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Comparative Observations on the Evolution of Gas from the Cathode in Helium and Argon

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CONTENTS

- I COMPARATIVE OBSERVATIONS ON THE
EVOLUTION OF GAS FROM THE CATHODE IN
HELIUM AND ARGON
Clarence A. Skinner 193
- II ON THE STRUCTURE OF THE PISTILS OF SOME
GRASSES
Elda Rema Walker 203
- III CORNEILLE: THE NEO-CLASSIC TRAGEDY AND
THE GREEK
Prosser Hall Frye 219
- IV ON THE COMPARISON OF ADVERBS IN ENGLISH
IN THE FOURTEENTH CENTURY
Alma Hosic 251

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I.—*Comparative Observations on the Evolution of Gas from the Cathode in Helium and Argon*

BY CLARENCE A. SKINNER

In previous reports¹ of investigations on the subject of evolution and absorption of gases by the electrodes in vacuum-tubes the writer has shown that during the first few minutes after starting a glow current through helium, hydrogen is given off by a metallic cathode at a rate determined by Faraday's law for electrolytes. Further, if a carbon cathode be used in helium, nitrogen is evolved by it, within certain time limits, according to the same law. But if a current be passed between metallic electrodes in hydrogen, or between carbon electrodes in nitrogen, the increase in gas pressure in the discharge-tube (by which the evolution is detected) is relatively small; in fact, under certain conditions, it decreases with duration of current. The difference between the observations with helium on the one hand and with hydrogen or nitrogen on the other was traced to anode absorption of the last two, that of helium being inappreciable. Under the *assumption* that the rate of evolution of gas from a given cathode is determined by the current alone, irrespective of the kind of gas in the discharge-tube, the experimental results indi-

¹*Phys. Rev.* XXI, 1, 169; *Physik. Zeitschr.*, 6 Jahrg., 610.

cate that the anode absorbs hydrogen and nitrogen, when these are used as filling, at a rate also determined by Faraday's law.

To verify the foregoing assumption is important. This of course can be done only in those gases which are not appreciably absorbed under the action of the current. In addition to helium, therefore, argon suggested itself as a gas which might fulfil this condition. This having proved true, the experiments described below were performed with the above mentioned intent.

EXPERIMENTAL ARRANGEMENT

The discharge-tube used was one which has served in the other investigations (*l. c.*). It was devised for making comparative tests of several different electrodes without, in the meantime, opening to the atmosphere. These electrodes could be removed for polishing or be replaced by new ones.

Helium and argon were obtained in sealed bulbs from Messrs. Thomas Tyrer and Co., London. Each gas was transferred from the bulb containing it to a storage chamber connected by a stop-cock to the system containing the discharge-tube, manometer, drying chamber, and pump connection.

The quantity of gas evolved being determined from the increase in pressure, it was necessary to measure the pressure very carefully. This was accomplished by means of a MacLeod gage, which multiplied it one hundred times, and with which single observations were seldom more than one-half per cent off the mean of several.

The volume of the chamber occupied by the gas was obtained by attaching to the system a chamber of known volume, measuring the pressure when a given quantity of gas occupied the unknown volume, then the known in addition, and from these data calculating the desired value. This was found to be 455 cc.

The electric current through the discharge-tube was furnished by a battery of small accumulators, measured by a Weston milliammeter, and regulated by a resistance of cadmium iodide in amyl alcohol.

Customary precautions were taken to avoid the presence of moisture and hydrocarbons.

The electrodes were given in all experiments a mirror polish, thereafter carefully cleaned with a dry cloth, then mounted in the discharge-tube, and this allowed to stand evacuated in connection with the drying chamber before making a test. To avoid the possibility of time changes in the metal the plan was followed of testing one sample of it in one kind of gas, then following this with a test of another sample of the same metal (which had been prepared in a similar manner) in the second gas. This method proved to be wholly satisfactory.

Earlier experiments (*l. c.*) having shown that both aluminium and magnesium give off hydrogen much more freely than the denser and more electropositive metals, these were chosen for making the comparative study in the two gases.

OBSERVATIONS WITH ALUMINIUM CATHODES

Six similar cathodes of aluminium (circular disks; discharge area, 1.8 sq. cm.) were prepared and mounted as already described. These were then successively tested during an uninterrupted series of experiments. With a fresh sample each time as cathode, an aluminium wire serving throughout as anode, a definite current was passed through the discharge-tube and the gas pressure observed at given time intervals. The test of one being completed, the system was thereupon immediately evacuated, filled with fresh gas, and the next tested. In this manner three samples were tested in helium under currents of 1.0, 2.0, and 3.0 milliamperes respectively; and three others in argon.

The results of these tests are incorporated in tables I, II, and III, the observed values being recorded in the first, second, and fourth columns, while in the third and fifth is given the pressure of the evolved gas; and in the sixth, the calculated value of the latter in case Faraday's law controls the rate of evolution from the start. At the top of each of the four medial columns is indicated the possible error of observation, though the probable error was not more than half as great.

TABLE I
Aluminium Cathodes. Current, 1.0 milliamperes

DURATION OF CURRENT (MINUTES)	SAMPLE NO. 1 IN HELIUM		SAMPLE NO. 2 IN ARGON		CALCULATED INCREMENT IN PRESSURE
	Gas pres- sure (mm.) ±.02	Pressure increment ±.02	Gas pres- sure (mm.) ±.01	Pres. in- crement ±.01	
0	3.76	0	2.21	0	0
1	3.79	.03	2.23	.02	.013
3	3.81	.05	2.26	.05	.04
5	3.83	.07	2.29	.08	.06
7	3.86	.10	2.31	.10	.09
9	3.87	.11	2.33	.12	.11
11	3.88	.12	2.345	.135	.14
13	3.90	.14	2.365	.155	.16
15	3.92	.16	2.385	.175	.19

TABLE II
Aluminium Cathodes. Current 2.0 milliamperes

DURATION OF CURRENT (MINUTES)	SAMPLE NO. 3 IN HELIUM		SAMPLE NO. 4 IN ARGON		CALCULATED INCREMENT IN PRESSURE
	Gas pres- sure (mm.) ±.02	Pressure increment ±.02	Gas pres- sure (mm.) ±.01	Pressure increment ±.01	
0	3.99	0	2.24	0	0
1	4.05	.06	2.27	.03	.025
3	4.10	.11	2.33	.09	.075
5	4.14	.15		...	.13
6		...	2.41	.17	.15
7	4.17	.18		...	.18
9	4.20	.21	2.46	.22	.23
11	4.22	.23		...	.25
12		...	2.50	.26	.30
13	4.26	.27		...	.33
15	4.29	.30	2.56	.32	.38

TABLE III
Aluminium Cathodes. Current, 3.0 milliamperes

DURATION OF CURRENT (MINUTES)	SAMPLE NO. 5 IN HELIUM		SAMPLE NO. 6 IN ARGON		CALCULATED INCREMENT IN PRESSURE
	Gas pres- sure (mm.) $\pm .02$	Pressure increment $\pm .02$	Gas pres- sure (mm.) $\pm .015$	Pressure increment $\pm .015$	
0	3.76	0	3.19	0	0
1	3.84	.08	3.27	.08	.04
3	3.90	.14	3.35	.16	.11
5	3.96	.20	3.37	.18	.19
7	4.00	.24	3.41	.22	.27
9	4.05	.29	3.435	.25	.34
11	4.08	.32	3.445	.26	.42
13	4.11	.35	3.48	.29	.49
15	4.15	.39	3.51	.32	.57

For the sake of clearness these results are also represented graphically in figs. 1, 2, and 3, the pressure of the evolved gas by the ordinates, and the corresponding duration of current by the abscissas. The values obtained in helium are indicated by circles, those in argon by crosses. The line *F* in each figure represents the value required by Faraday's law.

FIG. 1

Referring to fig. 1 we find for a current of one milliampere the values in helium and argon practically identical during the first seven minutes, and for the same period they coincide in direction, within the errors of observation, with the line *F*. After that time the evolution of gas falls gradually below the

calculated rate as indicated by the direction of the points dropping below that of the line. It may be noted that the values for argon are slightly nearer F throughout than those for helium. In both gases the results support very satisfactorily the view that the rate of evolution is controlled by Faraday's law. Fig. 2, representing the observations obtained under a current of two milliamperes, shows a marked divergence in the results from the two gases during the first minute after starting the current, but agreement in rate during the next few minutes, after which helium falls below argon and both as before below F . Here again the results in argon are very near the calculated values,

FIG. 2

until such a time is reached when we must conclude that the metal has been relieved largely of its available gas, namely, that in its surface layer. After the first minute helium gives equally satisfactory results until a similar condition is reached. The results obtained with a current of three milliamperes, fig. 3, are practically identical again in the two gases during the first five minutes of action, both giving here excessive values on starting the current, but following the line F during the next two or three minutes until depletion of the cathode makes itself evident. Contrary to the results in foregoing tests the sample of aluminum used in this case in argon became depleted before that used in helium.

We may conclude from these experiments that Faraday's law is the controlling factor in the evolution of gas from the cathode, although, as the current density increases, there is an excess given off at the start. This excess was inappreciable in the case of argon until a current of three milliamperes was reached, but was evident in helium for one milliampere. This suggests the possible cause, for with argon it was observed that the current density was at no time more than twice its "normal" value, while in helium it varied from about twice its "normal" value, at one milliampere, to six times at three milliamperes. The excess

FIG. 3

therefore may arise from the abnormally high current density. Another respect in which the two gases were remarkably different, namely, in their cathode fall, strengthens the belief that the evolution of gas is not merely incidental. For each current used the cathode fall in helium was at least three times that in argon; hence the energy dissipated at the cathode three times as great. If the evolution of gas were not controlled directly by the current we should expect it to increase with this energy dissipated, which evidently is not the case.

OBSERVATIONS WITH MAGNESIUM CATHODES

Experiments similar to the preceding were performed with magnesium cathodes of the same form as the aluminium and subjected to a similar treatment. The results obtained from

FIG. 4.

these are incorporated in tables IV and V, and represented graphically in figs. 4 and 5. The designations are the same as in the preceding figures. Fig. 4 exhibits the results with one milliamper in both helium and argon. Both sets of results fol-

FIG. 5

low the direction of the line closely, helium showing here also a slight excess, while argon holds closely to F until depletion makes itself evident. In fig. 5 the results from the two samples of magnesium tested in argon serve to show the extent of agree-

ment with Faraday's law, and also that within the errors of observation the values from two different samples are identical. They show further that magnesium does not possess as great a supply of available gas as aluminium.

The experiments with both kinds of metals support the assumption stated at the beginning, namely, *the rate of evolution of gas from the cathode is the same, irrespective of the gas-filling used*; hence also warrant the conclusion, derived from earlier experiments, that *the anode absorbs hydrogen and nitrogen* (when these are used as gas-filling in the discharge-tube) *at a rate determined by Faraday's law.*

TABLE IV
Magnesium Cathodes. Current, 1.0 milliamperes

DURATION OF CURRENT (MINUTES)	SAMPLE NO. 1 IN HELIUM		SAMPLE NO. 2 IN ARGON		CALCULATED INCREMENT IN PRESSURE
	Gas pres- sure (mm.) ±.015	Pressure increment ±.015	Gas pres- sure (mm.) ±.01	Pressure increment ±.01	
0	3.25	0	2.28	0	0
1	3.28	.03	2.30	.02	.013
3	3.31	.06	2.325	.045	.04
5	3.34	.09	2.35	.07	.06
7	3.36	.11	2.375	.095	.09
9	3.38	.13	2.39	.11	.11
11	3.39	.14	2.41	.13	.14
13	3.41	.16	2.43	.15	.16
15	3.43	.18	2.45	.17	.19

TABLE V
Magnesium Cathodes. Current, 2.0 milliamperes

DURATION OF CURRENT (MINUTES)	SAMPLE NO. 3 IN ARGON		SAMPLE NO. 4 IN ARGON		CALCULATED INCREMENT IN PRESSURE
	Gas pres- sure (mm.)	Pressure increment	Gas pres- sure (mm.)	Pressure increment	
	$\pm .01$	$\pm .01$	$\pm .01$	$\pm .01$	
0	2.27	0	2.22	0	0
1	2.30	.03	2.26	.04	.025
3	2.34	.07	2.30	.08	.075
5	2.36	.09	2.32	.10	.13
7	2.40	.13	2.35	.13	.18
9	2.42	.15	2.37	.15	.23
11	2.44	.17	2.38	.16	.28
13	2.45	.18	2.415	.195	.33
15	2.47	.20	2.42	.20	.38