SOME EXPERIMENTS ON THE CATHODE FALL.

Part I. In Neon and Helium,
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I. *Introduction.*

When an electric current is passed through a gas at low pressures, among other phenomena, two characteristic effects are always observed; firstly, an unilluminated space near the cathode and secondly a layer of bright glow. The space near the cathode, extending as far as the bright glow, is known as the "Crooke's Dark Space" and the glow, which is always distinctly visible on account of its characteristic colour, is called the 'cathode glow' or the 'negative glow'. This part of the electric field, which comprises the dark space and the cathode glow, has formed a subject of investigation for many observers. Warburg was the first to introduce the name "cathode fall" for the difference of potential between the front surface of the cathode and the bounding surface of the dark space, i. e., the surface where the glow begins.

Hittorf (Ann. d. Phys. u. Chem. 1883 *20*, 705) was one of the original experimenters in this field of research and his method was based on certain assumptions as to the use of small metallic sounds in the electric field.

Some of Hittorf's assumptions appeared very doubtful to Warburg (Ann. d. Phys. u. Chem. 1887, *31*, 545) who afterwards carried out experiments which led him to believe that although several of the assumptions were not altogether free from objections, still they did not affect the result to an appreciable extent. On the basis of these conclusions he measured the cathode falls for certain metals like platinum, copper, magnesium, aluminium and others in atmospheres of nitrogen and hydrogen

Later, Warburg (Ann. d. Phys. u. Chem. 1890, *40*. 1.) attempted to investigate the relation of the cathode fall to the pressure of the gas. His results led him to believe that the cathode fall was independent of the pressure of the gas and also of the total current, but in the latter case, subject to the condition that the cathode surface was not completely covered with the glow. This value he defined as the 'normal cathode fall' and found that it was almost the same for cathodes of platinum, zinc, copper, silver and iron. Aluminium and magnesium cathodes, however, showed very low values. Some of his later experiments were to investigate the effect of an impurity in a gas on the value of the cathode fall and he observed that an impurity generally raises it.

Using the same method of exploring wires, Mey (Verh. d. d. phys. Ges., 1903, *5*, 72.) worked on some alkali metals and found that their cathode fall potentials were strikingly low when the gas used was helium.

Experimenting on photo-electric effects, Gehlhoff (Verh. d. d. phys. Ges., 1910, *8*, 411.) observed that ultra-violet radiations falling on a potassium cathode lower its cathode fall from 64 to 38·5 volts in argon.

Defregger's (Ann. d. Phys., 1903, *12*, 662.) measurements on various metals in helium were done in the same way as Mey's and will be referred to later on.

Later, Skinner and his co-workers, (Skinner, Phys. Rev., 1915, *5*, 494; 1915, *6*, 158; Cheney, Phys. Rev. 1916, *7*, 241; Neuswanger, Phys. Rev. 1916, *7*, 253.) still using exploring metallic wires, made some measurements on aluminium, nickel, platinum, steel and zinc cathodes in atmospheres of hydrogen, oxygen and nitrogen. Some of the values obtained have been used by Skinner in the construction and verification of an elaborate theory of the cathode fall in gases.

In addition to the above investigations on the total cathode fall, a considerable amount of work has been carried out on the actual distribution of the electric force in the dark space.

Graham (Ann. d. Phys. u. Chem. 1898, *64*, 49.) observed certain maxima and minima in the electric force and an abrupt increase of the potential gradient at the cathode surface.

Wehnelt (Ann. d. Phys. 1903, *10*, 542.) repeated these experiments but could not find any irregularities in the electric force except that it was high near the cathode. He was

very uncertain about the point as to whether the potential gradient gradually dropped to zero at the cathode surface or whether it really assumed a characteristic high value, different for each metal, according to the expectations of Warburg.

Westphal (Verh. d. d. phys. Ges. 1910, *8*, 275.) observed a sudden drop of potential at the cathode surface which he called "Kathodensprung".

All these observers made use of the method of exploring wires introduced into the gas although it was realised by many of them that this procedure was open to objection. Wehnelt himself (Verh. d. d. phys. Ges. 1911, *11*, 505.) suggested that great care must be taken in making electric measurments by means of exploring wires, because of the deformation of the equipotential surfaces near the cathode due to the glass walls sending currents of Kanalstrahlen towards the middle of the tube and to the presence of the metallic points of the sounds themselves. Sir J. J. Thomson (Cond. of Elect. in Gases 2nd. ed. p. 531) pointed out that measurements with sounds were particularly open to objection when the pressure of the gas is very low (i. e. when there is not a plentiful supply of positive and negative ions in the gas) and when the sound is placed in the Crooke's dark space where the conductivity is very low. Aston (Proc. Roy. Soc. A. 1911, *84*, 533.) has discussed the subject at considerable length and has come to the conclusion that under certain conditions the errors resulting from the method of sounds may be very large.

To obviate these difficulties, Sir J. J. Thomson suggested a new method, which required no doubtful assumptions and did not introduce substantial obstacles in the path of the discharge. This method consisted in shooting a beam of cathode rays transversely through the discharge, their deflexion being taken as a measure of the electric force at that place.

F. W. Aston (loc. cit. p 526) used this method for the measurement of the distribution of electric force in the dark space and arrived at three main conclusions: firstly, that there is practically no potential gradient in the negative glow, its conductivity being very large like that of a liquid electrolyte; secondly, that the potential fall in the dark space varies according to a very simple law; and thirdly, that the so called "anode fall" does not exist. These experiments suggest a very accurate and a simple method for the measurements of the cathode fall, since according to Aston's results the cathode fall should be equal to the total difference of potential across the electrodes, when the anode is situated in the negative glow.

II. Apparatus.

The general arrangement of the apparatus is shown in Fig. I. The current was obtained from the Institute D. C. supply mains of 220 volts in combination with a battery of small secondary cells giving 252 volts. The potential accross the electrodes was measured by means of an accurate high resistance voltmeter (V) in series with another high resistance, the total resistance being 120,000 ohms. This could be easily read to 1 volt, and the current consumption was very small. A variable water-resistance (W) was placed in the main circuit and it will be seen by reference to the diagram that if the current is not passing through the discharge tube a varying E. M. F. may be applied to its electrodes, affording rough measurements of the sparking potential. A galvanometer with a low resistance shunt was used to indicate the magnitude of the current. This was not required with any degree of accuracy but was useful for comparison. A telephone (T) placed in series with the discharge tube was used to detect the existence of intermittent discharges. Measurements were made only when the telephone remained silent, as was always the case when the gases were pure, although impure gases tended to give an intermittant discharge. A small induction coil was used for illuminating a spectrum tube and in certain cases to start a discharge.

A large Toepler mercury pump (not shown in the diagram) of about a litre capacity was employed for evacuation. A mercury manometer was used to read pressures to tenths of a millimeter. Two charcoal bulbs (c_1 c_2) immersed in liquid air were used to purify and store up the gases during the experiments. A Geissler's tube (S) mounted on the apparatus near the manometer admitted of spectroscopic examination of the gas under investigation. Descriptions of the different forms of discharge tubes will be given later on.

III. Investigation of Experimental Conditions.

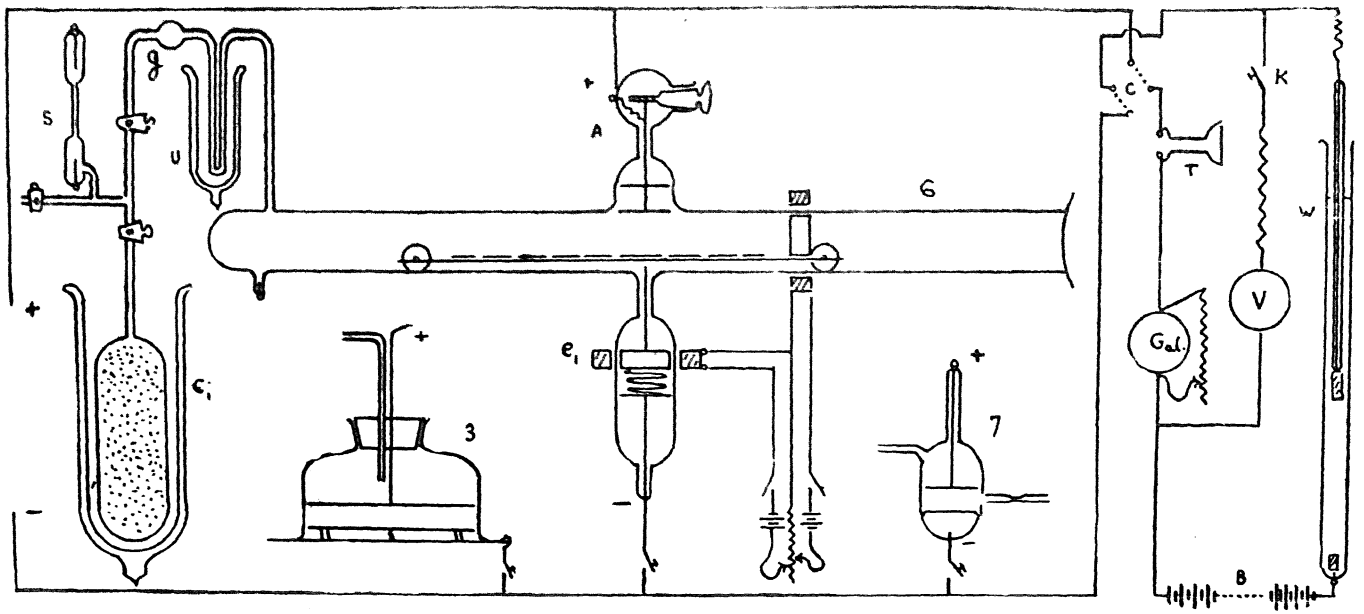
In a conducting gas at low pressure the total difference of potential between the electrodes may be divided into three portions in the most general case.

i. The potential difference between the cathode and the first bounding surface of the negative glow.

ii. The potential difference between the ends of the negative glow.

iii. The potential difference between the end of the negative glow remote from the cathode and the anode surface.

Figure 1.



A. Winding up anode.
B. Battery.
C. Commutator.
Gal. Galvanometer.
K. Voltmeter key.
S. Spectrum tube.
T. Telephone.
V. Voltmeter.
W. Water resistance.
c_1 Charcoal bulb.
g Gold leaf bulb
e_1, e_2 Electromagnets.
U. liquid-air cooled U-tube.
3, 6, 7 Different discharge tubes.

In general, a voltmeter placed across the electrodes will read the sum of all these three. The drop in potential in the second portion is negligible, while that in the third portion may be eliminated, as was shown by Aston, by placing the anode in the negative glow. Consequently it should be easy to measure the remaining portion or cathode fall by correct disposition of the anode. Preliminary experiments, however, showed that this apparently simple condition is not always to be attained in practice, or rather, it was found that the value of the cathode fall determined by this method was by no means constant. It was, therefore, decided to conduct a systematic investigation upon the requirements necessary to obtain reliable results. This will be described later.

The next consideration is the choice of gas. It is obviously unwise to use a gas which is likely to have any action upon the electrodes. For this reason, much of the work by other observers on the cathode fall has been carried out with hydrogen. It is well known, however, that hydrogen is occluded to a large extent by most metals and also given off again by them under certain conditions of the electric discharge. This is a drawback to its use, at least for the most fundamental experiments. The gases helium and neon present special advantages, in that they appear to have no action upon any metals, and what is even more important, they are very easy to obtain in a state of high purity. For this reason it was decided to use them at least for the preliminary experiments. To secure the greatest possible freedom of the gas from contamination the following precautions were adopted. All the joints and connections were made of glass where possible. In a few cases, where fused joints were impracticable, sealing wax was used to effect a connection. Considerable previous experience had shown that the use of this material had no appreciable effect upon the discharge in any way, provided that the wax was never directly in the path of the discharge and was not allowed to become warm. Taps were avoided wherever possible, especially as it is very difficult to keep them perfectly air-tight even with the best tap-grease in a warm climate. The gases, initially in a state of high purity, were let into bulbs containing cocoanut charcoal and allowed to remain for about half an hour before use, all the while cooled in liquid air. They were then admitted into the discharge tube, passing on the way through a bulb full of gold leaf and a U-tube immersed in liquid air to remove traces of mercury vapour. The further precautions necessary for obtaining the discharge in the gas while still uncontaminated will be discussed later, (p. 157).

As mentioned previously, Warburg has stated that the cathode fall is independent of the pressure of the gas, and of the total current, provided the cathode is not covered by the negative glow. In addition to the fact, however, that his results were obtained by the method of sounds, most of his measurements were made in gases which were moist or otherwise impure, and in many cases there were considerable variations between the results of different experiments. He also suggested that the walls of the tube might influence the readings, and in view of these sources of error, it was thought desirable to confirm his results and also to study the effects of the walls of the tube and of the distance between the electrodes on the discharge. For this purpose four discharge tubes were constructed with electrodes made from the same sheet of copper. To obtain the simplest conditions, the electrodes were in all cases plane and parallel. The dimensions of these tubes were as follows :—

No. 1 Electrodes 0·25 cm. in diam. 1·5 cm. apart.

No. 2 Electrodes 1·2 cm. in diam.

The distance between the electrodes could be varied by means of a thread which could be wound on a rod entering the tube through a ground glass joint, (cf. diagram on page 159)

No. 3 Electrodes 7·2 cm. in diam.

No. 4 Electrodes 1·2 cm. in diam.

In the three tubes 1, 2, 3, the electrodes were the same size as the diameter of the glass tube, while tube No. 4 had electrodes the same size as No. 2 but enclosed in a glass tube 3·5 cm. wide. All these four tubes were connected together so that they could be simultaneously filled with the same sample of gas.

No. 1 always showed a bright and striated positive column, at times as long as 12 millimeters, and the tube and the electrode surfaces were so small that it was impossible to regulate the current so as not to cover the whole surface of the cathode. It was also noticed that the negative glow was much shorter than in the large tubes. Under the most favourable conditions it was found that the potential difference across this tube was about 100 volts higher than that in the larger tubes, and it soon became obvious that no reliable results were to be obtained with such small electrodes

The large tube No. 3, however, was found to give very consistent results. In a preliminary experiment, when the distance

between the electrodes was 1·5 cm, the negative glow appeared like a luminous patch upon the cathode. But in many cases there appeared a distinct bright glow on the anode of exactly the same geometrical shape as the cathode glow and opposite to it. Consequently the distance was reduced to 0·6 cm. and an experiment was made with a slightly impure sample of neon, containing traces of hydrogen. Although the value for cathode fall was much higher than the one obtained afterwards with this gas in a high state of purity, still the experiment indicated that if all the necessary conditions were satisfied the cathode fall was a quantity constant over a wide range of pressures and current-strengths. Measurements were made of the sparking potential and of the minimum E. M. F. between the electrodes when the discharge was passing, at a number of pressures and the following values were obtained.

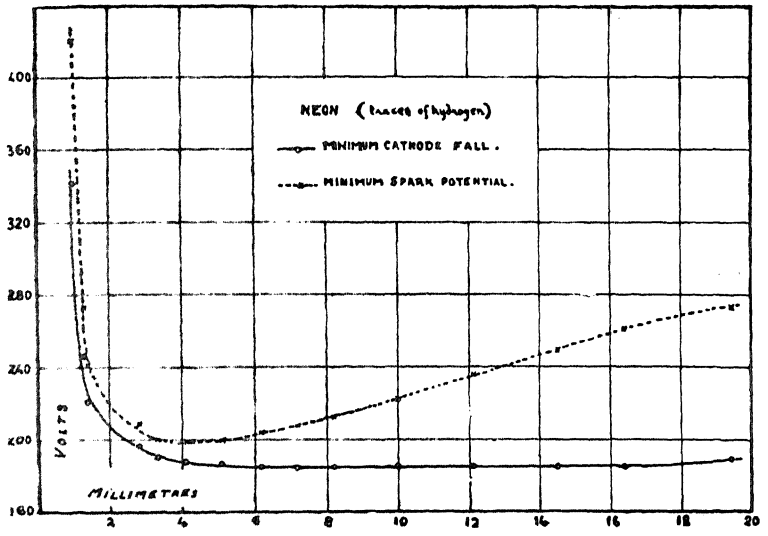
NEON (traces of hydrogen). Copper cathode.

Pressure mm.	Minimum cathode fall. Volts.	Minimum spark potential. Volts.
19·4	189	273
16·4	185	261
14·5	185	249
12·1	185	236
10·0	185	222
8·2	185	212
7·2	185	208
6·2	185	204
5·1	187	200
4.1	188	199
3·3	190	200
2·8	197	209
1·4	221	241
1·3	246	273
1·0	342	420

In column 2 is given the potential difference between the electrodes observed when the current was passing. All these figures were constant to 1 volt when the current was altered through a very wide range. At very low current densities there tended to be a slight rise and the shape of the discharge visibly altered, but when about 0·5 sq. cm. of the surface was covered by the glow the constant figure was attained and remained constant until the whole surface was just covered. The current, in this case was about 80 times the magnitude of the initial current, although, as has been shown by Wilson (Phil. Mag. vi, 1902, *4*,

608), the current density remained constant. It will be seen from the accompanying figure 2 that between pressures of 6 and

Fig. 2.



16 mm. the value of the cathode fall is quite constant within the limits of experimental error. At the high pressure of 19 mm. there is a slight rise which may be due to any one of several causes. All measurements of this type made with pressures of this order tend to become inaccurate and it was not considered advisable to endeavour to extend the range of pressures. At low pressures again it will be observed that there is an increase in the cathode fall. In column 3 are given some approximate determinations of the sparking potential or the lowest potential difference between the electrodes which will allow the current to establish itself. As is well known, this function decreases to a minimum as the pressure is lowered and then rises rapidly. This rise is undoubtedly due to the fact that at a certain point the length of the dark space begins to become comparable with the distance between the electrodes. The rise in the cathode fall starts at approximately the same pressure as the rise in the sparking potential and both are probably due to the same cause. If, however, the electrodes are drawn further apart this rise in the cathode fall does not begin until a lower pressure is attained. The same fact is known to hold good in the case of the spark potential.

It was not possible to make such an extended series of measurements with any one sample of gas in the highest state of purity attainable owing to the contamination which always

occurs when the discharge has been passing for some time, but results similar to the above were obtained for very pure helium and neon and there seems to be every reason to believe that the cathode fall in these gases is constant at least to 1 volt over a wide range of pressures.

As it was desired to carry out experiments with a large number of metallic electrodes, if possible in the same sample of gas, electrodes of the size of those in the tube just mentioned would not be practicable, and in order to see if the same results could be obtained with smaller electrodes tube No. 2 was constructed. This, as has been already mentioned, had electrodes 1·2 cm. in diameter and one of them was movable. In this tube, with 10 mm. distance between the electrodes, a coloured ring very often appeared at a distance of 6 mm. from the cathode. It disappeared when the anode was lowered to the position it had occupied. When the anode was above the position of the ring the potential difference aross the electrodes was much higher than the cathode fall and varied with the distance, as is known to be the case when a positive column is present. With the anode below the position of the ring the potential difference kept fairly constant, even when the electrodes were only 2·5 mm. apart. Naturally, the sparking potentials varied with the distance between the electrodes and the pressure of the gas. The following table gives the result of an experiment with a sample of neon, containing traces of hydrogen :—

Tube No. 2. NEON (traces of hydrogen). Copper cathode.

Pressure mm.		Distance cm.		Cathode fall Volts.
19·4	...	0·6	...	199
		0·35	...	183
16·4	...	0·5	...	189
		0·35	...	185
14·5	...	0·5	...	186
		0·4	...	186
12·1	...	0·5	...	185
		0·4	...	187
10·0	...	0·4	...	188

The variations are not very great. The anode column and glow could be made to vanish in certain cases by lowering the anode or even by gently tapping the tube. On the other

hand, if the electrodes were at first near together and then gradually separated, they could frequently be moved quite a long distance apart without the appearance of any positive column. The results obtained with this tube although not quite so consistent as in the larger one No. 3 appeared to differ from them in no important respects. The range of pressures over which reliable results can be obtained is somewhat more restricted but, provided that the distance between the electrodes is neither too large nor too small, satisfactory values seem to be obtained. The figures given above are for the same sample of gas as that used in the experiments given on page 150, for tube No. 3 and it will be seen that the minimum value is almost the same in each case. This result was confirmed by many other experiments both with pure and impure gas which are not given in detail. It seems, therefore, that with slightly increased precautions the correct value for the cathode fall can be obtained with plane electrodes only 1·2 cm. in diameter.

Only a few experiments were carried out with tube No. 4 in which the electrodes did not closely fit the walls. There appeared to be no advantage in using a tube of this type and in fact there were certain disadvantages owing to the tendency of the discharge to pass from the back of the cathode. Lower values for the cathode fall were not obtained and the experiments were discontinued.

To summarise therefore:-

1. As stated by Warburg and others, the cathode fall for any one metal has been found constant over a considerable range of pressures and remains unchanged with the current, provided the whole surface of the electrode is not covered.

2. The cathode fall can be conveniently measured by determining the potential difference between the anode and the cathode in tubes with plane and parallel electrodes under certain conditions, one of the most important of which is the distance between anode and cathode. Any departure from these conditions causes a rise in potential, so that the cathode fall must always be taken as the *minimum* value in any series of measurements. Needless to say, no results are given based upon one minimum only but always upon several concordant values obtained at different times.

3. Except for very small tubes measurements of the cathode fall made in this way are not affected by the size of the electrodes or the proximity of the glass walls.

IV. Effect of Impurities.

Before dealing with the final results it is necessary to discuss at some length the effect of impurities upon the cathode fall since the elimination of these is the most difficult part of the whole investigation.

Some interesting measurements by Rottgardt (**Ann. d. Phys. 1910,** *33*, 1185.) of the cathode fall in mixtures of argon with hydrogen, nitrogen and oxygen show that for mixtures containing 5 per cent of impurity and upwards, the effect of hydrogen is the least, and that of oxygen the greatest. Numerous references in the literature of the subject show, however, that the presence of mere traces of impurity exert a quite abnormal influence on the cathode fall and it is more particularly with these that we are at present concerned.

Even when a gas is introduced into a discharge tube in an absolutely pure condition it may rapidly become contaminated, firstly by gases evolved by the electrodes (apparently hydrogen) and secondly by gases from the walls of the tube (mainly carbon compounds and water vapour), so that it was advisable to study to a certain extent the difference these impurities produce.

It has already been mentioned that the cathode fall remains constant over a wide range of pressures both for a pure gas and also when traces of impurities are present.

A number of different measurements were unavoidably made during the course of experiments in which a gas was not quite pure and from these certain other deductions can be made.

Small quantities of impurities in the gas do not seem to affect the relative measurements for different cathodes or for changes of pressure, although they always seem to change the absolute value of the cathode fall. In the experiments no attempt was made to find the amount of impurity present, but the amount remained approximately the same during each of the cases quoted below.

On page 150, is given a table for slightly impure neon, containing traces of hydrogen, where the value is constant from 6 to 16 mm. pressure at 185 volts. Mercury was carefully excluded from the gas by means of a U-tube cooled in liquid air through which the gas was made to pass before entering the discharge tube. The following is a table for measurements in neon

where traces of hydrogen and mercury vapour were both present :—

NEON (hydrogen and mercury vapour)

Press. mm.	...	24·9	19·4	13·5	10·5
Cathode fall. volts	...	228	227	227	226

The final value obtained with this electrode (copper in tube No. 6) for pure neon was, as will be mentioned later, 147 volts.

Similar experiments in helium with traces of hydrogen and mercury vapour and some unknown impurities (oxygen, nitrogen) were made, the results of which are given below :—

HELIUM (traces of hydrogen)

Press. mm.	...	5·9	6·8	7·2	9·3
Cathode fall. volts	...	170	170	170	170

HELIUM (hydrogen and mercury vapour)

Press. mm.	...	8·5	10·7	14·4	18·1
Cathode fall. volts	...	214	212	212	213

The value for pure helium was 154 volts.

Further experiments similar to those mentioned above carried on in nitrogen and hydrogen show that among other impurities, which may tend to affect the cathode fall, hydrogen is the most difficult to avoid. Whether this is evolved from the electrodes or is produced by electrolysis of traces of water vapour is not certain, but the four following experiments make it appear probable that hydrogen itself actually produced a considerable effect.

(1) NITROGEN (pure)

Press. mm.	...	5·2	4·5	4·0	2·6	1·8
Cathode fall. volts		278	278	277	275	276

(2) NITROGEN (traces of hydrogen)

Press. mm.	...	7·0	5·8	5·3	4·0
Cathode fall. volts	...	307	307	307	308

(3) HYDROGEN (pure)

Press. mm.	...	3·2	2·6	2·3	1·5
Cathode fall. volts	...	263	263	264	267

(4) HYDROGEN (impure)

Press. mm.	...	5·3	4·5	3·4	2·4
Cathode fall. volts	...	269	265	264	266

In the second experiment, the nitrogen, prepared from ammonium chloride and sodium nitrite with potassium bichromate, was mixed with pure oxygen, and phosphorus ignited in the mixture; after standing for some time it was introduced into the discharge tube passing through liquid air on the way to remove mercury and water vapour. The spectrum showed the hydrogen lines strongly.

In the first case a sample of the same gas was absorbed in a little charcoal in liquid air and then allowed to warm up until gas was evolved. No hydrogen lines were visible.

In the fourth case the hydrogen was evolved from barium hydrate solution by electrolysis and merely dried by passing through a phosphorous pentoxide tube. It was then admitted into the discharge tube through liquid air, similarly to the nitrogen, while in the third case it was previously absorbed by charcoal.

The small difference produced in the value of the cathode fall by this procedure is interesting when compared with the case of nitrogen.

In none of these cases, however, were extraordinary precautions taken as to the purity of the gas and too much importance must not be attached to the above results, which admit of other interpretations than the one given. For each set of measurements the same copper cathode was used and the same tube No. 3.

Some of the earlier experimenters in this field did not exclude mercury vapour from the discharge tube, as some made the exploring wire float over mercury, and others did not use means to stop its passage into the discharge tube. The above examples will show that the presence of mercury vapour may exercise a large influence on the cathode fall and this was confirmed by other experiments as well as by the previous experience of many other observers engaged in similar measurements. Consequently, mercury was rigorously excluded from all tubes used for measurements with pure gases, and gas was never allowed to enter without previous passage through liquid air. It may be observed in this connection, that a bulb of gold leaf is quite useless for absorbing mercury vapour as an appreciable mirror was obtained on cooling the gas even after it had passed through such a bulb.

As suggested by Sir J. J. Thomson and others, a quantity of sodium potasium alloy was introduced in one of the preliminary experiments into a cavity in the discharge tube in which a

platinum wire terminal was fused so that the alloy could be used as a third electrode if necessary. The presence of the alloy in the tube was, however, suspected to be not free from objections. Soon after the alloy was let in, the values of the cathode fall went down considerably, in some cases by as much as 25 volts, (experiments were being done in helium) but after sending the current towards the alloy from the anode with an induction coil the values of the potential difference representing the cathode fall rose to the original amount without the alloy. After 20 minutes rest the values dropped again gradually through 25 volts. This and similar experiments seem to show that although the alloy might absorb impurities, yet under certain circumstances it might also evolve gas and so cause contamination, while there is also the possibility that the vapour pressure of the alloy alone may be sufficient to affect the discharge, or even attack the surfaces of the other metals. An effect of this nature was observed by Gehlhoff (Verh. d. d. phys. Ges. 1912, *10*, 960,) when using hot potassium vapour as a means of purifying the gases. Unless every trace of potassium were driven from the cathode by prolonged heating, abnormal values were obtained for the cathode fall. In our final experiments the alloy was not introduced.

With regard to the other impurities already mentioned as emanating from the electrodes and the walls of the tubes, the following precautions were adopted :—

Firstly, the metals were polished with glass paper and mounted in the discharge tube which was immediately afterwards carefully pumped out.

Secondly, it was found quite essential to allow the discharge tubes to remain evacuated completely for at least a week before use and to rinse them several times with the gas under observation. Owing to their construction, it was unfortunately impossible to heat them thoroughly.

Thirdly, a current sufficiently large to cover the electrode surface was run from each cathode for some hours before making any measurements in order to remove hydrogen and any other gases from the electrode. It seems likely that in spite of this treatment traces of gas were still given off while making measurements, but errors due to this were eliminated almost entirely by passing the current only for a sufficient period, usually a few seconds for taking a reading on the voltmeter. Fresh gas was introduced at various pressures and for each different cathode and the results obtained were very consistent and are probably correct. In the case of almuminium and one or two other

metals there was a change of two or three volts after running for about a minute, but on the other hand the platinum metals and many others showed practically no evidence of a change owing to evolution of gas.

It may be mentioned in this connection that the experiments of Neuswanger (*loc. cit.*) are open to very great objection. In the first place, a discharge tube was used in which there was a greased joint very near the path of the discharge, secondly, the tube was opened every few hours and the electrode 'cleaned', and thirdly, the author speaks of a rise in pressure *not exceeding four per cent* due to liberation of occluded gases or moisture. It is obvious to any one who has ever attempted to carry out experiments on electrical discharge in pure gases, that these samples cannot have been even approximately pure and for results, in which the absolute value of the cathode fall is concerned, measurements made in such impure gases are of little value.

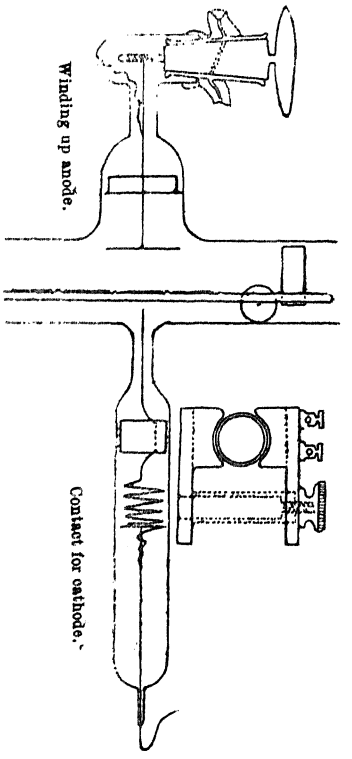
V. Experimental Results.

After having investigated the conditions of the experiments as regards, (i) the size of the electrodes,
(ii) the form and size of the discharge tube,
(iii) the distance apart between the electrodes
and (iv) the range of pressure and the regulation of the current,

in the case of copper, it was found desirable to extend the measurments of the cathode fall to as many other metals as possible and to carry out these measurements side by side in the same sample of gas. A tube was constructed for this purpose, shown as 6 in figure 1 (p. 147) but it was suitable only for such metals as could be obtained in sheet form. It was 70 cm. long and 2·5 cm. wide closed at one end. The other end could be closed with a watch-glass and sealing wax. There were two side tubes about the middle of its length at right angles to it and both in the same plane as the long tube. One branch was 5 mm. and the other 25 mm. wide at the junction. The wider branch carried an anode 21 mm. in diameter (made out of the same sheet of copper as in Nos. 2 and 3) which could be wound up and down as shown in figure 3. The other branch was connected to a wider tube containing mechanism for establishing contact with any desired metal. This was a platinum wire soldered on to a copper wire and an iron ring which was mounted on a copper spring and controlled by means of an electro-magnet. A straight carriage 34 cm. long and 1 cm. broad, made of glass rods and mounted on brass wheels, carried the metals under investigation. In most cases the metallic plates were not less than 1 sq. cm. in size and were held in position on the carriage by means of small glass

legs fused in the carriage bars. No sealing wax or other similar material was used to fix the metals. As many as 19 metals were mounted on a carriage at a time. These were copper, silver, gold, magnesium, zinc, cadmium, aluminium, tin, lead, iron, nickel, manganese, cobalt, silicon, platinum, palladium, rhodium, iridium, chromium, antimony and bismuth and were all the purest commercially obtainable, while copper, iron and cobalt were prepared electrolytically. One end of the carriage carried on it an elliptical iron ring and the other end an iron plate, so that it was possible to slide it along in the tube with the use of an electro-magnet from outside, and thus bring the required metal in position under the anode. (Silicon and manganese were replaced by antimony and bismuth in later experiments.)

Fig. 3.



Certain other metals, *viz*, mercury, selenium, tellurium, were examined each in a small separate tube of the type shown as 7 in figure 1 (p 147) Contact was made at the bottom with a platinum point and the anode was fixed at what appeared to be the most suitable distance judging by various experiments. If necessary it could be raised or lowered, but only after letting air into the

apparatus. A number of these tubes were connected to one common tube through which the gas was admitted.

While working with the metals in the long tube it was observed that measurements could not be made on all the metals in the same gas-filling without risk of introducing errors due to contamination. For this reason, the metals were divided into groups and only one group examined at a time with gas at different pressures. After this had been done, the tube was exhausted, refilled and another series of readings taken, and so on until the constant value for the cathode fall was obtained.

The annexed table will give a rough idea of the nature of the values obtained in this way. For the sake of brevity the results are given only for one pressure each time the tube was filled, although measurements were nearly always made at more than one pressure. The distance between the anode and the cathode was not constant, but approximately so. The gas was helium.

Helium.

Copper.	Silver.	Gold.	Rhodium.	Nickel.	Press. mm.	Time.	Date.
173	162	173	159	165	5·3	4-00 p. m.	16 1 '17
164	161	162	162	161	5·4	12-40 ,,	17 1 '17
162	160	161	160	163	8·7	4-30 ,,	,,
163	160	162	158	161	5·5	12-05 ,,	18 1 '17
161	158	160	157	156	5·3	2-15 ,,	,,
160	156	159	155	157	8·5	4-05 ,,	,,
158	156	158	152	157	8·8	12-30 ,,	19 1 '17
157	157	158	153	157	5·3	3-00 ,,	,,
157	157	158	152	157	5·4	3-50 ,,	,,
157	156	158	152	158	5·3	2-15 ,,	22 1 '17
157	156	156	152	156	5·5	3-30 ,,	,,
156	155	156	*150*	156	5·4	4-30 ,,	,,
156	154	156	152	*154*	5·4	11-30 a. m.	23 1 '17
156	*153*	156	151	155	8·6	12-20 p. m.	,,
155	154	155	152	154	5·3	2-15 ,,	,,
156	153	155	150	154	5·4	3-30 ,,	,,
154	153	154	150	154	8·5	4-25 ,,	,,
...	156	*153*	150	...	5·4	6-40 ,,	,,
...	...	154	...	...	5·5	11-30 a. m.	19 4 '17
...	...	153	150	153	6·1	12-30 p. m.	,,
154	...	...	150	153	5·1	3-00 ,,	,,
...	...	...	...	153	4·6	11-15 a. m.	20 4 '17
...	...	...	...	153	5·1	2-15 p. m.	,,

It will be observed that towards the end of the experiments, when it was possible to observe slight departures from constancy, higher values were usually obtained for the first experiment in a day. These are undoubtedly due to traces of impurity evolved from the tube in the night, but undetectable in any other way. As soon as consistent measurements were obtained with one set of metals, experiments were carried out with another series until all had been examined. The metals copper and platinum were also used as a check, by making measurements with them now and then, when the gas was judged to be in its final state of purity. These agreed exactly with the values found previously.

Occasionally also measurements were made with the current reversed, that is to say, with a copper cathode and anodes of all the metals under examination in turn. A perfectly constant value was always obtained, thus rendering it highly probable that the cathode fall alone was being measured, and that the anode fall does not exist.

Of the metals on the carriage some frequently refused to establish a steady glow discharge, but the current passed from one point, this being apparently an arc discharge In such cases the voltage was always very low (about 80) and the current very intense. Of these metals zinc and magnesium were most liable to do this and no explanation of their behaviour can be given, because in shape and smoothness they were very much like the others. Silicon and manganese had very rough surfaces and were very small as compared to the others. Only one or two reliable measurements could be obtained in consequence.

Cadmium appeared to form a film on its surface and the measurements were not satisfactory in the beginning, but after continued experiments it was possible to obtain with this metal a steady cathode fall.

Among the small tubes, bismuth and tellurium were made by melting the metal in vacuum in a side tube and then running it on the platinum wire in the bottom of the discharge tube. The branch in which the metal was melted was separated by sealing it off. Afterwards a place was found on the carriage for antimony and bismuth.

Selenium was converted into the conducting form by heating a few pieces of the metal to 200°C. and letting it cool very slowly.

Mercury was put in a tube of the same size as the others with a nickel anode and joined to the apparatus so that

the gas entered it before passing through the gold bulb and liquid air U-tube.

It is impracticable to give even an outline of all the results, since some four thousand measurements were involved. A few typical examples have already been given and now it is only proposed to tabulate the final values deduced for each metal from all the experiments. These are shown below.

Cathode.	Neon.	Helium.	Helium.
Magnesium	120	138	125 D.
Mercury	129	145	143 D.
Selenium	132*	151*	
Zinc	138	147	143 D.
Aluminium	140	151	141 D.
Iridium	137	150	
Rhodium	140	150	
Palladium	140	150	
Platinum	141	150	160 D. 226 S.
Gold	145	153	
Silver	144	153	162 D.
Nickel	145	154	
Copper	147	154	177 D.
Iron	145	155	
Tin	146	156	
Bismuth	146	158	137 D.
Antimony	147	159	
Chromium	149	159	
Cobalt	150	161	
Lead	151	161	
Cadmium	153	161	
Tellurium	157*	175*	
Silicon	160*	182*	
Manganese	172*	188*	

There are no available accurate determinations of the cathode fall in neon, but a number of measurements in helium have been made by Defregger (*loc. cit.*) and one or two by Strutt (Phil. Mag. v. 1900, *49*. 293). These are included above in the fourth column for the sake of comparison.

A number of the results are marked with an asterisk. These are determinations upon which not much reliance can be

placed. It has already been mentioned that the samples of silicon and manganese available were rather small and irregular, while the surface of cadmium could not be kept very clean. Selenium, tellurium and mercury were examined in small tubes with fixed anodes and it is possible that in all cases the values given are rather too high. In addition, mercury and selenium both have an appreciable vapour pressure and their own vapours doubtless affect the values somewhat. It was impossible to obtain a large number of definite values for magnesium in pure gases owing to the discharge taking the form of an arc. The purely tentative values given for manganese and silicon were only obtained by examining the difference between the figures for these metals and gold through a long series of readings in impure gases. This difference was approximately constant and so may afford a rough idea of the value.

The case of aluminium is interesting as this metal is so frequently used as an electrode. The values in the table are those obtained from experiments in the tube with the carriage. Some other measurements were made, however, with a piece of the same sheet of aluminium cut in the form of a quadrant and examined in the wide tube No. 3 together with similar pieces of copper, silver and gold. At first a value of 147 was obtained for this piece, but this soon rose and became constant at 152, only 1 volt higher than the value for the other sample. It is possible that the actual process of evolution of hydrogen greatly lowers the cathode fall, although the gas when evolved increases it, and this might acount for the initial low value.

With regard to the remaining metals it will be observed that there is a remarkable similarity between the values. With very few exceptions all of them have a cathode fall within five per cent of the mean value **145·5** for neon and **155·5** for helium. This remarkable result has already been hinted at by previous observers, although their deductions have been for other gases, fewer metals and have not agreed so closely.

The question at once arises, as to whether these figures would actually become identical with still more careful experiments or whether the variations are real. As far as can be judged at present, there actually is a difference, but it is one of the second order.

It is quite possible that further experiments would reduce somewhat the values given for the metals towards the end

of the table, but it is doubtful if they would fall quite as low as the mean values for the rest. On the other hand, it may be that the low values for mercury and selenium are due to the fact that these metals have an appeciable vapour pressure, but such an explanation would not hold in the case of magnesium.

With regard to the variation if it really exists, there appears to be no obvious connection between the cathode fall and the valency, atomic weight or reducibility of the metals. One possible clue may be found in the fact that there are indications that the cathode fall possesses a considerable temperature coefficient. Only a few experiments have been carried out so far in this direction, but they are being continued.

Another explanation may be connected with the 'fatigue' to which metals are known to be subject when a discharge is passed from them for some time. On the other hand it is possible that this fatigue is mainly the result of complete elimination of gases from the electrode. In any case, the present series of experiments was not of such a nature as to produce fatigue and no evidence was obtained of its existence. It is also noteworthy that if the metals are arranged in order of the cathode falls, as has been done in the table, this order is in nearly every case independent of the gas. In fact the only small deviations among the well determined metals are aluminium and copper.

It will have been noticed that no reference has been made to the alkali metals, which figure so largely in the literature of this subject. A considerable number of experiments have already been performed with each of them but so far the results are not satisfactory and it is not proposed to discuss them at present.

Finally it will be observed in the above results, that there is an approximately constant difference of about 10 volts in the cathode fall for any metal in helium and neon. This is exactly what would be expected if the cathode fall were independent of the metal.

The measurements are now being extended to other metals and gases.

Our best thanks are due to Mr. F. L. Usher for the loan of a quantity of helium.

VI. Summary.

1. Measurements of the cathode fall can be made by direct determinations of the potential difference between the anode and the cathode of the discharge tube.

2. The conditions necessary to obtain the above result have been fully investigated.

3. The laws governing the relation between the cathode fall, the pressure of the gas and the current have been examined by shis method and found to agree with those deduced by other obtervers using the method of 'sounds'.

4. The cathode fall in very pure helium and neon for 24 different cathodes has been determined.

5. It appears likely that the cathode fall for all easily reducible metals is the same to the first order of magnitude for the same gas; and consequently the difference between the cathode falls of one metal in two gases is approximately constant.

6. The second order difference between the values appears to be a real effect independent of the gas, that is to say, the order of the metals arranged according to their cathode falls is nearly the same in both gases.