

The Production of Neon and Helium by the Electrical Discharge.

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Last year two papers were published by two of the authors (J. N. C. and H. S. P.) "On the Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures"*; also a note by the third author (I. M.).† Since that time a very large number of experiments have been made, but the problem of where the neon comes from, and also the helium which was often noticed to be present, as yet has not been finally solved.

Last December a paper was read at the Royal Society by the Hon. R. J. Strutt, in which he described a new form of apparatus, and his unsuccessful attempts to obtain either neon or helium. The important point about the apparatus used was that all the operations were carried out so as to avoid transference of gases. These precautions were, as far as possible, to guard against atmospheric contamination of the gases under observation.

Of course, the authors, from the very beginning of the work, were keenly alive to the fact that the slightest leak in the apparatus meant neon and helium in the end-product. Obviously, therefore, they took every precaution to prevent it; and, as a result of the numerous control experiments to be described later, they believe that the precautions were successful.

Hitherto no description of the apparatus used has been published, and to do so in detail would be quite out of the question, for the form of the apparatus has been perpetually changed as circumstances suggested, each of the authors making his own, and more or less working along his own lines. It is necessary, however, to give as short an account as possible of the more important kinds used.

Experimental.

The coils used would each give a 12-inch spark; an ordinary hammer interrupter was used on one of them (J. N. C.), and mercury interrupters for the others. There seems to be little doubt that the nature of the break has some influence on the result of the experiment, and also that in the case of the mercury break better results have been obtained when a rectifier has been used, to produce a unidirectional discharge. Moreover,

* 'Chem. Soc. Trans.,' vol. 103, p. 419 (1913); 'Chem. Soc. Proc.,' vol. 29, p. 271 (1913).

† 'Chem. Soc. Proc.,' 1913, p. 233.

it is certainly a fact that, with the platinum break, up to July, 1913, much larger yields of neon and of helium were obtained than after this date, when new contacts were fitted. The currents used in the secondary circuit naturally varied considerably, but averaged a few milliamperes.

Forms of Discharge Tube.—These ranged from simple Plücker spectrum tubes and bulbs with disc electrodes to the more elaborate jacketed forms shown in figs. 1 to 4, as well as many others not represented.

Testing Apparatus.—Several types have been used. They may be classified as “transference” and “non-transference” types, according to whether the gas under examination was introduced from outside by means of an inverted siphon over mercury after having been pumped out of the experimental tube, or whether it was admitted to the testing apparatus directly, by simply opening a tap between this and the experimental tube.

If hydrogen is present in the gas, this has to be got rid of before examination, in order that its spectrum shall not mask those of other gases which may be present. At first this was done by exploding the gas with excess of oxygen, either in an explosion burette or in the small tube used for collecting it, which had platinum wires sealed through it; the residual gas was then transferred to the Ramsay apparatus, in which oxygen and moisture are removed by cooled charcoal, and the residual helium and neon are examined spectroscopically by forcing them over mercury into a fine capillary tube with a fine platinum wire sealed through the top.

One of the present types of “non-transference” apparatus is shown in fig. 5 (H. S. P.). A is the discharge tube, whence the gases can be admitted to the dead space, in which they can be driven up to the platinum wires F to be exploded under nearly atmospheric pressure with oxygen which has been admitted from a sealed-on tube (not shown). The resulting moisture is condensed by cooling the limb C in liquid air, and the excess of oxygen is taken up by sodium-potassium alloy in the bulb D. The residual gas is examined spectroscopically in the capillary tube B.

In the other forms now used, hydrogen is removed by copper oxide heated in a hard glass tube containing also phosphorus pentoxide, and numerous other modifications have been employed.

The capillary tubes used are of the finest bore, so fine that when the mercury is once admitted it can be drawn out again only by strongly heating the tube. Rough measurements of the volume of residual gases can be made by calibrating the capillary.

It is found that the minimum quantity of neon detectable probably equals that contained in a few cubic millimetres of atmospheric air. If, owing to defective working, the neon actually was atmospheric, the accompanying

argon could be very easily seen (as the ratio Ar : Ne in air is about 700 : 1), when the particular method used was such as might have eliminated nitrogen beforehand; in the apparatus depicted, nitrogen naturally made its presence at once evident if a very small part of a cubic millimetre of air was present.

Summary of Results.

In the first place, we wish to point out that a great many of our experiments have yielded negative results, for as yet unexplained reasons. In the following we give an account chiefly of the positive experiments.

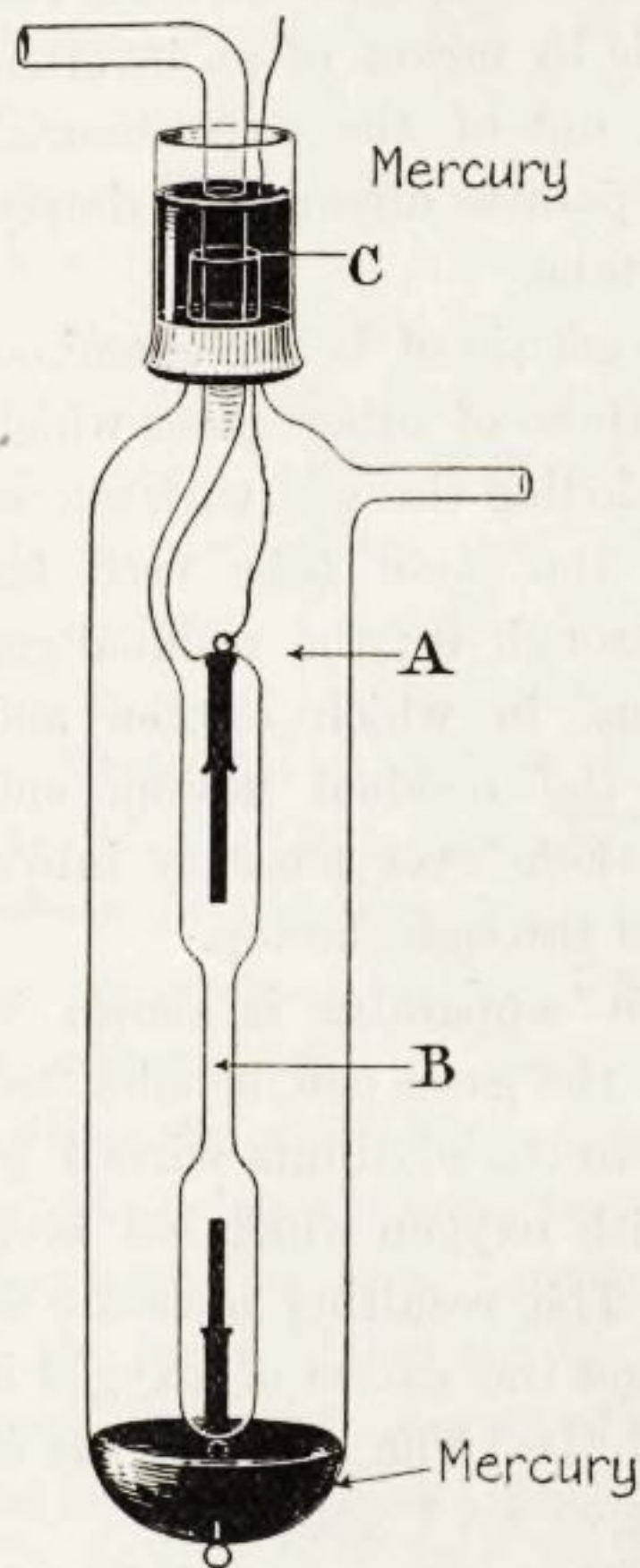


FIG. 1.

A. Different Electrodes—

Aluminium.—The apparatus used in the experiment where much helium and neon were found (J. N. C.) in the outer tube which surrounded the experimental tube* is given in fig. 1. B is the discharge tube, with moderately thick electrodes; A is the outer tube. Where the outlet tube of B passes through the neck of A, at C, was a thick piece of indiarubber tubing tightly wired and surrounded by a cup of mercury. Several modifications of this kind of tube were made later, but although small quantities of helium and neon were noticed in the outer tube, never again was the yield at all comparable with that obtained in the first experiment.

Fig. 2.—The description of an experiment with this apparatus (J. N. C. and H. S. P.) has been given.† It was designed in order that the wires connected to the electrodes in the inner tube A passed through the outer tube B

so that there were no live wires in the outer vessel. Helium and neon were found in the gases pumped off from the outer vessel. But the remarkable fact was noticed that the hydrogen (4.6 c.c.) admitted to the inner tube and sparked at the end of the experiment had diminished to about 0.4 c.c. Moreover, after breaking up the tube and melting the electrodes and the powdered ends of the inner tube in a hard glass tube, only 0.6 c.c. of

* 'Chem. Soc. Trans.,' vol. 103, p. 422.

† 'Chem. Soc. Proc.,' vol. 29, p. 217.

hydrogen was obtained. This apparent disappearance of hydrogen is always a noticeable fact during the discharge, and up to the present has not been entirely explained.*

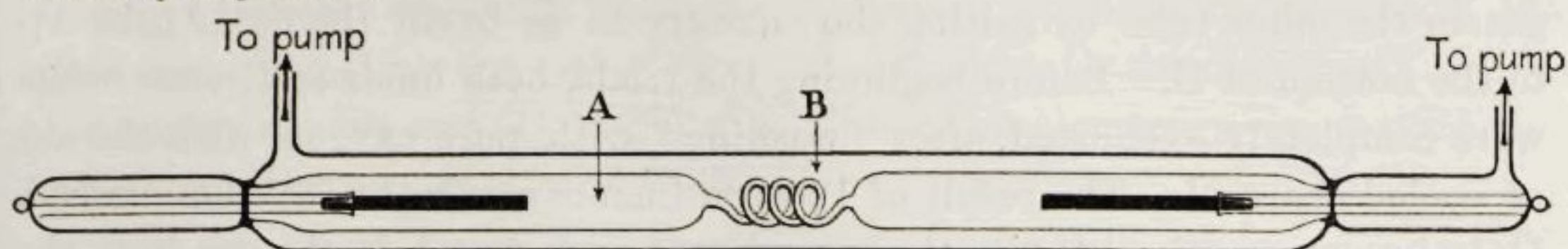


FIG. 2.

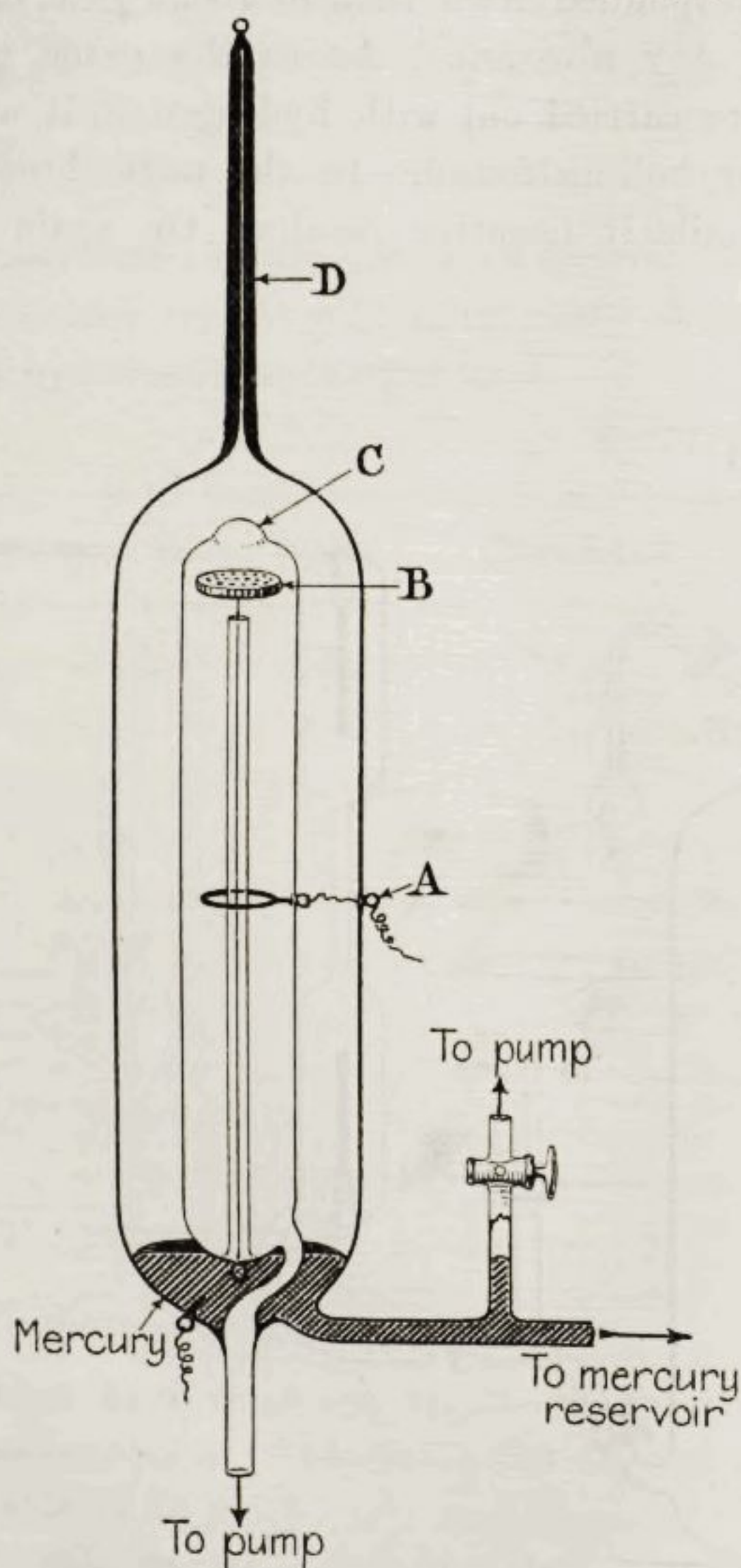


FIG. 3.

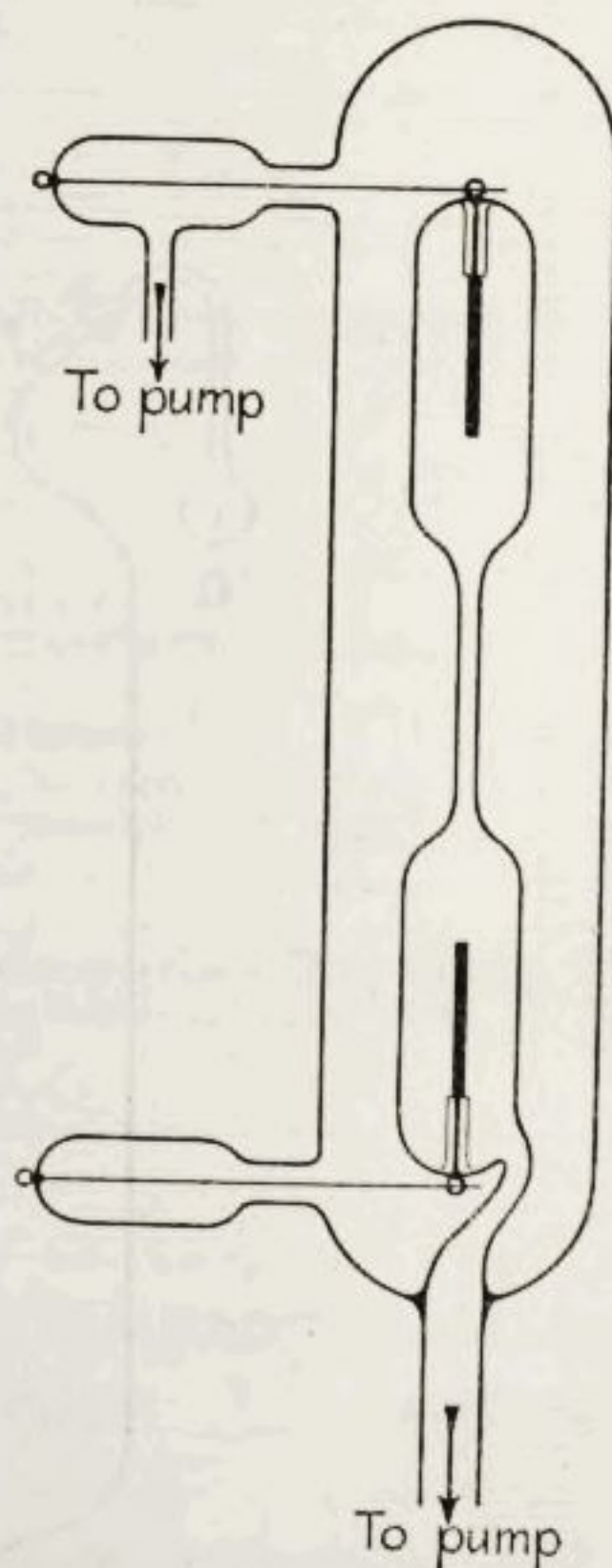


FIG. 4.

* The absorption of gases in vacuum tubes has been noticed by several people:—S. E. Hill ('Phys. Soc. Lond. Proc.,' Dec., 1912, p. 35) finds that hydrogen is absorbed in electrodeless tubes; Willows ('Phil. Mag.,' April, 1901), Campbell Swinton ('Roy. Soc. Proc.,' A, vol. 79 (1907)).

A series of experiments (I. M.) were conducted with the tube shown in fig. 3. A is the anode, B a perforated cathode, C the end of the inner tube blown out thin, D a capillary tube for examining spectroscopically any gas in the outer tube by raising the mercury so as to fill the outer tube up to the bottom of D. Before beginning the trials, both inner and outer tubes were completely exhausted, after "washing" with pure oxygen, with the aid of cooled charcoal. The result of 12 experiments can be briefly summarised. Only in one experiment, viz., the second, was neon found in the gas from the outer tube, where its amount corresponded with that in about $\frac{1}{4}$ c.c. of air: but it was not accompanied by any nitrogen. As to the gases in the inner tube, the first six tests were carried out with hydrogen in it, and in none of them was either neon or helium found. In the next three tests oxygen was used, and yielded similarly negative results. On again using

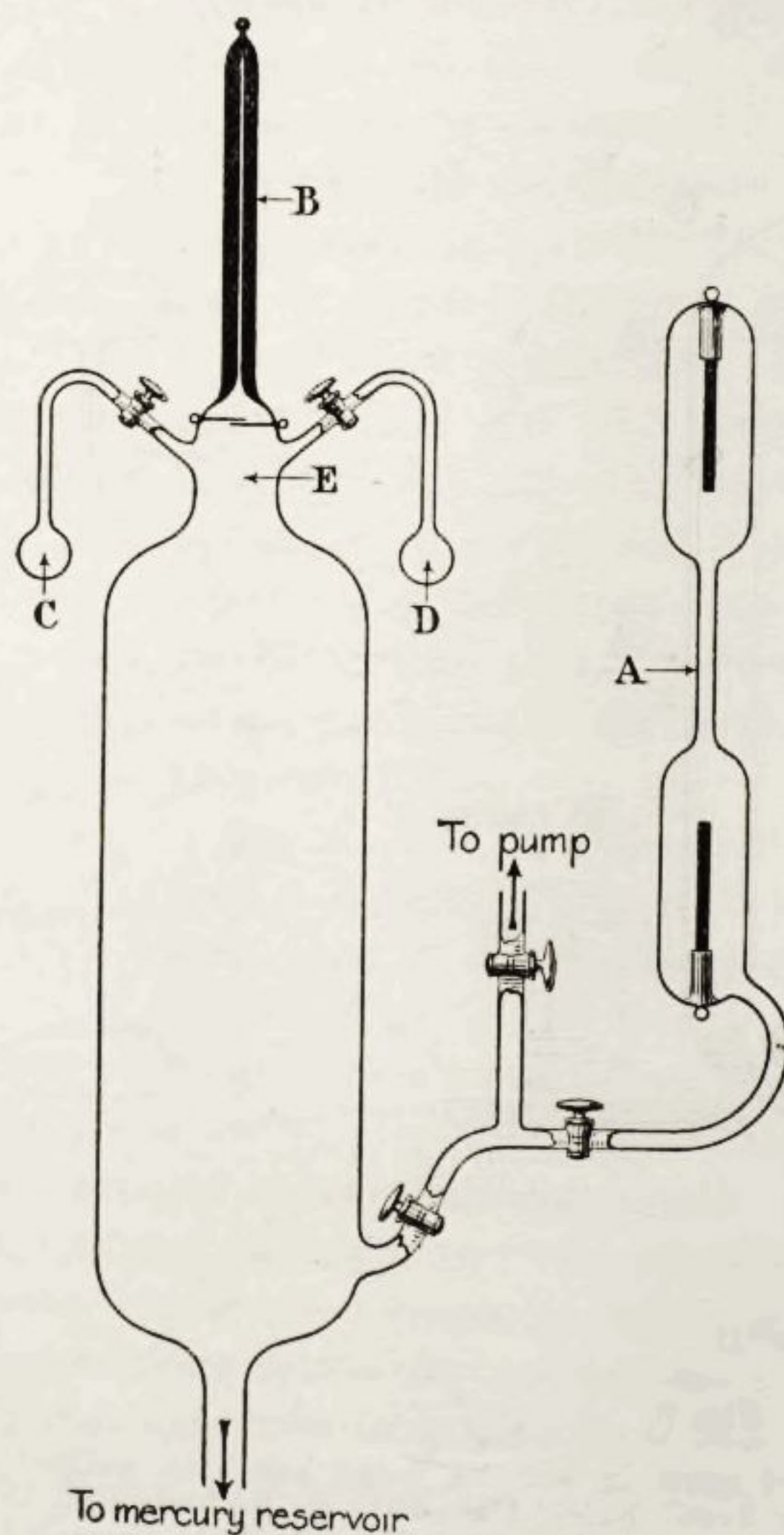


FIG. 5.

hydrogen (the same preparation as before), three experiments each yielded considerable amounts of neon. The quantities corresponded with that in about 1/10 to 1/5 c.c. of air; but in no case was nitrogen found in the gas. It may be remarked that in these three positive experiments, the top of the glass tube protecting the cathode rod was attacked by the discharge.

Another experiment (H. S. P.) with aluminium electrodes was carried out, using the testing apparatus of fig. 5 :—

(1) *Control*.—Hydrogen left in apparatus *without* discharge; then tested.

No Ne nor He.

(2) Discharge passed for 8 hours through hydrogen; tested as before.

Ne found.

(3) *Control*.—Procedure exactly as in (1). No Ne nor He.

These were repeated, with an identical result.

The chief results with other electrode materials may be tabulated. In all cases hydrogen was the gas used.

Table I.

Electrodes.	Tube.	Expts.	Gases found.	Notes.	Observer.
Pd	A	1	Much Ne	No N ₂ . Ar test not applied.	I. M.
	B	1	Strong Ne, some He	No N ₂ . Ar test not applied.	I. M.
	B	2-8	None	—	
Cu	A	1 and 2	None	—	J. N. C.
	A	3	He in jacket.....	—	J. N. C.
	A	4	Little He in jacket ...	—	J. N. C.
	B	1	Chiefly He, some Ne	No transference	H. S. P.
Pb		1-3	Chiefly He, some Ne	No transference	H. S. P.
Tl		1-4	He, trace Ne	No decrease in He yield ...	H. S. P.
Li	A	1-5	Good He, trace Ne ...	No decrease in 1 week	H. S. P.
	B	1-5	Same	Same	H. S. P.
Na		1	Chiefly Ne, some He	—	H. S. P.
K	A	1-4	Good He, trace Ne ...	{ No decrease in 4 days, when electrodes all volatilised }	H. S. P.
	B	1-4	Same		H. S. P.
Mg.....		1	None	—	H. S. P.

B. Bombardment Experiments—

Tubes have been set up in which various substances could be made the anticathode. The electrodes were of aluminium. The results are given in Table II on p. 36.

It will be seen that the results are in general agreement with those obtained by Sir J. J. Thomson by the use of the positive ray method; * the chief difference which is noticed is that in our experiments nearly all of

* 'Rays of Positive Electricity' (Longmans Green, 1913).

Table II.

Anticathode.	Experiments.	Gases found.	Notes.	Observer.
Pt	1-5	He, some Ne	No decrease in yield.	H. S. P.
Tl.....	1-10	Good He	Non-transference. No decrease in 100 hours' use.	H. S. P.
Ur	A 1	Good He, trace Ne	Non-transference.	J. N. C.
	A 2	Pure He	Non-transference.	J. N. C.
	B 1	Good He, trace Ne	Non-transference.*	J. N. C.
	B 2	Pure He	Non-transference.*	J. N. C.
KF	1-5	Good He	No decrease in yield.	H. S. P.
KCl	—	Good He	No decrease in yield.	H. S. P.
KI	—	Fair He, trace Ne	—	H. S. P.
RbCl	1	Strong He, some Ne ...	—	H. S. P.
	2	Slightly less of both ...	—	H. S. P.
	3-7	Constant yield, as in 2	—	H. S. P.
Cs ₂ CO ₃	1-4	Chiefly He, some Ne ...	—	H. S. P.
CaO	—	Doubtful traces	Long - continued bombardment.	
BeO	—	Same	Long - continued bombardment.	

* Ur powdered and heated to redness *in vacuo* beforehand.

the above substances gave yields of gas which did not seem to decrease even after long bombardment.

C. Mercury Arc—

The next experiments to be described arose from the observation that gas which was pumped out of an old silica mercury arc lamp contained a large quantity of both helium and neon. This lamp (for which we are indebted to Mr. C. Bastian) had a tantalum anode. It was in good order when we opened it after it had run for about 4000 or 5000 hours.


A discharge apparatus was then set up. It consisted of silica throughout. Essentially, it was a -shaped mercury arc lamp with barometer-leg leads which dipped into mercury reservoirs, whereby the current entered. A side tube on one of the limbs was connected to a pump by means of a mercury-jacketed ground joint. This is a perfectly reliable method of uniting silica to glass if good rubber grease is used as a lubricant. After pumping out and washing out the apparatus with pure oxygen, the arc was started by raising the mercury reservoirs. The current taken was 3½ ampères, from a 110-volt circuit.

Table III shows the results of the tests, which all yielded helium. A second series was then carried out, in which the arc was jacketed with cold water, with the object of testing the possibility that atmospheric helium had diffused through the hot silica. The current taken was 5 ampères. As the table shows, the production of helium remained unaffected.

Table III.—Mercury Arc (J. N. C. and I. M.).

	Hours' run.	Gas found.	Approx. quantity.
Arc unjacketed	12	Chiefly He; some Ne	cu. mm. at 1 atm. 0·001
	12	Chiefly He; less Ne	0·001
	20	Same	0·0005
	16	Same	0·0015
	30	Nearly pure He	0·001
Arc jacketed	5	Same	0·0005
	3	Same	Very small
	20	He, trace Ne	0·0005
	8	Same	Fresh mercury 0·0015
	32	Same	0·001

This series would seem to show that the source of the helium is not diffusion from air; to throw more light on the matter, however, another silica apparatus was devised and used (I. M.). This is seen in fig. 6. It is

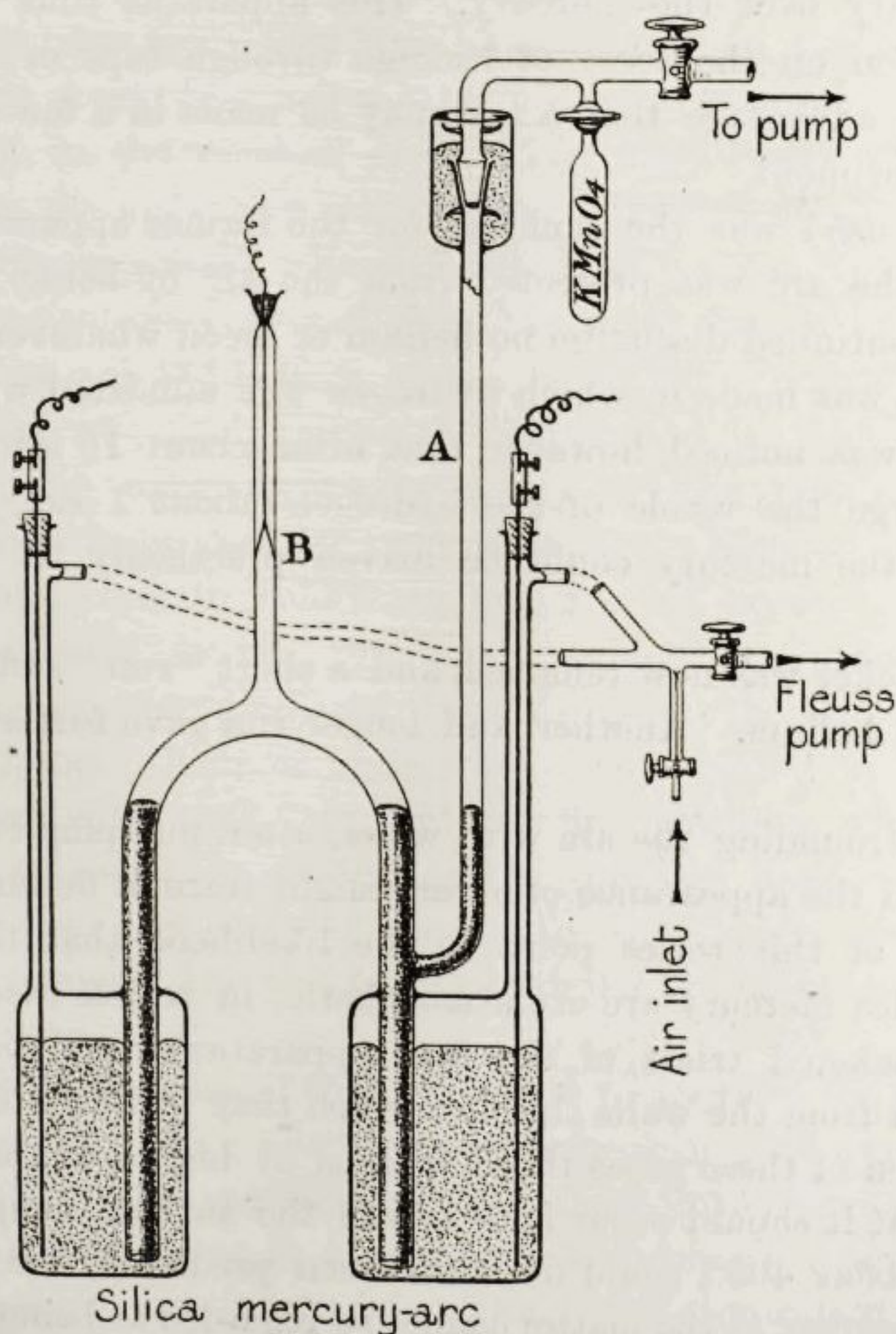


FIG. 6.

a \cap -shaped arc lamp as before, but the legs of the \cap are sealed into mercury reservoirs, each of which, besides bearing the wire for leading in the current, has also a connection with a Fleuss pump and an air inlet. By appropriately adjusting the pressure in the reservoirs the mercury can be set at any level in the bend. The apparatus can be exhausted by a Töpler pump connected to the tube A, which also carries a permanganate tube for generating oxygen to wash out the apparatus. The whole arrangement stands in a jar of water. During an experiment and the subsequent examination of the gas all possible communication with the outside is prevented by the mercury which cuts off from its surroundings the bend where the arc is in action. Finally, for testing the gas produced, it is simply necessary to admit air to the reservoirs so that the mercury rises into the tube B at the apex of the bend; the top half of this is very fine capillary tubing, at the top of which an extremely thin molybdenum wire is sealed through the silica to serve as one electrode in the spectroscopic examination of the gas which is thus forced into the capillary over the mercury. This apparatus thus is free from all possible objection on the score of leakage through taps or in transference and it has the advantage that a test may be made in a few minutes at any stage of an experiment.

The current used was the same as for the former apparatus. From the first, however, the arc was protected from the air by being water-jacketed, and even on continued discharge no helium or neon whatever was produced. An experiment was made in which hydrogen was admitted without affecting this result; it was noticed, however, that after about 10 minutes of passing the arc discharge the whole of the hydrogen (about 1 c.c.) had completely vanished, and the mercury could be driven practically to the top of the capillary.

The water-jacket was now removed, and a short "run" sufficed to produce a fair yield of helium. Another and longer run gave further helium and a trace of neon.

On again surrounding the arc with water, after pumping off these gases, a long run caused the appearance of a very slight trace of helium.

The results of this series point to the likelihood that the helium and neon in the silica mercury arc are atmospheric, in which case their appearance in the jacketed trials of the first apparatus would be attributed to their liberation from the walls through which they had been diffusing.

The diffusion of these gases through silica at higher temperatures is well known, but that it should occur here, where the surface temperature of the silica is only about 400° , could not have been predicted, and further experiments are in progress, as the matter cannot be regarded as being finally settled.

It was stated in the second of the earlier papers that the passage of the electrodeless discharge through hydrogen had yielded helium. This was undoubtedly the case in at least one set of experiments, where large yields were obtained (H. S. P.). In repeating the experiments with slight modifications (H. S. P. ; I. M.), negative results have been obtained, which seem to be related to the presence or absence of mercury vapour. Further work (H. S. P.) has partially confirmed the early results, but the conditions favourable to the production of helium are still uncertain.

Some remarks in the same paper dealt with a gas which showed a carbon spectrum, and which rapidly contracted when sparked in the examination capillary. This has been found to be merely a trace of oxygen (containing carbonaceous gas from the walls of the tube), which had remained uncondensed by charcoal cooled in liquid air, and which, when sparked with the mercury, was absorbed, forming solid oxide or ozonide of mercury.

Precautions.

It has already been mentioned that the presence in the apparatus of the slightest amount of air, even a few cubic millimetres, would mean that neon would be found in the residual gases. The most likely way in which air might leak into the apparatus was up the fall tubes of the mercury pump and of the testing apparatus. Small bubbles of air can creep up from the rubber tube between mercury and glass, but these can be arrested by using an efficient air trap at the bottom of the fall tube. For some time we have used not one, but two such traps. Another point is, that never since the beginning of these experiments have any of the pumps, apparatus, or electrode materials been used for neon or helium. Further, in order that no traces of air should remain before commencing an experiment, pure oxygen was always admitted to the completely exhausted apparatus, and then pumped out again, the discharge tube being at the same time strongly heated with a flame. Charcoal bulbs were always heated in boiling sulphur vapour before and after each test, and the fine platinum wire at the top of the capillary spectrum tube, as well as the capillary itself, were heated and sparked to drive out any occluded gases. By these precautions all residual gas is entirely removed, and this was proved, not once, but generally between each test of gases.

If gas had to be transferred from one place to another, the small test-tubes used were cleaned by being filled once or more with pure oxygen, which was then withdrawn into a gas burette, and these tubes, containing gas over mercury, were lifted about in a small glass spoon or a porcelain crucible. By the use of proper care it is most unlikely that atmospheric contamination

could occur, and this was continually being proved by direct tests, since gases so manipulated were found to be completely free of neon or helium when subjected to testing in the usual way. Moreover, in many of the experiments, the total volume of gas used was so small that even if it had been all atmospheric air, it could not have accounted for the quantities of the neon, and still less for those of the helium, which were obtained.

The controls just mentioned also attest the purity of the gases used. The oxygen was made usually from potassium permanganate, but also by electrolysis of barium hydroxide or sodium hydroxide solution in sealed vessels, which also provided the hydrogen for many of the experiments. Hydrogen was also prepared from sodium amalgam and boiled water, from aluminium and sodium hydroxide solution (*in vacuo*), by heating cut sodium (*in vacuo*), or from palladium. From whatever source they came, the gases were not used until they were found to be pure when tested in large quantity.

Finally, the mercury has always been purified by shaking it with mercurous nitrate solution, or, more usually, by sending it in a fine spray through a long column of dilute nitric acid. The fact that no neon or helium is contained in mercury so treated was proved by several experiments (J. N. C.), in which 1000 to 1500 grm. of mercury were boiled *in vacuo*. On examination in the usual way, no residual gases were found whatever.

Control Tests of the Sparked Gases.—The foregoing precautions and checks afford very strong security for the successful avoidance of an air-leak in any experiment; but more direct tests were considered necessary. The most obvious one, which was exclusively relied upon in our earlier work, was the search for nitrogen. In air the ratio $N_2 : Ne$ is about 80,000 : 1; hence if the neon detected in an experiment came from air, the nitrogen accompanying it would be found in relatively overwhelming quantity. Trials in which very minute amounts of air were deliberately admitted and tested in the usual way verified this.

It is necessary, however, to consider whether in all possible cases atmospheric nitrogen would necessarily remain in the gas after it had leaked in. Special trials were made (I. M.) in which air at low pressure was sparked in an ordinary Plücker spectrum tube connected with the pump. Even the minutest amounts of air gave a brilliant nitrogen spectrum in this comparatively coarse method of testing: hence it is apparent that in all the experiments which we have described, in which the discharge tubes were constantly kept under spectroscopic observation and never showed the nitrogen spectrum, air did not leak in before or during the discharge. But it was found that after continued sparking of air in the Plücker tube, a green phosphorescent vacuum resulted; so that if in an experiment $1/20$ c.c. of air

were to have leaked in unnoticed, after sparking for about 10 minutes there would have been no visible nitrogen spectrum. However, it was found that when the residual gas in the Plücker tube was transferred to an ordinary testing apparatus, nitrogen was plainly visible; hence, though this gas might possibly escape notice during a "run," it could be discovered in the final testing. It might be urged that even during this testing, in which the gas is spectroscopically examined over mercury, nitrogen might be absorbed so as to escape notice. Mercury was found to absorb only small quantities of nitrogen when sparked for some time with it at a low pressure, leaving a strong residual argon spectrum. A nitride of mercury was formed, which dissociated suddenly when moderately heated, and which reacted with Nessler's solution when wetted.

These considerations show that if atmospheric contamination occur at any point in an experiment *after* the "run," nitrogen must infallibly be detected during the examination. If any contamination occur *before* the "run," it would likewise instantly be made manifest on the first passage of the discharge through the experimental tube. It is only when an infinitesimally slow leak goes on *during* the "run" that it is possible that no nitrogen could be seen at any time; and to provide against this contingency an additional control is necessary, namely the absence of argon from the gas. It was proved that this is a reliable test by the trials made in the Plücker tube before mentioned. Though no argon spectrum could, with certainty, be seen in the Plücker tube after continued discharge, the residual gas when put into the testing apparatus gave a strong argon spectrum.

Besides this, it was found that if atmospheric gases have been bombarded into the aluminium electrodes of the Plücker tube, the neon can be extracted again (by heating and by passing the discharge) in a comparatively short time, together with much larger quantities of the argon. The whole of the absorbed argon is not, however, so readily extractable, and it appears that this gas is held with much greater tenacity than is neon when it has once been bombarded into the electrodes. This signifies that the argon test is in reality superfluously delicate as a control; nevertheless, it was used.

In all experiments where helium was the chief product, atmospheric contamination is *ipso facto* excluded; and as far as our tests have yet been carried, contamination seems to be thoroughly excluded in all the experiments. It must be mentioned, however, that in the less recent stages of the work, the disappearance of nitrogen during discharge was not properly understood; hence it is quite possible that some of the experiments in which the nitrogen test was exclusively relied upon may have been vitiated by a very minute and systematic leakage during discharge.

Possible Sources of the Gases.

Before coming to this question, we may make some tentative suggestions as to why Strutt's work proved unsuccessful; but at the same time it should be pointed out that many of our own experiments have been equally unsuccessful.

(1) A large charcoal bulb undoubtedly absorbs neon. A charcoal bulb of the same size as was used by Strutt in his testing apparatus, and a small one such as we always used, both with taps, were sealed on to a "non-transference" apparatus (J. N. C.). One cubic centimetre of air was taken, and the small bulb was cooled in liquid air. The residual neon occupied 26 scale-divisions of the capillary at about 1-2 mm. pressure. The gases were then boiled out of the small bulb and the large one was cooled instead for one hour. Residual neon = 8 divisions at as nearly as possible the same pressure. This residue was washed out with oxygen and rejected, meanwhile keeping the tap of the large bulb closed. The tap was now opened, the large bulb warmed up, and the gases from it exposed to the small bulb, which was once more cooled in liquid air. The residual gas was neon, and it occupied 15 divisions. Hence the large bulb had absorbed two-thirds of the relatively very large quantity of neon introduced. The experiment was repeated in several ways, always with the same result; and when only a very little neon was put into the apparatus, it was found that the large bulb absorbed it all, if small successive quantities of oxygen were admitted to the dead space so as to wash residual neon into the charcoal.*

(2) The capillary used by Strutt was closed with wax and had an outside electrode. We have always found it necessary to use a fairly strong discharge through the platinum wire which closes the top of the capillary; and further to be sufficiently sensitive the capillary tubes must be so fine that mercury can only be driven down out of them by strong heating.

(3) Any "splashed" metal in the experimental tube pertinaciously retains neon and helium unless it is strongly heated during withdrawal of the gas.

(4) The nature of the discharge through the experimental tube has, as was mentioned, a considerable influence upon the yield, and the necessity for a unidirectional current has already been pointed out.

Whatever the causes may be, it may be remarked that Strutt's results are in opposition not only to many of our own, but also to those of Sir J. J.

* It is necessary to qualify this criticism by mentioning that, despite the use of large charcoal bulbs, Strutt was able to detect the neon in 0.01 c.c. of air.

Thomson, which appear substantially to corroborate ours by an independent method.

A paper has recently been published by Mr. G. Winchester.* By using a very high potential discharge in tubes with a high vacuum he finds that the gases hydrogen, helium, and neon are set free. He also notices the uncertainty of production during experiment: in his paper he says:—"One thing noticeable in tubes of this kind is that, whereas some yield only comparatively small amounts of helium, others are very rich in this gas. One tube which at first gave only a small amount of helium in comparison with hydrogen, suddenly after running for 15 days gave out an enormous amount of helium for a few days and then suddenly became normal again. Since then I have found two tubes that showed the same phenomenon. Some electrodes seem to be very rich in helium and some very poor. All the aluminium electrodes mentioned in this paper were made of c.p. aluminium unless otherwise stated." Mr. Winchester believes that the helium and neon have been absorbed by the electrodes from the air, but that the case of hydrogen is different, and that there is a possibility of its being a disintegration product of the metal.

There remains the question: Since the neon and helium do not seem to come from leakage of air, what other origin is possible? Two hypotheses which suggest themselves are: Permeation from the air through the walls of the discharge tubes, and previous occlusion in the materials of the discharge tubes.

(1) *Permeation*.—It was conceivable that under the influence of heat and the discharge, glass might be permeable to helium and also to neon in much the same way as hot silica. It was proved that heat alone was unable to accomplish this, and experiments already described,† in which the discharge tubes were enclosed in atmospheres of helium and of neon with negative results, disprove this hypothesis. In any case the vacuum jackets with which most of the tubes were provided would have prevented any permeation. Nor do the platinum wires sealed through jacket and discharge tube act as avenues for the entry of these gases, as is shown by the positive results obtained with the gases sparked in tubes like that shown in fig. 4, where the outer sealed wire merely touches the inner one and is not continuous with it. These facts render the occasional appearance of helium and of neon in the outer jackets all the more unaccountable.

(2) *Occlusion*.—Especially in view of the fact that in some experiments the yield of neon appeared to cease after some time of running, the hypothesis

* 'Physical Review,' N.S., vol. 3, No. 4, April, 1914.

† J. N. C., *loc. cit.*, I, p. 422.

that the materials of the tubes already contained these gases is an obvious one. It has been experimentally put to the test, and so far appears to be untenable.

In the first place, the positive results with the electrodeless bulb and those with the mercury arc seem to be strong evidence against the metals used being the source—in the latter case, since boiling the mercury *in vacuo* yielded neither gas, as has been explained. This has been further studied, however, by examining aluminium. It has been melted *in vacuo* and the evolved gases tested (J. N. C.; I. M.). They contained no neon nor helium. To make perfectly certain, however, a fresh piece, about $\frac{3}{4}$ inch long, of the same wire as was used for electrodes in successful experiments, was allowed completely to dissolve in potassium hydroxide solution in an apparatus whence all traces of air had first been removed. The hydrogen was passed directly over hot copper oxide, thence the residual gases could be washed directly into the large dead-space of a “non-transference” apparatus with the help of a little oxygen from a sealed-on permanganate tube. There was neither neon nor helium in the gas (I. M.). This experiment has been made in other ways with the same result.

Since the metals contain neither of these gases, the only other possible store of pre-existing neon and helium would be the glass walls of the tubes. This has been tested as follows:—

Melting the glass *in vacuo* yielded neither neon nor helium. A large quantity of the same glass as was used for making the tubes was powdered and was acted on by potassium fluoride and strong sulphuric acid in an apparatus so arranged that no trace of air was present, the only gas being a little pure oxygen. Between 300 and 400 c.c. of silicon fluoride were collected and were frozen out by liquid air. The residual gases contained no neon and no helium (J. N. C.). To see if older glass contained the gases, two specimens were melted in a hard glass tube *in vacuo* and the gases tested. One was a green glass (Roman), probably from Egypt and presumably at least 1500 years old; the other was an opaque yellow glass (Chinese, Kien-lung period), about 150 years old. Neither specimen yielded neon or helium.

Valuable support is lent to these experiments, which negative the occlusion hypothesis, by tests described by Sir J. J. Thomson,* who found that aluminium salts gave the same quantity of helium on bombardment by cathode rays, whether they were made from ordinary aluminium metal or from the same metal which had originally had helium actually forced into it by being made the electrode of a helium spectrum tube. This shows, as he says

* *Loc. cit.*, p. 125.

that "solution can be relied upon to eliminate adsorbed gas." Again, the same author describes* how lead which is boiled *in vacuo* gives off no helium, but does so when bombarded; this appears to us to mean that no helium pre-exists in the lead.

It would be unreasonable in the extreme to suppose that, if helium and neon were present *as such* in any of the materials used, they would not be set free on dissolution which is accompanied by gas evolution. Solution of aluminium, for example, in potassium hydroxide entails a far more thorough physical disintegration of the piece of metal than does bombardment of its surface. The only tenable supposition is that any inert gases physically admixed must be set free; and we are not justified in assuming anything but a physical admixture in the case of inert gases pre-existing in aluminium or in glass. The proved absence of neon and of helium from the resulting products of chemical action must, therefore, mean that they are absent altogether.

We have endeavoured to put the facts of the case as fully as possible, without reference to any preconceived theory. It is not our view that our experiments rigidly exclude all the possibilities which have been mentioned; but it is evident that the trend of the results is towards conclusions which, if they turn out to be true, would be of very obvious importance.

We wish to thank Dr. H. T. Clarke for his assistance during part of the work.

* 'Nature,' vol. 90, p. 646 (1913).