

## XXXVII. The spectra of hydrogen, and some of its compounds

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To cite this article: Prof. John Trowbridge (1901) XXXVII. The spectra of hydrogen, and some of its compounds, Philosophical Magazine Series 6, 2:10, 370-379, DOI: [10.1080/14786440109462703](https://doi.org/10.1080/14786440109462703)

To link to this article: <http://dx.doi.org/10.1080/14786440109462703>



Published online: 08 Jun 2010.



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Similar experiments were made with Rochelle salt, and the spirals observed with a plate 1.75 cm. thick. Monochromatic light was found to be essential. The rotation was 12 deg. per cm. to the right. The value calculated from the specific rotation of a 20-per-cent. solution is 4 deg. per cm. in the same sense. On account of the symmetry of the crystal no difference between the two axes is to be expected.

XXXVII. *The Spectra of Hydrogen, and some of its Compounds.* By Prof. JOHN TROWBRIDGE \*.

[Plate VI.]

IN a late paper † I expressed the conviction that the so-called line-spectrum of hydrogen cannot be considered apart from the spectrum of water-vapour; and that one can never be sure that one is observing, with a condenser discharge, a pure spectrum of hydrogen. I am convinced from further experimentation, that this conclusion is correct; and I am also led to the conclusion that a certain amount of water-vapour is essential in all electrical discharges through gases.

Just as aqueous vapour seems to play an important rôle in most chemical reactions, so, it seems to me, its presence in rarefied gases, contained in ordinary glass tubes, enables a dissociation to take place which determines the strength and character of the electrical discharges.

I am led, moreover, to the conclusion that pure hydrogen is a perfect insulator; and that the passage of electricity through a gas depends upon the dissociation of the hydrogen and oxygen, by means of which change in the distribution of energy the gases are made luminous. Before proceeding to an account of my experiments, I will state some of the grounds upon which I base my belief that pure hydrogen is an insulator of electricity.

V. Schuman, in an important paper ‡, has shown that a column of pure hydrogen at atmospheric pressure transmits the ultra-violet rays as well as the most perfect vacuum he has been able to obtain. Now Maxwell's electromagnetic theory of light demands that the space between us and the sun, or, in other words, the vacuum of space, should be a perfect insulator, otherwise the electromagnetic waves would be completely absorbed, and the earth would remain in darkness. This observation of Schuman seems to me one

\* Communicated by the Author.

† Phil. Mag. Sept. 1900.

‡ Ann. der Physik, 1901.

of the most important in physical science; for it proves, I believe, incontestably that hydrogen cannot be a conductor.

Professor Dewar has also shown that liquid hydrogen is an insulator. The experiment sometimes shown, in which a wire, rendered incandescent by a current of electricity and surrounded by an atmosphere of carbonic dioxide, is suddenly diminished in brilliancy by supplanting this atmosphere by one of hydrogen, can be explained, in my opinion, not by the better conductivity of hydrogen for heat, but by the increased resistance of platinum due to the occlusion of this gas by platinum. A palladium wire increases often as much as 50 per cent. by the occlusion of hydrogen; and a platinum wire also shows a similar increase of resistance.

The increased length of the electric spark in an atmosphere of hydrogen is not due to an increased conductivity, but to a dissociation of water-vapour which is analogous to the dissociation which takes place in a voltaic cell.

These are some of the facts which lead me to believe that hydrogen is an insulator, and that water-vapour therefore plays a controlling part in the passage of electricity through gases. I am conscious that the conclusions in this paper are somewhat radical, and I have, therefore, worked assiduously during the past three years to test them in every way which my mind suggested; for it is not probable that many investigators have at present twenty-thousand storage-cells which would enable them to repeat my experiments. The strength of currents and the voltage I have employed have certainly reached the limit of glass tubes to withstand such powerful discharges. The form of tube figured in my previous article\* is the only one which I have found capable of withstanding steady currents of one-tenth to one-fifth of an ampere, and instantaneous condenser discharges of many hundred amperes.

The great advantage of the use of a storage-battery over the employment of a Ruhmkorff coil in the study of the ionization and molinization of gases is now generally recognized. This advantage is forcibly seen in the first experiment which I will bring forward in support of my view of the importance of the rôle played by water-vapour in the passage of electricity through gases. A wide tube, of the type I have referred to, the narrow portion being approximately 1 centimetre, was provided with massive copper ring electrodes, 1 inch in outside diameter and one-eighth of an inch thick, which were heavily electroplated with copper in order to avoid the impurities of commercial copper. The glass tubes

\* *Phil. Mag.* Sept. 1900.

were then exhausted and filled with hydrogen made by the electrolysis of distilled water and phosphoric pentoxide. The gas was sent through tubes filled with caustic potash and many drying-tubes filled with phosphoric pentoxide. The gas was kept in the drying-tubes many hours, and its flow was delayed by partitions of glass-wool: more than a litre of the gas was used in the process of flushing out the spectrum-tubes, so that the entire pump and connecting-tubes were for several hours presumably filled with hydrogen gas.

When the tubes, having been exhausted to the most luminous stage, were excited by a condenser-discharge and were examined by a straight-vision spectroscope, the ordinary four-line spectrum of hydrogen alone seemed to be present. When, however, the invisible portion in the violet was photographed, the bands beginning approximately at wave-lengths 3900 and 4315 were invariably present, unless the tube had been maintained, during the process of filling, at a temperature of more than  $350^{\circ}\text{C}$ . After such a process of heating the spectrum became that represented in fig. 2 (Pl. VI.), while before heating it was that shown in fig. 1. In both figures the normal spectrum is above the gaseous spectra. Further toward the ultra-violet under all conditions there were also faint nitrogen bands. Long heating diminished the strength of these bands. This process of experimentation shows that mere eye-inspection of glass tubes filled with rarefied gases is generally fallacious; we might conclude from this eye-study that the presence alone of the four-line spectrum of hydrogen denoted that we had this gas in a pure state; whereas the photography of the invisible portion would show that this was far from the truth.

When the glass tubes filled with rarefied hydrogen were submitted to the influence of a steady current of electricity, it was found that perfectly pure copper was deposited in a lustrous state on the glass walls of the tube which surrounded the negative terminal, while an olive-green oxide of copper covered the walls around the positive terminal. When the same tube was excited by a Ruhmkorff coil, no difference could be detected in the deposits around both terminals: they were both rusty-green, with here and there it may be streaks of pure copper. The mirrors produced by a strong, steady current at the negative terminal were very lustrous, and showed no trace of an oxide of copper. It was evident that the current had dissociated water-vapour in the presence of an excess of hydrogen, and had reduced the copper at the negative pole, and had set free oxygen at the positive pole which had, in turn, combined with copper. The rarefied gases thus acted like a voltaic cell.

When we examine the photograph of the discharge represented on fig. 1 (Pl. VI.), we see an interesting exhibition of ionization and molinization. The hydrocarbon bands at wave-length 4315 show a series gradually decreasing in length of waves; while another band, beginning at wave-length 3900, due probably to water-vapour, shows a series increasing in length of waves. It would seem that the carbon in one case endeavoured to throw off the hydrogen from the hydrocarbon molecule; and in the other case the hydrogen became loaded with oxygen molecules. This to and fro ionization and molinization continues until the oxide of copper at the positive terminal has taken up a large share of the oxygen of the water-vapour present. There is thus a critical point in the tube at which a sudden increase of resistance takes place. It is possible to exhaust glass tubes to such a degree by the mere passage of a strong steady current, that *x*-rays begin to manifest themselves.

When a similar tube, filled with hydrogen with great care, and prepared by long heating at a temperature a little below 500° C., is submitted to electrical discharges, the water-vapour bands become far less pronounced, and the hydrocarbon band at wave-length 4315 entirely disappears; while the light of the tube greatly diminishes in brilliancy. The hydrocarbon or cyanogen band at wave-length 3884 is present in all the tubes I have employed, and with all gases I have submitted to these strong discharges. Strong heating does not cause it to disappear, and it seems to be due to carbonaceous matter introduced into the tubes, probably in the process of blowing; for I cannot trace it to impurities coming from the pump. Professor Hartley, in a late communication in 'Nature,' has called attention to the constant presence of hydrocarbon spectra in Geissler-tubes. At a later point in this paper I shall return to a further study of these spectra due to the combination of hydrogen and nitrogen with carbon. At present I desire to dwell upon the point I wish to make: that all discharges in rarefied gases, contained in glass vessels, are conditioned by the amount of water-vapour present; and that a steady current passes through a gas at comparatively low pressure much in the same manner that it does through an electrolyte.

In an article on the production of the *x*-rays by a steady battery-current\*, I dwelt upon the phenomena presented in highly rarefied tubes, which represent, to my mind, the dissociation of water-vapour; and I will refer again at this

\* Phil. Mag. July 1900.

point to the phenomena already described. According to this hypothesis the rarefied water-vapour is dissociated at the surface of the anticathode, which is thus greatly heated ; the occluded hydrogen plays a part in this phenomenon.

The behaviour of large aluminium electrodes in glass vessels filled with ammonia-gas is also an interesting example of the dissociation of water-vapour. The gas was obtained by heating ammonia chloride, passing it over freshly slaked lime and through drying-tubes filled with phosphoric pentoxide. A sufficient amount of ammonia-gas was thus obtained for the purposes of spectrum analysis.

When a large condenser charged to a difference of potential of twenty thousand volts was discharged through the rarefied ammonia-gas, there being practically no self-induction in the circuit, and the main effect therefore was due to the pilot discharge, the light of the tube changed from a brilliant white to a rosy red, and eye-inspection with a straight-vision spectroscope showed only the line-spectrum of hydrogen. One would conclude from this inspection alone that there was pure hydrogen in the tube. One might also surmise that the oxygen of the water-vapour always present on the walls of the glass vessel had combined with the aluminium terminals, setting free the hydrogen which then carried the current. The pressure, however, in the tube increased : and therefore gas must have come from the aluminium. In the exhaustion of  $x$ -ray tubes provided with aluminium cathodes much time and long treatment with condenser discharges is necessary to drive out the gases from this cathode. The principal gas seems, from the experiment with ammonia-gas, to be oxygen. The same phenomenon is seen in tubes supplied with magnesium terminals, but to a much less extent. It is not seen when the terminals are of copper, iron, silver, platinum, or carbon. This behaviour of aluminium toward oxygen is very suggestive in regard to the ready passage of the  $x$ -rays through this metal.

I have been unable, with the conditions under which I have worked, namely the use of very powerful discharges, to obtain the spectra of hydrogen apart from water-vapour and hydrocarbons. The study, therefore, of the spectra of hydrogen compels one to study carefully the spectra of the hydrocarbons and that of cyanogen ; for I am forced to the conclusion that the combination of hydrogen with oxygen is a controlling factor in all discharges through rarefied gases. The following is a preliminary study of some of these compounds, which is added at this stage of my inquiry to illustrate this theory. When various gases are put in tubes provided with carbon

electrodes and these tubes are exhausted to a pressure of from one to two millimetres, the resultant spectra are very similar. The following gases have been studied in the neighbourhood of the great H H lines of the solar spectrum :

Hydrogen,  
Oxygen,  
Nitrogen.

In the hydrogen tube the only lines that appeared in the region from 4320 to 3200 were:

4268 very intense,  
3922 faint.

The tube was very thoroughly heated while it was being exhausted. The above-mentioned lines do not generally appear with hydrogen in tubes with metallic electrodes ; but with a tube with platinum electrodes, filled with hydrogen, and heated for two hours during exhaustion at a temperature of 350° C., the same two lines appeared, and in addition the following very faint lines :

3871  
3886

These same four lines also appear in carbon tubes when filled with oxygen. In addition, the following lines are present :

3936  
3971  
4077

All these lines appear in the nitrogen-tube, and, in addition:

3883  
3876  
3868  
3856  
3849  
3841

None of these lines appear in tubes with metallic electrodes filled with nitrogen ; and they are, therefore, not nitrogen lines. All the lines in the nitrogen-tube are more intense than those in the oxygen-tube, and it is possible that with a longer exposure these additional lines would come out in the oxygen.

To study the effect of the carbon terminals, the following gaseous carbon compounds were put into wide tubes provided

2 C 2

with copper terminals and rendered luminous by condenser-discharges :—

Cyanogen,  
Carbon monoxide,  
Carbon dioxide,  
Acetylene.

Cyanogen was prepared by heating mercuric cyanide, and passing the gas over sulphur to remove any traces of mercury-vapour. Carbon monoxide was prepared by heating potassium oxalate with concentrated sulphuric acid, and passing the gas over potassium hydroxide, and collecting over water. Carbon dioxide was prepared by treating potassium carbonate with dilute sulphuric acid and collecting over water. All of these gases were allowed to remain in contact with phosphoric pentoxide before introduction into the tubes.

With acetylene, carbon monoxide, and carbon dioxide, condenser-discharges being employed, the results appear to be identical with those obtained with hydrogen in the tube with carbon electrodes. With cyanogen, the same lines appear; and, in addition, the bands which are characteristic of these gases with continuous currents, which will be described later. In general, with condenser-discharges, all these spectra are the same; the differences which occasionally appear may be due to changes in pressure, time of exposure, &c.

The line 4268, in all these cases, is by far the most prominent line present in the region studied; and may be taken as characteristic of hydrogen, oxygen, and nitrogen in tubes with carbon terminals, and of gaseous carbon compounds in tubes with metallic terminals. This line does not usually appear in hydrogen in tubes with metallic terminals; occasionally it appears very faintly. It appears, however, very strongly in a tube provided with platinum terminals which is filled with hydrogen and heated for two hours during exhaustion to a temperature of 350° C. The spectrum, in this case, appears to be identical with the spectrum of hydrogen in a tube provided with carbon terminals. Were it not for this fact, it would seem as if this line were due to carbon in some form; but even with this fact, it is possible that there was enough foreign carbonaceous matter present in the platinum tube to produce the result noted.

Eder & Valenta\* find, among others, the following lines in the spectrum of an induction-coil between carbon terminals:

4268  
3921

\* *Beiblätter*, xviii. 1894, p. 753.



Apparently these are the same lines found in the tubes provided with carbon electrodes; and also in tubes with metallic electrodes which are filled with carbon compounds. Observed visually, with a straight-vision spectroscope, all the above cases appear identical. When, for instance, hydrogen was put into the tube with carbon terminals and submitted to discharges from an induction-coil, at first the line-spectrum of hydrogen appeared. After the discharge had passed for some time, this gradually changed into the characteristic band-spectrum of carbon. To the eye alone the change was equally noticeable; the light being, at first, reddish, and then changing to a white. Similar changes were noticed when nitrogen and oxygen were used in the carbon tube.

It seems to me that the following conclusions can be drawn provisionally from the above: when various elementary gases are introduced into wide tubes with carbon electrodes, and exhausted to a pressure of 1-2 mm., and submitted to condenser-discharges, compounds of carbon with the various gases are formed. With nitrogen this compound is probably cyanogen; with hydrogen, acetylene; but when a photograph of the spectrum in each case is taken, we get not the spectrum of the compound nor that of the elementary gas, but a carbon spectrum. This, however, does not mean that we get the line-spectrum of elementary carbon; for it is certain that there is water-vapour present in the tubes, notwithstanding the temperature to which it has been subjected. The carbon may then unite with the oxygen of the water-vapour, forming either carbon monoxide or dioxide; the hydrogen being occluded by the terminals or the glass walls.

Just as the spectra of gaseous carbon compounds in wide tubes with metallic terminals appear identical with the spectra of elementary gases in tubes with carbon electrodes submitted to condenser-discharges, so we should expect that the spectra produced would be the same in the two cases. This is found to be true. The general appearance of the photographs obtained with continuous currents is very different from those obtained with condenser-discharges. In the former case there is a marked band-appearance in addition to a line-spectrum. The most prominent of these bands, in the region studied, is the one beginning at 3884, fig. 2 (Pl. VI.). With the dispersion used this band consists of five prominent lines crowding together toward the ultra-violet. A somewhat similar band, apparently of six lines, begins at 4216. Another band, rather faint, consisting of a large number of fine lines, shading off toward the ultra-violet, begins at 4126. The bands beginning at 4216 and 3884 appear to be same as the

bands which Kayser & Runge\* designate respectively as the second and third cyanogen bands in the arc-spectrum of carbon in air.

Besides these bands, a number of single lines appear which are common to all the gases. Among these, the most prominent are :—

3652

4048

4080

4360

In the tube filled with cyanogen many of the same lines that appear in tubes with metallic terminals, filled with nitrogen, are present besides the above. This is true to a certain extent of the other gases ; and it is not surprising, since it is to be expected that some atmospheric air is always present as an impurity.

The conclusions to be drawn from these experiments with steady currents are similar to those we have deduced from condenser-discharges. When elementary gases are introduced into tubes with carbon terminals, and exhausted to a pressure of 1–2 mm., and are submitted to continuous currents, we obtain the spectrum of carbon, or some compound of carbon. From the above results very little information can be obtained as to what this compound is. The same spectrum is obtained whatever gas is introduced into the tube ; and, moreover, this is the same spectrum which is given by gaseous carbon compounds in tubes with metallic terminals. What, then, are the conclusions to be drawn from the present stage of my investigation with gases submitted to powerful electric discharges ? It seems to me that they are as follows :—

1. Hydrogen is an insulator.
2. The passage of electricity through hydrogen, nitrogen, oxygen, and their gaseous compounds is conditioned by the water-vapour present.
3. The dissociation of this water-vapour in the case of tubes filled apparently with pure hydrogen, under the effect of a strong steady current of electricity, shows an electrolytic action closely analogous to that of the voltaic cell. In the case of electrolytic copper terminals in an atmosphere of hydrogen, pure copper is deposited from the negative terminal, and a suboxide of copper at the positive terminal.
4. Under the effect of powerful condenser-discharges,

\* *Abhandlungen der Akademie der Wissen. zu Berlin*, 1889.

oxygen is set free from commercial aluminium and magnesium.

5. Certain carbon bands are always present in glass tubes filled with hydrogen, nitrogen, oxygen, and ammonia gas, notwithstanding the greatest care which may have been taken in submitting them to a high temperature during the process of exhausting, when powerful discharges are employed.
6. The brilliancy of the light of tubes filled with hydrogen diminishes as the process of the dissociation of water-vapour goes on and the resistance of the tube increases. It is possible to raise such a tube to the  $x$ -ray stage from a pressure of 1-2 mm. merely by the application of a strong steady current.
7. The  $x$ -rays excited by the application of a steady current are due to the radiations set up by the dissociation of highly rarefied water-vapour.

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### XXXVIII. *On the Complete Emission Function.*

*By* P. G. NUTTING\*.

THE relation between emission, temperature, and wavelength, developed theoretically by Wien† and by Planck‡, and empirically by Paschen§, expresses the amount of the radiation from a black or perfect radiator, in regions of temperature and period in which the emission-period function is continuous. Von Kövesligethy|| has given a function by which the emission of a limited class of substances may be represented in the optical region. By means of the modern theory of functions, a function more general than either may be developed; expressing the emission of all wave-periods, of both complete and partial radiators, as well in the lined as in the banded and continuous spectra. The Wien formula will be developed by the same method, as a preliminary step in the development of the complete function.

The intensity of the emission from a body, being a function of the entirely independent arguments, temperature and wave-period, we may construct each function separately and

\* Communicated by the Author.

† W. Wien, *Wied. Ann.* lviii. p. 632 (1896).

‡ M. Planck, *Berl. Berichte*, May 1899.

§ F. Paschen, *Wied. Ann.* lviii. p. 491 (1896).

|| R. v. Kövesligethy, *Astr. Nachr.* No. 2805, cxvii. p. 330 (1887); *Math. u. Nat. Berichte Ungarn*, xvi. p. 40 (1899); *Beibl.* 1900, p. 1280.

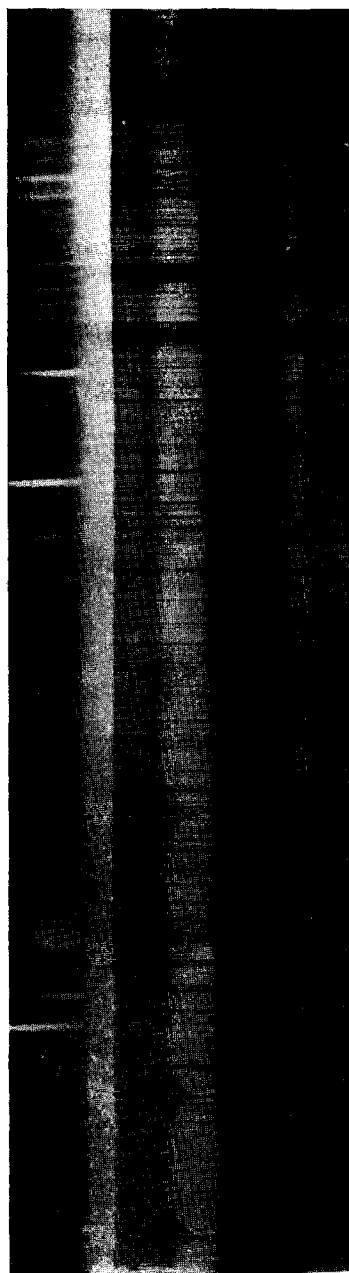


Fig. 1.

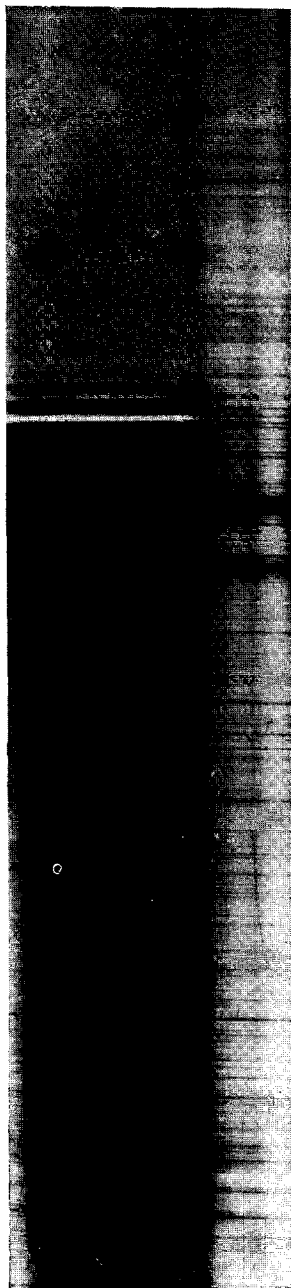


Fig. 2.