XXXIX. On the second spectrum of hydrogen

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By Dr. B. Hasselberg[*].

[Plate X. figs. 1–3.]

PLÜCKER and Hittorf, in their celebrated paper "On the Spectra of Ignited Gases and Vapours"[†], were the first to call attention to the remarkable system of lines which almost always appears, together with the characteristic hydrogen-lines H_α H_β H_γ and H_δ, in tubes containing hydrogen, under small pressure, when traversed by the electric discharge. These groups of lines, which are distributed through the whole spectrum from H_α to H_γ, but are especially bright and characteristic in the neighbourhood of D, have since been made the subject of numerous investigations, especially to decide the question of their origin, since the views of the discoverer upon this point had been rendered doubtful by later experiments. The result of these investigations was not altogether satisfactory, since even now the question can hardly be regarded as settled. On the contrary, two opposite opinions upon this point are held by spectroscopists, one of which, held by Plücker, Hittorf, and Wüllner, represents the lines in question as a spectrum belonging to hydrogen at a low temperature ; whilst the second, represented by Berthelot, Ångström, Salet, and recently Ciamician, finds the source of these

* Translated from the *Mémoires de l'Académie Impériale des Sciences de St. Pétersbourg*, vol. xxx. No. 7.
† Phil. Trans. 1864.

radiations in acetylene. This circumstance may be regarded
as a sufficient reason for a renewed study of the subject, in
view of the great importance which attaches to an exact
knowledge of the spectroscopic phenomena exhibited by this
gas ; the more so since it offers opportunity to give a more
accurate description of the spectrum than those which spec-
troscopic literature offers at present, and which are in no way
fitted to give even a moderately satisfactory idea of the spec-
trum in question. It is, indeed, surprising that so little has
been done towards the exact knowledge of a subject which
has so often given occasion to discussion ; and I should be
even inclined to regard this very circumstance as the reason
of more than one of the differences in opinion which still
exist upon this subject. As complete an examination of the
spectrum as possible, as it appears under different conditions,
will then, in my opinion, not only supply a gap in the spec-
troscopic literature concerning this gas, but will facilitate in
no small degree the solution of the problem concerning the
origin of the spectrum. In order to make this clearer, I will,
in the first place, and before passing to the description of
my own experiments, consider somewhat fully the inves-
tigations upon this spectrum published up to the present
time.

As already mentioned, the first description of the spectrum
is to be found in the paper of Plücker and Hittorf referred
to above. This gives in few words as exact a description of
the main features of the spectrum as possible without mea-
surements and drawings, and shows at any rate that the
subsequent designation of the spectrum as a band-spectrum,
belonging to the same category as the band-spectra of
nitrogen, sulphur, &c., is to be regarded as altogether in-
admissible. The description is as follows :—" Even in the
old spectral tubes enclosing highly-rarefied hydrogen, the
ground, from which the three characteristic lines rise, did not
appear always of the same darkness ; in some instances new
bright lines appeared, especially in the neighbourhood of the
sodium-line. In resuming the subject we pointed out the
existence of a *new hydrogen spectrum* corresponding to a
lower temperature, but having no resemblance at all to the
spectra of the first order of nitrogen, sulphur, &c. In this
spectrum, of a peculiar character if fully developed, we ob-
serve a great number of well-defined bright lines almost too
numerous to count and represent by an engraving, but bril-
liant enough to be examined with a magnifying power of 72,
after the light has passed through four prisms." It is clear
from this that the spectrum possesses a character altogether

different; and, indeed, the employment of more powerful instruments does not reveal in its whole extent a single line of similar nature to the band characteristic of the so-called spectra of the first order of other gases. On the contrary, the spectrum consists entirely of sharply-defined lines distributed upon a feebly-illuminated background without any definite order, which neither in appearance nor in intensity differ essentially from the four characteristic lines of hydrogen.

If, then, we take into account only the appearance of the spectrum, we find no reason for distinguishing it as a separate spectrum of hydrogen from the four lines $H_\alpha \ldots H_\delta$. It would be more simple to assume the existence for hydrogen of only one line-spectrum, consisting of all these lines together with the lines $H_\alpha \ldots H_\delta$, always assuming that they can be shown to possess identical origin. This view of the matter is, to a certain extent, justified by the circumstance that with hydrogen, in opposition to what is found with other gases giving double spectra, the two spectra almost always appear together, whereas in other cases the appearance of the one spectrum is accompanied by the disappearance of the other, or at least by its greater or less diminution. We may, for example, recall the behaviour of a tube filled with, nitrogen the pressure of which is caused to vary: as long as the pressure is small or there is no air-break in the circuit, the well-known band-spectrum only is seen; whereas if the pressure be increased, or if an air-break be introduced, the spectrum gives place to the line-spectrum. Between these two cases there is always a transition-point at which a sort of conflict takes place between the two spectra, in which sometimes the one, and sometimes the other, spectrum partially starts up; but we never have the two spectra completely developed at the same time. Although these conditions do assume somewhat different forms with hydrogen, yet one difference between the two spectra, based upon the different temperatures at which they are produced, may be pointed out. Plücker has already shown that in wide tubes, where the temperature of the discharge is certainly less than in capillary tubes, H_β is the only one of the chief lines of hydrogen which makes its appearance, whilst the groups of the second spectrum in the red and orange are still distinctly to be seen. On the other hand, by the introduction of an air-break or Leyden jar, even at extreme rarefaction, it is possible to entirely extinguish the second spectrum, whilst the characteristic lines at the same time assume a more or less expanded and diffuse appearance. Now, since this arrangement involves an increase in the potential of the quantities of electricity which

unite in each discharge, the mechanical equivalent of the discharge is greater, and consequently its temperature is higher. The expansion of the lines is therefore to be regarded only as the consequence of this rise in temperature *; and if the same effect is produced by increase of pressure, this is only because then a higher potential is necessary in order that the discharge shall take place.

If, instead of the induction-coil, we employ an influence-machine as source of electricity, then, as E. Wiedemann † has shown, the simpler process of discharge which takes place with the machine permits the two spectra to be much more clearly separated from each other, by gradually lengthening the included air-break, than is possible with the more complicated process of discharge in the induction-coil. The second spectrum, which appears with no air-break, or only a small one, becomes gradually less bright as the air-break is increased, whilst the characteristic lines become more distinct, until finally, with a certain length of spark, the second spectrum disappears almost suddenly. These conditions are exactly suited to make the phenomena obtained with the induction-coil more intelligible. Since, on account of the gradual flow of electricity to the electrodes which takes place, each opening or closing of the primary current, besides the chief discharge, produces also a whole series of feebler partial discharges, it is probable that the second spectrum is due to these smaller discharges, whilst the primary discharge at greater potential produces the characteristic lines. Consequently, in more completely exhausted tubes, where the resistance is not sufficient to prevent the passage of the smaller discharges, both spectra should be visible; whilst as the pressure is increased a point is at last reached at which only the principal discharge takes place, and the spectrum due to it, consisting of the lines $H_\alpha \ldots H_\delta$, is seen. If this is so, then in one and the same tube, in which the exhaustion is gradually increased, when currents of different strengths are employed, that pressure at which the second spectrum begins to show itself must be greater the greater the intensity of the current, and consequently the potential of the partial discharges. But this is confirmed by experiment. Thus, for example, on passing the current from a large induction-coil excited by means of five Bunsen cells through a tube containing hydrogen, and then passing the current of a small induction-coil through it, I found that on gradually exhausting, the first traces of

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* Compare Salet, *Sur les spectres des Métalloïdes* (Paris 1872), p. 17 ; Fievez, *Bull. de l'Académie de Belgique*, 3 sér. t. 1, No. 3, 1881.

† Wiedemann's *Annalen*, vol. x. 1880, p. 202.

the second spectrum appeared at pressures of 22 millim. and 2 to 3 metres respectively.

These views of the connexion between the process of discharge and the nature of the spectral phenomena obtained have already been propounded by Ångström[*], being supported by observations of the image of the tube produced by a rotating mirror. But if we observe in this manner, not the tube itself as is generally done, but the spectrum of the tube, it would seem that we ought to obtain a still sharper criterion of the admissibility of the above view than is afforded by experiments hitherto described. If the three principal lines are to be referred exclusively to the momentary chief discharge, and the system of lines forming the second spectrum to the series of partial discharges, then, in the revolving mirror, the first should appear as isolated lines upon a continuous background formed by the latter. However simple the experiment theoretically considered may appear, its actual performance is attended by such considerable difficulties, in consequence of the small luminous intensity of the spectrum, that my attempts in this direction have not given any certain result.

Plücker and Hittorf, from their experiments with wide tubes, drew the conclusion, in respect to the origin of the second spectrum, that it is to be ascribed to hydrogen just as much as the four lines undoubtedly characteristic of this gas. In their method of experimenting there is, in fact, no uncertainty upon this point arising from possible influence of the material of the electrodes or of the glass envelope. Although no details are given of the method of preparing the gas, yet it is clear that Plücker and Hittorf have certainly bestowed due care upon this point, so that their conclusions need not fear criticism upon this ground. Since these conclusions were very completely confirmed some years later by the experiments of Wüllner [†], there was every reason to regard this question as settled. But other views were expressed almost at the same time, based upon chemical investigations on the conditions of equilibrium of gaseous systems, by Berthelot and Richard [‡], which not only caused the reopening of the question, but so hindered a definite decision that even now there is no agreement among spectroscopists upon this point. I will now consider these views more closely.

It is known that every compound body is decomposed into

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[*] *C. R.* t. lxxiii. (1871), p. 371.

[†] Pogg. *Ann.* vol. cxxxv. p. 497, cxxxvii. p. 337. *Festschrift der Niederrhein. Ges. f. Natur- und Heilkunde,* Bonn, March 1868.

[‡] *C. R.* lxviii. pp. 810, 1035, 1107, 1546.

its elements under the influence of the electric discharge. On the other hand, compounds are formed under the same influence; and between these opposite actions there is produced in certain cases a condition of unstable equilibrium, in which no further change is produced by the continued action of the electric current. Acetylene, amongst others, is, according to Berthelot, one of the bodies which behave in this way. If a continuous series of electric discharges be sent through this gas, decomposition occurs, which, however, is not complete, but ceases at a certain point, depending upon the pressure at which the composition of the gaseous mixture remains the same. Since, moreover, with constant change of pressure the percentage composition of this mixture does not change gradually but suddenly, this composition is within certain limits independent of the pressure. Thus, for example, Berthelot found in 100 volumes of the resulting mixture, at a pressure of from 3·46 to 0·41 metres of mercury, 12 volumes of acetylene; at 0·31 metre, 6·5 volumes; and between 0·23 and 0·10 metre, 3·5 volumes : the last mixture retained its stability even at a pressure of only a few millimetres.

We see from this that the equilibrium between acetylene, carbon, and hydrogen in the resultant gas-system changes only abruptly with the pressure in multiple proportions ; and since, consequently, those complications which would otherwise result by continuous change in the composition of the gas under the influence of the discharge are, for the most part, · avoided, Berthelot and Richard have justly regarded the spectroscopic examination of this and similar mixtures as specially adapted to give clearer evidence as to the spectroscopic conditions of compound bodies. The results of these investigations, so far as the mixture of gases at present under consideration is concerned, on the interpretation given to them by Berthelot and Richard, can hardly be brought into agreement with the results of later spectroscopic research, and consequently cannot, in my opinion, be made to serve as an argument against the admissibility of Plücker's view of the second hydrogen spectrum.

The mixture employed contained 1·7 per cent. of acetylene, and 98·3 per cent. of hydrogen. These proportions were so chosen in order to be as far as possible from the limits given above. The gas having been introduced, under a pressure of a few millimetres, into a Geissler's tube, the discharge of a powerful induction-coil was passed through the tube, and the spectrum observed. It is described * by Berthelot and Richard as follows :---

* *Loc. cit.* p. 1548.

" Le spectre de notre mélange gazeux a présenté :

" (1) Les raies brillantes de l'hydrogène.

" (2) Les raies et les bandes lumineuses du carbone, conformes au spectre de l'oxyde de carbone dessiné par MM. Plücker et Hittorf et au spectre du carbone de M. Morren. Nous avons vérifié l'exactitude remarquable de ces dessins en opérant sur une tube de Plücker remplie d'oxyde de carbone raréfié.

" (3) En outre nous avons reconnu l'existence d'un groupe particulier de bandes et de raies, qui n'ont été signalées à notre connaissance par aucun observateur *.   En effet, depuis le jaune jusqu'au vert on aperçoit une multitude de bandes étroites et brillantes équidistantes ou à peu près séparées par de fines raies noires.   Le tout offre l'aspect d'une série de cannelures délicates et extrèmement reserrées : elles sont surtout manifestes à partir de la division 25 de notre micromètre et jusque vers la division 65.   La portion jaune du spectre, voisine de la raie du sodium, les présente avec le plus grand éclat."

As far as the first point is concerned, there is no doubt of its correctness, since the mixture contained more than 98 per cent. of hydrogen.   But it is different with the second.   The bands mentioned here can no more be ascribed to the element carbon, but form the spectrum common to all hydrocarbons, which was first exactly studied by Swan †, and has since formed the subject of investigation by many spectroscopists. In my paper " On the Spectra of Comets, &c." ‡ I have given the history of this spectrum somewhat fully, and have given reasons (chiefly from the researches of Ångström and Thalén §) why the above interpretation appears to me the right one. Since, according to these investigations, which have been recently confirmed by the exhaustive researches of Liveing and Dewar ‖, the acetylene which always forms in hydrocarbons under the influence of the electric current is to be regarded as producing these radiations, its appearance in the spectrum of the mixture in question was not to be expected, but forms a direct proof of the correctness of the explanation of the spectroscopic phenomena observed with hydrocarbons first given by Ångström and Thalén.

But if, as, strange to say, is still the case with most spectro-

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* It is remarkable that the passages treating of this point in Plücker and Hittorf's paper should have escaped the notice of the authors, since, from the remarks made above under No. 2, we must assume that this paper was known to them.
   † Edinb. Trans. vol. xxi.
   ‡ *Mémoires de l'Acad. de St. Pétersbourg*, vol. xxviii. No. 2.
   § *Acta Upsal.* ser. 3, vol. ix.   ‖ Proc. Roy. Soc. No. 201 and 205, 1880.

scopists, we regard Swan's spectrum as that of carbon, we might ascribe the *third* spectrum appearing in the above gaseous mixture to the *third* component of the mixture, viz. acetylene, as Berthelot and Richard do. But the matter is not so. Against such an assumption we have not only the arguments already brought, but also the circumstance that the spectrum does not at all bear the character usual to spectra of chemical compounds, since it does not consist, as Berthelot and Richard maintain, of a system of channelled spaces, but, on the contrary, must be placed in every respect in the category of the line-spectra of the elements. Since, moreover, it appears always in those cases where not only has no acetylene been mixed with the gas, but where the greatest care has been bestowed upon the purification of the gas, it seems much more reasonable to ascribe it to hydrogen itself than to assume for a compound body such as acetylene spectral peculiarities having no analogy with those in any other known case. Against what has here been said, the objection may possibly be raised that even the greatest care in the preparation of the hydrogen does not afford any complete guarantee that the gas may not, after all, be rendered impure by the presence of hydrocarbons, since it must of necessity come repeatedly into contact with the different parts of the air-pump. That carbon compounds may actually be introduced into the gas in this way is not to be denied ; but it is not *necessarily* the case, and I shall presently adduce experiments which completely prove this.

It need scarcely be mentioned that there is no doubt of the identity of the spectrum mentioned by Berthelot and Richard under No. 3 with Plücker's second hydrogen spectrum. Since, on the scale of their spectroscope, the hydrogen-lines H_α, H_β, and H_γ fell respectively upon the divisions 13·5, 144·5, and 229·0, the divisions 25 and 65, which the authors give as the limits upon the same scale of the most conspicuous part of the spectrum, correspond to the wave-lengths $\lambda = 633$ and $\lambda = 570$; and these are in fact, according to my measurements, the limits within which the part of the spectrum in question is included.

The views of Berthelot were at the time shared by Ångström [*], which may appear surprising, since it was from his investigations, made conjointly with Thalén, that the identity of Berthelot's second spectrum with that of acetylene appears. But one or two remarks must be made upon this point. In the first place, Ångström has not altogether taken it as settled

* *C. R.* lxxiii. p. 372 (1871); Pogg. *Ann.* cxliv. p. 300.

that Berthelot's third spectrum belongs to acetylene; he has only inferred, from the processes of discharge in the appearance of this spectrum on the one hand, and of the ordinary spectrum of hydrogen on the other hand, that we have to do in the first case with a *compound* of hydrogen, "soit avec lui-même soit avec un corps étranger;" and then, on account of the stability of the mixture of acetylene and hydrogen as shown by Berthelot, he takes the latter alternative as the more probable. If, now, in consequence of evidence already brought forward, and further on account of evidence still to be adduced, the assumption of a compound with a foreign substance appears to be little probable, there is no reason that we should lose sight of the possibility of the other alternative suggested by Ångström, according to which the spectrum is to be ascribed to a compound of hydrogen with itself. On the contrary there are, as we shall presently see, reasons which are decidedly favourable to such an assumption.

If further, in the second place, we remember that the investigations of Ångström and Thalén, which treat, amongst other things, of the spectroscopic relations of carbon compounds, and give the first rational explanation of the spectroscopic phenomena of hydrocarbons, were not published until four years later, viz. in the year 1874, and moreover, in consequence of Ångström's death, were not so complete as was intended, we have the explanation of the fact that Ångström did not subject his first theory of the second hydrogen spectrum to further proof.

Berthelot's theory receives a confirmation, which, at first sight, seems of great weight, from the researches of Salet [*]. If, in fact, Plücker's spectrum really belongs to acetylene, then this spectrum cannot appear in a hydrogen-tube which is free from all impurity of carbon compounds. In order to test this, Salet allowed a current of pure dry oxygen to circulate for a long time through the tube to be used before it was filled with hydrogen, the tube being all the time heated to a low red-heat. In this way it was believed all traces of carbon compounds must have been removed. Further, in order to eliminate all possible influence of the electrodes, they were omitted altogether, and instead the wide parts of the tube were coated with tinfoil : when these were connected with the poles of the induction-coil, or with the combs of the Holtz machine, the gas became luminous. Under these circumstances spectroscopic examination of the tube showed only the three principal lines of hydrogen without any trace of the second

[*] Salet, *Spectres des Métalloïdes* (Paris, 1872), p. 17.

spectrum; and Salet concludes therefore that Berthelot's view is shown to be correct. However natural this may appear at first sight, there is yet an objection which may be made, and which appears to me to essentially alter the state of the case, and to deprive Salet's experiments of most of their force. We know that if a gas is rendered luminous in the way described the temperature is comparatively low, or at least decidedly below the limits it may attain when the discharge passes directly through the tube. Consequently the intensity of the light and of the spectrum will be smaller, and, unless the coatings are very strongly charged, may be even so small that only the stronger lines of the spectrum (in this case the principal lines H_α, H_β, H_γ) are visible. In order further to test the admissibility of this explanation of Salet's experiment, I have made the two following experiments :—A hydrogen-tube (purchased ready filled), which showed the second hydrogen-spectrum very vividly when a powerful current was sent through it, was provided with tinfoil coatings and excited in the manner described. The light emitted by the tube, usually brilliant and nearly white, was now feebly red, and showed in the spectrum, besides mere traces* of the second spectrum in the green, only H_α and H_γ of small intensity, and H_β relatively bright and diffuse. The same experiment was then repeated with another tube, of the form shown in fig. 2 (Plate X.). This tube was closed at one end, A, by a plate-glass disk ground air-tight and cemented, in order that it might be placed before the slit in a longitudinal position (*i. e.* in the direction of the axis of the collimator), and was united to the air-pump by means of the tube B. After being repeatedly filled with pure hydrogen and exhausted, it was finally excited, in the same way as before, with the gas at a few millimetres' pressure, and examined with the spectroscope. If the tube was placed in the ordinary way before the slit the spectrum was exactly that described, whilst it was only necessary to place the tube longitudinally in order to see the second spectrum fully developed. It follows therefore that the absence of this spectrum in Salet's experiments affords no certain proof that it belongs to the eliminated carbon compounds and not to the hydrogen ; but their explanation may just as well, and even with greater probability, be sought in the diminution in intensity of light in the whole phenomena due to the experimental conditions employed, a diminution by which the already feeble lines of the second spectrum must be first affected.

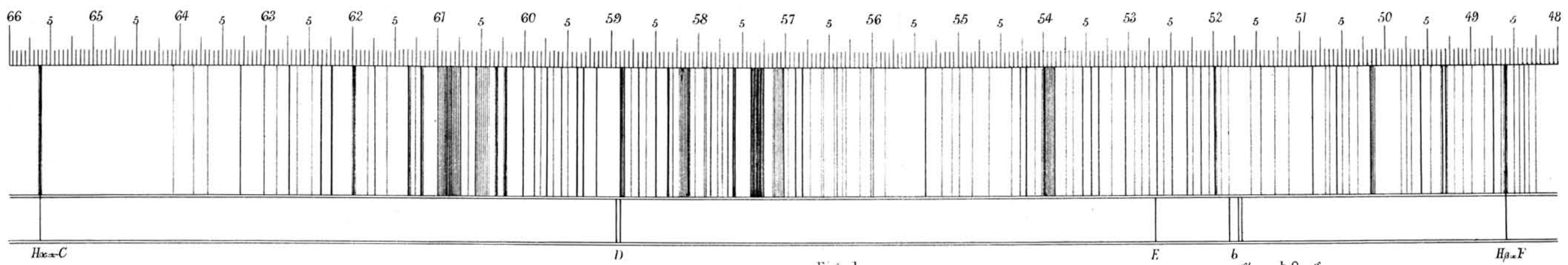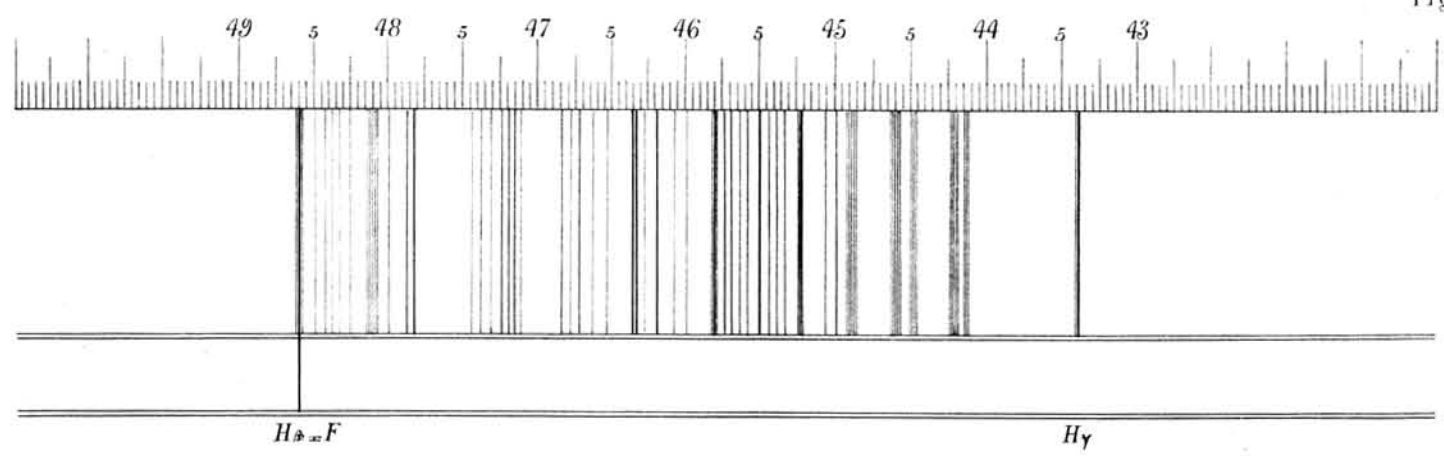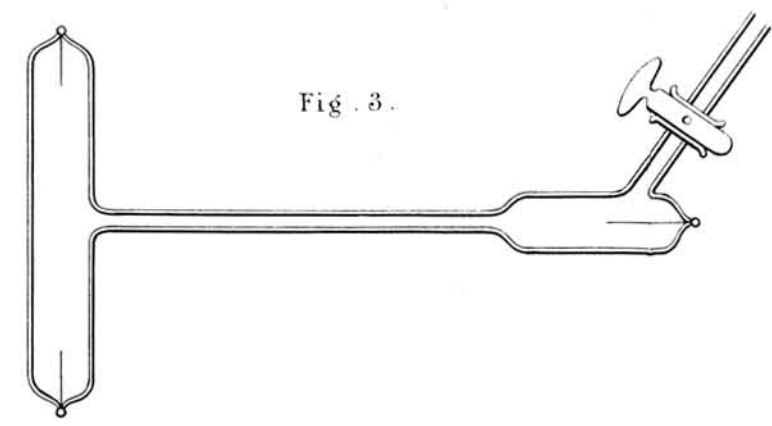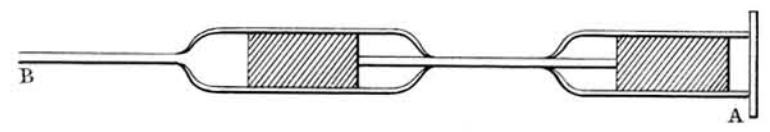* The lines $\lambda = 5015$, 4930, 4635.
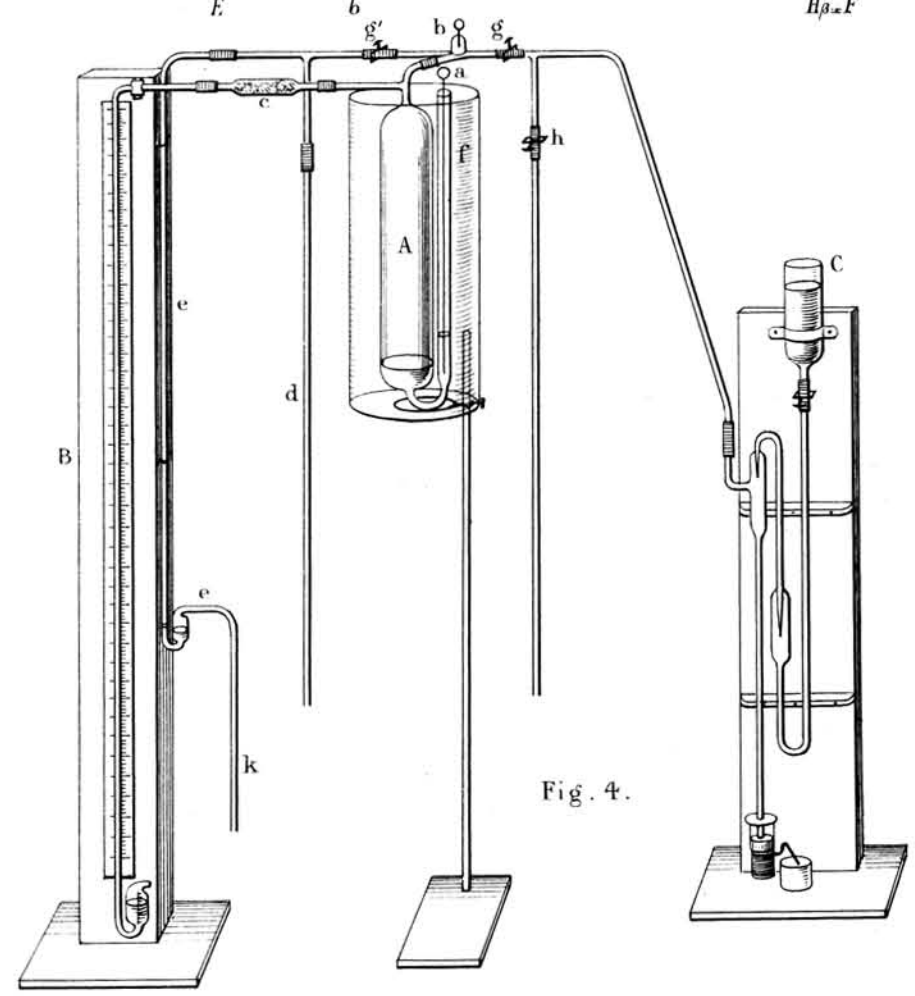
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Mintern Bros. lith.

After the foregoing explanation I cannot but regard the explanation of Berthelot's spectrum given by Plücker and Wüllner as by far the best founded. In this opinion I am still further confirmed by numerous experiments of my own. That nevertheless this view has not yet received universal assent, is indeed perhaps not shared by the majority of spectroscopists, is seen from the circumstance that Ciamician[*] has recently given Berthelot's explanation as the correct one, and that Schuster[†] regards the question as still open. This last circumstance has induced Wüllner [‡] also to undertake new experiments upon this subject, the results of which require further notice here in conclusion.

Wüllner's experiments are designed to show directly that the spectrum of acetylene is quite different from the second spectrum of hydrogen, and could not be confused with it. For this purpose acetylene, prepared from cuprous acetylide with careful observation of the precautions necessary to secure the purity of the product, was introduced into a spectral tube, exhausted to a pressure of 1 or 2 millimetres. The spectroscopic examination of the greenish-white light produced by the passage of the induced current revealed a somewhat complicated spectrum, which Wüllner considers to be that of acetylene ; and the difference between which and that of hydrogen he further endeavours to show by means of a complete description based upon measurements. That there is a difference there is no doubt, but not because the spectrum belongs to acetylene, the spectrum of which is altogether different, but because it is formed by the simple superposition of the spectra of carbonic oxide and of hydrogen ; of which last spectrum, just because of this superposition, only the strongest lines are perceptible. In order to show this, I here compare Wüllner's description of the spectrum with the measurements of the carbonic-oxide spectrum made by Ångström and Thalén, and with those of the second hydrogen spectrum made by myself, omitting nevertheless those spectral regions which, according to Wüllner, form the boundary of the bright carbon-oxide bands on the more refrangible side of the spectrum, since these, under varying circumstances, have no significance as characteristic of the spectrum. The wave-lengths of the lines here given of the second hydrogen spectrum are taken from complete tables of wave-lengths of this spectrum given further on.

* *Wien. Sitz. Ber.* lxxxii. part ii. p. 425 (1880).
† Report of the British Association, 1880, p. 287,
‡ Wiedemann's *Annalen*, xiv. p. 355 (1881).

Wüllner's Acetylene Spectrum.		Spectrum of Carbon Oxide.		Spectrum of Hydrogen.	
Description.	λ.	λ.	Remarks.	λ.	Remarks.
The spectrum begins with a tolerably bright field at nearly the same place at which the spectrum of carbonic acid begins. In the middle of this field a bright line is faintly seen, probably Hα	6620 6567	6622·0 ...	Commencement of one of the chief bands.	6562·1	Hα (Å.).
After a feebly illuminated field a second bright field begins at ...	6475	6469	Weaker bands.		
A dark field 5′ broad follows, upon which appears a single bright line	6330	...	......	6328·7	Distinct line.
Another bright field begins at	6305	6298·5	Bright band begins.		
bounded on its more refrangible side by a bright line	6235	...	......	6235·0	Bright line.
In the dark space following of 3′ breadth a bright line	6204	...	......	6198·9	Very bright line.
A band begins at	6192				
bounded by a double ⌠ line at .... ⌡	6136 6124	... ...	....	6134·1 6119·7	⎱ Very bright ⎰ lines.
The next dark field contains a bright line at ...	6097	...	......	6100·1	Limit of group of lines.
A very bright orange field begins with an ill-defined bright line at	6089	6078	A principal band of CO.		
which extends with diminishing brightness through a breadth of 13′. This field contains at ⌠ two bright lines, and ⌡	6037 6023	... ...	....	6032·4 6021·6	⎱ Very bright ⎰ lines.
further a bright line at	5978	...	......	5978·1	⎰ Centre of a ⎱ double line.
A shaded field begins at	5950	...	......	5950·1 5939·6 5932·5	⎰ Bright lines.
of 11′ breadth, and which shows several ⌠ lines at .... ⌡	5873 5838 5804	... ...	....	5887·4 5834·7 5811·3	⎱ Principal lines ⎰ of the hydrogen spectrum.
The last of these lines bounds the fields on its more refrangible side. The spectrum, consisting of beautifully shaded fields showing faint lines, continues until at.........	5609	5607·5	Very bright band.		
there appears the well-known greenish-yellow					

Table (*continued*).

Wüllner's Acetylene Spectrum.		Spectrum of Carbon Oxide.		Spectrum of Hydrogen.	
Description.	λ.	λ.	Remarks.	λ.	Remarks.
channelled band occurring in the spectra of all gases containing carbon, showing the fine lines which are so beautifully seen in the bands of the carbonic-acid and carbonic-oxide spectra. This band, however, is distinctly narrower than in the spectrum of carbonic acid. It is bounded by a sharp line at.........	5550	...	......	5536·6	?
A broad green field, which, like the first hydrogen spectrum, shows a large number of lines, follows, and then the green band finely shaded, as in the carbonic-acid spectrum, begins at	5200	5197	Brightest band of CO.		
which, however, like the greenish-yellow band, is only half as broad as in carbonic acid.					
The same holds good of the following carbon bands: the blue one beginning at	4834	4833·5			
the first violet at	4510	4509·0			
the second violet at	4393	4394·0			
Between these bands the spectrum is similar to the band-spectrum of hydrogen; as is also the case with ethylene and marsh-gas, although there are differences in detail.					

We see from this comparison that Wüllner's so-called acetylene spectrum contains scarcely a single line or band which does not occur either in the spectrum of carbon oxide or in the second hydrogen spectrum. It is exactly the brightest lines of this last spectrum which appear here ; as indeed must be the case, since the weaker lines are concealed by the broad bright bands of the superposed carbon-oxide spectrum. That these bands belong to carbon oxide, and not to carbon as Wüllner thinks, may be considered as a settled matter. Their

appearance in Wüllner's tube is completely explained by the small pressure of the gas, since under these circumstances the complete exclusion of oxygen is attended with considerable difficulty. The true spectrum of acetylene, on the other hand, is, according to the investigations of Angström and Thalén and Liveing and Dewar, an altogether different one, and coincident with the well-known flame-spectrum of gases containing carbon observed. In the spectrum under discussion there is no trace of these bands, unless we identify the band 6192 with the hydrocarbon band 6187, which appears to me somewhat doubtful, since the much stronger bands at 5633, 5164, and 4736 are absent.

These experiments do not therefore prove directly, in the way intended by Wüllner, that the second spectrum observed in hydrogen tubes really belongs to hydrogen and not to acetylene, though they do so indirectly; since, according to Wüllner's observations, this spectrum gradually predominates during the observation over that of carbonic oxide, until finally it takes its place almost completely. This observation agrees completely with Berthelot's experiments, according to which the continued action of the electric discharge gradually converts acetylene into the stable mixture of hydrogen and acetylene, the percentage composition of which in the present case is expressed by the numbers 97 and 3. It is exactly this ultimate great preponderance of hydrogen which shows that the spectrum in question belongs to this gas and not to acetylene; and its gradual production sufficiently explains the gradual fading of the carbonic-oxide bands.

From this account of the older investigations I pass now to the description of my own experiments. They were designed, in the first instance, to determine the origin of the spectrum, if possible, more certainly than had already been done, and then, further, to investigate as fully as possible the different conditions under which they are produced. It is not necessary to insist upon the close connexion of these two problems. In fact it is exactly the complete identity of the spectral phenomena of the gas prepared in different ways, taken together with the above criticism of previous investigations, which has convinced me that this spectrum must be ascribed to hydrogen itself. But how little these investigations have contributed to the more accurate knowledge of the spectrum appears from the fact that, with the exception of a few isolated measurements by Seabroke[*] and Vogel[†], no actual measurements were made. The drawing given by Wüllner a few years ago

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[*] Monthly Notices, vol. xxxii. p. 63.
[†] Pogg. *Ann.* vol. cxlvi. p. 569.

is also not suited to satisfy the requirements of spectroscopic science, since in the absence of numbers, or even of a scale, not even approximate wave-length determinations of the few lines given can be obtained from it. The measurements given below and the drawing constructed from them (Pl. X. fig. 1) will supply this deficiency, at least to some extent.

The spectroscope which I employed is of the usual Steinheil model, and when a powerful Rutherfurd prism is employed, shows the spectrum in great detail.

The dispersion, which was somewhat greater than that of two ordinary flint-glass prisms of 60°, might, with the means at my command of rendering the gas luminous, have been somewhat increased ; but little would have been gained by that, since the rest of the spectrum was not of sufficient intensity to bear a higher dispersion. The magnifying-power of 9·3 employed in the first series of observations was increased to 17·0 with the remaining series, since the brightness of the spectrum proved to be sufficient to permit such an increase.

The wave-lengths of the lines were determined by micrometric measurement with reference to suitable metallic lines chosen from Thalén's tables. These lines were always so chosen that the errors of interpolation might influence as little as possible the reliability of the wave-lengths determined. It would certainly have been an advantage if the lines of the gas could have been directly determined from those of the solar spectrum ; but with a spectrum of such feeble intensity as the one in question, this method is attended with considerable difficulties, and may, in my opinion, even introduce greater errors than those which are to be apprehended from the employment of the metallic spectra as references.

It is well known that a Geissler tube, placed immediately in front of the slit of the spectroscope, acts as a cylindrical lens, and every small displacement produces a greater or less apparent change in place of the lines of the spectrum. This circumstance in the present case, when, in order to observe the comparison-spectrum, the tube had to be pushed on one side, would have given rise to extremely prejudicial irregularities in the measurements ; and I have therefore, in order to avoid this source of error, employed an achromatic lens of short focus, so as to throw a sharp image of the tube or of the spark used for comparison upon the slit. In this way, the projecting lens being fixed, the spectrum remains altogether fixed in the field of view, and the source of error mentioned is avoided.

The source of electricity employed was, in all cases, a large Ruhmkorff's coil, made by Keyser and Schmidt, of Berlin, excited by a battery of six large Bunsen cells. Commonly

the simple induced current only was employed; but cases have occurred, particularly with wider tubes, when the introduction of a small air-break and Leyden jar has increased the distinctness of the spectrum. This air-break must, however, be taken so small that the characteristic lines do not appear hazy, since in this case the second spectrum loses in brilliancy instead of gaining. Four different tubes in all were employed for the measurements. The *first* was a small tube containing hydrogen, about 3 inches long, of the usual form, whose capillary was about 30 millim. long, and possessed an internal diameter of about 0·5 millim. It was exhausted to a few tenths of a millimetre. The *second* tube was a purchased hydrogen-tube. The *third* tube had the well-known form introduced by Wüllner ; but with the modification that a globe about an inch in diameter, containing phosphoric anhydride, was attached to it by grinding. The *fourth* tube, in order that it might be placed longitudinally before the slit, was provided with a wide cylinder at one end and at right angles to the capillary, which was about 55 millim. long, as will be understood from the figure (fig. 3, Plate X.). The internal diameters of the capillaries of these two tubes were respectively 1 and 2·5 millim., and the pressure of the gas in the two cases 2 to 3 millim.

It scarcely needs to be specially mentioned that in preparing the gas used, as well as in filling the tubes, all the precautions upon which its purity depends were strictly observed. The gas evolved from zinc and sulphuric acid was therefore carefully freed from impurities by the use of known methods, and introduced directly from the evolution-apparatus into the tube, which had been repeatedly heated and exhausted. Not until the tubes had been in this way repeatedly washed out with hydrogen were they closed at the pressure mentioned above, and used for observation. The results of all the measurements made of the spectrum are given in the following tables. They contain the wave-lengths of all the lines visible under the conditions employed, of which a large number, especially in the green and blue portions of the spectrum, are so extremely weak that they approach the limits of visibility. It might be thought superfluous to give here any more than the final mean, but I have thought it desirable to give the separate series of measurements, first, because the accuracy attained can best be judged from them, and, secondly, because they show the complete identity of the spectral phenomena with the gas obtained in different ways. For the yellowish-red part contained in Table A, which forms the characteristic portion of the spectrum, the four series of measurements were obtained by the use of the before-mentioned four tubes ;

whilst the measurements of the rest of the spectrum given in Table B have been made by means of the tubes Nos. 2 and 4. The employment of a higher magnifying-power with the Series III. and IV. of Table A is the reason why single fine lines occur in these Series which are absent in the Series I. and II. All the values of Table B were obtained by employing the higher magnifying-power.

As far as the general arrangement of the tables is concerned, it is only necessary to remark that the wave-lengths are expressed in ten-millionths of a millimetre, and that the numbers in column J give the estimated intensities of the lines ; the numbers 1 to 6 being employed, 1 to denote the weakest scarcely perceptible line, and 6 the strongest. Certain lines having a somewhat hazy appearance are marked *v.* Lastly, under V and S are given the somewhat older determinations of Vogel and Seabroke, of which the latter have been reduced from Kirchhoff's scale to wave-lengths.

TABLE A.

From λ = 6400 to λ = 5630.

Series I.	Series II.	Series III.	Series IV.	Mean.	J.	Remarks.	Older determinations.	
							V.	S.
...	...	...	6408·0	6408·0	1	Very difficult to see.		
...	...	...	6383·5	6383·5	1	λ in consequence		
...	...	...	66·8	6366·8	1	somewhat uncertain.		
6328·0	6327·8	...	30·4	6328·7	2			
02·3	00·2	...	02·4	6301·6	1—2			
...	...	...	6286·5	6286·5	1			
6274·7	6273·3	...	74·0	6274·0	2			
...	...	...	62·8	6262·8	1			
...	...	...	46·1	6246·1	1			
34·8	34·0	...	36·3	6235·0	4			
22·9	22·9	...	23·4	6223·1	4			
6199·0	6199·4	6197·4	6199·9	6198·9	5	*v.*		
77·4	80·2	83·6	84·5	6181·4	2			
...	...	72·6	75·6	6174·1	3			
60·1	60·2	59·5	62·6	6160·6	3	Perhaps oxygen.		
32·9	34·7	34·0	34·8	6134·1	5—6	There is a fine line	} 6129	
19·3	20·1	18·6	20·8	6119·7	4—5	between these lines.		
01·3	01·7	6097·3	6099·6	6100·1	...	Boundary of a bright		
...	..	...	90·5	6090·5	2	region on which the		
6085·3	6086·4	79·8	82·4	6083·5	3	three following lines		
74·7	73·1	...	69·1	6072·3	4	are placed.		
...	...	66·5	63·9	6065·2	2			

Table A (*continued*).

Series I.	Series II.	Series III.	Series IV.	Mean.	J.	Remarks.	Older determinations. V.	S.
...	...	6055·7	6055·0	6055·3	3	} Background feebly illuminated.		
...	...	40·0	42·8	6041·4	1			
6036·9	6032·7	30·6	29·7	6032·4	6	v.		} 6026
26·6	22·7	18·0	17·1	6021·6	6	v.		
5997·4	06·6	03·4	5999·8	6001·8	2			
...	...	5991·2	86·2	5988·7	3			
80·3	5972·8 { 82·1	78·8	5980·4	2 } Mean 5978·1.				
	74·0	71·9	5973·0	4				
65·8	64·0	68·0	65·7	5965·9	1			
...	...	58·9	56·3	5957·6	3			
51·8	53·7	48·5	46·5	5950·1	2			
39·7	42·3	38·4	37·1	5939·4	4			
26·0 { 36·5	31·4	29·6	5932·5	4 } Mean 5925·1.				
20·5	17·1	15·6	5917·7	3				
5887·6	5887·1	5887·7	5887·3	5887·4	4	Double { 5889·7. / 5884·9. }		5879?
...	...	76·2	78·0	5877·1	1			
70·0	66·4	68·9	70·3	5868·9	3			
62·7	...	59·4	61·5	5861·2	2			
50·4	47·9	49·0	48·8	5849·0	3			
35·1	32·7	35·2	35·8	5834·7	5	....	...	5828·3
...	...	...	29·9	5829·9	1			
...	...	22·5	22·8	5822·6				
11·7	10·3	11·0	12·4	5811·3	'6'	Complicated assemblage of lines. Several weak lines on both sides.	5813	5811·2
...	...	03·1	04·1	5803·6	2			
...	5790·9	5791·4	5793·8	5792·0	2	Double.		
5785·2	...	83·2	86·1	5784·8	3			
...	...	...	77·6	5777·6	1	Seen in Series I. & II.		
73·0	71·0	69·0	74·6	5771·9	2			
...	...	65·5	66·5	5766·0	3			
57·8	57·3	58·0	58·0	5757·8	4	Double.		
41·9	40·5	36·3	44·0	5740·7 }	4 {	In this space five equal sharp lines.	}	5730·6
28·0	22·4	28·7	25·0	5726·0 }				
16·9	14·1	14·0	15·0	5715·0	2			
03·7	00·2	03·5	02·6	5702·5	3			
...	...	...	5696·0	5696·0	2			
5685·7	5684·8	5688·2	87·7	5688·0	3 } Mean 5684·6.			
		81·9	80·5	5681·2	3			
70·6	69·9	72·0	...	5670·9	1			
...	...	59·4	...	5659·4	2			
58·1	56·1	55·1	...	5656·4	2			
...	...	43·0	...	5643·0	1			
32·4	...	33·5	...	5633·0	2			

TABLE B.
From λ = 5630 to λ = 4410.

Series I.	Series II.	Mean.	J.	Remarks.	Older determinations. V.	S.
5633·5	5635·8	5634·6	2—3	{ The same line as 5633·0 of Table A.		
...	27·9	5627·9	2			
13·3	...	5613·3	2			
00·3	01·9	5601·1	2			
...	5598·6	5598·6	2	The line given by	5596	
...	84·5	5584·5	2	Vogel at 5555		
5536·1	37·1	5536·6	2—3	was not seen.		
18·4	...	5518·4	1			
05·7	05·8	5505·7	1			
5497·7	...	5497·7	1			
84·7	5482·8	5483·7	1			
...	63·3	5463·3	1			
37·5	36·4	5437·0	1—2	⎧These lines stand upon a somewhat brighter back-		
27·5	26·2	5426·8	2	{ ground than the	5422	
20·7	19·0	5419·8	3	⎩ rest of the spectrum.		
12·2	08·9	5410·5	1	⎫Upon a brighter		
5399·9	5398·8	5399·3	2	{ background.		
87·9	86·3	5387·1	2—3	⎭		
75·8	71·4	5373·6	1			
...	64·6	5364·6	1			
53·8	55·2	5354·5	1—2			
...	43·8	5343·8	2			
34·3	36·3	5335·3	2			
18·8	20·3	5319·5	1—2			
04·0	04·8	5304·4	2—3			
5293·0	5293·6	5293·3	1—2			
84·4	85·5	5285·0	1			
74·6	74·5	5274·5	1—2			
66·2	66·3	5266·2	2—3	⎫		
58·7	58·3	5258·5	2	}	...	5261·3
46·8	47·2	5247·0	1—2	{ Hazy towards the violet.		
31·4	30·4	5230·9	2			
24·7	22·9	5223·8	1			
...	14·8	5214·8	2			
...	05·6	5205·6	1			
5197·8	5197·9	5197·8	3	......	5189	5192·5
...	91·1	5191·1	1			
82·0	81·9	5182·0	1			
70·3	...	5170·3	...			
56·8	57·3	5157·0	1			
44·7	44·8	5144·7	1			
...	28·5	5128·5	1			
10·5	14·3	5112·4	1			

2 A 2

Table B? (*continued*).

Series I.	Series II.	Mean.	J.	Remarks.	Older determinations.	
					V.	S.
5083·6	5084·3	5084·0	2—3			
70·2	70·3	5070·2	1			
...	65·0	5065·0	1			
55·9	57·0	5056·4	2			
49·0	50·1	5049·5	1			
41·3	40·3	5040·8	1			
31·4	31·7	5031·5	1			
16·6	17·2	5016·9	3	{ Probably corresponds to the line 5008 of Vogel's. }	}5008	5012·5
4980·5	4983·8	4982·1	1			
73·8	75·2	4974·5	1			
67·3	69·0	4968·1	1	{ Remarkable that Seabroke should have seen this line.		}4968·5
...	58·1	4958·1	2			
47·2	...	4947·2	1			
34·2	35·5	4934·8	3			
28·2	29·9	4929·0	2—3	......	4929	4931·5
20·1	21·0	4920·5	1			
07·1	10·3	4908·7	1			
...	4897·8	4897·8	1			
...	85·4	4885·4	1			
4873·4	74·0	4873·7	2	......	...	4872·0
64·3	65·2	4864·7	1			
49·5	50·2	4849·8	1			
43·4	43·5	4843·5	1			
37·6	37·7	4837·7	1			
32·6	32·1	4832·3	1			
24·7	25·2	4825·0	1			
4797·8	4798·8	4798·3	1—2			
...	86·5	4786·5	2			
81·8	82·4	4782·1	1—2			
42·8	44·0	4743·4	1			
...	36·8	4736·8	1—2			
...	30·7	4730·7	1			
23·0	24·6	4723·8	2	......	...	4725·7
19·8	19·0	4719·4	1—2			
...	14·5	4714·5	1—2			
11·6	10·3	4711·0	1			
4683·9	4686·1	4685·0	2			
...	79·0	4679·0	1			
71·9	72·2	4672·0	1—2			
62·7	62·8	4662·7	1			
54·0	54·7	4654·3	1—2			
34·4	{ 35·5	4635·5	4	} In Series II. the components sharply divided.	}4632	4626·6
	{ 33·0	4633·0	4			
27·7	28·6	4628·1	1—2			
18·7	18·8	4618·7	2—3			
07·0	07·2	4607·1	1—2			

Table B (*continued*).

Series I.	Series II.	Mean.	J.	Remarks.	Older determinations.	
					V.	S.
4599·3	4597·8	4598·5	1			
80·0	81·3	4580·6	4	Hazy on both sides.	4581	4576·1
73·3	73·2	4573·2	2			
67·4	68·3	4567·8	2			
62·7	63·1	4562·9	1			
57·5	58·3	4557·9	1			
50·7	50·6	4550·6	2	*v.*		
...	43·5	4543·5	1			
38·6	38·9	4538·7	1			
31·8	33·5	4532·6	1			
22·8	...	4522·8	1	*v.*		
06·3	...	4506·3	1	......	4506	
4498·3	...	4498·3	2	......	...	4498·5
91·9	...	4491·9	1	*v* tolerably broad.		
59·7	...	4459·7	1	*v* broad, middle.	...	4454·7
47·7	...	4447·7	1	Feeble maximum.		
22·4	...	4422·4	1	Feeble maximum.		
13·5	...	4413·5	1—2	*v* middle.	...	4414·2

As we see, the agreement between the values in the separate series is in general very satisfactory; only in the yellowish-red portion there are occasionally more important deviations, but yet not greater than may be easily explained in view of the smaller dispersion of this portion of the spectrum. We may therefore regard the accuracy of the definitive wave-lengths as in general quite satisfactory, and for most of them we may estimate the probable error as not more than a unit of Ångström's scale. Those wave-lengths which occur in only one series of observations are included in the column of mean values; because, since each of them (as of all the other determinations) is the mean of at least three separate observations, they are in fact mean observations.

Since the identity of the spectral phenomena of hydrogen from different sources may be said to be put beyond doubt by the numbers of the above table, it appears to me absolutely impossible to ascribe the spectrum to any foreign substance whatever. This is further confirmed by the fact that a fifth tube which I filled with electrolytic hydrogen, carefully observing all precautions, showed identically the same spectrum.

The single circumstance which can be alleged against what has been here said by those who nevertheless regard this spectrum as that of acetylene, is the always possible contamination of the gas by some carbon compound from the taps of the air-

pump. But to this objection may be replied, first, that if this were the case the carbon-monoxide spectrum must also show itself, since, as is well known, this spectrum is nearly as ubiquitous in highly exhausted spectral tubes as that of sodium is in flames. In all the tubes prepared by me there was, however, no trace of it to be seen. Secondly, it is to be observed that if our spectrum belonged to acetylene proceeding from such impurity, we must expect to find the same more or less completely in every tube prepared with the same pump. But this is not the case ; for when the tube No. 3 was filled with dry air and exhausted to about 1 millim., I observed a perfectly pure and beautifully developed band-spectrum of nitrogen, whilst the admission of moist air after removal of the phosphoric anhydride at once gave rise to the above spectrum.

It is therefore impossible to attribute it to any carbonaceous gas derived from the pump.

As the result of all these experiments, I confidently express the opinion that the spectrum described here certainly belongs to hydrogen and not to acetylene. If we examine the series III. and IV. of Table A as well as Table B more closely, we find that in both cases the number of observed (that is, of visible) lines is very nearly the same ; in other words, that increasing the layer of radiating gas about sixty times has not caused any perceptible change in the spectrum. This appears to be in direct opposition to the experiments described above on page 338, since the longitudinal use of the tube there described showed the spectrum perfectly distinctly, whilst only traces were otherwise to be seen. The apparent contradiction disappears, however, at once when we consider that in the latter case the temperature was decidedly lower. We easily see from Zöllner's well-known formula

$$E = \{1 - (1 - A_\lambda)^\delta\} \, \epsilon,$$

which gives the intensity of the light of wave-length λ radiated from an incandescent layer of gas of the thickness δ, that this intensity will be less affected by an increase in the value of δ the higher the temperature is.

It follows from the two equations,

$$\frac{dE}{d\delta} = -\epsilon \log (1 - A_\lambda)(1 - A_\lambda)^\delta,$$

$$\frac{d^2E}{d\delta \, dA_\lambda} = \epsilon (1 - A_\lambda)^{\delta-1} \{1 + \delta \log (1 - A_\lambda)\},$$

that $\dfrac{dE}{d\delta}$ increases with A_λ so long as $A_\lambda < 1 - e^{-\frac{1}{\delta}}$, but de-

creases as A_λ increases, if $A_\lambda > 1 - e^{-\frac{1}{\delta}}$. Since, then, for a given wave-length, A_λ is only a single function of the temperature, which, of whatever form it may be, must at least possess this property—that, within limits determined by its nature, it increases with the temperature—we see that so long as the temperature is so low that A_λ does not attain the value $1 - e^{-\frac{1}{\delta}}$, an increase in the thickness of the radiating layer and an increase in the temperature both produce an increase of E ; whilst for those temperatures for which A_λ exceeds the value mentioned, a further increase of temperature produces the opposite effect to the increase of δ. Consequently at high temperatures a spectrum will be considerably less affected by change in the thickness of the radiating layer than at lower temperatures, exactly as shown by the above experiments.

But we may perhaps go further still, and in these experiments obtain even an experimental confirmation of the peculiarity of the function A mentioned above. I am the more disposed to do so, since it appears to me altogether unintelligible how a continual rise in temperature can have any other effect, at least so long as no dissociation and consequent alteration in the arrangement of atoms in the radiating system, has taken place. If this is admitted, we shall be obliged to assume such a dissociation as the explanation of the displacement of a spectrum by a new one with rise of temperature, and must therefore ascribe the first spectrum to a more complicated arrangement of molecules, or to a compound of the body with itself. Since, according to the investigations of Wiedemann*, in the case of hydrogen a continual rise in temperature produces first a gradual diminution of the spectrum above described, and then upon reaching a certain limit its almost sudden disappearance, these considerations lead us to the view proposed as a second alternative by Ångström, according to which the spectrum belongs to a compound of hydrogen with itself. The heat-equivalent found by Wiedemann for the quantity of energy necessary to transform this spectrum into that consisting of the three characteristic bright lines, would therefore be nothing else than the thermal equivalent of the corresponding work of dissociation.

If the views thus explained of the spectroscopic conditions of hydrogen are regarded as justified by facts, we have an easy explanation of the fact that in the spectra of the sun and most stars only the characteristic lines of this gas appear as bright lines or absorption-lines, as the case may be, whilst no

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* Wiedemann's *Annalen*, vol. x. p. 202.

trace of the second spectrum is to be detected. The reason is to be found in the enormous temperature existing in these bodies. But in the case of stars such as α Orionis, α Herculis, &c., which, judging from their complicated spectra, are in a more advanced stage of cooling, the appearance of the second hydrogen spectrum would not, under these circumstances, be remarkable, since observation shows that the characteristic spectrum is either entirely absent in these stars, or only feebly present. Nevertheless the verification of this expectation by observation must always be nearly or quite impossible on account of feeble intensity of light; and the same is *à fortiori* true of the nebulæ, in which the appearance of the second hydrogen spectrum, together with the characteristic line H_β, might have been expected, upon other grounds, with a certain degree of probability.

XL. *On the Rate of Chemical Absorption of Gases, with regard to their Interdiffusion.* By JOHN J. HOOD, *B.Sc., Assoc. R.S.M.*[*]

[Plate X. fig. 4.]

WITH the exception of Graham's work on the diffusion of gases, their rates of passage through porous diaphragms or minute apertures into a vacuum, and Loschmidt's experiments on free diffusion[†], no measurements of any note have been made bearing on this important subject. The former chemist has shown that the lighter a gas is the more rapidly does it pass through a porous diaphragm, or, as it is expressed, the rate of diffusion varies as the reciprocal of the square root of the density. The experiments of Loschmidt, which were performed by placing two tubes containing different gases over each other, opening a channel between them, and after a certain time determining the amount of the gases that had exchanged places, gave measurements of the rate of interdiffusion of the one gas into the other. The results obtained by this method of studying diffusion, a physical process somewhat different from that of the passage of a gas through a porous diaphragm or minute aperture into a vacuum as worked out by Graham, show a relation to exist between the molecular weights of the gases and their rates of interdiffusion, but which relation is not quite clear[‡].

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[*] Communicated by the Author.
[†] *Wiener Sitzungsberichte,* 1870; extended by Wretschko and by Benigar, Bd. lxii.
[‡] Meyer, *Kinetische Theorie der Gase,* 1877, p. 164.