

Part II.—In Argon, Hydrogen and Nitrogen.

By Gopal Paranjpe (Springer Research Scholar of the University of Bombay).

Measurements of the cathode fall from different metals, as described in part I for helium and neon, have now been extended to other gases using the same method as before. The gases selected were argon, hydrogen and nitrogen, and it is thus possible to compare the values of the cathode fall found for each metal in five different gases.

A certain number of such measurements, the most extensive series of which was made by Rottgardt (*Ann. d. Phys.*, 1910, 33, 1161) are on record. This author concluded that the cathode fall of a metal depended on its valency, and that each group of metals in the periodic table had a characteristic cathode fall, thus fulfilling Stark's expectations based on the theory of valency electrons. (*Jahrb. d. Radioakt.*, 1908, 5., 124).

Experimental.

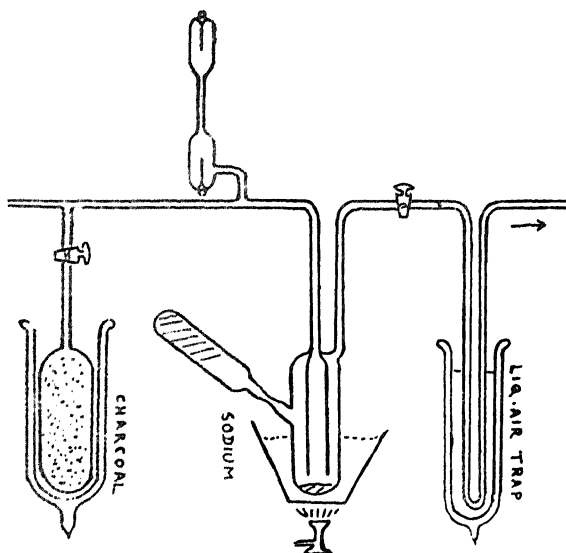
The apparatus used in these experiments was the same as before, the discharge tube consisting of a long glass tube, containing a carriage, on which were mounted various metallic electrodes, which could be moved by an electro-magnet. The anode was a circular plate of copper which could be placed at any desired distance from the cathode, thus satisfying one of the principal conditions for the successful working of this method of measurement. A few slight modifications were necessary owing to the different methods adopted for purifying the gases, and these are described under the heading of the individual gases.

Argon was made by passing dry air over hot calcium carbide and copper oxide according to the method described by F. Fischer (*Ber.* 1910, 43, 1435, 1442) The gas obtained in this way—when the temperature of the hard glass tubes containing carbide and fresh calcium turnings was maintained at a bright red heat—was practically free from nitrogen but contained hydrogen and carbon compounds. To remove these, the gas was passed backwards and forwards over hot copper oxide and then it was absorbed in a charcoal bulb in liquid air. Traces of hydrogen and nitrogen still remained in the gas as an impurity; it was therefore mixed with a large quantity of pure oxygen and sparked over strong caustic potash for some hours. The remaining free oxygen

was removed by the ignition of phosphorus. This procedure of sparking in oxygen over caustic potash had to be repeated during the course of the experiments whenever the gas became contaminated.

Since charcoal bulbs cooled in liquid air could not be used for purifying this gas on account of its high freezing point, it was decided to treat the gas with clean metallic sodium. Means were also devised for introducing the gas into the discharge tube in a high state of purity, and free from sodium vapour, as the previous experiments, in which a quantity of sodium potassium alloy was kept in the discharge tube close to the metals under investigation, had given unreliable results. Before admission into the discharge tube, the gas was passed very slowly over long cylindrical surfaces of metallic sodium, obtained by the condensation of the vapour and then through a U-tube cooled in liquid air. This condensed both sodium and mercury vapour (Figure 4). During the passage of the gas, the tube containing the sodium was heated to about 200° and at the end of the day after completing the experiments the tube was allowed to cool down to room temperature, the liquid air vessel under the U-tube was removed and the apparatus exhausted.

Fig. 4.



This method was found to be very effective in reducing the gas to a certain definite state of purity, in which, ultimately, the values of the cathode fall kept constant between pressures of 1.9 mm. and 6.3 mm. through a long series of experiments. It

was not possible to work at higher pressures than these, because the dark space became very short, so that the minimum values for the E. M. F. could only be obtained when the electrodes were inconveniently close together.

The final results, when consistent and steady figures were obtained, are given in Table II, column 6, p. 171.

These measurements are almost as satisfactory and consistent as those in helium and neon (vide p. 171). The difference between the values of the cathode fall for the same metal in argon and neon is on an average 33 and is almost the same for all metals except aluminium and magnesium, for which the cathode fall is very low and antimony for which it is very large.

Hydrogen was made by electrolysis of a freshly prepared solution of barium hydroxide. It was carefully dried by passing through a long phosphorus pentoxide tube and then stored up in a large bulb containing charcoal and immersed in liquid air.

The gas thus obtained was very pure and when it was let into the discharge tube, under the usual precautions, constant values of the cathode fall set in very quickly. These results are given in Table II, column. 10, p. 171.

Nitrogen was made from ammonium chloride and sodium nitrite with potassium bichromate. After carefully drying, it was mixed with a quantity of pure oxygen and a piece of phosphorous was ignited in the mixture. By these means traces of hydrogen and excess of oxygen were removed simultaneously.

It was observed by Warburg (*Ann. d. Phys. u. Chem*, 1890, 40, 1) and also by Rottgardt (*loc. cit.*) that the removal of the last traces of oxygen from nitrogen had a large effect on the cathode fall. For example, the former author found that this quantity fell from 343 to 232 volts on careful purification of the gas by circulating it over a clean sodium surface to absorb the oxygen.

According to Strutt (*Proc. Roy. Soc. A*, 1913, 81, 540) phosphorus, even in the cold, will remove traces of oxygen from nitrogen to the extent of less than one part in a hundred thousand so that the method mentioned above should give satisfactory results. However, in order to remove volatile phosphorus compounds and other possible impurities, the gas was submitted to a further process of purification by being let into a bulb immersed in liquid air and containing a small quantity of charcoal. This was not sufficient to absorb the nitrogen completely, but may be assumed to have removed any other impurities.

The nitrogen was admitted from the charcoal bulb to the discharge tube through a U-tube cooled in liquid air to remove any mercury vapour which may have been in the connecting tubes.

The results given in column 16 of Table II were for nitrogen purified in this manner. These were fairly constant on different occasions, although not quite so steady as in the case of other gases.

At a later date another series of experiments was carried out using nitrogen treated as follows:—

After standing over mercury in contact with phosphorus for a long time, the gas was let into a bulb containing clean metallic sodium at liquid air temperature. The sodium was then heated to a temperature of 200° in an oil-bath for half an hour, after which it was cooled again by immersing the bulb in liquid air. The gas was now led into the discharge tube through a tube coated with a mirror of sodium, described in connection with argon, and a U-tube in liquid air. Experiments with this gas were, however, quite unsatisfactory, since the values of the cathode fall were invariably very high and inconsistent. There could hardly be any doubt as regards the purity of the gas after it had received the above drastic treatment. The main source of error, however, was supposed to be in some change which had occurred in the metallic surfaces. Between the two series of experiments the discharge tube had been standing in a highly evacuated condition for several months, and on making a control experiment with pure helium, the values found were much higher than before and irregular.

TABLE I.

Cathode fall in Nitrogen.

Electrode	I	II	Difference.
	(26-2-'17)	(27-11-'17 to 7-12-'17.)	
Magnesium	216	260	44
Copper	228	297	69
Aluminium	232	309	67
Rhodium	242	304	62
Platinum	247	309	62
Iron	265	315	50
Cadmium	274	330	56

Table I shows these results. The figures entered in the third column were obtained as an average of about 25 different series and it can be seen that they are all higher than those in the second column. The order of the metals in both columns is almost the same, and the difference between the values shown in the last column is approximately constant. The greatest discrepancies are in the cases of iron and magnesium, indicating that the value 265 may be nearly 12 volts too high, and that the figures for magnesium may be incorrect.

Copper seems to be quite an exception in nitrogen. It has a strikingly low cathode fall as compared with other metals.

Soon after this unexpected change in the surfaces of the electrodes, and the consequent rise in the cathode fall, the experiments had to be discontinued, so that the exact reason for the change is undetermined. It seems certain that the cathode fall is very largely influenced by some unknown condition of the metallic surface, but the nature of this must be left for a future investigation.

Results.

The figures entered in Table II give the final values obtained for the cathode fall in argon, hydrogen and nitrogen in addition to those previously found for neon and helium (p. 162.) These were quite steady and within certain limits independent of of the pressure of the gas. The values obtained by other observers are also given for the sake of comparison.

On examining this table it will be seen that there is a considerable difference between the values of the cathode fall for one metal in different gases, but that with one or two exceptions, different metals have nearly the same cathode fall in the same gas. The variation amounts to 16, 14, 20, 15 and 23 volts for neon, helium, argon, hydrogen and nitrogen respectively. In the case of hydrogen it will be noticed that four values, namely those for zinc, iridium, tin and chromium, marked with an asterisk fall into a group by themselves, while those for iron and antimony are considerably higher, and for magnesium and aluminium very much lower than the rest of the figures which lie between 270 and 285. No such effect is to be observed in the other gases, although the value for magnesium is low in all cases. In nitrogen, aluminium and copper have very low values.

Neglecting for the moment these apparently abnormal values, the question to be decided is whether the remaining

TABLE II.
Cathode fall Potentials.

	NEON		HELIUM			ARGON.			HYDROGEN.					NITROGEN.					
	P. & W.	P. & W.	Defreg-ger.	Strutt.	P.	Rottgardt. K.	Strutt. P.	P.	Warburg.	Skinner '01	Rottgardt. K.	Cheney. P.	P.	Warburg.	Skinner. '01	Rottgardt. K.	P.		
Magnesium	120	138	125		156	119	163		201	183	266	153	185		216	207	228	188	223
Mercury	129	145	142.5		167														
Zinc	138	147	143		171	119	159		249*		326	242	278	273	252		265	216	253
Aluminium	140	151	141		161	100	153	100	204	190	260	171	199	197	232		217	179	215
Iridium	137	150			167				254*						246				
Rhodium	140	150			173				277						242				
Palladium	140	150			173				280						247				
Platinum	141	150	160	226	173	131	157	167	281	300		276	311	302	247	232	252	216	247
Gold	145	153			175	131	161		283		386	265	347		249		258	233	261
Silver	144	153	162		176	131	163		284	295	406	295	326		251		258	233	265
Nickel	145	154			173	131	167		270		395	276	316	322	249		237	197	229
Copper	147	154	177		175	131	160		277	280		263	312		228		258	208	244
Iron	145	155			180	131	175		297	230		250	285		235		255	215	257
Tin	146	156			180	123.5	171		249*		389	255	303		253			216	246
Bismuth	146	158	137		183	135.5	168		281			240	296		257		255	210	242
Antimony	147	159			189	135.5	176		297			294	328		259		254	225	251
Chromium	149	159			187				249*						261				
Cobalt	150	161			184										259				
Lead	151	161			186	123.5	173		285		382	276	332		251		243	210	236
Cadmium	153	161			182	119	167		282		359	264	312		274		266	216	251

Skinner (1915) Al in hydrogen 197; Neuswanger (1915) Al in nitrogen 218; Capstick (1898) Pt in hydrogen 298.

figures should be actually the same for each gas, or whether the variation is really due to some property of the metal. The differences observed are well beyond the limit of experimental error as far as actual measurement is concerned but they are not outside the variations which may occur owing to traces of impurity in the gas. It is however possible to obtain a little insight into the matter by comparing the values in another way. Table III shows the differences between the cathode falls of the various metals in neon, and those in the remaining gases. Certain figures are marked with an asterisk. These differ by more than 5 volts from the mean of the remaining figures which is shown at the end of the Table.

TABLE III.

(Showing differences of cathode falls from those in neon.)

	Helium.	Argon.	Hydrogen.	Nitrogen.
Magnesium	18*	36	81*	94*
Mercury	16*	38	—	119*
Zinc	9	33	111*	114*
Aluminium	11	21*	64*	92*
Iridium	13	30	127*	109
Rhodium	10	33	137	102*
Palladium	10	33	140	107
Platinum	9	32	140	106
Gold	8	30	138	104
Silver	9	32	140	107
Nickel	9	28	125*	104
Copper	7	28	130*	81*
Iron	10	35	152*	120*
Tin	10	34	103*	107
Bismuth	12	37	135	111
Antimony	12	42*	150*	112
Chromium	10	38	100*	112
Cobalt	11	34	—	109
Lead	10	35	134	100*
Cadmium	8	29	129*	121*
<i>Mean</i>	<i>10</i>	<i>33</i>	<i>137</i>	<i>108</i>

In the first place it will be seen that the differences for neon and helium are remarkably constant, the total variation for all but two metals being only 6 volts. In Table II the metals are

arranged approximately in order of their cathode falls, but in the difference table the high and low figures are irregularly situated indicating that there is no simple connexion between the absolute values of the cathode fall and these differences. This is what would occur if the cathode falls varied by any amount for the different metals provided that there was a constant difference for the same metal in two different gases. The differences for neon and argon, as has been already pointed out, are not quite so constant but there are still only two values which lie outside the limit of 5 volts from the mean. There is no regularity in the figures and this again suggests that the differences may be really constant. The case of nitrogen is similar, but the number of metals for which the difference is approximately constant is now only eleven. It has already been mentioned that it was difficult to get consistent results in this gas and that the figures in Table II are based upon a few experiments only, consequently the experimental error is larger than in the case of the inactive gases. The high values for iron and cadmium are probably due to this cause, as in the other series of measurements quoted on p. 169 they fall more nearly into line with the other metals. The outstanding feature of the series is however the very low value for copper for which no reason can be assigned. It is interesting, in this connexion, to note that Rottgardt's figure is 21 volts lower than that for silver as compared with 23 in the present experiments, although Skinner's values for the two metals are identical.

On turning to hydrogen it will be seen that there is much greater irregularity, the differences for only seven metals are within 5 volts of the mean. The measurements in hydrogen offered no difficulty and readily gave consistent values while, as pointed out in part I, impurities did not appear to cause such large variations as in the other gases. Consequently it seems as if in this case there is some effect due to chemical action or occlusion. Unfortunately there is nothing in the values to throw light on the nature of the effect, for example, metals differing so widely in reducibility as tin and chromium appear to be the same, while palladium, and platinum, which are known to occlude hydrogen readily, are in no way abnormal.

On the whole, it seems likely that there is a constant difference between the value of the cathode fall for all metals in any two gases except when disturbing influences are present; for the gases so far examined these are least in the inactive gases, and greatest in hydrogen. At the same time there seems little doubt that magnesium has a low cathode fall in all cases, while several experimenters have found very low values for the alkali

metals. These have been confirmed, using the present method of determination, although the results are not yet complete. If, however, it be granted that some metals have distinctly lower cathode falls than others, it is not possible to state that the cathode fall is independent of the nature of the cathode however close together the figures for the remaining metals may be. It is true that magnesium and the alkali metals are particularly readily oxidised, but there are also great differences in the oxidisability of say, lead and platinum, and yet the latter has the lower cathode fall. It seems necessary therefore to assume that the observed differences in cathode fall for any one gas are real effects, although the origin of them is obscure.

Rottgardt (Ann. d. Phys. 1910, 33, 1161) who gives an extensive series of measurements in air, nitrogen, hydrogen and argon, concludes from his results that "the metals belonging to the same group of the periodic system possess the same cathode-fall". This, he says, is in accordance with Stark's hypothesis (*loc. cit.*) which requires that the number of valency electrons lying in the surface of an atom is the same for all members of a vertical column in the periodic system and the number changes by one from one vertical column to another. One can, therefore, imagine that when a definite number of positive Kanalstrahlen strike any monovalent electrode, the number of electrons detached in this process will be the same for all monovalent electrodes, thus the resulting concentration of positive and negative ions in the gas will be the same and consequently the cathode fall for all monovalent metals will also be the same. In the case of a divalent electrode exactly the same conditions hold, but the number of valency electrons will be different and this fact will cause a different cathode fall which will remain the same for all metals of the same group.

Rottgardt's results in argon seem to justify this hypothesis but his results in nitrogen and hydrogen lend no support to his conclusions.

It can be seen from the values for neon, helium and argon that in every gas the individual figures are all within 3% of the mean and hence it is possible to group them in any desired way to this degree of accuracy. The same thing holds even in the case of hydrogen and nitrogen, where omitting some very divergent metals, the cathode fall is nearly the same for all. Even if it be assumed that the figures are absolutely correct a

definite relationship between the cathode fall and the position of the metal in the periodic system cannot be established as an examination of Table II will show.

It must, however, be noted that the quantity K termed by Rottgardt the 'normal cathode fall' is not a value which has been measured by any previous observers. This K is the E. M. F. between the cathode and a point which appears to the eye to be the boundary between the negative glow and the dark space. Aston (*Proc. Roy. Soc.*, A. 1907, 79, 80.) has pointed out the difficulty of seeing the edge of the dark space from a cylindrical cathode when viewed from the side, and this difficulty is enormously increased when dealing with the inactive gases in which the boundary is very poorly defined. It is moreover generally agreed that the negative glow is a region of high conductivity, whereas according to Rottgardt there was a considerable drop of potential between the point from which K was measured and a point a few millimeters further from the cathode; so that the former point was in the dark space as usually defined. It is quite possible for consistent results to be obtained in this way, but they probably have no physical meaning, and would have different values with plane electrodes. On the other hand, measurements made from a point 1.5 to 3 mm. outside the apparent edge of the dark space are probably approximations to the true cathode fall. These Rottgardt denotes by P . The figures given show that P was not constant but increased as the pressure of the gas fell. This is what would be expected owing to the use of a sound, as at high pressure the supply of ions to the sound is greater. In Table II the figures under P (Rottgardt) are all minimum values and it will be seen that they agree approximately with the values found in the present experiments, marked P , except in the case of hydrogen. As the variation in P amounted sometimes to 20 volts, they cannot be considered as reliable as our figures which were always constant to one volt.

One would expect from the diatomic structure and the chemical natures of hydrogen and nitrogen that they might be characteristically different from the rarer gases as regards the cathode fall. This is not to be seen in nitrogen, but the case of hydrogen is uncertain. Rottgardt gives two series of values for this gas, one when the current is freshly started and the other when it has been running for some time. This difference is undoubtedly due to occlusion, as Sir J. J. Thomson (*Discharge of electricity through gases*, 2nd ed. p. 551) and other observers

Holman, (*Phys. Rev.* 1907, 25, 81.), R. Ladenburg (*Jahrb. d. Radioakt.* 1909, 6, 454), Hallwachs. (*Ann. d. Phys.* 1907, 23, 459) have shown that the effect of occluded gases on the measurement of the cathode fall is considerable.

When a current passes from a cathode containing occluded gas, the gas is evolved and appears to facilitate the liberation of ions, thus diminishing the cathode fall.

If the evolved gas is allowed to mix with the gas under investigation in the discharge tube, then it is found that there is a large increase in the cathode fall, owing to the presence of impurity. As however, the evolved gas is mainly hydrogen, the effect is not to be observed to any extent in this gas.

If the occluded gases are removed as far as possible, either by keeping the electrodes in a vacuum for a long time, or by passing heavy currents from them, before admitting a gas to the discharge tube, then steady values for the cathode fall quickly set in.

The photo-electric sensitiveness of a metal is supposed to be responsible for the lowering of the cathode fall in one case more than in another; but recent experiments by Ladenburg (*Verh. d. deut. phys. Ges.* 1907, 9, 165.) indicate that even the photo electric sensitiveness of a metal is dependent on the amount of occluded gas. An electrode that has been very thoroughly 'exhausted' is shown to be less photo-electric, although it was highly sensitive before exhaustion.

In the present experiments as much occluded gas as possible was removed so as to eliminate all the above effects and the double set of readings, as observed by Rottgardt, with hydrogen was not obtained. Nevertheless, as already remarked, the values in this gas do not fall into line with those in the others, and there is moreover a great want of agreement with the results of other observers. It is evident that there is, in this case particularly, much room for further investigation.

I should like to express my deep gratitude to Dr. H. E. Watson for his very valuable advice and interest in the progress of this work. My best thanks are also due to Dr. J. J. Sudborough for allowing me to work in the Institute Laboratories.

SUMMARY.

1. Measurements of the cathode fall of potential from 20 different metals have been made by a new method, without the use of exploration sounds, in the case of argon, nitrogen and hydrogen.

2. In any one gas, most metals have very nearly but not exactly the same cathode fall.

3. For any two gases the difference between the cathode falls of any metals appears to be constant, when no disturbing influences are present.

4. There is no simple relationship between the cathode fall of a metal and its valency or position in the periodic table.

5. In the case of hydrogen there are secondary effects which prevent correct measurements of the cathode fall.

DEPARTMENT OF GENERAL AND ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.