they place carbonic acid differently. This may be due to the difference in the nature of the discharge employed, which may have decomposed the substance in the one case and not in the other.

Masson's* values were obtained by means of the method of Faraday. It is interesting to note that the value he gives for oil of turpentine is, as it ought to be, equal to the square of the specific resistance which I have given.

XLVII. *On the Thermic and Optical Behaviour of Gases under the Influence of the Electric Discharge.* By E. WIEDEMANN.

[Concluded from p. 380.]

5. *Connexion between Spectral Phenomena, Elevation of Temperature, and Quantity of Electricity.*

I HAVE attempted to solve the problem of the connexion between the quantity of electricity passing through a gas of given pressure, the quantity of energy produced, and the corresponding changes in the spectral phenomena only in one particular case, which, however, seemed to me to be of especial interest. I have determined *what amount of energy is necessary to change the band spectrum of hydrogen into the line spectrum.*

The observations were made in the following way:—A calorimeter was passed over the horizontal capillary tube of a discharge-tube, and the spectrum was observed, as near as possible to the place where it fitted on the tube, by means of a spectroscope with a horizontal slit. The band spectrum was then changed into the line spectrum by interposing air-sparks. If the spark-length is gradually increased, beginning with none, the band spectrum is at first very bright; but soon the three hydrogen-lines make their appearance beside it, then the ground becomes fainter and the hydrogen-lines brighter, until at last the band spectrum disappears almost suddenly. The change is so sudden that it may often be recognized by the eye without the spectroscope. This order of phenomena has already been observed by Wüllner and others. When the spark-length necessary had been determined, the rise in temperature of the calorimeter t and the number of discharges were determined. From this the rise of temperature for one discharge at the given pressure was calculated, and then, by dividing by the pressure, what the rise of temperature would have been if the pressure had been only 1 millim.

If a denote the rise in temperature of the calorimeter in a minute caused by a current of deflection 100, W the water-equivalent, z the number of discharges in a second with the

* *Ann. de Chim. et de Phys.* 3rd ser. t. xxx. p. 25.

same current, and p the pressure, then the value

$$A = \frac{a}{60pz} W$$

expresses what quantity of heat must be evolved in order to change the band spectrum into a line spectrum in a gas of unit-pressure, in which of course the assumption is made that for a given volume the above quantity of heat is proportional to the pressure. The measurements were made with two different tubes, of radii 0.304 and 0.183 millim., and are given in the following tables *without exception*, and in the order in which they were made. The length of the portion of tube in the calorimeter was 42 millims.; the water-equivalents of the two calorimeters were 11.84 and 12.08. Some of the numbers were certainly too small, since at the moment the striking-power of the machine did not rise sufficiently to cause a complete disappearance of the band spectrum. These are marked with an asterisk, and are left out in determining the mean. Two different series of observations were made with the first tube, of which one includes the first three observations and the other the last four.

I.

p .	a .	z .	A .
5.8	0.50	166	0.0000086*
2.2	0.28	184	0.0000116
0.9	0.19	181	0.0000191
15.3	0.745	100	0.0000081*
5.4	0.50	96	0.0000158
2.1	0.28	160	0.0000139
0.9	0.21	233	0.0000167
Mean			0.0000155

II.

p .	a .	z .	A .
9.4	0.52	250	0.00000369*
3.6	0.26	200	0.00000615
1.7	0.20	270	0.00000726
6.2	0.35	160	0.00000587
14.1	0.60	133	0.00000533
Mean			0.00000565

Two determinations at pressures 2.2 and 0.7 millims. gave for the tube I, whilst bands were still plainly to be seen, $A=0.0000052$ and 0.0000057 .

The numbers in the last columns of I and II agree as well as the complicated conditions of experiment allow. They show that "the quantity of energy absorbed from the discharge to change the band spectrum into the line spectrum for a given quantity of hydrogen is independent of the pressure." The ratio of the quantities of heat necessary per unit of area in order to convert band spectrum into line spectrum in I and II is, since the lengths of tubes giving off heat are equal,

$$\frac{(0.183)^2 \times 0.0000155 \times 11.84}{(0.304)^2 \times 0.00000565 \times 12.08} = \frac{617 \times 10^{-8}}{631 \times 10^{-8}} = 0.979;$$

a number as nearly equal to unity as can be expected in experiments of such unusual difficulty.

We may hence conclude that the quantity of heat to be given up by the discharge to the unit weight of gas in order to change the band spectrum into the line spectrum is independent of the pressure and of the section of the tube. We may also easily calculate (1) *how great the quantity of heat is in absolute measure necessary for 1 gr. hydrogen to effect this change*; (2) *how great a quantity of electricity is necessary at any given pressure.*

The water-equivalent of the calorimeter I is 11.84, the rise of temperature for each discharge 0.0000155, the length of the portion of tube in the calorimeter 4.2 centims.; so that the quantity of heat given per unit length in each discharge is

$$\frac{11.84 \times 0.0000155}{4.2} \text{ calories.}$$

The volume of the gas per unit length is, since the section of the tube is 0.0029 square centim., 0.0029 cubic centim., and

its weight at 1 millim. pressure $\frac{1}{760} \times \frac{1 \times 0.0029 \times 0.069}{773.38}$ gr.

The quantity of heat necessary for 1 gr. hydrogen is therefore

$$\frac{11.84 \times 0.0000155 \times 760 \times 773.3}{4.2 \times 0.0029 \times 0.069} = 128300 \text{ calories.}$$

Let us further determine the quantity of electricity per unit area of 1 square millim. to convert the band spectrum into the line spectrum.

If we choose the case when the pressure was 2.2 millims. in the first tube, the number of discharges for a deflection of 100 (when the band spectrum changes to the line spectrum) was about 200. A deflection of 0.5 corresponds therefore to one discharge in which the quantity of electricity passes across a section of 0.29 square millim.; so that the quantity of electricity per square millimetre corresponds to a deflection 1.73,

$$= \frac{0.000336 \times 1.73}{100} = 0.00000581 \text{ Daniell-Siemens.}$$

Experiments on the Discharge in very high Vacua.

1. Reitlinger and Urbanitsky*, Spottiswoode†, and others have found that on approaching the finger to, or on touching a *highly exhausted* Geissler's tube, the discharge is deflected. I have further shown‡ that this phenomenon occurs especially with the positive discharge, and that sometimes the inner and sometimes the outer surface of the tube phosphoresces with green light.

By new experiments I have established that the point of the tube put into contact with the ground behaves in every respect like a negative electrode; for

(a) a faint reddish light shows itself on the inner face of the tube-wall, the spectrum of which is exactly similar to that of the red glow which forms about the negative electrode;

(b) the discharge given off from the wall by a positive or insulated electrode throws images on the opposite wall, which are displaced on the approach of a magnet.

(c) if the apparatus (fig. 10) be employed, and *a* be connected with the positive pole of the machine, *b* with the negative pole, and if the wall be touched at *d*, then at *f* there is formed a magnified shadow of *b*, in the same way as one negative electrode throws a shadow of another. The properties and forms of these shadows have been thoroughly studied by Goldstein§.

The discharge sometimes loses the property of sensitiveness in a very remarkable manner, as Spottiswoode has observed. An experiment which I have made shows this very plainly. The tube used was 5 metres long and 5 millims. wide. It was covered with a spiral strip of tinfoil for a distance of about half a metre. If the discharge was rendered sensitive by interpolating air-sparks, and the tinfoil strip connected with the ground, there was produced on the glass wall opposite to it a similar spiral of phosphorescent light, which became continually feebler from the positive electrode towards the negative, and at last disappeared. Also at points more than two metres from the point of contact there was hardly any green light produced by approach of the finger. It was as if the discharge had changed its form of motion, and lost the power of producing phosphorescence.

It is to be noticed that the green light of the glass does not appear most brilliantly in the parts of the tube traversed

* Reitlinger and Urbanitzky, *Beibl.* i. p. 416 (1877).

† Spottiswoode, *Beibl.* iii. p. 643 (1879).

‡ E. Wiedemann, *Wied. Ann.* ix. p. 157 (1880).

§ Goldstein, *Berl. Ber.* p. 284 (1876), and *Eine neue Form electrischer Abstossung* (Berlin, T. Springer, 1880).

by the current, but at points where blind branch tubes are placed, as, for example, in the pieces joined on for the purpose of securing the joints (Pl. IX. fig. 6).

2. It was further examined whether the negative discharges which excite the green light, the so-called kathode-rays, do really propagate themselves only in straight lines. For this purpose the apparatus fig. 11 was employed. If a was negative and b positive, the discharge from a struck first upon the glass wall at s , causing it to shine brightly, and then upon the bend at m (when the angle at m was about 30°), where bright green light also appeared. On the other hand, the tube was only feebly illuminated from s to m and m to l ; whilst on the surface d , exactly opposite the mouth of the tube sml , there appeared a bright green spot, in the midst of which there was a sharp shadow of the electrode e .

That this spot of light is not produced by light which has undergone several reflections in the interior of the tube sml may be seen in two ways: first, there was no violet spot when the positive discharge traversed the tube without the production of green light; and, further, the green spot alters its position under the influence of a magnet.

If the angle at m is chosen greater than 45° , and, moreover, the tube ml is taken tolerably long, the spot is at first faint, but appears with greater brilliancy as soon as the part of the tube surrounding a is touched directly with the finger. At the same time the discharge issuing from a within as is hardly affected by the magnet. Touching a point at some distance from a is without influence.

Whether we have to do here with an actual bending of the kathode-rays, or whether the result is due to secondary action, must be further investigated. It is possible that the wall at m acts as a negative electrode, and so causes the deviations of the rays. This supposition is supported by the fact that, if a glass rod or a narrow metallic plate be brought into the path of the bundle of rays diverging from a plane surface and near to the kathode, the rays diverge from it in a high degree, as if it were itself a negative electrode. The divergence is increased by interpolating air-sparks in the circuit.

3. Further, to determine whether the negative vibrations which excite the green light could traverse the ordinary positive discharge, the following experiment was made:—

a (fig. 12) is an electrode in the form of a disk, b is a point. When a is negative and b positive, a bright green spot appears at m , corresponding to the opening of the tube at c ; at the same time the tube at c shines with violet light of the same colour as a tube through which no kathode-rays pass.

An experiment to determine whether there was any difference in time between the appearance of the violet light and of the green gave no reliable result—partly, no doubt, because of the feebleness of the light at *c*.

4. I have, further, made experiments to determine whether the kathode-rays propagate themselves with a measurable velocity; and employed for this purpose a discharge-tube 1 metre long, provided with a disk electrode at one end, which at a sufficient exhaustion sent the kathode-rays through the entire tube. When the tube was viewed in a revolving mirror, the phosphorescence appeared at the same instant at both ends of the tube.

5. In order to examine the influence of the shape of the electrodes on the number of discharges, and the potential necessary to produce them, the following experiments were made.

The following pieces of apparatus were connected together by fusion onto a forked tube:—1st, the apparatus fig. 11 from *a* to *m*; secondly, the apparatus fig. 10; thirdly, a discharge-tube similar to fig. 11, except that at *b* there was a disk parallel to *a*. The whole was exhausted, so that when the disks were negative the whole tube shone brightly with green light. In the revolving mirror the following results were obtained:—

(*a*) With the apparatus fig. 10, no difference whether the positive or the negative electrode was put to earth; the green band of light appeared almost entirely continuous.

(*b*) With the apparatus with the two disks the same is the case.

(*c*) With the apparatus fig. 11, when the disk is negative no discontinuity is observed in the revolving mirror; but if it is positive, then the appearances represented in fig. 13 are observed. They consist of single, sharp, very bright images of the tube, e. g. *b* and *d*; at the side of which is seen a much feebler preceding discharge, *aa*, *cc*, sharply bounded at its commencement and of nearly equal intensity throughout. If the velocity of rotation of the electrical machine be increased, the appearance is not altered. If the outside of the tube be connected with the earth, the broad strips are resolved into separate images. The appearance is probably to be explained by the charge taken by the tube. At very small pressures, therefore, not only the number of the discharges, but the whole mechanism depends to a great extent on the form of the electrodes.

6. In order to measure the influence of the kathode-rays radiating from the negative electrode on the intensity of the current, a mica disk provided with a hinge was so placed between two disk electrodes opposed to each other at a distance

of about 40 centims., that without altering the connexions it could be brought between the electrodes or removed. In the former position it intercepted the kathode-rays issuing from the negative electrode, whilst in the latter they had a free path. The intensity of the current was the same in both cases.

7. Reitlinger* has shown that when stratifications form about the positive electrode in a tube traversed by a current, their number is considerably increased by the approach of a magnet from the negative pole. The increase is caused by the advance of those nearest the negative electrode, and the appearance of new ones at the positive pole. I have observed that the mean distance of the layers is not much altered in the process. When, by carrying the exhaustion far enough, all the stratifications have been made to disappear, I have succeeded in producing new ones by approaching a magnet to the electrode. The phenomenon is especially beautiful when the positive electrode is a point; the stratifications seem then to float up round it.

The phenomena are seen most distinctly when the quantities of electricity passing in the discharge correspond accurately to the potential necessary to cause discharge through the tube, and are not increased by interposition of air-sparks in the circuit.

Action of different Sources of Electricity.

The conditions of discharge are certainly the most simple in *friction- or electrophorus-machines*. The electricity is produced uniformly, it flows into the electrodes, after a certain time reaches the potential necessary to discharge, and discharges itself, and the process begins anew. So little electricity is collected upon the disks, conducting-wires, &c., or the flow of electricity is so rapid, that the discharge may be considered almost instantaneous. It is only in quite exceptional cases at very low pressures that we see sometimes how a discharge is made up of a series of partial discharges.

But for our investigations we must have such instantaneous discharges; for only with such can we assume that the discharge gives up its energy to the gas so rapidly that no perceptible transference of energy from the gas to its envelope takes place during the process.

The quantities of electricity produced by Töpler's machine are abundantly sufficient for all thermic measurements, while, on the other hand, they are not so great that the images of the separate discharges cannot be distinguished in the revolving

* Reitlinger, *Wien. Anz.* p. 795 (1876).

mirror. It is, further, of importance that the quantity of electricity produced can be varied simply by a change in the velocity of revolution of the machine and without alteration of the connexions. The introduction of resistances (which would cause complications in the processes of discharge) is therefore rendered unnecessary.

By the introduction of resistances into the circuit the mode of discharge is in general not altered, but the quantity of electricity which passes suddenly in each discharge is increased. Conditions are much more complicated when the induction-coil is employed*.

At each breaking and closing of the primary current we have, besides the principal discharge, a whole series of partial discharges of decreasing intensity. That we have not only a single discharge traversing the tube is seen by the use of the rotating mirror. But each of the partial discharges lasts a certain length of time, during which the electricity flows gradually from the coil to the electrodes; it will therefore again either be itself composed of a series of partial discharges, or correspond to a more or less continuous discharge of electricity. The images of the discharges do not consist of separate sharp lines, as with the electrophorus-machines, but of more or less broad bands in which maxima and minima occur.

The total heating in the tube is, as shown above, always dependent upon the total quantity of electricity transmitted, without reference to the quantity in each discharge; so that the result obtained by Naccari and Bellati† is intelligible without further explanation.

Hence it results that at different pressures of the gas in the discharge-tube the duration of the induced currents, and the quantity of electricity furnished by the inductorium in each discharge, is essentially different, since the potentials at the ends of the coil must rise to different magnitudes before the flow of electricity takes place. If the pressure of the gas be very high, then no doubt only the principal discharge passes through.

From all these considerations, it follows that the induction-coil is not suitable for the quantitative study of the discharge or of spectral phenomena; for each of the partial discharges, being of a different strength, will produce a different spectral phenomenon, so that one may produce a line spectrum and another a band spectrum.

Exactly similar remarks hold good also for the discharges of large batteries of Leyden jars, only that here another circum-

* Compare G. Wiedemann, Pogg. *Ann.* clviii. p. 286 (1876).

† Naccari and Bellati, *Beibl.* ii. p. 720 (1878).

stance must be taken into account. A part of the very large quantity of electricity passing in each discharge charges the surface of the tubes and discharges itself only very gradually (in ten or more minutes), as is clearly shown by the afterglow of the tubes. This is particularly striking when very long tube conductions (30 metres and more in length) are employed.

In considering *galvanic batteries*, such as Hittorf employed in his beautiful investigations, we must first examine whether, with the large quantities of electricity produced, the gas returns after each discharge to its original condition.

In order not to complicate the inquiry unnecessarily, let us imagine the tube replaced by an indefinite space bounded by two parallel planes. Let the whole of the gas be heated by the instantaneous discharge to the same initial temperature A . Let the distance of the walls be c , their temperature constant and equal to zero, the temperature of the separate points between the plates u , their distances from the one plate x , and the time t . Then the flow of heat, if a^2 is a constant, is determined by the partial differential equation

$$\frac{du}{dt} = a^2 \frac{d^2u}{dx^2},$$

where

$$u = f(x) = A \text{ when } t = 0,$$

$$u = 0 \quad \text{when } x = 0 \text{ and } x = c,$$

The solution gives, if r be a whole number,

$$u = 4A \sum_{r=0}^{\infty} \frac{e^{-a^2 \left(\frac{(2r+1)\pi}{c}\right)^2 t}}{(2r+1)\pi} \sin \frac{2r+1}{c} \pi x.$$

Let us consider only the temperature U in the middle of the plates, then $x = \frac{c}{2}$. If we expand the series and content ourselves with the first term, we have

$$U = 4A \frac{e^{-\frac{a^2 \pi^2}{c^2} t}}{\pi}.$$

For a pressure p in air,

$$a^2 = \frac{0.25 \cdot 760 \text{ centim.}}{p} \frac{\text{sec.}}{\text{sec.}},$$

according to Stefan*.

If we take the pressure at $\frac{1}{100}$ atmosphere, which corre-

* Stefan, *Wien. Ber.* lxx. (2) p. 45 (1872). See also Kundt and Warburg, *Pogg. Ann.* clvi. p. 194 (1875).

sponds to ordinary conditions in our discharge-tubes, then $a^2=25$; and if, further, we bring together the constants in U , we have, nearly,

$$U=1.3Ae^{-245\frac{t}{c^2}}.$$

If we take two tubes, of which the one is about 1 centim., the other about 1 millim. wide, then for these, if A_1 and A_2 denote the initial temperatures,

$$U'=1.3A_1e^{-245t}, \text{ and } U''=1.3A_2e^{-245\times 100t}.$$

A numerical calculation, neglecting the factor 1.3, shows that in the middle of a tube of 1 centim. width, after $\frac{1}{100}$ second the rise of temperature will have sunk about $\frac{1}{11}$, after $\frac{1}{1000}$ second $\frac{1}{13}$, and that, on the other hand, in a tube of 1 millim. diameter the same changes will have taken place after the $\frac{1}{10000}$ and the $\frac{1}{100000}$ second. If we assume that in the narrow tube the gas has attained a temperature of 1000° , a case easily realized, then (again neglecting 1.3) after the lapse of the times t the temperatures θ (which, it is true, give only a measure of the order of magnitude of those actually present) would be

$$\begin{array}{cccc} t=10^{-6} & 10^{-5} & 10^{-4} & 10^{-3} \\ \theta=980 & 815 & 133 & 1.4\times 10^{-6}. \end{array}$$

If, therefore, there are 1000 discharges in the second, the gas is after each almost in its original condition; if there are 100,000, this is not the case.

These considerations hold good for the case of a capillary tube, where, in fact, a considerable rise in temperature accompanies the luminosity. As yet no afterglow has been recognized with certainty following the separate discharges. Also in wider tubes experiment shows us that, contrary to theory, no afterglow occurs—a fact to which we will return later.

The above discussion can of course only furnish a measure of the order of the magnitudes in question. An exact discussion is as yet not possible, the constants not being certainly determined. Similar methods would hold good if we desired further to take into consideration the radiation of the gas.

The experiments of my father, of Röntgen, myself, and others have shown that with a uniform supply of electricity a perfectly definite potential is necessary to discharge—that, further, the electricity passes in separate discharges which are almost instantaneous, and which do not appear lengthened in the rotating mirror. With a galvanic battery the electricity used in each discharge is rapidly supplied again; and it is a

question whether we have to do here with discontinuous or continuous discharge.

The current from a Hittorf's cell, when newly put together, will liberate a maximum of 90.2 milligrammes of silver in a minute; so that this would in general represent its maximum strength of current*.

The current of my Töpler's machine corresponded to 0.0006 Siemens-Daniell for a deflection of the galvanometer of 100 millims., and would therefore separate about 77×0.0004 milligramme of silver. It is therefore $\frac{90.2 \times 10000}{77 \times 4}$ or about 3000

times as weak as that employed by Hittorf. But with this current I obtained, with electrodes widely separated by capillary tubes, about 2000 discharges in a second at a pressure of about 5 millims. If we assume that Hittorf's battery would furnish the same quantity of electricity as given above when used with the discharge-tube, we should have $3000 \times 2000 = 6,000,000$ discharges in the second. If the part of the tube seen in the revolving mirror have a breadth of 1 millim. and the mirror make 100 revolutions per second, then, when the observer and the tube are each at a distance of half a metre from the mirror, the image would appear to move $1000 \times 100 \times 2 \times 3.14$, or 600,000 millims. in a second. Accordingly, six separate discharges would appear to fall upon each millimetre of the image. But as the impression of the light on the retina lasts more than one seventh of a second, we see the images corresponding to 14 revolutions of the mirror at the same time; so that the images of 126 separate discharges are seen together in each millimetre.

In the tubes employed by Hittorf the electrodes were much nearer together, and the pressures were lower; so that the number of discharges would be further considerably increased.

With so large a number of discharges the heating and luminosity of the gas does not sink again to nothing between each two discharges; so that the separate images appear lengthened out in the mirror. Hence it is here quite impossible to draw conclusions about continuity or discontinuity of discharges. Moreover the criterion given by Hittorf to decide the question of continuity—the want of sensitiveness of the discharge on approach of the finger—is not always applicable, as experiments with the Töpler's machine have shown that the discontinuous discharges are almost altogether non-sensitive; but they can be made more or less sensitive by the interpolation of air-sparks of definite length. Most probably, in most

* Hittorf, *Wied. Ann.* vii. p. 557 (1880).

cases, the discharge of the battery, according to the conditions existing in the battery itself, is either altogether discontinuous, or takes place in such a way that stronger discharges cause the chief discharge, upon which follows a continuous discharge gradually becoming weaker, and so on.

But even if the discharges are completely continuous, I do not believe that they can be employed in spectroscopic investigations, since the final temperature of the gas depends on so many circumstances which cannot be exactly determined—for example, upon the radiation-coefficient, which varies with the temperature.

Theoretical Considerations.

If we endeavour, from the above facts and others yet to be mentioned, to represent to ourselves the mode in which the electric discharge takes place through a gas, we see, in the first place, that the theory proposed by G. Wiedemann and R. Rühlmann is not supported by these facts. According to this theory, the discharge is carried on by molecules charged with electricity which are driven off from the electrode, and which, upon collision with other molecules, yield up their electricity to them. The same theory has been adopted, in a somewhat different form, by Crookes to explain the phenomena described by him, but most of which, though no doubt without his knowledge, had been long ago made known by Hittorf, and then by Goldstein and others. According to this theory, the molecules must possess velocities corresponding to the velocity of propagation of electricity in gases. But we know, from Wheatstone's* experiments on the discharge in gases, that this is certainly greater than 200,000 metres, or 30 (German) geographical (=124 British statute) miles. But it is quite certain that the molecules do not possess so great a velocity of translation measured in the direction of the current. Dr. von Zahn has observed the lines of the spectrum given by a Geissler's tube, first when the axis of the tube and the axis of the collimator of his spectroscope were parallel, and then when they were at right angles, and observed no displacement of the lines, although the dispersion was so great that a displacement of $\frac{1}{40}$ of the distance between the D-lines could have been observed. A displacement of this magnitude would, in accordance with Doppler's principle, have corresponded to a velocity of 4 geographical miles; and a velocity of 30 geographical miles would have produced a displacement nearly equal to the entire interval between the

* Wheatstone, *Pogg. Ann.* xxxiv. p. 464, 1835.

two D-lines. So great an increase of the normal velocity of the molecules is therefore quite improbable*.

According to my view, we may imagine to ourselves the phenomena of the discharge somewhat as follows:—The electricity produced by the machine, which we may imagine as free æther, is accumulated on the surface of the electrodes partly as free electricity, and there is prevented from passing into the surrounding gas by the mutual action between it and the molecules of the metal; and a transference can only take place when its density has reached a sufficient magnitude. At the same time the electricity produces a dielectric polarization in the surrounding medium in such a manner that the æther envelopes of the separate gas-molecules become deformed, and, in consequence of the rotation of the molecules on their axes, maintain a definite position. If a discharge takes place, the sudden change of the dielectric polarization thereby produced propagates itself from the electrode through the æther envelopes of the gas-molecules, and thereby puts them into vibration. At the same time a transference of free electricity from the electrode may no doubt take place from molecule to molecule.

As a ray of light produces in the æther envelopes of the molecules of phosphorescent and fluorescent bodies oscillatory movements whose *vis viva* is considerably greater than corresponds to the temperature, so also the case is here; as there the motions of the æther which produce the luminosity gradually transfer themselves to the molecules and produce heat-motions, so also, in an exactly similar manner, with the electric discharge a secondary elevation of the total temperature results.

If in consequence of this transference two molecules of the gas have a greater motion of oscillation than corresponds to their temperature, in accordance with the normal relationships between motion of translation and motion of oscillation (rotation), then upon their collision a portion of the internal motion resolves itself into motion of translation, until at last the normal condition is restored†.

* These considerations, which I had already (Wied. Ann. ix. p. 160) brought forward to prove that there is no propagation of molecules in the direction of the current, have been again adduced by Goldstein in a paper (Phil. Mag. September, 1880) on the phenomena which take place at the negative pole, which only came to my knowledge since the above was in type.

† In the paper cited above I have compared the luminosity of the gas under the influence of the discharge with the light of a fluorescent substance. Hittorf, in discussing it, has expressed the opinion that one should speak of phosphorescence. The two terms, however, are only dif-

That there is really such an excess of internal motion in gases rendered luminous by electricity is shown by their low temperature. The change of motion of oscillation into motion of translation takes place with very great rapidity. I have shown on p. 416 that, according to the laws of conduction of heat, in a tube 1 centim. wide, even after $\frac{1}{1000}$ second, a perceptible fraction of the original energy must exist in the centre of the tube, yet nevertheless it is seen in the rotating mirror to be discontinuously illuminated, just as a narrow tube would be; so that we must conclude that the transference of the internal motions produced by the current into heat is much more rapid than the conduction of heat itself in the gas.

The vibrations produced by the electric discharge may become so energetic that the molecules themselves fall to pieces and are resolved into their constituent atoms, just as we observe decomposition when we receive the chemically-active rays on silver chloride, or an increase of affinity when they fall upon chlorine.

If the oscillatory motions produce a decomposition of the molecules, the energy necessary for the decomposition is brought to the molecules from the source of electricity, and is again given up to the calorimeter when they reunite. Whether the whole quantity of heat produced in this case results from the latter process cannot be decided off hand.

ferent names for the same phenomenon. Fluorescence and phosphorescence differ only in degree. Fluorescent light lasting really for only an instant could never be observed. The time during which the luminosity lasts is determined by the rapidity with which the internal motions of the molecules equalize themselves, and consequently by the mutual influence of the molecules in their internal motions. With solid bodies this is certainly relatively small: the molecules vibrate about their positions of equilibrium; and the elongations are so small that the actions of neighbouring molecules on the different parts of the same molecule are very little different. Only thus can we explain and understand the appearance of sharp absorption-bands in the case of solid bodies, since light emitted by solid bodies can still interfere when there is a great difference of path (compare Wied. *Ann.* v. p. 500, 1878). The same holds good for fluids: here also, besides the motion of translation of the molecules, we have vibrations of the whole molecules; for otherwise the law of change of friction with temperature would be the same for gases and for fluids, whereas it increases with the temperature in the former case and decreases in the latter. With liquids also the time during which a molecule vibrates uninfluenced is therefore relatively large, and the transference of energy follows relatively slowly. This will take place with gases most easily and rapidly, where the mean path-length alone is of account; and therefore the name fluorescence is first applicable here. But here also the fluorescent light will last at least as long as the mean interval between two collisions.

It is possible that a first fraction of the electricity transmitted is used up in producing an increase of the mean temperature resulting from a transformation of oscillatory motion, that by this an unstable condition of the molecule is brought about, and the remainder of the electricity completes the decomposition.

There is a remarkable parallelism between the production of heat caused by a ray of light in a feebly absorbing medium and that which is caused by the electric discharge.

(1) If a conically enlarging beam of light propagate itself in a feebly absorbing medium, the quantity of heat developed is nearly the same in every section of the beam; in the same way the heat produced by an electric discharge is the same in each section.

(2) If we increase the intensity of the ray of light, but allow it to pass for a proportionately smaller time, an equal quantity is absorbed in the two cases; the same holds good for the discharge when we increase its strength, but decrease its frequency.

(3) If we increase the optical absorption by, for example, increasing the number of absorbing particles in the absorbing solution, the quantity of heat produced is increased in proportion; so also the electric evolution of heat in a gas becomes greater for the same section as the pressure increases.

It seems therefore very probable that the absorption of energy in both cases follows in the same way, that therefore the discharge consists in a propagation of vibrations which give up a portion of their energy to the gas-molecules. But then we must make the assumption that the amplitude caused by a quantity of electricity e is proportional not to e , but to $\sqrt{e}$.

But even under this assumption the phenomena of the electric discharge cannot be explained so well as the optical phenomena, since so many disturbing causes occur.

Amongst them must be mentioned, first of all, the statical charge of the glass walls, which largely affects the transmitted discharge, and produces by itself a definite polarization of the gas-molecules, sometimes increasing and sometimes diminishing the energy given up by the discharge. These exterior charges produce most effect with wide tubes, in which the motion produced by the discharge itself is much less rapid than in narrow tubes. Here should be mentioned the interesting fact discovered by Hittorf, that a gas which is traversed in one direction by a discharge conducts the current in a direction at right angles to that much better than when this is not the case.

The great differences in the behaviour of positive and negative electricity may perhaps be explained by assuming that the propagation of negative electricity alone depends upon the communication of electric polarization, whilst that of positive electricity is associated with a transference of free æther from molecule to molecule, as indeed Von Ettingshausen* has recently concluded from the experiments of Hall†.

We should thus have explained at once the difference in potential necessary for the commencement of discharge from the negative and positive electrodes. At the negative electrode the resolution of the dielectric polarization alone is necessary, whilst at the positive the attraction of the material molecules for the æther has also to be overcome.

The propagation of the discharge issuing from the negative electrodes obeys nearly the laws of light. From each point of the electrode there apparently issues a feebly diverging bundle of kathode-rays, which behaves in its further course almost exactly like a beam of light, casting shadows, producing phosphorescent light, and so on. But we must not look upon the electrode as itself the source of light, but as a surface parallel to a wave-surface. For in the source of light the displacements of the æther envelopes of the separate molecules are still altogether without law, and take place indifferently in all directions. The wave itself, all of whose parts vibrate isochronously, is first formed at a definite distance from the electrode; whilst at the electrode the dielectric polarization possesses a perfectly definite position, and is simultaneously resolved at all points. The superficial molecules of the electrode itself do not form a wave; for the displacements do not occur in them in the same manner as, for example, when the kathode-rays issuing from the negative electrode produce phosphorescent light when they strike the glass wall in the same way as light-waves. If, for example, a part of the outer wall of an exhausted glass tube be covered with a metallic coating and this be connected with the induction-coil, the inner wall of the tube at this point becomes alternately negative and positive; nevertheless I have never been able to observe the green light on it. Leonh. Weber‡ has also recently employed such exterior coatings for the study of Hittorf's phenomenon.

The deviation of the positive discharge, by connecting the outer surface of the tube at any point with the earth, would be an effect of the altered potential produced by the altered dis-

* Von Ettingshausen, *Wien. Ber.* lxxxi. March 4, 1880.

† Hall, *Phil. Mag.* [5] vol. ix. p. 225, 1880.

‡ L. Weber, *Carl. Rep.* xvi. p. 240, 1880.

tribution of the free electricity on the walls of the tube on the free current-electricity. The wall, turned towards a positive discharge, then naturally plays the part of a negative electrode. In what way the discharges issuing from the two electrodes equalize themselves is still an open question.

I have already shown*, and also mentioned above, that the phenomena produced by the kathode-rays cannot be caused by projected molecules. If we were even to assume that the thickness of a layer of such projected particles amounted to a whole centimetre, that it therefore possessed a mass relatively great, yet, in order to produce the observed heating of the tube above the negative electrode, it must possess velocities of 100,000 metres or more.

Gintl† and Puluj‡ seek to refer the phenomena to a projection of the substance of the electrodes; but since with aluminium electrodes, for example, no decrease of the electrodes is observed, the velocity must be immense. This view is therefore scarcely tenable. Moreover all the other phenomena observed may be explained by the propagation of æther-waves of very great energy; thus, for example, the mutual influence of two rays may be explained by the pressures occurring on the anterior surface of advancing waves§, which in our case may be of considerable magnitude.

Let us turn, lastly, to the results in spectrum-analysis which may be drawn from the above investigation. In a previous investigation|| I have endeavoured to show, in continuation of the investigations of Lockyer, Lecoq de Boisbandran, and others, that the band spectrum corresponds to the individual molecule, the line spectrum to the separate atoms. The same quantity of heat which is necessary to change the band spectrum into the line spectrum gives, therefore, a maximum value for the heat of decomposition of the hydrogen molecules, of which, besides the work expended in the dissociation, another portion is employed in heating the gas.

We find that about 128,000 gramme-calories must be communicated to 1 gramme of hydrogen of ordinary temperature in order to separate it into its atoms. This number is to be regarded as only a rough approximation, since its determination is affected by so many sources of error; it must remain for further investigations to determine this number more exactly.

It corresponds to values such as we frequently have in

* E. Wiedemann, Wied. Ann. ix. p. 157, 1880.

† Separate Publication.

‡ Puluj, Wiener Anzeiger, p. 76, 1880.

§ Maxwell, 'Electricity and Magnetism,' ii. p. 391.

|| E. Wiedemann, Wied. Ann. v. p. 512, 1878.

thermochemical decompositions. A determination of the quantity of heat necessary for the decomposition of the molecules of the elements must be important for the science of chemistry. If, for example, we have the reaction

the thermic effects are of three kinds:—first, heat is absorbed in separating one atom of hydrogen from the other; a further quantity of heat is absorbed in separating one atom of chlorine from the other; and, lastly, twice as much heat is produced as corresponds to the formation of one molecule of hydrochloric acid.

Until now only the total result has been measured. It is now possible, by spectroscopic methods, to determine the first two portions by themselves, and so to determine the true heat of combination.

If we assume, as is in the main confirmed by the preceding investigations, that the spectra are conditioned by the quantity of electricity given to each molecule and the energy absorbed by it, the known dependence of spectra on the pressure may be explained as follows:—

When the pressure is great in a discharge-tube, the number of gas-molecules is large also. As at the same time the number of discharges for an equal supply of electricity is comparatively small, the energy given up by each separate discharge must be relatively very large. At the same time this may be confined to a few molecules, in consequence of the formation of a small spark. A very great quantity of energy is given to each molecule; it decomposes into its atoms, and we have a line spectrum.

If the pressure falls, the number of discharges increases, the energy given up decreases, and, moreover, all portions of the gas are put into motion: hence the number moved is larger, a smaller quantity of energy is given to each molecule; it is no longer sufficient for the decomposition of molecules into atoms, and the spectrum is a band spectrum.

If now we include air-sparks in the circuit, the quantity of electricity transmitted in each discharge is increased, and consequently the energy given up; hence the band spectrum is converted into the line spectrum. At very low pressures complications occur which cannot be dealt with till we possess a complete theory of the discharge.

If we find in the experiments (p. 407) that the line spectrum appears together with the band spectrum, first weak and then increasing in strength, this is in entire accordance with the conclusions which follow from the kinetic theory of gases.

Of all the molecules present in the gas, there are always some in which the atoms perform such vibrations that a very small impulse is sufficient to separate them. Such impulses are communicated to the atoms by the discharge in abundance; hence the hydrogen-lines appear already in tubes of relatively great width, with a very small supply of electricity to each molecule. So, on the other hand, there are molecules present for the separation of whose atoms comparatively powerful impulses are necessary; the complete disappearance of the band spectrum takes place therefore only very gradually. In exactly the same way we understand why, with the discharges of the induction-coil, we have the line spectrum and the band spectrum present together: it is to be observed that the discharge of an induction-coil always consists of partial discharges of varying strength.

It was shown on p. 372 that, when electrodes of different forms are employed, the heat produced in a capillary tube is the same, and moreover the number of discharges does not alter much. This fact shows that in a capillary tube, if we have to do with discontinuous discharges, we can never have spectra corresponding to quantities of electricity less than a certain minimum value.

The spectra which result from the smallest quantity of electricity transmitted in each discharge, and the smallest quantities of energy given off, are obtained by placing the two electrodes close to each other and exhausting till the spark-discharge ceases and the silent discharge alone takes place. A cylindrical portion of the gas of several millimetres diameter becomes luminous, and is traversed by a large number of discharges. The energy given off may indeed fall so far that scarcely any light at all is to be seen.

The only means which we have of obtaining spectra of small energy of internal motion with the necessary brilliancy consists in the employment of wide tubes. We may get rid of the influence of thickness by employing tubes with axial line of sight; but I have never been able to observe any difference between nitrogen seen in this way and nitrogen seen transversely. Hittorf has found similar negative results with sodium-vapour.

In order to compare the action of the induction-coil with that of the electrophorus-machine in producing spectra, I excited a Stöhrer's induction-coil of medium size by the current from four Bunsen cells, and employed as current-break an automatic tuning-fork giving 100 complete vibrations; the one pole of the coil was connected directly with the earth, and

the other connected by a discharge-tube and galvanometer with the earth.

The deflection amounted to 145 millims., with a pressure of about 10 millims. in the discharge-tube; so that a deflection of about 1·5 millim. would correspond to a discharge. The quantity of electricity given by each discharge would therefore be sufficient to convert the band spectrum into the line spectrum in a tube of 1 to 2 millims. width (p. 409). But if we have even a very powerful excitation of the coil, and replace the metallic contacts by a mercury break, we shall hardly succeed in bringing to bear on unit surface in a tube 10 times as wide, and consequently of 100 times the section, so much electricity that the same change would take place. This only takes place when we employ Leyden jars; and then the conditions become so complicated that their discussion has hitherto been impossible.

Wüllner*, from a series of careful experiments, has urged objections against the above view of the origin of spectra, and has employed the spectrum of nitrogen as his starting-point. As he had not these separate measurements of the influence of the thickness of the layer, of the intensity of the discharges, of the pressure, and of the quantity of energy given off, it is not possible to follow the discussion of his experiments into details. The appearance of single nitrogen-lines together with the bands may be explained by the reasons given above. An objection formerly raised by me against Wüllner's theory has been set aside by recent experiments of Dewar and Scott†. But that with hydrogen a change of line spectrum into band spectrum cannot be brought about by change of the thickness of the radiating layer may be seen from the remark of Lockyer, that a layer of incandescent hydrogen only a fraction of a millimetre thick in a Geissler's tube shows the same bright lines as the layer in the sun's photosphere thousands of kilometres in thickness. Moreover the gases would have to possess an enormous absorption-coefficient for the luminous rays corresponding to the bands, whereas exactly the opposite follows from the experiments of Gouy‡. Moreover Wüllner has always taken the change of temperature into account.

My next problem will be to examine further the region sketched out in this research—namely, to determine the relation between the intensity of the separate lines of the spectrum, the quantities of electricity, and the quantities of energy given

* Wüllner, *Wied. Ann.* viii. p. 590 (1879).

† Dewar and Scott, *Beibl.* iv. p. 309 (1880).

‡ Gouy, *Beibl.* ii. pp. 349, 411 (1878), iii. p. 611 (1879), iv. p. 476 (1880).

up. It will in this be necessary first of all to further examine the proposition previously stated, and probably to expand it into the following general statement:—

“In order that definite changes in quality and quantity may take place in the spectrum of a gas produced by electric discharges, equal quantities of energy must be communicated to each molecule, which are, within tolerably wide limits, independent of the pressure of the gas and of the width of the tube.”

Leipsic, March 1880.

XLVIII. *On the Space protected by a Lightning-Conductor.*
By WILLIAM HENRY PREECE*.

[Plate X.]

ANY portion of non-conducting space disturbed by electricity is called an electric field. At every point of this field, if a small electrified body were placed there, there would be a certain resultant force experienced by it dependent upon the distribution of electricity producing the field. When we know the strength and direction of this resultant force, we know all the properties of the field, and we can express them numerically or delineate them graphically. Faraday (Exp. Res. § 3122 *et seq.*) showed how the distribution of the forces in any electric field can be graphically depicted by drawing lines (which he called *lines of force*) whose direction at every point coincides with the direction of the resultant force at that point; and Clerk Maxwell (Camb. Phil. Trans. 1857) showed how the magnitude of the forces can be indicated by the way in which the lines of force are drawn. The magnitude of the resultant force at any point of the field is a function of the potential at that point; and this potential is measured by the work done in producing the field. The potential at any point is, in fact, measured by the work done in moving a unit of electricity from the point to an infinite distance. Indeed the resultant force at any point is directly proportional to the rate of fall of potential per unit length along the line of force passing through that point. If there be no fall of potential there can be no resultant force; hence if we take any surface in the field such that the potential is the same at every point of the surface, we have what is called an *equipotential surface*. The difference of potential between any two points is called an electromotive force. The lines of force are neces-

* Communicated by the Author.