

# Extension of the Spectrum Beyond the Schumann Region—I\*

## Difficulties Encountered and Methods of Procedure Followed

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I HAVE recently published a brief statement of the result of my investigations on the extension of the spectrum.<sup>1</sup> Since the appearance of that article my researches in this field have been directed toward clearing up certain doubtful points. Although these experiments have not resulted in pushing the spectrum beyond the limit already announced, and although the investigation is by no means at an end, it now seems time to make a fuller statement than was possible in a preliminary notice. Such a statement is all the more desirable since an understanding of the difficulties which have been encountered is necessary if one is to estimate the probability of future progress. The first part of this article, therefore, will be found to contain substantially the same material as the earlier notice, while the later parts are devoted to a rather detailed description of the experimental procedure.

The violet limit of the spectrum determined by direct eye-observation lies in the neighborhood of  $\lambda$  4000; with a glass prism and lenses, the spectrum may be followed photographically to  $\lambda$  3000 or thereabout; with a quartz system or with a reflecting grating, the limit may be pushed to  $\lambda$  1850. Victor Schumann showed that the absorption of the air and of the gelatine of the photographic plate were responsible for the abrupt termination of the ultra-violet spectrum near  $\lambda$  1850. By employing a vacuum spectroscopy and a special photographic plate, the emulsion of which was very poor in gelatine, he was able to push his observations to  $\lambda$  1230. At this point he was stopped by the opacity of the flourate of which his lenses were made. I have employed a concave diffraction grating arranged in such a manner that the lightpath from the source to the photographic plate is wholly in gas. Briefly, the containing apparatus may be described as a brass tube about 11 centimeters in diameter and rather over a meter long.<sup>2</sup> This tube is closed at each end by brass plates ground to fit suitable flanges. In my most recent experiments the light is generated electrically in a discharge tube of quartz provided with tungsten electrodes. This discharge tube fits air-tight on one of the two brass plates just mentioned; light from it, having passed through a slit, traverses the length of the apparatus and falls upon the diffraction grating by which, having been analyzed into its component colors, it is brought to focus on a special photographic plate placed in close proximity to the slit.

As the discharge tube is in no way separated from the body of the spectroscopy, it is obviously necessary to choose for the experiment some gas which will not only yield radiations in the region under investigation, but which will be transparent to these radiations. My earlier experiments were conducted with hydrogen, since it had shown the necessary characteristics in that part of the spectrum investigated by Schumann. With this gas at a pressure of 2 or 3 millimeters and by employing a strong disruptive discharge, in May, 1914, I was able to extend the spectrum<sup>3</sup> to  $\lambda$  900.

A rather tedious investigation having convinced me that nothing more was to be expected from the use of hydrogen, at least in this neighborhood, I turned my attention to helium, being guided by some of my earlier experiments which had proved that this gas possesses the necessary transparency.<sup>4</sup> At the same time I made some improvements in my apparatus which, though they left its general form unchanged, resulted in making it far more air-tight than ever before. The success of this improvement may be judged by the fact that I have been able recently to leave the spectroscopy for over fourteen hours at a pressure of about 3 millimeters without being able to detect any leak, either by a McLeod gage reading to 0.007 millimeter or by the appearance<sup>5</sup> of impurities in the spectrum of the gaseous content. I also took particular pains to purify the helium which I employed.

I have been rewarded for my trouble by a very considerable extension of the spectrum, for with helium free from nitrogen, at a pressure of 2 or 3 millimeters, by the use of the disruptive discharge, and with an exposure of about 10 minutes, I have repeatedly ob-

served a number of new lines, the most refrangible of which has a wave-length of 600  $\text{\AA}$ . All this has been accomplished with a grating ruled on speculum and with photographic plates prepared exactly as recommended by Schumann. The line  $\lambda$  600 represents an extension beyond Schumann's limit greater than that which Schumann himself achieved beyond the region of  $\lambda$  1850.

The relations of the spectra of hydrogen and helium have recently come into prominence through the theoretical researches of Bohr, Nicholson, and others. It so happens that the region on the more refrangible side of  $\lambda$  1250 offers an important ground for the study of these relations. In order that the conclusions may be of value, however, it is necessary that the gases under observation should be free from impurities. In the best form of closed discharge tubes the difficulties, arising from the contamination of the gas by the material of the tube or by the electrodes, are very considerable, especially when a disruptive discharge is used. In my apparatus, where the brass spectroscopy and quartz discharge tube communicate directly, these difficulties are considerably increased. I trust in time to overcome them, but for the present I must confine myself to the following statements.

Prominent in the spectrum of hydrogen is the line at  $\lambda$  1216 which forms the first member of a series predicted, on theoretical grounds, by Ritz.<sup>6</sup> I have also found the two next members near  $\lambda$  1026 and  $\lambda$  972. With pure hydrogen,  $\lambda$  972 is not visible and  $\lambda$  1026 is best seen when a disruptive discharge is used, but singularly enough, with helium containing a trace of hydrogen, both lines occur quite strongly with a simple alternating current from a 60-cycle transformer. This may be an illustration of the curious behavior of helium, for an atmosphere of this gas seems to facilitate the production of the spectra of other gaseous substances which occur in it as impurities.

In addition to these lines predicted by Ritz there are a number of others of equal prominence which always appear with a disruptive discharge in hydrogen. Two of these are of special interest, for their frequencies may be calculated rather exactly from the formula:

$$v = N \left\{ I - \frac{I}{(n + 0.5)^2} \right\}.$$

They persistently occur at  $\lambda$  1086 and  $\lambda$  929. Though the matter is perhaps not entirely settled, all the evidence seems to indicate that the two lines in question are due to an impurity.

The radiations from atmospheric nitrogen and from argon have also been examined. With both substances the disruptive discharge is necessary to produce the best results. The spectrum of the former gas with this type of excitation possesses some strong lines between  $\lambda$  1050 and  $\lambda$  1250; the spectrum terminates, however, near  $\lambda$  975. With a simple 60-cycle alternating current, argon shows a spectrum terminating near  $\lambda$  915. The extent of its spectrum is thus superior to that of hydrogen or of helium when subjected to similar electric conditions. With a disruptive discharge argon gives a strong spectrum of many lines terminating abruptly near  $\lambda$  800.

As far as I am able to observe, with one exception all the lines seen with helium when excited by a non-disruptive discharge are also found in hydrogen; a disruptive discharge is necessary for the production of the new lines of extremely short wave-length. The intensity of these lines seems to depend in a critical way on the electrical conditions in the exciting circuit, for it is only when the pressure in the discharge tube, the external spark-gap, and the capacity are all nicely adjusted that the extreme lines appear to the best advantage. The nature of the adjustments suggests that the radiations of the shortest wave-lengths require for their production that the atoms or molecules within the gas possess a very high velocity at the moment of collision. Some of the points in the preceding paragraphs are illustrated in the accompanying plate.

Spectrum *a* is the spectrum obtained from hydrogen when a spark-gap of about 3 millimeters is placed in series with the tube and when a capacity of 0.014 microfarad is shunted across the terminals of the transformer. Pressure about 1 millimeter. Time of exposure about 12 minutes.

Spectrum *b* is the spectrum of helium containing hydrogen under the same electrical conditions as for spectrum *a*. Pressure 1.7 millimeter. Time of exposure 8 minutes.

Spectrum *c* is the spectrum of hydrogen excited by a 60-cycle alternating current, there is no capacity in the system beyond that of the leads; current about 15 milliamperes. Pressure 2—3 millimeters. Time of exposure one hour.

Spectrum *d* is the spectrum of helium under the same electrical conditions as for spectrum *c*. Pressure 2.2 millimeters. Time of exposure 30 minutes.

The extreme lines in the helium spectrum are probably not visible in the reproduction. The scales are intended only to give the position of the lines approximately. I crave the reader's indulgence for the blemishes which disfigure the spectra; they are almost unavoidable under the conditions of the experiment.

The wave-length of the X-rays, as determined by the Braggs, is of the order of one angstrom. There is therefore a gap of some 600 units between the region of the ordinary Roentgen rays and the limit which I have reached. Several attempts have been made recently to produce less refrangible X-rays, but there is no satisfactory way of estimating their wave length unless perhaps one relies on the Planck-Einstein formula  $Ve = h\nu$ . Taking  $V$  as the potential drop which gives the cathode particle the velocity necessary to produce a very soft X-ray,  $e$  as the charge on the particle, and giving to  $h$  the usual value ascribed to Planck's constant, the experiments of Dember<sup>7</sup> were made to yield a wave-length for the X-ray longer than that which I have determined. Such speculations, though they are very interesting, cannot be given any great weight. There is still a considerable region between  $\lambda$  600 and wave-length 1 angstrom which must be experimentally explored. My present limit is probably due rather to difficulties of technique than to any fundamental fault in method. Now that we know that a Schumann plate can be used and that the speculum grating is efficient, I see no insuperable difficulty to a still further extension by purely spectroscopic means.

The following pages contain a detailed description of my experimental procedure. A table of the wave-lengths of the lines is given at the end of the paper.

The vacuum grating spectroscopy with which this research has been carried out has been already fully described.<sup>7</sup> The changes on which the success of the present research largely rest are simple in character, but of fundamental importance. Their object was to improve the air-tightness of the containing vessel and to guard the purity of the gas content. To this end, the plate which closed the working end of the container was of the simpler form used in my earlier work. It was of brass 1.3 centimeters thick, ground to fit the flange which it was destined to cover; of its two windows, one was permanently provided with a quartz disk through which comparison spectra were obtained, the other was fitted with a cup into which a brass cone, destined to carry the discharge tube, was ground. The plate was attached to the flange of the spectroscopy in the following way: A string of pure beeswax, some 2 millimeters in diameter, was bent into a circle of the required size; the flange of the receiver was then slightly warmed and the wax was lightly pressed against it; a photographic plate having been put in place, the face plate, also slightly warmed, was pressed against the wax. On the receiver being exhausted, the pressure of the air forced the face plate against the flange and thus squeezed the wax into a thin gasket. This device was suggested to me by Prof. R. J. Strutt; by its means it has been possible to reduce the leak in the apparatus to a value far smaller than I have been able to attain by any other method. An example of its efficiency has already been given. As a high degree of air-tightness is fundamental to the success of the whole research, the importance of the wax gasket is evident. It is obvious that the nature of the arrangement just described necessitates the removal of the face plate whenever the plate-holder is to be withdrawn from the apparatus. At present there seems no escape from this rather inconvenient procedure.

In order to secure radiations of the shortest wave-

\*Lyman, "Spectroscopy," p. 108.

<sup>1</sup>Lyman, *op. cit.*, p. 34.

<sup>2</sup>The *Astrophysical Journal*.

<sup>3</sup>Proceedings of the National Academy of Sciences, 1, 368, 1915; *Nature*, 95, 343, 1915.

<sup>4</sup>Lyman, "Spectroscopy of the Extreme Ultra-Violet" (Longmans, Green & Co.), p. 34.

<sup>5</sup>*Ibid.*, p. 78; *Nature*, 93, 241, 1914.

<sup>6</sup>*Ibid.*, p. 69.

<sup>7</sup>W. Ritz, *Gesammelte Werke*, p. 105.

length, it is necessary to employ a disruptive discharge; under these electrical conditions the gas-filling is always more or less contaminated by material torn from the discharge tube. To reduce this cause of error, quartz has been employed in place of glass. A change of form as well as of material has also been made, for the internal capillary type, so well suited to some previous investigations,<sup>8</sup> cannot be employed when a violent disruptive discharge is used, because the propinquity of the end of the capillary to the inside of the spectroscope encourages a spreading of the discharge with a consequent fatal fogging of the photographic plate. The form of discharge tube finally arrived at was of the simple "end-on" type with a capillary 4.5 centimeters and about 3 millimeters in diameter. The tungsten electrodes, provided by the kindness of the General Electric Company, were in the form of cylinders 1.5 centimeters long and about 3 millimeters in diameter. They were bound with fine tungsten wire to stouter wires of the same material which, in turn, were clamped in brass rods. These rods, covered with quartz sleeves, were contained in legs of the discharge tube and were sealed into these legs with Khotinski cement, the seals being kept hard by baths of mercury. The object of this arrangement was to restrict the electric discharge to the tungsten alone in the hope that thereby the contamination of the gas might be reduced to a minimum. The whole discharge tube thus constituted was sealed into a brass cone which, in turn, fitted air-tight into the cup on the face plate.

It is well known that tungsten if properly treated can be freed from occluded gases; this material, therefore, if employed for electrodes in a discharge tube, affords an escape from the contamination of the gas by the hydrogen which is so freely given off by most metals. In practice, I have found tungsten far more satisfactory than any other material which I have employed, always provided that it has been freshly treated.

Atmospheric nitrogen, argon, hydrogen, and helium have been used in this investigation. I am indebted to my colleague, Prof. Baxter, for the first-named gas. It was free from impurities save for those rare gases whose presence its atmospheric origin rendered inevitable.

I am indebted to the General Electric Company for my sample of argon. They informed me that the gas contained less than 1 per cent of impurity. As judged by spectroscopic observations in the visible spectrum, some hydrogen and a trace of nitrogen were present.

The hydrogen employed was prepared by electrolysis from amalgamated zinc and hydrochloric acid in an automatic generator of special type.<sup>9</sup> This method was recommended to me as one of the best available. After passing through towers of fused potassium hydroxide, the gas was collected over water. It was found necessary to prepare the hydrogen immediately before it was required for use, for, by standing over water, it is sure to become contaminated with air. Before being introduced into the phosphorous-pentoxide drying system, the gas was passed over platinized asbestos heated to redness in a quartz tube to insure the removal of the least trace of oxygen. A delicate test for the presence of a trace of air in the spectroscope is afforded by the appearance of the nitrogen lines near  $\lambda$  5005 with disruptive excitation. Judged by the appearance of its visible spectrum the hydrogen seemed free from impurities.

The helium employed has been obtained from three sources. The first sample was prepared from cleveite in the usual way and was purified over charcoal plunged in liquid air; the second was obtained from Professor Cady, of the University of Kansas; the third I owe to the generosity of Professor Boltwood. This last specimen I treated with pyrogallic acid and then passed over hot copper, then over hot calcium, and finally it was exposed to charcoal and liquid air. All the specimens were free from nitrogen and oxides of carbon, but contained a trace of hydrogen. Charcoal cannot be trusted to remove the last remnant of this gas, but as the helium was bound to be exposed to some admixture of hydrogen from the walls of the spectroscope and from the discharge tube, it seemed useless to go into the greatest refinement of purification at the present stage of the investigation. It must be noted that after the gas had been admitted to the spectroscope it sometimes showed a trace of oxides of carbon, but it appeared to be free from nitrogen.

About 100 cubic centimeters of helium are necessary for a single experiment; part of this gas is used in washing the spectroscope and part in the final observations.

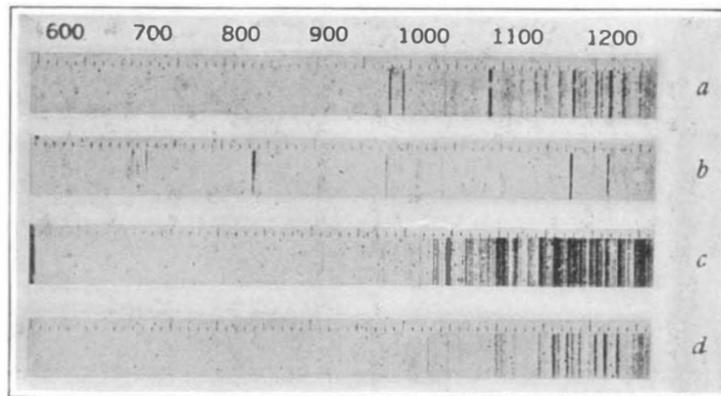
In order to guard the spectroscope from mercury and to reduce the presence of hydrocarbons as far as possi-

ble, a U-tube with legs, each about 35 centimeters long, was plunged in liquid air and interposed between the spectroscope receiver and the rest of the system; this latter consisted of the gas reservoir, the McLeod gage, and the Trimount oil pump.

When a disruptive discharge was required, the current was obtained from a  $\frac{1}{2}$  kilowatt Clapp-Eastham transformer run from a 60-cycle, 110-volt circuit. A capacity of 0.014 microfarad was placed across the terminals of the secondary, while a spark-gap of about 3 millimeters was used in series with the discharge tube. Under these circumstances, the equivalent spark-gap between needle-points at the discharge tube was 8.5 millimeters. When the non-disruptive discharge was employed, the current through the tube was of the order of 15 milliamperes.

With the idea of eliminating altogether the difficulties which arise from the introduction of electrodes into a radiating gas, some attempts have been made to use the electrodeless discharge. In this experiment a Chaffee gap<sup>10</sup> was connected in series with the primary of a Tesla coil, the arrangement thus formed being shunted by a condenser which, in turn, was placed across the leads of a 500-volt circuit, one of the lines of which contained a choking coil. The capillary discharge tube was provided with armatures of tinfoil at either end and these were connected to the secondary of the Tesla. Thanks to the regular behavior of the Chaffee gap, a very brilliant and steady illumination resulted.

The successful reconnaissance of Saunders<sup>11</sup> into the region of extremely short wave-lengths suggested the advisability of trying a calcium arc in quartz. The arrangement was very similar to that described by



Photograph of Spectra obtained by the apparatus described

Saunders except that the lamp was operated from the 500-volt circuit. The chief technical difficulty arises from the rapid deterioration of the quartz. In these experiments magnesium as well as calcium electrodes were employed.

If of the many experimental difficulties of the subject there is one which seems at present more troublesome than the others, and to which the limit of the spectrum may be directly traced, it is a luminosity in the gas content of the spectroscope excited by the disruptive discharge. The phenomenon makes its appearance when the pressure is of the order of 1 millimeter and produces a background of fog on the photographic plate in which faint lines are lost. This luminescence is especially aggravating since the low pressure at which it appears seems particularly favorable to the production of the lines of the very shortest wave-length. As a result of this difficulty long exposures are out of the question. It seems probable that if a window could be interposed between the discharge tube and the spectroscope, the excited luminosity would vanish.

Unfortunately, material for such a window is not at hand. A test with a bit of fluorite 1 millimeter thick, of proved transparency in the Schumann region, showed that this substance was opaque from  $\lambda$  1230 to the extreme end of the spectrum at  $\lambda$  600. A similar test with quartz 0.5 millimeter thick demonstrated that this substance shows no signs of transparency in the extreme ultra-violet.

Lyman<sup>12</sup> has interpreted some of his experiments on the ionizing power of light from an aluminium spark as proving the existence of radiations from this source lying on the more refrangible side of the quartz absorption band and transmitted to some extent by air. I have made an attempt to find these radiations by placing an aluminium spark in air outside my spectroscope and about 2 millimeters distant from a quartz window 0.2 millimeter thick which closed the apparatus. The result of the experiment was entirely negative, the adjustment of the apparatus being such that the field covered by the photographic plate extended to  $\lambda$  250.

<sup>10</sup>E. L. Chaffee, *Proceedings of the American Academy*, 47, 270, 1911.

<sup>11</sup>*Astrophysical Journal*, 40, 377, 1914.

<sup>12</sup>Lyman, *op. cit.*, p. 107.

After this account of the apparatus and the methods employed, it seems important to discuss the various spectra in some detail, paying particular attention to the circumstances under which they were produced.

(To be continued.)

### Purification of Running Water by Ozone

THE Prussian city of Königsberg has established an experimental laboratory in water purification, in which there has been developed a process of ozonization at once cheap and effective. The raw water, of yellowish color and often muddy, is first freed of silt and discoloration by treatment with aluminium sulphate in the proportion of 80 grammes per cubic meter, and by gravel filtration. The water is then run from below into a de Frise tower, a small portion being deflected, mixed with ozone in a compressor, and let into the tower on the opposite side.

In order to ascertain the limits of the tower's conductivity, there were introduced into the water enough coli-bacilli to give it a germ content of from 30,000 to 9,000,000 per cubic centimeter; and after each such injection the number of germs still alive after passage through the tower was determined. These tests confirmed the suspicion that the ozone in the tower was not being sufficiently well mixed with the water—that in addition to the many tiny bubbles desired, others were being formed, the size of a cherry, or even larger, which passed through the tower so rapidly that all effect upon the germs was lost.

In order to bring about closer contact of water and ozone, the two lowest celluloid sieves of the tower were covered with a layer of small pebbles and gravel to a depth of 25 centimeters. After this alteration, the bacteriological effect of the tower was excellent; the use of 5.4 grammes of ozone per cubic meter of water reduced the number of germs from nine million per cubic centimeter to ten. Even with a proportion of ozone of only 1.8 grammes per cubic meter, very good results were attained. This was likewise the case even when the water was run through the tower without previous treatment with alum, and without filtration; and also when the bacteria were not single, but in clusters.

It appears that the strength of the ozone is not so much of prime importance as is the reduction to a minimum of the thickness of the sheet of water between two gas bubbles. It is vitally necessary that the ozone shall circulate rapidly through the water, replacing that which has been used up in oxidizing the bacteria and other organic matter.

By simultaneous use of alum and ozone, under this method, it is found possible to convert water of very high organic content into a clear, colorless drinking water with no taste whatever, very free from germs, entirely free, in fact, from pathogenic ones. In every case the result of ozonization is distinctly to be preferred to that of the chlorine treatment; and the increased cost is very slight.—*Die Umschau*.

### Behavior of Iron Toward Water and Aqueous Solutions in the Steam Boiler

EXPERIMENTS were made under normal working conditions, at a pressure of 15 atmospheres, in an experimental boiler of about 30 liters capacity, using test plates of mild steel of 400-500 grammes weight suspended from the cover of the boiler. The electrolytic method of removing rust, described by Jakob and Käsbohrer (this J. 1911, 1063), proved useful for determining the amount of corrosion. Freshly-boiled distilled water, free from carbonic acid, produced the least corrosion. Sodium carbonate in small concentrations caused rusting, but in concentrations above 1 per cent showed a pronounced protective effect. Zürich tap water corroded the iron to a greater extent than ordinary distilled water. Sodium hydroxide showed a protective action even at a concentration of only 0.01 per cent, while at 0.1 per cent it prevented corrosion entirely. Sodium hydroxide is formed slowly from sodium carbonate in the steam boiler, and this accounts for the fact that small proportions of sodium carbonate, which produce corrosion at first, exert a protective action after some time. Of the salts which may occur in boiler feed water, chlorides and magnesium salts are especially active in causing corrosion; sodium carbonate at a concentration of at least 1 per cent is an effective protective agent. Sodium hydrosulphite exerts a protective action when added in small quantities, but at a concentration of 1 per cent causes pronounced corrosion of boiler plate even in presence of sodium carbonate.—*E. Bosshard and K. Pfenniger. Abstract from Jour. of the Soc. of Chem. Ind.*

<sup>8</sup>Lyman, *op. cit.*, p. 41.

<sup>9</sup>Cook and Richards, *Proceedings of the American Academy*, 23, 149, 1887.