials were determined over a range of pressures extending from 51 millims. down to ·35 millim. of mercury. The spark potentials corresponding to

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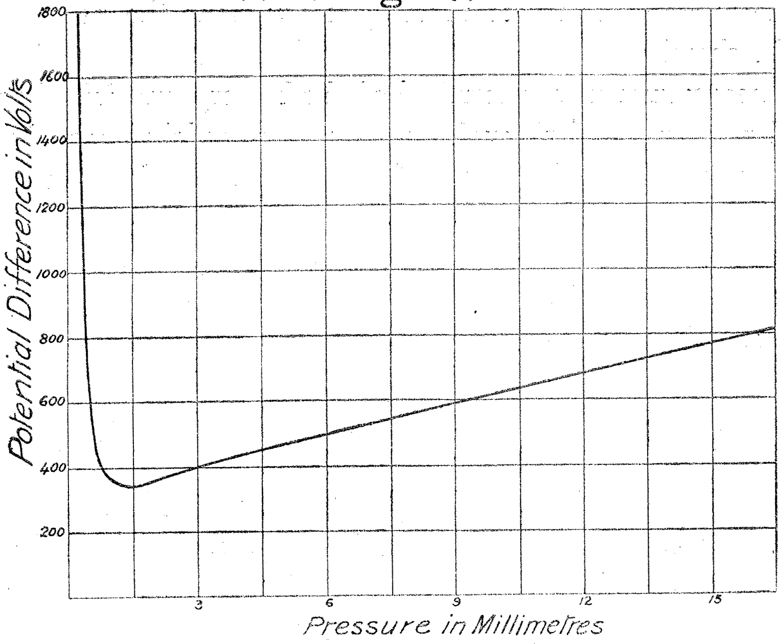
* WARBURG, 'Ann. d. Phys.,' vol. 62, p. 385.

the various pressures are recorded in Columns V. and VI. of Table I., and the results are represented graphically in fig. 2A.

Fig. 11 (a)



In making these determinations, the precaution was always taken of allowing eight or ten minutes to intervene between consecutive readings, in order to make certain that the air was in its normal condition when the discharge occurred. As can be seen from the figure, the curve is quite regular and exhibits all the peculiarities already noted by Peace,* Strutt,† and Bouty.‡ The curve, however, is carried much higher than those drawn by any of these experimenters, discharges corresponding to potential differences of over 1800 volts being recorded.

The distance between the electrodes was then varied and five different sets of readings were taken, in air, with the electrodes 1, 2, 3, 5, and 10 millims. apart, respectively. The complete set of numbers for these different spark lengths is given in Table I., and curves showing the readings taken over that portion of the range of pressure below 5 millims. of mercury are exhibited in fig. 2B.

It is apparent from the relative positions of these curves in the figure, that at points at and below the critical pressures, with a given potential difference applied to the electrodes, the pressures at which discharges occurred regularly decreased as the distance between the electrodes was increased. But a critical examination of the curves and also a reference to the numbers which they represent show that Paschen's law is rigidly applicable over the whole series of discharge potentials recorded.

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* Peace, 'Roy. Soc. Proc.,' vol. 52, p. 111.

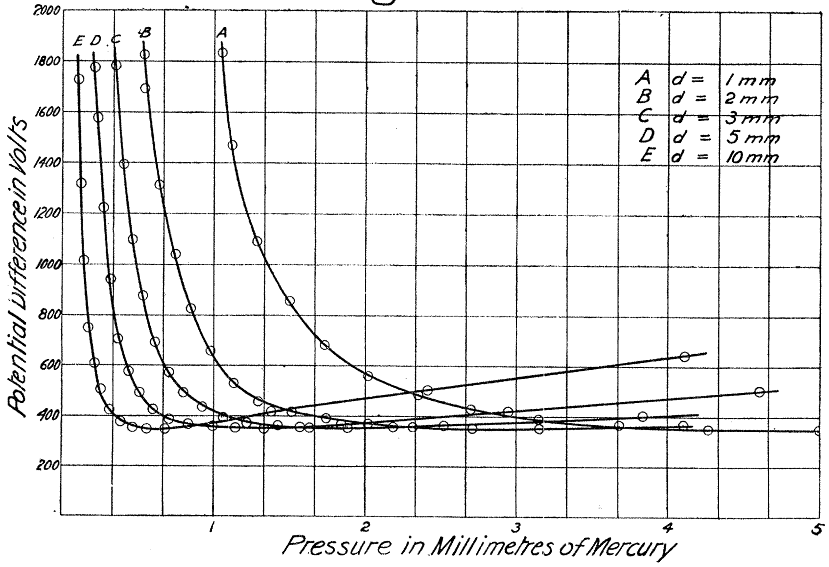
† Strutt, 'Phil. Trans.,' A, vol. 193, p. 384.

‡ Bouty, 'Compt. Rend.,' vol. 131 (2), p. 446.

TABLE I.—Air.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.
150	1510	20	620	51	1480	7·34	600	7·09	831
120	1265	13·2	527	41·5	1275	4·61	504	4·12	645
90	1025	8·73	455	31·5	1015	2·95	418	2·39	504
61	784	5·52	400	21·4	790	1·85	368	1·39	420
40·8	634	4·11	373	14·1	630	1·57	356	·982	372
21·6	489	3·16	355	9·31	526	1·34	349	·805	355
19·4	477	2·71	351	5·99	452	1·14	352	·679	348
12·4	417	2·32	357	3·84	405	·982	359	·562	351
7·77	367	2·02	371	2·51	371	·839	370	·466	359
6·66	357	1·75	389	2·18	361	·714	388	·384	377
5·80	352	1·52	419	1·89	356	·607	427	·312	425
4·98	349	1·30	460	1·64	358	·517	484	·259	504
4·27	355	1·13	534	1·42	364	·440	575	·219	605
3·67	368	·982	654	1·22	375	·375	705	·180	757
3·15	392	·857	826	1·06	397	·321	935	·152	1020
2·70	429	·750	1042	·928	441	·276	1223	·125	1315
2·35	481	·643	1312	·804	494	·232	1585	·105	1730
2·02	558	·549	1695	·710	576	·216	1774	—	—
1·74	681	·536	1829	·616	691	—	—	—	—
1·51	855	—	—	·536	863	—	—	—	—
1·29	1090	—	—	·465	1092	—	—	—	—
1·12	1463	—	—	·411	1395	—	—	—	—
1·05	1826	—	—	·357	1786	—	—	—	—

Fig. 11b– Air



For example, the pressures at which discharge took place with an applied potential of 1800 volts were, for the different distances between the electrodes, approximately:

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	1·05
2	·536
3	·351
5	·216
10	·105

and it will be seen that the numbers in Column II. are almost exactly in inverse proportion to the numbers in Column I.

Again, with an applied potential of 500 volts (say), the approximate pressures at which discharge occurred were:

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	2·35
2	1·30
3	·804
5	·517
10	·259

where the pressures are in the ratio 1·00 : ·55 : ·34 : ·22 : ·11, numbers which are again very nearly inversely proportional to the distance between the electrodes.

Further, we notice that the spark potential corresponding to the critical pressure in all cases was practically the same, 350 volts, and the values of the critical pressures for the different spark lengths were, from Table I.:

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	4·98
2	2·71
3	1·89
5	1·34
10	·679

and these numbers, while not exactly in the ratio 10 : 5 : 3 : 2 : 1, are still very close to it.

In finding the values for portions of the curves around the critical pressures the results given in Table I. show that a small variation in potential difference was associated with a relatively very large change in the pressures, so that a very small error in reading the potential difference would result in a large error in the pressure readings. It is interesting to note, however, that even under these unfavourable conditions a striking agreement is presented between the results obtained at critical pressures and the results demanded by Paschen's law.

In order to make the agreement between the numbers demanded by Paschen's law and those obtained in these experiments still more evident, the results recorded in Table I. are again given in a slightly different form in Table II., where each potential difference is associated with the product of the pressure at which discharge took place and the corresponding spark length. Paschen* found that at high pressures these products were constant for different distances between the electrodes, as long as the applied potential difference was the same.

The numbers recorded in Table II. show that the same law is rigidly applicable to all pressures, both high and low.

Table II.—Air.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.
150	1510	40	620	153	1480	36·7	600	70·9	831
120	1265	26·4	527	124·5	1275	23·0	504	41·2	645
90	1025	17·4	455	94·5	1015	14·7	418	23·9	504
61	784	11·0	400	64·2	790	9·25	368	13·9	420
40·8	634	8·22	373	42·3	630	7·85	356	9·82	372
21·6	489	6·32	355	27·9	526	6·70	349	8·05	355
19·4	477	5·42	351	17·9	452	5·70	352	6·79	348
12·4	417	4·64	357	11·5	405	4·91	359	5·62	351
7·77	367	4·04	371	7·53	371	4·19	370	4·66	359
6·66	357	3·50	389	6·54	361	3·57	388	3·84	377
5·80	352	3·04	419	5·67	356	3·03	427	3·12	425
4·98	349	2·60	460	4·92	358	2·58	484	2·59	504
4·27	355	2·26	534	4·26	364	2·20	575	2·19	605
3·67	368	1·96	654	3·66	375	1·87	705	1·80	757
3·15	392	1·71	826	3·18	397	1·60	935	1·52	1020
2·70	429	1·50	1042	2·78	441	1·38	1223	1·25	1315
2·35	481	1·28	1312	2·41	494	1·16	1585	1·05	1730
2·02	558	1·09	1695	2·13	576	1·08	1774	—	—
1·74	681	1·07	1829	1·84	691	—	—	—	—
1·51	855	—	—	1·60	863	—	—	—	—
1·29	1090	—	—	1·39	1092	—	—	—	—
1·12	1463	—	—	1·23	1395	—	—	—	—
1·05	1826	—	—	1·07	1786	—	—	—	—

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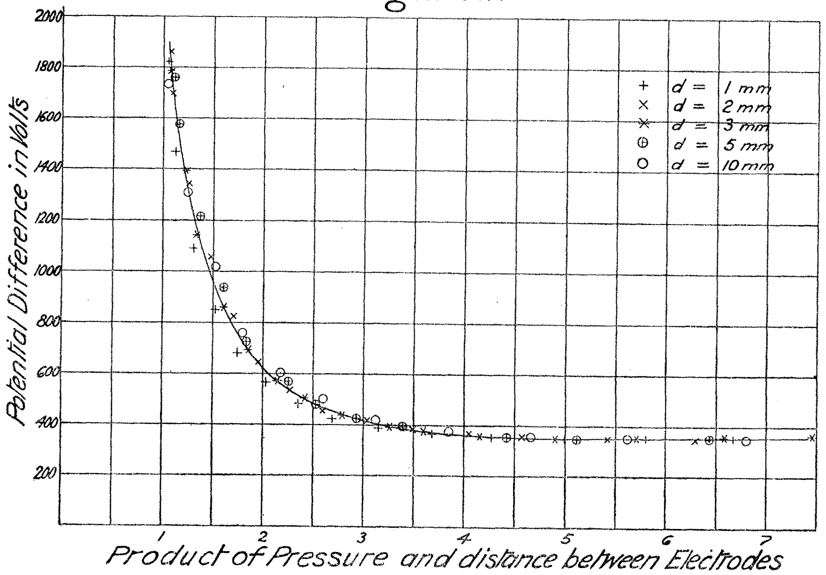
* Paschen, 'Ann. d. Phys.,' vol. 37, p. 69.

A like conclusion must be drawn from the curve shown in fig. 3, which graphically represents the numbers in Table II. In plotting this curve the products of spark lengths and discharge pressures were taken as abscissæ and the sparking potentials

Fig. III–Air



as ordinates. The regularity of the curve which represents the products for the five different electrode distances shows clearly that there can be no doubt regarding the applicability of Paschen's law to electric discharges, in air, at pressures at and below the critical point as well as at pressures above it.

IV. *Experiments in Hydrogen.*

In order to demonstrate, if possible, the generality of the law which has just been proven to hold for discharges in air, a series of measurements were made on the spark potentials in the gases hydrogen and carbon dioxide.

In these experiments exactly the same apparatus was used as in the previous experiments in air.

Preparatory to making the measurements in hydrogen the apparatus was first exhausted of air to a pressure of 1 millim. of mercury, or less, and then filled with hydrogen to atmospheric pressure. It was then exhausted and refilled with hydrogen several times to make certain that all air was removed.

The hydrogen was prepared from zinc and sulphuric acid in a Kipp apparatus, and, in order to ensure purity and freedom from moisture, was passed through wash-bottles containing potassium permanganate and caustic potash, and through a tube tightly packed with phosphoric pentoxide, before being led into the discharge chamber.

Also, just as in the experiments in air, the gas was always allowed to stand for several hours, at a pressure of about 20 millims. of mercury, in the presence of phosphoric pentoxide before any readings were recorded.

TABLE III.—Hydrogen.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.
21·7	328	23	435	13·6	415	13·6	469	7·58	526
16·2	300	14·8	360	8·54	356	9·35	415	4·37	427
11·9	281	11·0	323	5·40	301	6·02	350	2·55	335
10·3	278	8·08	299	4·66	286	3·80	300	1·77	299
8·94	287	6·95	285	4·02	278	3·28	287	1·46	283
7·74	306	5·93	279	3·44	282	2·80	281	1·22	287
6·52	335	5·04	284	2·93	292	2·41	282	1·01	295
5·57	374	4·30	293	2·52	310	2·05	285	·846	313
4·73	487	3·72	305	2·15	356	1·76	293	·700	343
4·11	649	3·23	333	1·85	440	1·51	305	·575	426
3·54	905	2·77	399	1·59	564	1·26	345	·470	595
3·04	1275	2·36	523	1·35	780	1·09	410	·390	850
2·60	1781	2·03	727	1·16	1054	·928	539	·330	1142
—	—	1·73	1010	1·00	1382	·808	706	·276	1477
—	—	1·48	1380	·861	1789	·700	975	·264	1710
—	—	1·33	1746	—	—	·600	1373	—	—
—	—	—	—	—	—	·516	1775	—	—

In the experiments with this gas, readings were taken for the same electrode distances 1, 2, 3, 5 and 10 millims., and the values of the spark potentials and their corresponding pressures are given in Table III. These numbers are also graphically set forth in fig. 4.

We see from this table that the readings corresponding to the spark potential 1800 volts are :

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	2·60
2	1·33
3	·861
5	·516
10	·264

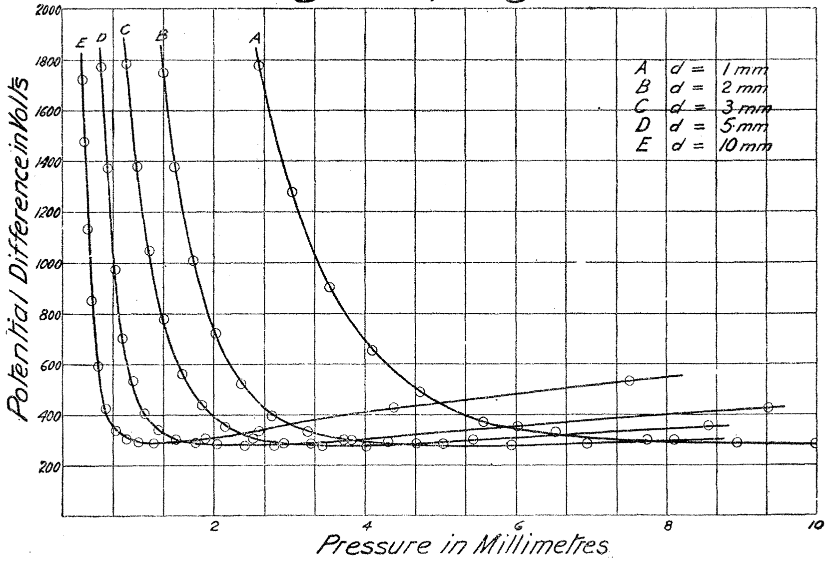
which pressures are in the ratio 9·9 : 5·0 : 3·2 : 2·0 : 1.

Again, with a spark potential of 500 volts the readings give :

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	4·7
2	2·4
3	1·7
5	·94
10	·51

the pressures being in the ratio 9·3 : 4·8 : 3·3 : 1·9 : 1.

Fig. IV—Hydrogen



The minimum spark potential in hydrogen was about 280 volts, and the critical pressures corresponding to the different spark lengths were:

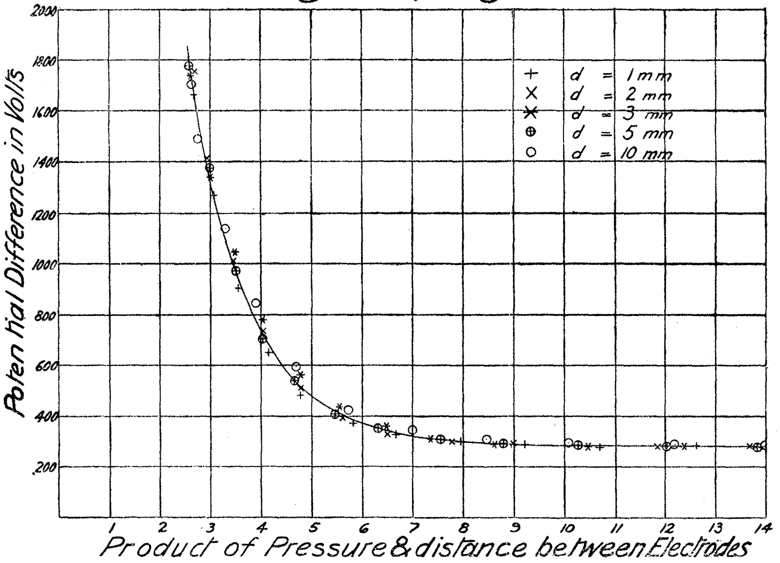
Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	10·3
2	5·93
3	4·02
5	2·80
10	1·46

where the various discharge pressures are once more nearly inversely proportional to the distance between the electrodes.

TABLE IV.—Hydrogen.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.
21·7	328	46	435	40·8	415	68	469	75·3	526
16·2	300	29·6	360	25·6	356	46·7	415	43·7	427
11·9	281	22·0	323	16·2	301	30·1	350	25·5	335
10·3	278	16·1	299	13·9	286	19·0	300	17·7	299
8·94	287	13·9	285	12·0	278	16·4	287	14·6	283
7·74	306	11·8	279	10·3	282	14·0	281	12·2	287
6·52	335	10·0	284	8·79	292	12·0	282	10·1	295
5·57	374	8·60	293	7·56	310	10·2	285	8·46	313
4·73	487	7·44	305	6·45	356	8·80	293	7·00	343
4·11	649	6·46	333	5·55	440	7·55	305	5·75	426
3·54	905	5·54	399	4·77	564	6·30	345	4·70	595
3·04	1275	4·72	523	4·05	780	5·45	410	3·90	850
2·60	1781	4·06	727	3·48	1054	4·64	539	3·30	1142
—	—	3·46	1010	3·00	1382	4·04	706	2·76	1477
—	—	2·96	1380	2·58	1789	3·50	975	2·64	1710
—	—	2·66	1746	—	—	3·00	1373	—	—
—	—	—	—	—	—	2·58	1775	—	—

Fig. V – Hydrogen



To indicate further that the law is applicable at all points, a table of products, similar to that recorded for air, was calculated, and is given in Table IV. A single curve, fig. 5, represents these five sets of readings, and again the close grouping of the different results about this common curve shows that the law is equally applicable above and below the critical pressure to all spark potentials.

It is evident, then, that with hydrogen, just as with air, PASCHEN's law is rigidly applicable over the whole range of pressures.

V. *Experiments in Carbon Dioxide.*

These further experiments were made with a view to corroborate the results already obtained in air and hydrogen. The same apparatus as had been used with these two gases again served for the experiments in carbon dioxide, and the distance between the electrodes was varied as before, so that readings were obtained at the five different distances 1, 2, 3, 5, and 10 millims. The carbon dioxide was prepared by treating marble with hydrochloric acid, and was purified and dried by being bubbled through a wash-bottle of water and passed through a tube tightly packed with phosphoric pentoxide before reaching the discharge apparatus. In each case the operation of exhausting the whole discharge apparatus to 1 millim., or less, of mercury, and then refilling with carbon dioxide was repeated five or six times, and finally the gas was allowed to stand as in both previous cases, in the presence of a bulb of phosphoric pentoxide for several hours.

The complete set of results is given in Table V., and the corresponding curves set forth in fig. 6, and if we again compare the discharge pressures and spark lengths corresponding to any value of the applied potential, the same law is seen to hold here also with even greater rigidity than in the other cases.

TABLE V.—Carbon Dioxide.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.
19·8	516	21·3	802	8·75	674	9·10	790	7·27	993
12·6	480	13·8	645	5·57	563	5·77	674	4·26	790
9·41	443	8·76	519	3·55	477	3·64	579	2·43	656
6·83	425	5·41	464	2·25	427	2·33	498	1·44	553
5·86	421	4·02	439	1·91	420	1·45	438	·860	473
5·02	419	3·46	426	1·63	419	1·25	423	·612	428
4·31	420	2·95	421	1·41	425	1·07	421	·510	423
3·73	427	2·52	419	1·20	432	·919	428	·409	440
3·18	443	2·15	420	1·02	449	·786	441	·340	470
2·73	475	1·84	427	·875	487	·678	464	·280	506
2·34	503	1·58	443	·758	542	·572	495	·239	563
2·00	559	1·34	473	·651	599	·492	533	·196	639
1·72	636	1·16	525	·558	699	·419	599	·162	761
1·47	763	·980	605	·482	815	·360	704	·134	973
1·26	916	·848	702	·420	971	·310	820	·111	1219
1·08	1127	·728	847	·362	1162	·266	969	·094	1550
·946	1432	·625	1026	·314	1445	·232	1159	·089	1730
·817	1801	·536	1258	·274	1756	·196	1373	—	—
—	—	·455	1574	—	—	·169	1662	—	—
—	—	·421	1762	—	—	·164	1770	—	—

For 1800 volts the figures are approximately :

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	·817
2	·421
3	·274
5	.164
10	·0892

where the pressures are almost in the required ratio, being 9·2 : 4·8 : 3·0 : 1·9 : 1.

For 500 volts the numbers are :

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	2·34
2	1·23
3	·84
5	·57
10	·28

where the pressures are as 8·4 : 4·4 : 3 : 2 : 1.

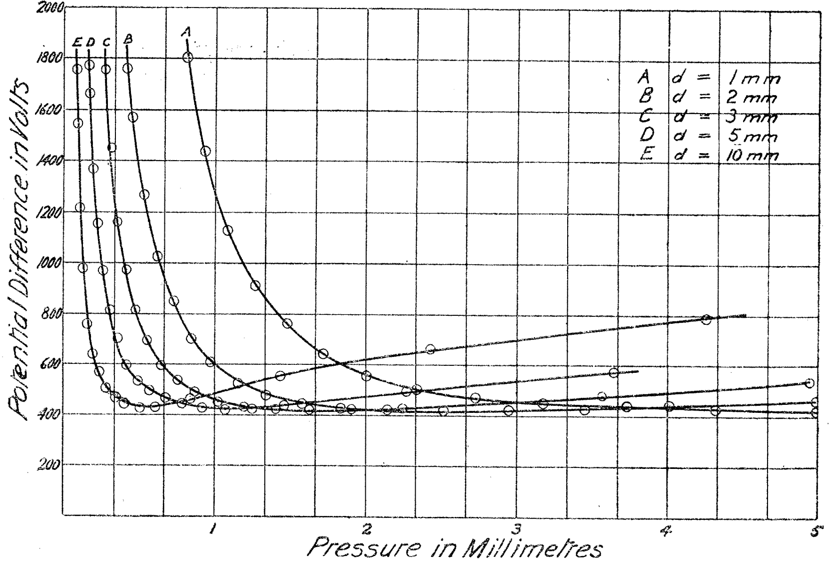
And at the minimum discharge potentials, which are again constant, 420 volts, the readings given are :

Distance between electrodes in millims.	Discharge pressures in millims. of mercury.
1	5·02
2	2·52
3	1·63
5	1·07
10	·510

Special attention is directed to these latter results, inasmuch as the exactness of the ratio indicated by the pressures is very remarkable. The ratios of the pressures are practically 10 : 5 : 3·1 : 2 : 1, the nearest approximation to the numbers demanded by PASCHEN's law which has been shown by any of the comparisons, and this result is all the more convincing in that these figures were obtained at the critical points, where, in the other two gases, the results obtained indicated the law in a somewhat less marked degree.

Though it would appear that further evidence was unnecessary, the table of products was again calculated and is given in Table VI. Also the corresponding curve is shown in fig. 7.

Fig. VI—Carbon Dioxide

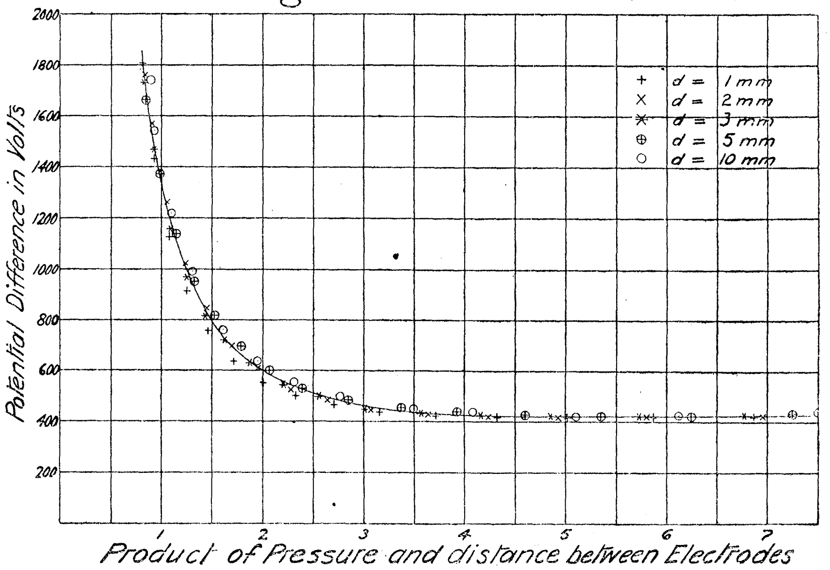


Once more the regularity of the curve shows that, as in air and hydrogen, so in carbon dioxide, PASCHEN's law is rigidly applicable to all spark potentials both above and below the critical pressure.

TABLE VI.—Carbon Dioxide.

Spark length = 1 millim.		Spark length = 2 millims.		Spark length = 3 millims.		Spark length = 5 millims.		Spark length = 10 millims.	
Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.	Product of pressure and spark length.	Spark potential in volts.
19·8	516	42·6	802	26·2	674	45·5	790	72·7	993
12·6	480	27·6	645	16·7	563	28·8	674	42·6	790
9·41	443	17·5	519	10·6	477	18·2	579	24·3	656
6·83	425	10·8	464	6·75	427	11·6	498	14·4	553
5·86	421	8·04	439	5·73	420	7·25	438	8·60	473
5·02	419	6·92	426	4·89	419	6·25	423	6·12	428
4·31	420	5·90	421	4·23	425	5·35	421	5·10	423
3·73	427	5·04	419	3·60	432	4·59	428	4·09	440
3·18	443	4·30	420	3·06	449	3·93	441	3·40	470
2·73	475	3·68	427	2·62	487	3·39	464	2·80	506
2·34	503	3·16	443	2·27	542	2·86	495	2·39	563
2·00	559	2·68	473	1·95	599	2·46	533	1·96	639
1·72	636	2·32	525	1·67	699	2·09	599	1·62	761
1·47	763	1·96	605	1·44	815	1·80	704	1·34	973
1·26	916	1·69	702	1·26	971	1·55	820	1·11	1219
1·08	1127	1·45	847	1·08	1162	1·33	969	·946	1550
·946	1432	1·25	1026	·942	1445	1·16	1159	·892	1730
·817	1801	1·07	1258	·822	1756	·98	1373	—	—
—	—	·910	1574	—	—	·845	1662	—	—
—	—	·842	1762	—	—	·820	1770	—	—

Fig. VII Carbon Dioxide



VI. *Spark Potentials with different Electrodes.*

It has now been shown, using brass electrodes of constant size, that, for discharges in a uniform field, in any gas, the values of the spark potentials are determined solely by the product of the pressure of the gas and the distance between the electrodes. From this result it appeared that if the size or material of the electrodes did not affect the results, the spark potentials were dependent only upon the quantity of the gas per unit cross section between the electrodes.

In order to determine this point, the brass electrodes which had been used up to this time were replaced in turn by electrodes of iron, zinc and aluminium, of exactly the same size. The results of the experiments showed that there was no variation in the different sets of readings, and it was evident that there was not the slightest effect produced in any case by a change in the material of which the electrodes were made.

In order to see if the size of the electrodes affected the values of the spark potentials for the different pressures, provided the discharge took place in a uniform field, a reduction was made in the surface of the electrodes exposed to the gas. This was done by replacing the ebonite rings C, C, fig. 1, which had an inner diameter of 3 centims., by others whose inner diameter was but 1 centim. By this device the areas of the electrodes exposed to the gas were reduced to about $\frac{1}{10}$ of their value in the early experiments, and the condition that the discharge could only take place in a uniform field still held. Using this apparatus with air, no difference could be observed in the values of the discharge potentials corresponding to the different pressures, and it was therefore certain that the value of the spark potential was in no way influenced by the size of the electrodes.

It is therefore clearly established that the only factors affecting the spark potentials are pressure and the distance between the electrodes, and hence PASCHEN'S law is most accurately expressed by saying, "that, with a given applied potential difference, discharge in a uniform field, in any gas, is dependent solely on the constancy of the quantity of matter per unit cross section between the electrodes."

VII. *Minimum Spark Potentials.*

An interesting result in connection with these experiments is the almost constant value obtained for the minimum spark potential with the different electrode distances in each of the gases.

PEACE,* in the paper already referred to, was able to point to the probable existence of such a condition, but his results were not sufficiently regular to allow him to speak with certainty from the evidence at that time in his possession. This is seen from the following table of results taken from his paper, which appear to be the readings upon which he based his conclusions :—

PEACE'S Table of Minimum Spark Potentials.

Spark length in millims.	Minimum discharge potential in volts.
·01	326
·025	330
·05	333
·1	354
·2	370
·3	390
·5	400
·7	428
1	458
2	475

While these results are of the same order, it will be noticed that the spark potential rapidly increases with the distance between the electrodes, and that the smallest value differs from the greatest by nearly 150 volts.

In the results recorded in the present experiments, however, it cannot be said that there is any indication of an increase in spark potential for an increasing spark length.

The minimum spark potentials observed in these experiments, for the three different gases, are given in the following table :—

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* PEACE, 'Roy. Soc. Proc.,' vol. 52, pp. 107, 112.

Observed Minimum Spark Potential in Volts.

Spark length in millims.	Air.	Hydrogen.	Carbon dioxide.
1	349	278	419
2	351	279	419
3	356	278	419
5	349	281	421
10	348	283	423

where it will be seen that the values of the minimum spark potentials, for air, over this large range of spark lengths vary by only 7 volts. The values for hydrogen, over the same large range of spark lengths, vary by only 5 volts, and those for carbon dioxide by only 4 volts.

These results, then, seem to establish the fact that the least spark potential required to break down a gas is entirely independent of the spark length.

It is evident, too, from figs. 3, 5 and 7, that the constancy of the minimum spark potential is a necessary condition to Paschen's law holding for discharges at different electrode distances.

R. J. Strutt,* in his paper "On the Least Potential Differences required to produce Discharge through Gases," has drawn the conclusion that the minimum spark potential for discharges in any selected gas is probably equal to the cathode fall, in the same gas, measured over the whole extent of the negative glow in the vacuum tube. Since the cathode fall in any gas has been shown by Warburg† to be a constant, over a very large range of pressures, the constancy of the values obtained in these experiments for the least spark potential gives strong support to Strutt's conclusion.

Moreover, the value of the least spark potential found by Strutt in air, using a spark length of $\frac{3}{4}$ millim., was 341 volts. This agrees very well with the numbers given above, the difference being only about 8 or 9 volts. For hydrogen, however, the agreement between the results is not so good, his values for the least spark potential, 302–308 volts, being somewhat higher than those found for hydrogen in these experiments.

In this connection it may be pointed out that special precautions were taken in the neighbourhood of the critical pressure to make certain that the gas was in its normal condition when the discharge occurred, and so make sure that the spark potential obtained was not too small. The procedure followed was to apply a low voltage to the electrodes, and then gradually increase it until the discharge passed. By this procedure there could be no doubt that the gas was always in its

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* Strutt, 'Phil. Trans.,' A, vol. 193, p. 393.

† Warburg, 'Ann. d. Phys.,' vol. 31, p. 545.

normal state, and that therefore no discharge could occur until the correct potential difference was reached.

After discharge did occur the gas was allowed to stand for a considerable time before the operation was repeated.

On account of the "delay" in the discharge, already referred to, special care was taken at the critical pressure to see that no voltage applied to the electrodes was replaced by a higher one, until a sufficient time had elapsed to make sure that discharge would not occur with the lower voltage.

VIII. *Connection between Spark Lengths and Spark Potentials.*

In the preceding experiments the spark potentials and corresponding pressures have been found for spark lengths ranging from 1 to 10 millims. It is evident from PASCHEN'S law, which has been shown to govern these discharges, that the different curves in figs. 2, 4 or 6 are interdependent, and that if one were given in each figure all the others could be deduced. It is clear, too, providing PASCHEN'S law applies, that curves can be deduced for spark lengths not included within these limits. This has been done in fig. 8, where curves corresponding to a number of spark lengths, in air, ranging from 1 millim. down to 5 micra* have been plotted.

The numbers corresponding to these curves were calculated by PASCHEN'S law from the experimental results obtained with a spark length of 1 millim. The values for spark lengths shorter than 5 micra have not been calculated, as there is evidence to show that PASCHEN'S law does not apply beyond this point. It can be seen that as the spark length is gradually decreased a length will be reached finally when the gas between the electrodes will consist of but two surface layers. It will then be subject to special molecular forces and, in all probability, a departure from the laws governing electric discharges in a gas under normal conditions will appear when this limiting spark length is reached.

This point has been well brought out by EARHART† in a paper on spark potentials for very short distances. He has shown, for a series of pressures, that a direct proportionality exists between spark potential and spark length, down to a spark length of about 5 micra. For shorter lengths than this he has shown that, while a law of proportionality still holds between spark potentials and spark lengths, the spark potentials diminish more rapidly for the same change in the spark length than they do in the range of longer distances.

It is true this critical spark length of 5 micra is of a higher order than most of the values found by a number of experimenters for the distance over which molecular forces act. The value of this distance given by QUINCKE,‡ deduced from the results

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* 1 micron = ·001 millim.; EARHART, 'Phil. Mag.,' January, 1901.

† EARHART, 'Phil. Mag.,' January, 1901.

‡ QUINCKE, 'Pogg. Ann.,' 1869, vol. 137, p. 402.

of experiments on capillary phenomena, is about ·05 micron. REINOLD and RÜCKER* found that the range of unstable thickness of a film began somewhere between ·096 and ·045 micron. A value of the same order is given by PLATEAU,† who fixes the superior limit of the radius of the sphere of molecular action at ·118 micron.

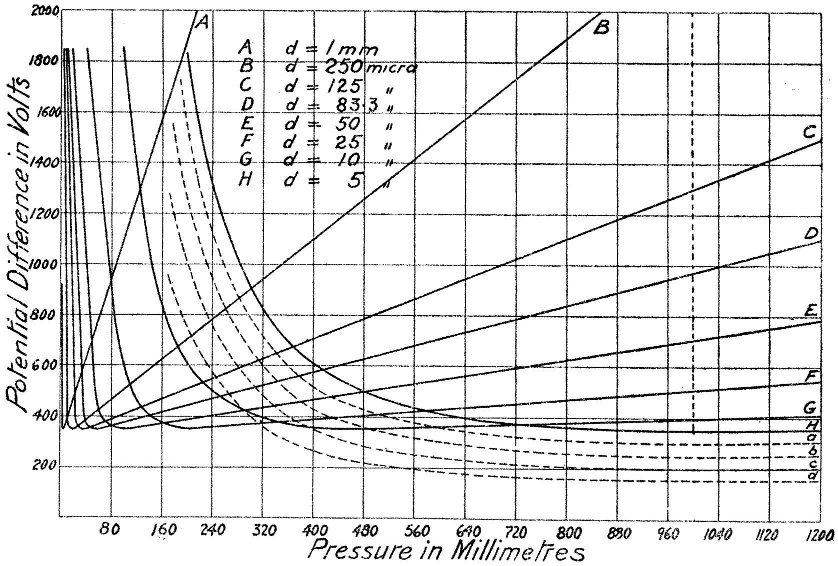

Fig. 8.

Results of a higher order, however, were obtained by MÜLLER-ERZBACH‡ and KAYSER.§ The former of these made experiments on the thickness of water and carbon bisulphide films, and finally concluded that the radius of the sphere of molecular action is at least 1·5 micron. KAYSER, experimenting on condensation of gases on glass threads, fixed the range of molecular action at from 2 to 3 micra.

Now the distance between the electrodes when the air film is reduced to the two surface layers is equal to the diameter of the sphere of molecular action, and there is thus strong experimental evidence from the data given above to support our adopting EARHART'S value of 5 micra for the smallest length to which we can legitimately apply PASCHEN'S law.

The experiments described in this paper have been made with a view to finding the relation between spark potentials and corresponding pressures for a constant spark length in air and other gases, but, as all the results for different spark lengths are connected by PASCHEN'S law, it is easy to deduce curves, for any gas, expressing the relation between potential differences and corresponding spark lengths at selected pressures. Such curves, for air, deduced from those exhibited in figs. 2 and 8, have been plotted for a series of different pressures and are shown in fig. 9.

It will be seen that these curves present a number of points of special interest.

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[*] REINOLD and RÜCKER, 'Phil. Trans.,' vol. 177, Part II., p. 684, 1886.

[†] PLATEAU, 'Statique des Liquides,' 1873, vol. 1, p. 210.

[‡] MÜLLER-ERZBACH, 'Wied. Ann.,' vol. 28, p. 696, 1886.

[§] KAYSER, 'Wied. Ann.,' vol. 14, p. 468, 1881.

The curve B, corresponding to a pressure of 1000 millims., which is the critical pressure for the spark length of 5 micra, fig. 8, is a straight line and shows that the spark lengths are directly proportional to the spark potentials for the whole range of spark lengths. It will be noticed, too, that at this pressure the minimum spark potential, 350 volts, to which special attention has been drawn in this paper, is that potential necessary to break down the gas for the shortest spark length to which we have considered Paschen's law is applicable.

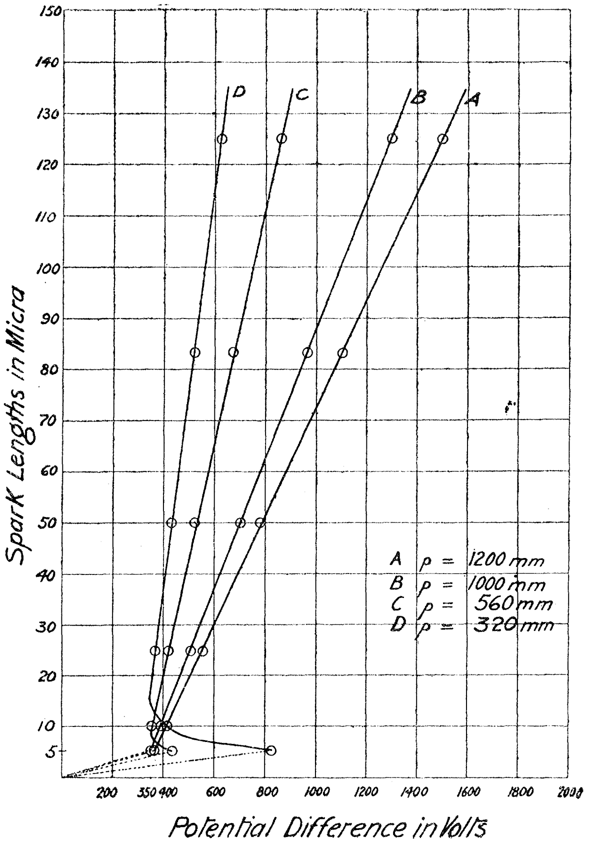

Fig. 9.

Again, the curve D, which is typical of all the curves for pressures below 1000 millims. of mercury, expresses the relation between spark potentials and spark lengths for a pressure of 320 millims.

It shows that the ratio of spark potential to sparking distance is constant for all spark lengths greater than 15 or 16 micra. For shorter spark lengths the spark potential increases with decreasing spark lengths until finally the 5-micra line is reached at a potential of about 820 volts.

The curve A, which is a type of those which can be drawn for pressures above 1000 millims. of mercury, differs from B in but one feature. The law of proportionality again holds throughout for this pressure down to the shortest spark length, but it will be seen that a potential difference of about 365 volts is necessary to produce discharge when the spark length of 5 micra is reached.

While the three types of curves which have been described all present different characteristics, it will be seen that all are confined to spark lengths above 5 micra, and to spark potentials greater than 350 volts.

Earhart has shown that for spark lengths below 5 micra the spark potentials again decrease as the spark lengths are shortened, until finally the two electrodes come together and direct electrical contact is established. Throughout this lower range of spark lengths his results also show, for a series of pressures, that the spark potentials vary directly with the spark lengths.

These experimental results of Earhart give an indication of the forms the curves in fig. 9 would have taken had the experiments with the apparatus used in this investigation been extended to the shorter set of spark lengths. Had this been done, it is highly probable that the curves in fig. 9, on reaching the 5-micra line, would have followed courses such as are indicated by the dotted straight lines in the figure.

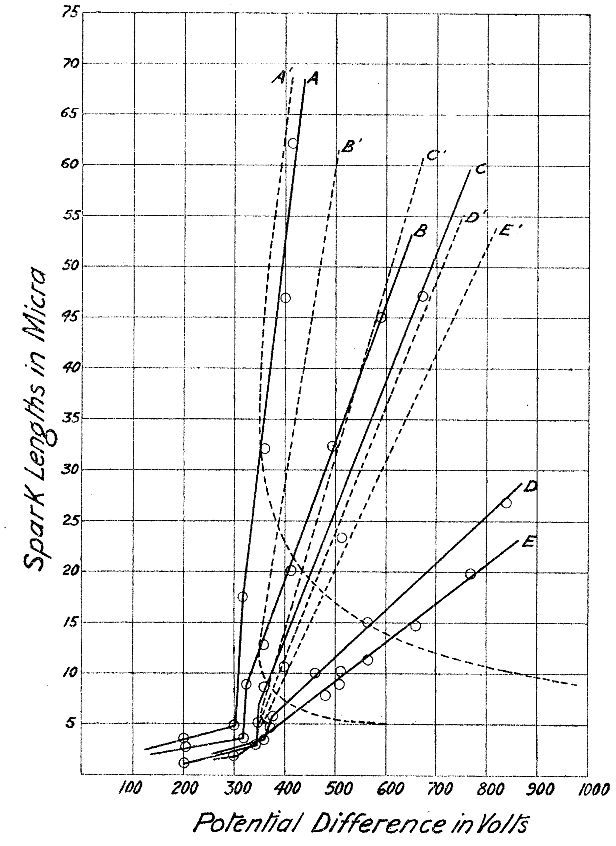

Fig. 10.

On this view it is of interest to examine the character of the pressure-spark potential curves that can be drawn in fig. 8 for spark lengths shorter than 5 micra.

It is clear that all these curves will lie below the 5-micra curve for every pressure, and since a law of proportionality applies between spark length and spark potential, at all pressures, it is easy to show that they fall off regularly down to the zero potential line. The dotted lines *a*, *b*, *c*, *d*, shown in fig. 8, indicate the relative positions of these curves.

In order to make a direct comparison between EARHART's curves and those which we have deduced, in fig. 9, by PASCHEN's law, a series of each is reproduced in fig. 10. In this figure, A, B, C, D, and E are drawn from the numbers given in EARHART's paper and correspond to pressures of 15 centims., 40 centims., 1, 2, and 3 atmospheres, respectively, while the dotted curves A′, B′, C′, D′ and E′ are deduced from fig. 8 for the pressures 15 centims., 40 centims., 1 atmosphere, 1000 millims. and 1200 millims., respectively.

For the higher range of spark lengths it will be seen that EARHART's values are invariably larger than those deduced for the same pressures in this investigation. This difference is especially noticeable in connection with the curves B and B′, which correspond to a pressure of 40 centims. With a spark length of 50 micra, for example, EARHART's spark potential for this pressure is 625 volts, while that indicated by the curve B′ is but 470 volts, a difference of about 25 per cent. This difference, however, is exceptionally great, and extends over a very limited range of spark lengths. For distances greater than 100 micra, the values of the spark potentials do not appear to differ by more than 8 or 10 per cent. It is evident, too, from EARHART's diagram, that an irregularity exists in regard to his curve for this pressure, as it does not take up the position one should expect from his curves for higher and lower pressures.

A comparison of the curves corresponding to pressures of 15 centims. and 1 atmosphere also shows that the average difference between the spark potentials for each of these curves, over the higher range of spark lengths, does not exceed 8 per cent. This constant difference in the two sets of results in all probability is due, at least in part, to the difference in the form of the electrodes used in the two investigations, as both BAILLE* and PASCHEN† give results which show that, for spark lengths of this order, the spark potentials obtained with spherical electrodes are in every case considerably higher than those obtained when the electrodes are parallel plates.

When spark lengths slightly greater than 5 micra are reached, EARHART's curves A, B, C, and D become more nearly vertical, and indicate that over a considerable range of spark lengths the spark potentials remain approximately constant. It will be seen, too, that the vertical portion of the curves becomes shorter and shorter with increasing pressures, until finally, at 3 atmospheres, curve E, it disappears altogether.

The deduced curves A′, B′, C′ also present some characteristic features over the same range of spark lengths. They each exhibit a minimum spark potential which is reached in each case at approximately the spark length where the constancy of spark

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* BAILLE, 'Annales de Chimie,' (5), vol. 25, p. 531, 1882.

† PASCHEN, 'Wied. Ann.,' vol. 37, p. 79, 1889.

potentials first appears in the corresponding curves of Earhart. These deduced curves then indicate rapidly increasing spark potentials down to the 5-micra line. It will be seen, too, that this feature of the curves extends over a range of spark lengths which diminishes with increasing pressures and finally disappears, as the curves D′ and E′ show, when a pressure of 1000 millims. is reached.

It is evident also from fig. 8 that the potential-spark length curves for all pressures greater than 1000 millims. (which is the critical pressure for the pressure-potential curve corresponding to 5 micra) will be similar in form to D′ and E′.

It thus appears that the two sets of curves, though differing widely in form for the lower range of pressures, yet present a resemblance as higher pressures are selected which becomes more and more marked. This can be seen very clearly from fig. 10, where each of the curves D′ and E′ has practically the same form as the curve E down to the 5-micra line and shows no indication of not following a course similar to E for spark lengths below 5 micra.

The explanation of the vertical portion of Earhart's curves seems evident. The results are in reality precisely what one should expect to obtain for low pressures when electrodes other than parallel plates were used. Take, for example, a pressure of 500 millims., fig. 8, which is the critical pressure for a spark length of 10 micra. With parallel plates as electrodes, it is clear that the spark potential-spark length curve would consist of a straight line down to a spark length of 10 micra, at which distance the spark potential is 350 volts, the minimum spark potential for a gas under normal conditions. If the distance between the electrodes is still further reduced, the resistance offered by the gas increases and a potential difference higher than 350 volts will be necessary in order to obtain discharge. At a pressure of 500 millims., therefore, a spark length of 10 micra is the one which offers least resistance. With spherical electrodes, for all spark lengths above 10 micra, the shortest distance between the electrodes is that of least resistance, and the discharge will take place along this line. But when the shortest distance between the spherical surfaces is less than 10, but greater than 5 micra, this distance is no longer the one which offers least resistance to the passage of the discharge, and under these circumstances a longer, but less difficult path will be followed. The path which offers least resistance is clearly the one which corresponds to the minimum spark potential. It follows, then, that while the shortest distance between the electrodes is decreased from 10 to 5 micra and the gas is kept at a pressure of 500 millims. discharge will always occur with a constant spark potential of 350 volts and will follow the path which corresponds to this difference of potential. As Earhart's experiments were performed with electrodes one of which was spherical and the other plane, the explanation will, in all probability, account for the ranges of constant spark potentials, which his results for different pressures indicate.

The explanation which has just been given evidently requires that the constant spark potential corresponding to the vertical portions of Earhart's curves should be the same, 350 volts, for all pressures. But it will be seen that he obtained, for pressures up to two atmospheres, values varying from 325 to 370 volts. This discrepancy, however, though marked, is not large and possibly is within the range of experimental error.

The results which Earhart obtained for spark lengths shorter than 5 micra cannot in any way affect the validity of this explanation, for he has shown without doubt that the discharges in this range are governed by a law which does not apply to the gas under ordinary circumstances.

IX. *Spark Potentials in Different Gases.*

In a paper on the cathode fall of potential in gases, by Capstick,* an attempt has been made to show that the cathode fall in a compound gas is related to the cathode falls in the elementary gases of which it is composed by a simple additive law. Experiments were made with hydrogen, oxygen, nitrogen, ammonia gas, and water vapour. The results, though not conclusive, were yet of sufficient weight to lead the author to the observation that the cathode fall is approximately an additive quantity and is probably a property of the atom rather than the molecule of a gas.

Owing to the difficulties experienced by Capstick and others in overcoming the intermittence of the current in the case of compound gases, the effort to extend his investigations to compound gases other than those mentioned was abandoned, and the question up to the present time has remained unsettled.

As already pointed out in this paper, experimental evidence has been brought forward by Strutt to show that the minimum spark potential should be equal to the cathode fall measured in the same gas. In view of this conclusion it seemed desirable to extend the experiments described in the first part of this paper to include a larger number of compound gases, in order to throw light, if possible, on the question raised by Capstick. Measurements were therefore carried out with the gases oxygen, nitrous oxide, hydrogen sulphide, sulphur dioxide and acetylene. A constant spark length of 3 millims. was used throughout in order that a direct comparison could be made between the results obtained with these gases and those already recorded for hydrogen and carbon dioxide. The results obtained with all the gases, using this spark length, are recorded in Table VII., and curves corresponding to the readings at the critical and lower pressures are shown in fig. 11.

All the curves present the general characteristic of a minimum spark potential, followed, at lower pressures, by rapidly increasing spark potentials. It will be seen, also, that the critical pressures and the minimum spark potentials vary with the different gases. The curves, too, cut each other in regular order, and at the lowest pressures their relative arrangement with regard to the ordinate axis is practically the inverse of that assumed by them with reference to the abscissa axis above the critical pressures.

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* Capstick, 'Roy. Soc. Proc.,' vol. 63, p. 356.

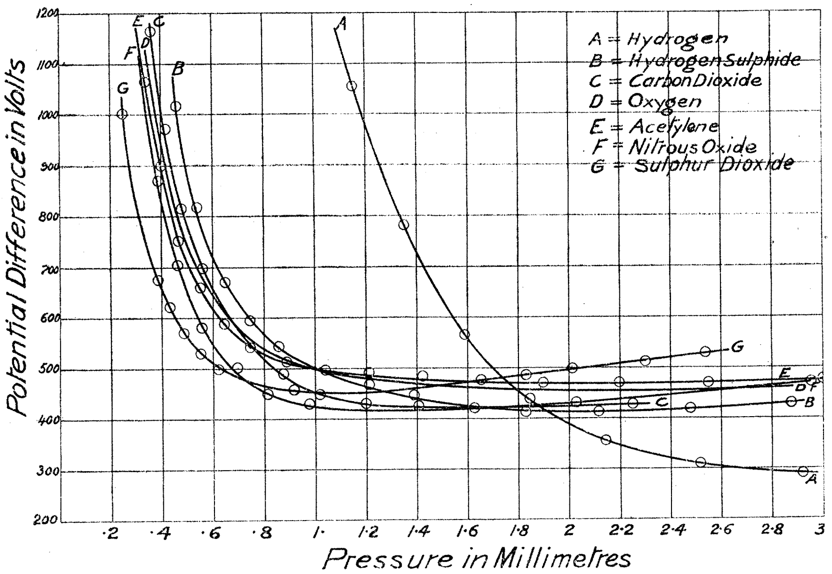

Fig. 11.

The values of the minimum spark potentials obtained in these experiments for the different gases are given in the following table :—

Gas.	Minimum spark potential in volts.
H_2	278
O_2	455
H_2S	414
CO_2	419
N_2O	418
SO_2	457
C_2H_2	468

Owing to the special precautions taken by STRUTT* to obtain an accurate value for the minimum spark potential in nitrogen, measurements were not taken with this gas. Adopting STRUTT's value of 251 volts for nitrogen, it will be seen that, with the exception of oxygen, all the minimum spark potentials given above obey an additive law ; that is, if H′, N′, O′, &c., represent the spark potential constant corresponding to an atom of the gases H_2, N_2, O_2, &c., respectively, the minimum spark potential for any compound gas whose formula is $H_x \, . \, N_y \, . \, O_z$, &c., will be equal to $xH' + yN' + zO' +$ &c.

If we assume the truth of this law and calculate H′, N′, O′, &c., from the minimum spark potentials for H_2, N_2, H_2S, SO_2 and CO_2 we find :

$$H' = 139, \quad N' = 126, \quad C' = 98, \quad S' = 136, \quad O' = 161,$$

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* STRUTT, 'Phil. Trans.,' A, vol. 193, p. 385.

TABLE VII.—Spark Length = 3 millims.

Hydrogen.		Carbon dioxide.		Nitrous oxide.		Acetylene.		Hydrogen sulphide.		Sulphur dioxide.		Oxygen by electrolysis.		Oxygen from potassium permanganate.		Oxygen from potassium chlorate.	
Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.	Pressures in millims. of mercury.	Spark potential in volts.
13·6	415	8·75	674	8·64	716	14	765	9·73	617	13·5	1145	8·42	576	8·07	556	8·75	596
8·54	356	5·57	563	5·00	560	8·7	633	5·29	467	7·7	842	4·85	523	4·71	494	4·92	524
5·40	301	3·55	477	2·95	470	7·4	583	3·90	442	4·5	651	3·42	483	3·25	466	3·44	477
4·66	286	2·25	427	2·03	430	6·4	555	2·88	428	2·54	531	2·82	468	2·72	456	2·86	464
4·02	278	1·91	420	1·70	420	5·5	530	2·48	418	2·30	511	2·34	461	2·27	453	2·37	439
3·44	282	1·63	419	1·41	418	4·7	509	2·12	414	2·01	501	1·94	458	1·88	462	1·97	457
2·93	292	1·41	425	1·18	422	4·1	490	1·83	414	1·83	486	1·60	455	1·57	474	1·62	457
2·52	310	1·20	432	·982	430	3·5	480	1·57	432	1·61	471	1·33	456	1·30	486	1·35	467
2·15	356	1·02	449	·816	450	3·0	474	1·39	457	1·40	466	1·10	463	1·08	501	1·12	484
1·85	440	·875	487	·670	500	2·55	468	1·20	472	1·23	461	·910	493	·901	516	·941	503
1·59	564	·758	542	·560	581	2·2	468	·86	543	1·20	459	·759	533	·750	536	·782	544
1·35	780	·651	599	·466	706	1·9	471	·73	592	1·04	457	·625	631	·616	566	·646	621
1·16	1054	·558	699	·389	866	1·66	476	·63	668	·92	459	·517	766	·501	645	·535	711
1·00	1382	·482	815	·326	1061	1·42	483	·54	817	·80	465	·428	1001	·428	763	·446	832
·861	1789	·420	971	·277	1370	1·21	490	·46	1013	·70	481	·354	1250	·357	987	·366	1003
—	—	·362	1162	·251	1830	1·04	498	·39	1286	·62	498	·294	1578	·303	1289	·305	1283
—	—	·314	1445	—	—	·89	513	·33	1650	·55	531	·268	1802	·260	1726	·255	1710
—	—	·274	1756	—	—	·65	588	—	—	·43	621	—	—	—	—	—	—
—	—	—	—	—	—	·47	754	—	—	·27	1000	—	—	—	—	—	—
—	—	—	—	—	—	·34	1064	—	—	·23	1590	—	—	—	—	—	—
—	—	—	—	—	—	·28	1302	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	·24	1650	—	—	—	—	—	—	—	—	—	—

and if we use these values to calculate the minimum spark potentials in the remaining gases, we obtain :

Gas.	Value found by experiment.	Calculated value.
C_2H_2	468	474
N_2O	418	412
O_2	455	321

The agreement between the observed and calculated values for each of the gases N_2O and C_2H_2 is very marked, and is a strong evidence that the additive law holds. The only case in which there is any serious difference between the observed and the calculated values is that of oxygen. Judging that this discrepancy might be due to impurities, three specimens of this gas were prepared by independent methods. It was prepared in turn by electrolysis, by heating potassium permanganate, and by heating a mixture of potassium chlorate and manganese dioxide. In every case the gas was purified by being passed through a mixed concentrated solution of potassium iodide and caustic potash and through concentrated sulphuric acid. It was also carefully dried in the usual way. It will be seen from Table VII. that the three sets of readings practically coincide at every pressure, and, since it is not possible that the same impurity could be present in each of these specimens to the same degree, it does not seem reasonable that the irregularity in oxygen could be traced to impurities arising from any lack of precaution in the preparation of the gases.

It is well known, however, that when an electric discharge is passed through oxygen, a considerable quantity of ozone is produced. It is in fact by this method that ozone in its purest form can be obtained. It is highly probable, then, that after the first discharge had passed between the electrodes, in the experiments on oxygen, a considerable percentage of ozone was present in the gas, and it may be that the discrepancy noted above is due to this cause. The experimental value of 455 volts found for oxygen seems to bear out this conclusion, for, ascribing the value of 161 volts to the atom of oxygen, we get by addition 483 volts as the calculated value of the minimum spark potential for ozone. The difference between the two values is but 28 volts, and assuming that the discharge occurs initially through the dissociation of ozone rather than of oxygen, the result is not in opposition to the additive law which has been shown to hold for the other gases. This large influence of a small amount of a denser gas when mixed with one less dense is in accord with the results obtained by previous experimenters, for WARBURG* and CAPSTICK† in their experiments on the cathode fall, and STRUTT‡ in his experiments on the

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* WARBURG, 'Wied. Ann.,' vol. 31, p. 545.

† CAPSTICK, 'Roy. Soc. Proc.,' vol. 63, p. 360.

‡ STRUTT, 'Phil. Trans.,' A, vol. 193, p. 385.

minimum spark potential, found that a very small percentage of oxygen increased their values for nitrogen by an amount out of all proportion to the quantity of the denser gas present.

The calculated values for the minimum spark potential in water vapour and in ammonia are 439 volts and 543 volts respectively, and the values found by CAPSTICK for the cathode fall in these gases are respectively 469 and 582 volts. When we consider that the values in the one case are calculated from the measurements made on one effect, while the values in the second case are the direct experimental results on an entirely different effect, this comparatively close agreement not only forms a corroboration of STRUTT's conclusions, but also lends support to the view that the minimum spark potential has to do with the atoms rather than the molecules of a gas, and is determined, in any special case, by the application of a simple additive law.

In this connection it may be mentioned that the value found by STRUTT* for the cathode fall in the monatomic gas argon, 167 volts, corresponds very closely with the constants which we have ascribed to the atoms of the various gases mentioned above. His value, 226 volts, for the monatomic gas helium, however, is considerably larger than any of the atomic constants we have deduced.

In performing these experiments, all ordinary precautions were taken to ensure the purity of the gases. The nitrous oxide was prepared by heating ammonium nitrate in a flask, and the gas was collected over water, but was well dried with phosphorous pentoxide before being passed into the discharge tube. The sulphur dioxide was prepared from copper and sulphuric acid. In order to purify it the better, the gas was dried and then liquefied. It was further dried by being passed through a phosphoric pentoxide tube before reaching the discharge apparatus.

Acetylene was obtained in the usual way by the action of water on calcium carbide, and was carefully dried with sulphuric acid and phosphoric pentoxide. Hydrogen sulphide was prepared in a Kipp apparatus from ferric sulphide and sulphuric acid. It was slowly bubbled through wash-bottles of water and then carefully dried in the usual way.

In every case, as in the early part of the experiments, the gas remained in the discharge chamber in the presence of phosphoric pentoxide for several hours before any readings were taken.

X. *Summary of Results.*

1. The law governing electric discharges between parallel plates, in a uniform field, in any gas, for pressures at and below the critical pressures, is that which PASCHEN found to hold with spherical electrodes for high pressures, viz., that, with a given spark potential, the pressure at which discharge occurs is inversely proportional to the distance between the electrodes.

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* STRUTT, 'Phil. Mag.,' March, 1900.

2. The values of the spark potentials are not influenced at any pressure by the size of the electrodes, provided the discharge takes place in a uniform field.

3. Plates of iron, zinc, aluminium, and brass were in turn used as electrodes, but the material out of which the electrodes were made was not found to affect the values of the spark potentials at any pressure.

4. When the discharge was compelled to pass in a uniform field between parallel plates the minimum spark potential in any gas was found to be a physical constant for that gas, being independent of the pressure and of the distance between the electrodes.

5. Evidence has been adduced which indicates that Paschen's law is applicable to discharges in a uniform field between parallel plates as long as the distance between the electrodes is greater than the diameter of the sphere of molecular action.

6. The minimum spark potential has been shown to vary with different gases. The results obtained with a large number of elementary and compound gases show that the minimum spark potential is a property of the atom rather than the molecule, and that for any selected gas it may be calculated by the application of a simple additive law.

In conclusion, I desire to thank President Loudon for the kindly interest he has always shown in my work by placing at my disposal every facility the laboratory afforded.

To Dr. J. C. McLennan, also, under whose immediate supervision these experiments were carried out, I am deeply indebted for valued assistance. I cannot adequately express how much I owe to his encouragement and advice.