II. On the conductivity of the hot gases from flames

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effect on the value obtained for J . An error in the standard of electromotive force of about $\frac{1}{10}$ per cent. would therefore suffice to account for the entire difference between Rowland's results and Griffiths'.

The most interesting result of the present comparisons is that Rowland's corrected curve shows the same rate of change in the specific heat of water with the temperature between 15° and 25° that Griffiths' does, as can be seen at a glance by an inspection of the curves as drawn in fig. 4. This fact also suggests the possibility of the difference being due to an error in the standards used, rather than in the experiments themselves.

A short abstract of the results of these comparisons was published in the Johns Hopkins University Circular for June 1897, giving the corrected values of the mechanical equivalent of heat. There was a slight error in the values as published, owing to the use of an incorrect method of reducing the readings of Rowland's Baudin thermometers. The error was not discovered until after the abstract had been published. This incorrect abstract was reproduced in the *Philosophical Magazine* for August 1897.

The author wishes to express his appreciation of Professor Rowland's kindness in allowing the use of his thermometers for these comparisons, and his obligation to Professor Rowland and Professor Ames for their frequent aid and advice in the course of the work.

Although the general plan of the apparatus described here is the author's, he wishes to express his deep sense of obligation to Dr. W. T. Mather, at that time Fellow of Johns Hopkins University, for his aid at almost every step in the mechanical details of its design and construction.

II. *On the Conductivity of the Hot Gases from Flames.*

By J. A. McCLELLAND, M.A., Cavendish Laboratory, Cambridge.*

IT is well known that a charged body loses its charge when a flame is brought near it, even if there is not actual contact with the flame but only with the hot gases coming from it.

The subject of the conductivity of flames has been studied by many experimenters, and an account of their results is given in Wiedemann's *Lehre von der Electricität*, vol. 4 B, and in a later paper by Arrhenius (*Wied. Ann.* xlii. 1891).

In the following paper the nature of the conductivity not

* Communicated by Prof. J. J. Thomson.

in the flame itself but in the gases taken from the flame has been investigated: here the conditions are simpler and the nature of the electrodes used is not so important. For papers on this part of the subject see Giese, *Wied. Ann.* xvii. 1882, xxxviii. 1889.

The method used in the experiments is simple; the gas is drawn along a brass tube inside which is placed an insulated terminal which can be raised to any required potential, and the conductivity of the gas passing this terminal is measured by the rate of fall of potential of the terminal as given by an electrometer. For experiments on conductivity inside a flame a sensitive galvanometer may be used, but when one is dealing with the conducting gas drawn from the flame the conductivity is too small to permit the use of a galvanometer. The electrometer method enables us to work with the gas at distances from the flame convenient for the experiments.

1. *The Relation between the Current and the Electromotive Force.*

To determine the manner in which the current through the conducting gas depends on the E.M.F., the arrangement in fig. 1 was used. A is a metal tube 3.7 cm. in diameter

Fig. 1.

with a funnel attached to it. Beneath this funnel an ordinary rose bunsen-burner is placed and regulated to give a steady flame. The products of combustion pass up the tube A with a velocity constant at each point as soon as the tube has attained a steady temperature, and the bunsen-burner is large enough to ensure that the stream of conducting gas is as nearly as possible the same at all points in a horizontal section of the tube. B is a brass rod 10 cm. long and .5 cm. diameter, placed in the axis of A and insulated by an ebonite plug C. It is connected to one pair of quadrants of an electrometer E. A is connected to earth, and the two pairs of quadrants are first connected together and to one pole of a battery of storage-cells, the other pole of which is to earth;

the quadrants connected to B are then separated from the cells, and the motion of the spot of light gives a measure of the current for the E.M.F. of the cells used.

Table I. gives the numbers for one experiment, the current being expressed in arbitrary units.

TABLE I.

E.M.F.	Current.
10 volts	3
20 "	6
40 "	12
80 "	25
120 "	34
156 "	38
188 "	39

Table II. gives the numbers for a similar experiment with the same apparatus when the velocity of the stream of hot gas up the tube A has been diminished by placing on top of A a piece of board pierced with a number of small holes.

TABLE II.

E.M.F.	Current.
20 volts	10
40 "	18
120 "	23
200 "	24

Fig. 2.

Curves I. and II. (fig. 2) are plotted from Tables I. and II., and show at once that the conduction does not follow

Ohm's law, but that the current tends to a maximum value which is not increased when the E.M.F. is further increased.

This is the form of curve we should expect to get if we regard the conductivity of the gas as due to its ionization in the flame, so that we have a number of positively and negatively charged ions in the gas passing the electrode B. If the terminal B be positive, then the negatively charged carriers are deflected to it and give up their charge, causing the observed leakage of the charge from B. If we suppose that one of these carriers of electricity moves with a velocity of v centimetres per second under an electromotive force of 1 volt per centimetre, and that the stream of carriers takes a time t to pass along the length of the electrode B, the carriers inside a radius ρ will be discharged to B, where ρ is given by

$$t = \frac{1}{vV} \frac{\rho^2 - r_0^2}{2} \log \frac{r_1}{r_0}$$

(r_1 =radius of tube A; r_0 =radius of B; V =potential of B),
and

$$t = \frac{l}{v'}$$

(l =length of B; v' =velocity of the stream of gas up the tube A).

Therefore if q be the charge carried by the carriers of one sign in unit volume in the tube at B, the amount of electricity given up to B in unit time is

$$\pi(\rho^2 - r_0^2)v'q = \frac{2\pi qlvV}{\log \frac{r_1}{r_0}}.$$

The current is therefore proportional to the E.M.F. until $\rho = r_1$ (the radius of A), when all the carriers are discharged to B.

We have neglected in this calculation the rate at which the positive and negative carriers are recombining; as we go up the tube the recombination diminishes the conductivity, so that a large E.M.F. by discharging the carriers sooner to B increases slightly the current, so that the curves do not become perfectly flat at the point where the E.M.F. is sufficient to discharge all the carriers before they pass the electrode.

In curve II. the maximum current is reached for a smaller E.M.F. than in I., because the velocity of the stream is less and the carriers take a longer time to pass the electrode.

In the following table (III.) the numbers are given for an

experiment in which the conducting gas is passed up a much wider tube (4 cm. radius) with a velocity of over 100 cm. per second and the leakage from a terminal in the axis of the tube taken as before.

TABLE III.

E.M.F.	Current.
40 volts	8
80 "	15
120 "	23
160 "	31
200 "	37
240 "	43
280 "	50

Curve III. is drawn from these numbers and shows that up to the voltage used the current is approximately proportional to the E.M.F. On the other hand, with a narrower

Fig. 3.—Curve III.

tube and a smaller velocity of the carriers up the tube, the maximum value of the current has been reached for an E.M.F. of a few volts.

If a second terminal C be placed in the tube above B and connected to the electrometer and charged to a potential sufficiently great to give the maximum rate of leak ; then if

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we raise the potential of B the leak from C diminishes until, when the potential of B is high enough to give the maximum leak from it, we get no leakage from C. All the carriers have been discharged before they pass B, and the gas above it possesses no conductivity. The maximum rate of leak from B is the same whether it is charged positively or negatively, showing that equal amounts of positive and negative electricity are carried by the ions.

We can calculate the amount of electricity on the carriers of one sign per unit volume of the gas from the flame. A terminal placed in the axis of a cylinder through which the gas was moving and joined to a capacity (including that of the quadrants of the electrometer) of 280 C.G.S. units fell in potential at the rate of 5 volts per second, which corresponds to $\frac{14}{3}$ electrostatic units of charge per second. We know that the gas in a cross-section of 3 sq. cm. around the terminal was discharged, and the velocity of the stream of gas past the terminal was 130 cm. per second, so that the charge per unit volume was $\frac{1}{83}$ electrostatic unit. If each carrier has the atomic charge, the number in unit volume is of the order 10^9 . Or the ratio of the number of charged carriers to the number of molecules is of the order 10^{-12} . These numbers refer to the conducting gas at a point about 17 cm. from the flame; closer to the flame the number of dissociated atoms is, of course, much greater, and the number falls away rapidly as the gas moves away further from the flame.

2. *Recombination of the Ions.*

We can measure the rate at which the positive and negative ions recombine by determining the conductivity of the gas at different times after it is drawn away from the flame. To do this, the gas from the flame passes up a cylindrical tube which is connected to earth, and an insulated metal rod is lowered into the tube from the top and placed in its axis. This rod is connected to a pair of quadrants of an electrometer, and charged to a potential high enough to ensure that all the carriers are discharged in a short distance after reaching the lower end of the rod. By lowering the rod further and further into the tube, and measuring the rate of leak in each position, we get the conductivity at different distances from the flame. By measuring the temperature at different points of the tube, and therefore knowing the relative velocities of the current of gas at these points, we can express the conductivity of the gas in terms of the time since it left the flame. The following table shows the result of an experiment :—

Conductivity proportional to	Distance from flame in cm.	Time from flame proportional to
50	9	18
25	14	28
14	19	39
8.5	24	51
6.5	31	69
6	34	77

Fig. 4.—Curve IV.

Curve IV. *a* is plotted from the above numbers, and shows the way in which the conductivity falls away, owing to the recombination of the positive and negative carriers.

The rate at which the conductivity falls away evidently diminishes with the conductivity. If n be the number of ions per unit volume at any time, and if we assume that

$$-\frac{dn}{dt} = \alpha n^2,$$

we get

$$\alpha t = \frac{1}{n} - \frac{1}{N},$$

where N = number of ions when $t=0$.

If we use the points A and B on the curve *a* to determine the constants in the above equation and plot the curve, we get the curve *b*.

The two curves agree approximately, which would show that the rate of recombination of the ions is proportional to the square of the number present in the dissociated gas. We should expect the conductivity to fall off in this way, as the number of collisions between positive and negative carriers will be proportional to the square of the number present, and each collision means a definite loss of conductivity. The curve *a* must diverge considerably from the curve *b* nearer to the flame, since *b* if continued back would give an infinite conductivity before the flame is reached. The rate of recombination closer to the flame would not seem to be as rapid as it should be if it continued to be proportional to the square of the number of ions.

In the experiment from which the above curve is drawn the absolute velocity of the current of gas up the tube was not determined, so that the time is only expressed in arbitrary units. In another experiment, however, where a wider tube was being used, and the velocity of the current up it was measured by a wind-gauge and found to be 130 cm. per second, the conductivity fell to half its value between two points 17 cm. and 27 cm. distant from the flame. The conductivity thus fell to half its value in $\frac{1}{13}$ of a second. Of course the rate of loss of conductivity rapidly diminishes with the conductivity, so that for electrometer determinations it is quite convenient to work with the gas more than 1 second after it has been drawn away from the flame.

3. *Velocity of Carriers under an Electromotive Force.*

We can easily determine the velocity with which the positively and negatively charged ions travel under an electric force. The apparatus shown in fig. 5 was used.

A is a cylindrical tube .85 cm. radius, with two terminals B and C placed one above the other in the axis of the tube—each 6.5 cm. long and .2 cm. radius. These terminals are insulated and supported by ebonite plugs. To prevent the insulation of the ebonite being spoiled by moisture depositing on its surface, it is convenient to shape the ebonite as shown in the figure, so that the insulating surface is not exposed directly to the current of the gas.

A piece of tubing T leads from A to an ordinary water-pump P connected to the water-mains. The pump is connected by a glass tube as shown with a large glass vessel V, which is fitted with the two tubes *a* and *b*—*a* just passing through the cork, and *b* going to the bottom of V. The water and air from the pump enter by *c*, and the tap in *a* can easily be set so that the vessel remains about half full of

water, the water escaping by *b* and the air by *a*. It is kept so during an experiment; then by closing *a*, and taking the time in which the level of the water in *V* sinks through *a*

Fig. 5.

short distance, and knowing the cross-section of *V*, we get the volume of air drawn through *A* in a given time. Knowing the cross-section of *A*, and also the temperature inside it at any point, we get the velocity of the current of gas through *A* at that point. The temperature is determined by pulling out the plug of ebonite and inserting a thermometer.

A is connected to earth and *C* is charged by storage-cells, and the rate of leak measured as described previously. *C* is charged sufficiently high to ensure that the gas is completely discharged in passing it. The rate of leak of *C* is thus determined (1) when *B* is connected to earth, (2) when *B* is charged to such a potential that the rate of leak from *C* is about halved. These two determinations enable us to calculate the velocity of the carriers. The carriers of opposite sign to *B* in a part of the cross-section of the tube are discharged to *B*; the area thus discharged is given, as we have seen above, by

$$t = \frac{1}{vV} \frac{\rho^2 - r_0^2}{2} \log \frac{r_1}{r_0},$$

where the letters denote the same quantities as before. We can determine ρ from the rate of leak of *C* in the two cases

when B is to earth, and when it is charged to potential V; t is equal to the length of the terminal B divided by the velocity of the current past it which we measure. The velocity v of the carrier under an electric force of 1 volt per centimetre is therefore given by the above equation.

In practice V is made such as to diminish the rate of leak from C by about one half. We can check the value of v thus calculated by finding what value of V is just sufficient to give no conductivity at C.

This method gave the velocity of the carrier,

·2 cm. per second,

under a potential gradient of one volt per centimetre. A large number of experiments were made, and the results of different determinations agreed to less than 10 per cent. The velocity of the stream past the terminal B was varied between 15 and 30 cm. per second in the different determinations, and the potential of B varied from 1 to 4 volts.

Another set of determinations of the velocity of the carrier was made with a large cylindrical tube of 4 cm. radius, in which were placed two terminals, B and C (as in the previous case), the lower one (B) being 43 cm. long and 4 cm. radius. This tube was placed above the flame, and the velocity of the stream of gas up it was measured with a wind-gauge which fitted into the tube. A determination with the apparatus gave the following numbers :—

Leakage from C :

200 divisions in 11 seconds when B is at zero potential,
200 „ „ 18 „ when B is at 40 volts potential.

The velocity of the stream past the terminal B was 122 cm. per second.

This gives the velocity of the carrier to be

22 cm. per second.

The determinations with the two sets of apparatus agreed as closely as could be expected from the nature of the experiments.

All the above determinations of velocity of the carrier were made in the gas soon after leaving the flame and when its temperature was about 200° C. This is important, as appears from some work later on.

This velocity is much less than that found for the carrier of electricity in the case of a gas which has been exposed to Röntgen rays. (See Rutherford, *Phil. Mag.* Nov. 1897.)

If we regard the charge on the carrier as unalterable, we

must assume that in our case the charged carrier has joined on to it a number of uncharged particles which increase its mass without increasing the charge, thus lowering its velocity under an electric force. We have not data enough to determine the size of the carrier even if we assume that it carries the atomic charge, as the carrier is so small that the equations of viscous motion do not apply.

4. *Difference of Velocity between Positive and Negative Carriers.*

As we have seen, the above method of determining the velocity of the carrier under an electric force gave results which did not vary in a number of determinations by more than 10 per cent.

These determinations seemed to point to a difference in the velocity of the positive and negative carriers; and a large number of experiments were made to settle the point.

The velocities of the positive and negative carriers were determined alternately a number of times by charging the terminals alternately negatively and positively in the method described above. As the method involves the ratio of two rates of leak in the same direction in determining each velocity, any want of symmetry in the deflexions of the electrometer is eliminated. The results showed that the velocity of the negative carrier was about 15 per cent. greater than that of the positive carrier.

The following experiment would be easily explained by the negative carrier having a greater velocity than the positive. The gas from the flame is drawn up a tube A connected to earth, and through a metal box B which is insulated and filled with a loose plug of glass wool. B is joined to a pair of quadrants of an electrometer, the other pair being to earth. In the tube is a terminal C, which can be joined to one pole of an alternating circuit, the other pole being earthed. The positive and negative carriers, passing through the glass wool, give up their charge to it.

When C is to earth the box B gets a small negative charge; we always do get a small negative charge from the gas from a Bunsen flame. (Kelvin, 'Nature,' April 22nd, 1897.)

When now the terminal C is joined to the alternating E.M.F., if the negative carriers move faster than the positive, and the intensity and frequency of the E.M.F. be such that not all the carriers of both signs are discharged, we get more negative carriers discharged than positive, and the box B gets an excess of positive.

In the experiment the electrometer showed a positive charge rising rapidly to a value at which it remained constant. This was because the conducting gas entering B caused a discharge to A, and equilibrium was produced when the discharge was equal to the gain of positive electricity from the carriers.

Fig. 6.

This experiment is difficult to explain except on the theory that the negative carrier moves faster than the positive under the same force. As the charges of the positive and negative carriers are probably the same, the positive carrier must have more uncharged particles attached to it.

5. *Change in the Velocity of the Carrier.*

In all the experiments described above on the velocity with which the carrier moves under an electric force, the experiments were made on the gas at a short interval after it left the flame and when its temperature was always well over 100°C . Further experiments showed that this velocity does not remain constant, but falls away rapidly when the gas has cooled down at a distance from the flame. The gas is drawn up a tube with a number of terminals placed along this axis at different distances from the flame, so that the velocity of the carrier can be determined at each of these points. Knowing the velocity of the current of gas up the tube, we know the time which has elapsed since it left the flame; and the temperature can be found by inserting thermometers.

The following table shows the result of an experiment :—

	Velocity of the carrier.	Temp.	Conductivity of the gas proportional to	Distance of the terminal from the flame.
At terminal A	cm. ·23 per sec.	° C. 230	26	cm. 5·5
At terminal B	·21 „	160	3	10
At terminal C	·04 „	105	1	14·5

Evidently for some distance from the flame the velocity of the carrier was very little altered, and then began to rapidly diminish. This diminution of velocity seems to depend principally on the cooling of the gas, and would point to a rapid condensation on the charged carrier of some uncharged body greatly increasing its mass.

To test whether a similar falling away of the velocity would occur in the case of a flame which burns without the production of water-vapour, a CO flame was tried; and a similar diminution of velocity was found.

The velocity of the carrier in the CO flame was found to be

·16 cm. per second,

under an electric force of 1 volt per cm., and at a distance of 30 cm. from the flame, where the temperature was 55°, this velocity had fallen to

·03 cm. per second.

Some other experiments are in progress to investigate more fully this falling away of the velocity of the carrier.

6. *Discharging Power of Fine Gauze.*

When the velocity of the carrier under an electric force has diminished at a distance from the flame, it can pass through gauze without being discharged much easier than if the gauze is placed closer to the flame.

In one experiment a charged terminal placed in the tube, at a distance of about 35 cm. from the flame, leaked at the rate of 50 scale-divisions in 30 sec. One layer of fine gauze placed in the tube just below this terminal, and therefore at a point where the velocity of the carrier was small, scarcely diminished the rate of leak. The same gauze when placed 10 cm. from the flame reduced the leak from the same terminal to 50 divisions in 75 seconds.

This means even a greater difference in the discharging-power of the gauze in the two positions than the above numbers indicate, because in the second position the loss of conductivity by recombination while passing up the tube is less than in the first case.

The difference in the discharging-power of the gauze is explained by the fact that when the carrier has a smaller velocity under an electric force fewer of the carriers come into contact with the gauze by diffusion. It can be shown that for such a gas, when enclosed between parallel planes or in a cylinder, the ratio of conductivity at time t to the initial conductivity varies as e^{-avt} , where v is the velocity of the carrier under 1 volt per cm. (See Townsend, *Phil Mag.* May 1898) Hence we see that when v is smaller fewer of the carriers are discharged by diffusion as the gas comes up to the gauze and passes through the meshes.

In conclusion, I wish to thank Prof. Thomson for his valuable criticisms and suggestions.

III. *On the Properties of Liquid Mixtures.*—Part II. By R. A. LEHFELDT, *Professor of Physics at the E. London Technical College*.*.

IN a previous article (*Phil. Mag.* (5) vol. xl. p. 398) an attempt was made to follow out the consequences of a certain thermodynamic relation between the composition of a liquid mixture, and that of the vapour in equilibrium with it, and the saturation pressure of the system. Experiments were there described on mixtures of benzene with ethyl and methyl acetates in which a small fraction of each mixture was distilled, as nearly as possible at a constant temperature, and the distillate analysed; these led to an empirical expression connecting the composition of liquid and vapour. Experiments were afterwards made to determine the vapour-pressure of similar mixtures by the dynamic method, but they led to unsatisfactory results owing to decomposition of the esters on prolonged boiling. I was able to resume the work in 1897, and then chose more stable compounds to work on, viz., benzene and toluene mixed with carbon tetrachloride, as types of normal organic compounds, and benzene and toluene mixed with ethyl alcohol, as type of a so-called "associated" liquid. The experiments to be described here were carried out at the Davy-Faraday laboratory, which the managers of the Royal Institution very obligingly placed at my service.

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