



LXXXVII. On the nature and velocity of migration of the carriers of electricity in flames containing metallic vapours

E. N. da C. Andrade B.Sc. Ph.D.

To cite this article: E. N. da C. Andrade B.Sc. Ph.D. (1912) LXXXVII. On the nature and velocity of migration of the carriers of electricity in flames containing metallic vapours , Philosophical Magazine Series 6, 23:138, 865-884, DOI: [10.1080/14786440608637288](https://doi.org/10.1080/14786440608637288)

To link to this article: <http://dx.doi.org/10.1080/14786440608637288>



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THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1912.

LXXXVII. *On the Nature and Velocity of Migration of the Carriers of Electricity in Flames containing Metallic Vapours.* By E. N. DA C. ANDRADE, B.Sc., Ph.D., 1851 Exhibition Scholar of University College, London*.

§ 1. *Introduction.*

THE experiments here described, which were carried out in the Radiologisches Institut of the University of Heidelberg, are primarily concerned with the velocity of migration and origin of the positive carriers of electricity which are formed when a metallic salt is brought into the Bunsen flame. Lenard† has shown that if a bead of a salt of one of the alkali metals be brought into the Bunsen flame, the coloured streak so formed is deviated in an electric field, and behaves as if positively charged. He estimates the velocity of migration of the carriers in unit field from the inclination of the luminous streak, and the upward velocity of the flame. Previously to Lenard's paper H. A. Wilson‡, using two horizontal electrodes in the flame itself, had measured the velocity of the positive carriers by driving them down against the current of the flame gases: he estimates the field required to bring them to the lower electrode by the current between the electrodes. The value obtained by Wilson is about 1000

* Communicated by Prof. Sir J. J. Thomson.

† P. Lenard, *Ann. der Physik* (4) ix. p. 642 (1902).

‡ H. A. Wilson, *Phil. Trans. A.* cxcii. p. 499 (1899).

times as great as that of Lenard, e. g. for lithium he finds $63 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ and Lenard $0.08 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$. From this

Lenard (*loc. cit.* p. 647) infers the probability of the existence of two kinds of positive carriers, but there appears to have been no attempt made to demonstrate this with certainty, or to explain the discrepancy.

It seemed to me desirable to establish clearly the simultaneous existence of, and distinguish the difference between, the two kinds of positive carriers, and especially to show the existence of both kinds with a common method. The arrangement adopted was similar to that used by Lenard for deflecting the coloured streak, the electrodes being vertical and outside the flame: the Wilson carriers, which are invisible, are then driven sideways out of the flame, and detected as described later. Their velocity has been measured, and found to be smaller than that given by Wilson; experimental and theoretical grounds are brought forward for supposing that Wilson and subsequent experimenters using his method have made an erroneous assumption as to the origin of these carriers, which makes the velocity work out too high.

It has been shown in the course of the work to be described that the faster positive carriers are metallic, like the slower ones, probably metal atoms, thus contradicting the theory that the positive carriers in flames are hydrogen. Experiments have also been made on the negative carriers, showing, among other things, that metallic negative carriers exist.

For convenience the slower positive carriers which form the luminous streak, whose velocity was measured by Lenard, will often in the following be called "carriers of the first kind"; the faster carriers, not seen as luminous, measured by Wilson, "carriers of the second kind."

A critique of previous work on the subject will be found at the end of the paper.

§ 2. *Method and Apparatus.*

The essence of the method is as follows: the flame is placed between two plate electrodes, one earthed, and the other insulated and connected with an electric machine; the fast moving positive carriers are in this way driven sideways out of the flame, and some of them fall upon an insulated platinum strip, which is connected to earth through a high resistance galvanometer, and is fixed close to the earthed

electrode, so that the uniformity of the field is not disturbed by it. The presence of the carriers is detected by the current through the galvanometer caused by the introduction of the bead of salt into the flame.

The earthed electrode is a massive brass plate, 6 cm. \times 8 cm. \times 0.5 cm.; to this is fastened a strip of brass pierced by a vertical slot, in which runs a brass piece holding an amber insulation: through the amber passes a stout wire holding the horizontal strip of platinum foil, 4 mm. \times 50 mm., close to and parallel to the electrode. The brass piece can be clamped by a screw at any given height, and its position read off on a scale fastened to the slot. The other electrode is a brass plate similar to the earthed electrode, but insulated on amber; it is joined up to a "Mercedes" influence machine, through a reverser arranged so that either pole can be connected to the electrode, the other to earth. Between the electrodes, not touching either of them, burns a non-luminous flame of air and gas from a burner provided with a quartz flame piece, giving a flat flame about 20 mm. wide and 6 mm. thick, the plane of the flame being at right angles to that of the electrodes. By means of a small electromagnet, the current through which is controlled by a variable resistance, a platinum loop containing the given salt can be brought gradually into the flame; the platinum wire is insulated from the iron armature which supports it. The galvanometer, one pole of which is connected to the insulated platinum strip, the other to earth, is of the D'Arsonval type, with a resistance of 10,000 ohms: it is usually shunted with a resistance of 1900 ohms.

The potential of the insulated electrode is kept constant by a spark-gap connected in parallel. This potential is measured on a rough electrometer; the potential fall in the flame by means of two parallel "probes" of fine platinum wire placed in the flame itself, and connected to a small aluminium leaf electrometer, which is insulated, the outer case being connected to one probe and the leaf to the other. The electrometer is protected by an earthed net. For the smaller potential falls used in the final and more accurate experiments on the velocities of the faster carriers, a bifilar electrometer is used, the two threads being in this instrument surrounded by an insulated cylinder inside the outer metal case, which outer case is earthed.

The probes are placed in the flame between the luminous streak and the negative electrode; it then makes practically no difference in the potential fall whether the streak is present or not. If the potential difference is measured in the

luminous streak itself, it is found to be smaller than in the pure flame, but, with such amounts of salt as were used, by not more than 20 per cent. It is to be noticed that this is the case when the potential is maintained by cold electrodes *outside the flame*; when the electrodes maintaining the potential are platinum glowing in the flame, as in all previous experiments on the velocity of the faster positive carriers, the case is very different, the distribution of potential being very much altered by the presence of the salt in contact with one or both of the glowing electrodes.

§ 3. *Determination of the Velocity from the distribution of the faster carriers.*

When the insulated platinum strip is opposite the flame, and the insulated electrode is positively charged, there is a deflexion of the galvanometer, which remains constant as long as the field remains on: this is due to positive carriers present in the pure flame being driven out onto the strip. On the introduction of the bead of salt into the flame a further deflexion in the same direction is observed, showing that there are positive carriers which can be driven out of the flame contained in the metal vapour. The amount of this further deflexion gives a measure of the number of metallic carriers arriving at the particular region occupied by the strip. The extra current due to the introduction of the metal salt into the flame will in future be referred to as the "metallic current," and the corresponding deflexion of the galvanometer as the "metallic deflexion."

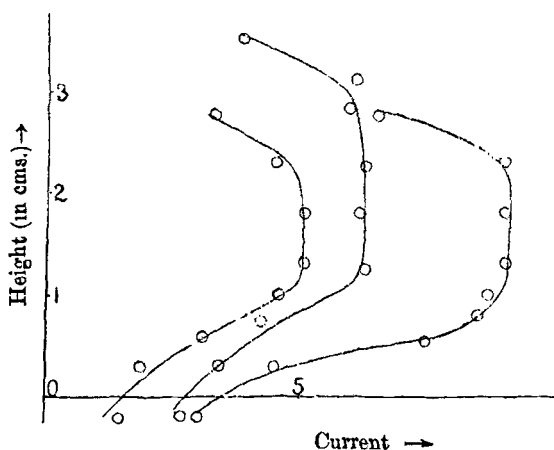
The fields used were usually not strong enough to produce a marked deflexion of the coloured streak: this could always be produced by increasing the field, but the smaller fields were used as being steadier. Some measurements of the velocity of the Lenard carriers deduced from the deflexion of a just visible streak of vapour gave $0.04 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for strontium*: Lenard gives $0.08 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for lithium, and states that the velocity for strontium is smaller.

The distribution of the faster carriers was investigated by measuring the number of carriers, as measured by the metallic current, to be observed with the platinum strip at

* Since these measurements were made G. Ebert has published a paper (Heidelberg Dissertation, 1911) where he gives $0.042 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for Sr.

different heights. When the strip was below or on a level with the bead of salt a small deflexion corresponding to positive carriers arriving on the strip was observed on the introduction of the bead, but for a certain portion above the bead this metallic current increased very rapidly with the height of the strip, and then remained approximately constant until the strip was in the neighbourhood of the top of the flame, when it again decreased. Typical distribution curves are shown in fig. 1. The ordinates are the vertical height of

Fig. 1.



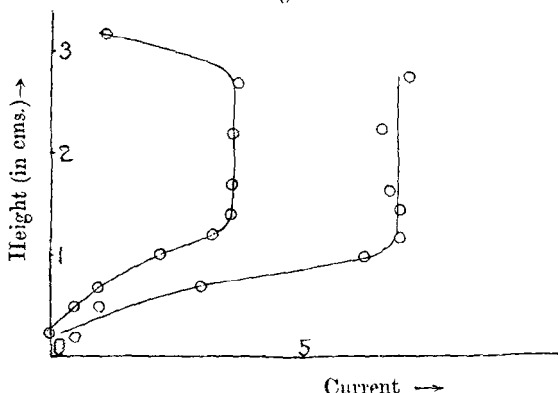
the mid line of the strip above the centre of the bead, the abscissæ the metallic deflexions*.

It seems reasonable to assume that the sudden increase of current is due to the strip being brought into the paths of the carriers coming from the lower part of the luminous vapour streak. The much smaller deflexions (which are, however, always present) for positions of the strip below this are then to be ascribed to positive carriers which have diffused down from the bead against the flame velocity. To test this point a screen, consisting of a very carefully insulated rectangle of thin platinum foil, was brought into the flame between the bead and the earthed electrode, so as to cut off the carriers below a certain point. The level of the top of the screen was well above the bead. The curves obtained are

* The three typical curves given were obtained on different days, when the height of the luminous streak was somewhat different. This accounts for the different extents of the flat maxima.

shown in fig. 2. The level of the top of the screen corresponds to the ordinate 0, and it will be observed that below this there is no current.

Fig. 2.



We make then the assumption that the height at which the flat maximum begins corresponds to the point at which the positive carriers from the lower part of the luminous streak (or from just above the screen, when the screen is used) arrive at the earthed electrode*. Then the velocity of migration of the carriers in the given field can be estimated from the vertical height of the strip above the screen for the position in which the large metallic current is first given. To do this we must, however, consider the effect produced by the portion of the path of the carriers lying in the hot air between the flame and the earthed electrode.

In the light of modern experiment it seems that positive carriers of molecular size do not become appreciably loaded with air molecules in such a case†. We have then to consider the effect of (1) the variation of the electric field, which is smaller in the flame than in the air-gap; (2) the variation of temperature; (3) the variation of the upward velocity of the gases.

* That there are present lesser currents between the point at which the maximum begins and the level of the top of the screen is due to the fact that the platinum strip is of finite breadth (4 mm.). The maximum first begins when the whole breadth of the strip is in the path of the carriers. By the height of the strip above the screen is therefore meant the height of the bottom of the strip above the top of the screen.

† See e. g. P. Lenard and C. Ramsauer, "Über die Wirkung sehr kurzwelliges ultraviolett Lichtes," *Berichte der Heidelberger Acad.* Part IV. (1911) page 19.

The variation of the velocity of a carrier of molecular size in a gas with the temperature can be deduced from a formula given by Lenard *

$$\omega = \frac{3}{2\pi\sqrt{2}} \frac{eF}{Ds^2W},$$

where e is charge, F the potential gradient, D the density of the gas, s the sum of the radii of carrier and gas molecule, and W the mean molecular velocity of the gas. Thus, assuming that the charge remains constant, we can find the ratio of the velocity in the hot air to that in the flame.

The upward velocity of the hot air will be less than that of the flame gases. The greater intensity of the field and the smaller upward velocity of the gases, together with the fact that the path in air is much shorter than that in the flame, tend to make the vertical rise of the carriers during their passage through the air-gap much smaller than that in the flame. Against this we have in the air a diminished horizontal velocity in unit electric field, owing to the lower temperature: this tends to increase the vertical rise in the air. Measurements were made to find the relative magnitudes of these effects. The strength of the field in the air-gap was estimated by measuring the field in the flame, and the potential difference between the electrodes; the difference between the latter and the total fall in the flame gives the fall in the air-gaps. The temperature at different places in the air-gap was measured with a thermo-couple, and the upward velocity of the air at the same places compared with that of the flame by a method worked out by Becker †. It was found that, with the distances of our experiment, *i. e.* path in flame = 1.2 cm., path in hot air 0.8 cm., the vertical rise of a carrier in the air-path would be only $\frac{1}{15}$ of the total rise, on the above assumptions. This is chiefly due to the field being seven times as strong in the air, and the average upward velocity of the gases less than half that of the flame. (Later, we shall assume that the measured velocity is less than that given by the formula of Lenard's already quoted, because the positive carriers are not charged all the time, but are during a certain fraction of their journey neutralized by electrons present in the flame. Now there are far fewer electrons in the hot air than in the flame; consequently the ratio of the horizontal velocity in the hot air to that in the flame will probably be greater than that assumed in the

* P. Lenard, *Ann. der Physik* [4] iii. p. 313 (1900). The original formula is more general.

† A. Becker, *Ann. der Physik*. [4] xxiv. p. 823 (1907)

calculation. Hence the vertical rise in the air will be still smaller.) The rise in the air can be neglected, as being not more than 7 per cent. of the total rise: our other measurements do not allow an assumption of greater accuracy. The whole vertical rise may, therefore, for purposes of calculation be assumed to take place in the flame.

For example, if we take the case for which the distribution curve is *a*, fig. 2, the whole vertical rise

$$= 0.95 \text{ cm.} = \frac{1}{\omega F} (360 + 26)$$

where ω = velocity of carrier in unit field in flame,

$$F = \text{strength of field in flame} = 150 \frac{\text{volt}}{\text{cm.}}$$

$$\left(\text{field in air} = 1100 \frac{\text{volt}}{\text{cm.}} \right),$$

and of the term in the bracket the first, 360, is proportional to the vertical rise in the flame, and the second, 26, to that in the hot air, which, as will be seen, is negligible.

$$\text{Hence} \quad \omega = \frac{386}{150 \times 0.95} = 2.7 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}.$$

The other curve in fig. 2 gives for ω $2.5 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$; while two careful experiments without the screen give 2.4 and $2.6 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$. Hence we may take the velocity of migration of the positive carriers of the second kind in the flame to be approximately $2.5 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$.

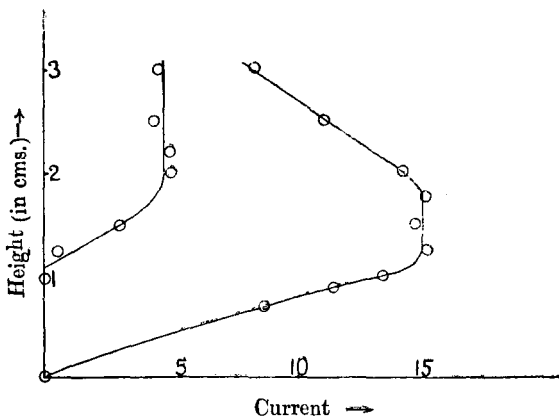
§ 4. Calculation of the Velocity without an Air-path.

An experiment made to see if the metallic current was markedly lessened by making the carriers pass through a greater distance in the flame (*i. e.* if many carriers were permanently neutralized) enables us to estimate roughly the velocity of the carriers without making any assumptions as to what takes place in the air-gap. The curves in fig. 3 show the resultant deflexions for the two cases:

- (1) in which the carriers pass through about 0.5 cm. in the flame;
- (2) in which the carriers pass through 1.4 cm. in the flame.

The bead was moved horizontally from one position to the other without altering the relative positions of the flame and the electrode. It will be observed that the metallic currents are very much less for all positions of the strip in the case when

Fig. 3.



the carriers pass through the extra centimetre in the flame, but further, that the maximum is reached at a lower position in the case where the path in the flame is short. If we assume that the vertical distance between the points at which the maxima begin in the two cases (0.65 cm.) is the vertical rise taking place in the 0.9 cm. of flame between the two positions, we can calculate the mobility. The potential gradient in the flame being $230 \frac{\text{volt}}{\text{cm.}}$,

$$\omega = \frac{0.9 \times 300}{230 \times 0.65} = 1.8 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}.$$

This is in as good agreement as we can expect with our previous values.

§ 5. Action of Glowing Platinum on Metallic Vapours.

It was also attempted to measure the velocity of the carriers without making them pass through air by bringing the earthed electrode into the flame itself. For this purpose the brass plate electrode was replaced by a very fine platinum net, fixed in the flame: an insulated platinum strip was so arranged that it could be moved in the flame vertically and close to the net. When, however, the net was earthed, and the strip connected to earth through a galvanometer, a

current, large compared with the usual metallic current, was obtained without any field being applied. The direction of this current corresponded to the assumption that negative charges were received by the strip, and was, no doubt, due to electrons shot out by the net (which from its fineness was much hotter than the strip) being received by the strip. If the net was insulated and earthed through the galvanometer, a current was observed if an earthed strip was present in the flame; if the strip was insulated or absent no current was obtained. In this case there must be approximate equilibrium between the accumulated electrons in the flame and those given out by the net, but as soon as an earthed strip is in the flame the electrons can escape as they are produced, and fresh ones are given out by the net, producing the observed current.

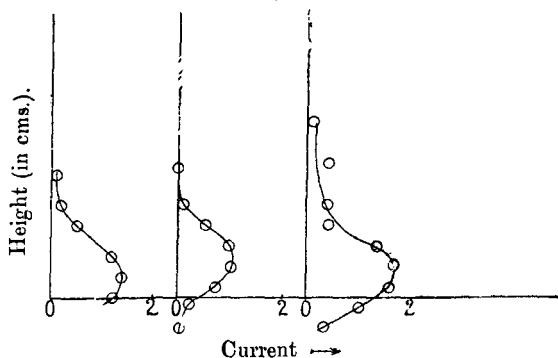
If the net is earthed, and the strip connected through the galvanometer to earth at a distance of about 1.5 cm. from it, the introduction of a bead of salt (SrCl_2) into the flame makes no appreciable difference to the observed current unless the luminous metallic vapour is in contact with the net, when the current observed from the strip is very much increased (four or five fold). If the strip in the flame is directly earthed, and the net earthed through the galvanometer, when the streak of luminous metallic vapour is brought into contact with the net, the current observed is increased in a similar manner. This shows that the impact of the metallic atoms of the vapour against the platinum must be able to liberate electrons in large quantities from the metals. The process may, of course, be considered not as direct impact, but as "Nähewirkung" (see P. Lenard, *Annalen der Physik*, [4] xvii. 1905, p. 244).

§ 6. *The Faster Carriers come only from the edge of the Luminous Vapour.*

To see if the fast moving positive carriers were driven out from throughout the volume of the metallic vapour, or only from the edge of the luminous streak remote from the positive electrode, as was suspected, a second bead of salt was brought into the flame between the first bead and the positive electrode, and level with the first bead. It was found, with the platinum strip in various positions, to produce no appreciable increase in the galvanometer deflexion. Hence it may be assumed that the faster carriers do not proceed from the volume of the vapour, but travel out from the neighbourhood of the edge only. This is most important for our theoretical considerations.

The insulated screen of thin platinum foil, pierced with a rectangular horizontal slit (3 mm. \times 12 mm.), was brought into the flame between the bead and the earthed electrode, and arranged in different experiments with the slit at various heights above the bead. Curves of the type shown in fig. 4

Fig. 4.



were obtained in all cases ; the maxima are sharp considering the breadth of the slit. (These curves are taken at random as typical ; they are not all three made with the same bead.) This indicates that the carriers have all approximately the same velocity ; the fact that curves made at different heights with the same streak of vapour give all about the same maximum deflexion indicates again that the carriers proceed only from the edge of the luminous streak, for the streak increases in breadth as we go upwards. The very flat maxima in the curves obtained for the unscreened streak offer additional confirmation of this point. (See fig. 1.)

The effect of increasing the air-gap between the flame and the earthed electrode was examined. It was found to diminish markedly the metallic current for all positions of the platinum strip. An example of the effect is shown in fig. 6 ; the solid and dotted curves on the right of the figure represent respectively the metallic current obtained with an air-gap of 8 mm. and 18 mm. respectively. The same figure exhibits the effect for negative carriers to be referred to later. This shows that a certain number of the carriers become permanently neutralized, and pass upwards.

§ 7. *The Faster Carriers are Metallic.*

It was observed that if the platinum strip was carefully cleansed in the Bunsen flame before being used to detect the carriers, yet it afterwards gave the sodium colour in the

flame (if a bead of a sodium salt were employed), indicating that the faster carriers are metallic. Owing to the difficulty of avoiding small traces of sodium, the point was systematically investigated with strontium. With a bead of this metal in the flame, after a quarter of an hour in the field, a large metallic current being observed all the time, the strip showed the strontium lines very distinctly on testing in the Bunsen flame with a pocket spectroscope. Control experiments (1) with the bead in the flame, but no field, (2) with the field, but with the strip in a position in which no metallic current was observed (*i. e.* below the bead), (3) with the isolated plate charged negatively, gave no strontium. To put the matter to a rough quantitative test the galvanometer was calibrated, and the amount of strontium corresponding to a unit deflexion for a unit time calculated on the assumption that the strontium atom had two elementary positive charges, as in electrolysis. Solutions of SrCl_2 were made, one drop of which from a given pipette held a known quantity of strontium. Drops of the different solutions were brought successively upon a platinum strip similar to that used to receive the carriers, and slowly evaporated; the brightness and duration of the strontium lines produced on bringing this strip into the Bunsen flame were compared with the lines given by the electrically deposited strontium. The experiments showed that the amount of strontium deposited was, very roughly, that calculated: the experimental errors of this method are, of course, large, but it would probably detect a difference if one of the amounts were double the other.

Further experiments were then made on the transport of sodium. As a control, two platinum strips were arranged close to the earthed electrode, one being earthed through the galvanometer as usual, the other being connected with the insulated electrode, which was then maintained at a positive potential for some minutes. The earthed strip showed the sodium colour strongly in the flame, the other strip did not. The strips were interchanged, with the same result. Hence there seems no doubt that the transport of sodium is connected with the metallic current.

Measurements were made of the time in which, for a given galvanometer deflexion, enough sodium was transported to give a just perceptible coloration of the flame. Åselman* has given for the amount of sodium which will give a perceptible coloration for one second in the Bunsen flame in a dark room, 1.5×10^{-8} mg. NaCl , which is equivalent to

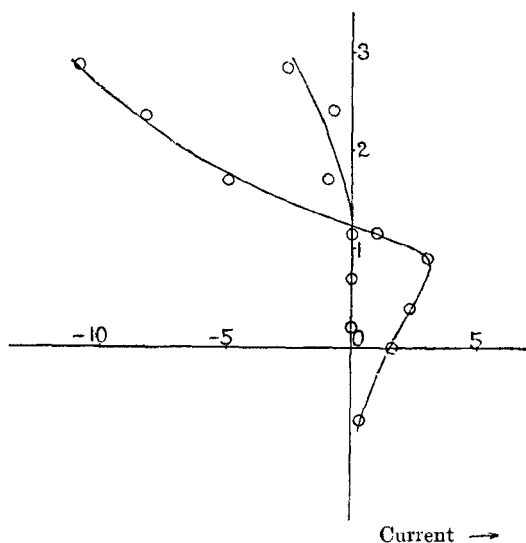
* E. Åselman, *Ann. der Physik* [4] xix. p. 960 (1906).

0.6×10^{-8} mg. Na. Our experiment was slightly modified to allow the tests being carried out under the same conditions as those of Aselman: on the assumption that each sodium atom conveyed one elementary charge, our observations of the current and time corresponding to the strip giving a just perceptible colour for one second on subsequent testing, gave 1.0×10^{-8} mg. Na as the amount, which is in moderate agreement, considering the nature of the experiment.

§ 8. *Experiments on the Negative Carriers.*

Measurements of the current produced by the introduction of a bead of salt into the flame for various positions of the platinum strip were also made with the same arrangement of apparatus, but with the insulated electrode charged negatively. In this case, if the strip be horizontally level with the bead, the introduction of the bead causes the current to diminish. As the strip is raised, a point is reached where the introduction of the bead causes no change in the current, and after this the metal vapour produces the usual increase of current found for the positive carriers. A typical curve is shown in fig. 5.

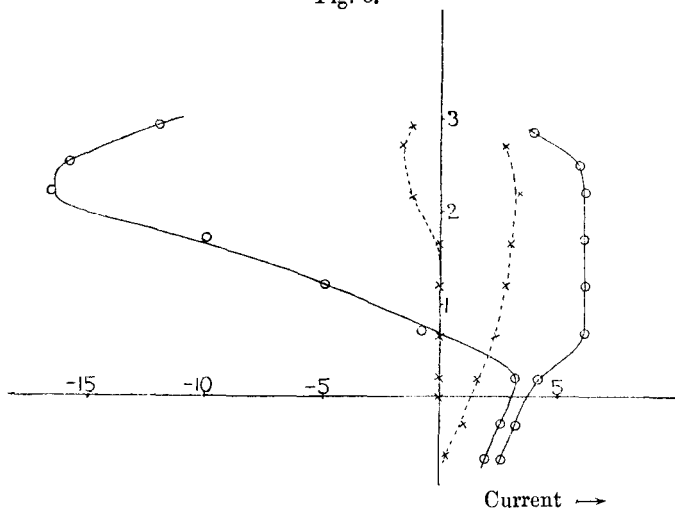
Fig. 5.



If the earthed electrode be further removed from the flame, the deflexions all decrease in the same way as with the positive carriers, but a path of 1 cm. extra in air decreases the maximum deflexion for the negative carriers to $\frac{1}{16}$, while

for the positive carriers it decreases it only to $\frac{1}{2}$. This is because the free electrons, which form the greater part of the negative carriers, become rapidly loaded with air molecules, and pass upwards with the current of air. For this, among many reasons, the velocity of the electrons cannot be estimated by this method. In fig. 6 are given curves for both positive

Fig. 6.



and negative, made for two different distances of the electrode and strip from the flame, the smaller distance being 0.8 cm., the greater 1.8 cm. Positive and negative readings were taken alternately by changing the sign of the electrode.

With Sr, as before mentioned, metal was not detected on the strip, when the electrode was negatively charged. With Na, however, the colour was unmistakably obtained with a run of a few minutes, though not nearly as bright as when the insulated electrode was positive for the same time.

The controls before enumerated rendered it certain that there really was a transport of metal on the negative side, though far less than on the positive side. This, together with the fact that about a thousand times as much Sr as Na is necessary to give a perceptible colour in the flame, would account for the Sr not being detected on the negative side. The presence of these metallic negative carriers enables us to explain the decrease of current which takes place on the negative side on introducing the bead if the strip is horizontally in the neighbourhood of the bead; this decrease is plainly shown in figs. 5 and 6. We assume that some of the

electrons of the flame get absorbed by neutral metallic atoms, which diminishes their velocity considerably: hence a certain number of electrons which before, in consequence of their high velocity, travelled almost horizontally out from the lower part of the streak of metallic vapour, now, combined with metal atoms and travelling slowly, arrive at the earthed electrode at a place higher than before: hence we get a diminished current for low positions of the platinum strip, but a considerable extra current above.

§ 9. *Theoretical.*

It has now been clearly established that when metallic vapour is present in a flame there exist positive carriers of two classes, distinguished by their having very different velocities of migration, the velocities of the one class being about $2.5 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ as compared with $0.04 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for the other class in the case of strontium. Both kinds of carriers are metallic; the slower kind form a luminous streak. The faster kind produce no visible coloration in the flame when driven sideways out of the luminous streak; this is to be anticipated, since they are present in relatively very small numbers, as can be deduced from the time required to deposit a quantity of metal on the strip sufficient to produce strong coloration in the flame. The faster carriers are produced throughout the height of the streak, and hence their presence is not connected with the contact of glowing platinum, but inherent in the luminous vapour itself.

As a result of much experimental and theoretical work, Lenard has put forward with strong support the view that any single carrier of the class whose presence is detected by the visible deflexion of the luminous streak is not positively charged always, but only for a short fraction of the time*. We may now explain the difference of velocity of the two classes by supposing that in both cases the carrier is only charged for a fraction of the time, alternating the positive state with the neutral state, but that the fraction is very much greater for the one than for the other. We can calculate the theoretical velocity of a permanently charged carrier of atomic size from the formula given by Lenard already cited (p. 871), which has proved very successful†.

* *E. g.*, P. Lenard, *Ann. der Physik* [4] ix. 1902, p. 648, and [4] xvii. 1905, p. 238.

† For a short account of the formulæ for the mobility of carriers in a gas, see A. Becker, *Ann. der Physik* [4] xxxvi. p. 217 (1911).

Lenard gives as the mobility calculated from this formula the value $2.3 \frac{\text{cm.}}{\text{sec.}}$ in nitrogen at 2000°C.^* , but the diameter of the metal atom assumed by him is, according to work which has since appeared, too large, and the value of e too small. Taking for e the value 4.7×10^{-10} c.g.s. electrostatic units (Planck), and calculating the radius of the strontium atom from the value given by Becker \dagger for the radius of the sodium atom, we have for the mobility of a permanently charged metallic atom $17 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$ (or for a molecule of SrO $15 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$). Thus we must assume, as we have

done above, that even the faster carriers cannot be always positively charged, but alternate the charged state with a neutral state caused by recombination with a free electron.

Evidence has been given for the assumption that the faster carriers come from a region near the edge of the luminous streak. Now in the streak itself we may assume that the impact of the metallic atoms against one another is the main cause of the liberation of an electron, and the consequent rendering of an atom positive; impact between a metal atom and a molecule of the flame-gases can also be sufficient to render an atom positive, but is a far less active cause \ddagger . In consequence of the large number of free electrons produced in the streak itself, the positive atom is quickly neutralized again; in fact from the velocity of the carriers in the streak the atom can, on the average, be positive for only about $\frac{1}{400}$ of the time. Now a metallic atom which is near the edge of the streak may, while it is positively charged, be driven out of or diffuse out of \S the luminous streak, where the metal concentration is high, into the free flame remote from the positive electrode, where the number of free electrons must be small. Hence the average positive life of an atom which has arrived into the free flame near the earthed electrode will be much longer than that of an atom in the dense streak. From the calculated mobility of a permanently charged metallic atom, a carrier of the faster kind must be positive for about $\frac{1}{6}$ of the time.

* P. Lenard, *Ann. der Physik* [4] xvii. p. 197 (1905).

\dagger A. Becker, "Über die Diffusion leuchtender Metaldämpfe etc.," *Sitzungsberichte der Heidelberger Acad.* 1911, p. 16.

\ddagger E. N. da C. Andrade, "Some Experiments on the Electrical Behaviour of Metallic Vapours etc.," shortly to be published; and P. Lenard, "Über die Elektrizitätsleitung und Lichtemission etc.," *Sitzungsberichte der Heidelberger Acad.* 1911.

\S Cf. p. 869.

It is interesting to compare the positive carriers in the flame with the canal rays in a vacuum-tube, which are also charged atoms. In both cases we have the constant alternation of the positive and neutral states*. Similarly, we have found in flames a result already known for canal rays, namely, that there exist metallic atoms in flames, in comparatively small numbers, which are negatively charged. These are analogous to the negatively charged atoms found in canal rays by Wien†, whose energy was much less than that of the positive ones.

In the following we give a critical resumé of previous work on the subject. H. A. Wilson, in the work already

quoted (p. 865), obtained the value $60 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ as the

velocity of the positive metallic carrier, a value about 20 times as large as that found here for the carriers of the second kind. It is difficult, however, to determine exactly the smallest electric force which suffices to drive the carriers against the current of the flame-gases. Wilson measured the distribution of potential in the flame *without the presence of metallic salt*; he drew the potential curve and assumed that the smallest gradient here shown was sufficient to give the carriers the velocity of the flame. This smallest gradient lies, however, close by the positive upper electrode, in the place occupied by the metallic vapour in the experiment itself, and, since the carriers which come into account here proceed, as we think to have demonstrated, from the edge of the luminous vapour (*i. e.* in this case from the lower boundary of the vapour), and not from the upper electrode, this smallest gradient occurs in a region where the carriers are not necessarily driven down against the flame.

Moreau‡ measured the velocity of the positive carriers with two vertical electrodes, one standing in metal vapour, the other in free flame, and assumed that the potential gradient was approximately uniform between the electrodes. This is far from being true (as Lusby has shown, for instance, in work to be quoted immediately); it is not to be wondered

at that his value, $80 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$, does not agree with mine.

* W. Wien, *Ann. der Physik* [4] xxvii. 1903, p. 1025. The result was first obtained by Lenard for flames (*Ann. der Physik* [4] ix. 1902, p. 649) and found again for canal rays by Wien, *cf.* W. Wien, *Ann. der Physik* [4] xxx. p. 368 (1909).

† W. Wien, *Ann. der Physik* [4] xxxiii. p. 871 (1910).

‡ G. Moreau, *Ann. de Chimie et de Physique* [7] xxx. p. 39 (1903).
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E. Marx * has also measured the velocity of the positive carriers; he assumes, however, for the purpose of simplifying his calculations, that the whole ionization takes place in the body of the vapour, which is certainly incorrect when electrodes of glowing platinum stand in the metallic vapour, as in his experiments (*cf.* p. 874). His work is of great interest, but it is not adapted to give a correct value of the velocity.

When this work was practically completed a paper by Lusby † on the subject came to my notice, and a second paper by this author, including his previous results, has just been published ‡. He brings forward criticism essentially agreeing with that already given here against the previous work. He has made measurements with Wilson's original method, but has measured the gradient of potential in the flame from one electrode to the other, with the salt vapour present in the flame. At normal flame temperature the gradient in the vapour is very small, that in the free flame large: Lusby takes the gradient in the vapour as the one relevant, which seems to be erroneous as already

explained. With this he gets a value of $290 \frac{\text{cm.}}{\text{sec.}}$. As he has given the curve of potential for one case in his paper §, we can obtain the correct velocity according to the views here advanced. Taking the gradient in the flame just beneath the salt ($50 \frac{\text{volt}}{\text{cm.}}$), we get as the value of the velocity $4.1 \frac{\text{cm.}}{\text{sec.}}$, which agrees pretty well with our average value of $2.5 \frac{\text{cm.}}{\text{sec.}}$

His assumptions as to the gradient in question will account for a peculiar effect noticed by Lusby. He has made measurements at different temperatures, and finds that down to 1450° absolute the velocity is roughly proportional to $\sqrt{\theta}$, but that below this the values of the velocity are very much smaller than those given by $\sqrt{\theta}$. Now down to 1450° abs. the distribution of potential varies very little with the temperature, but below this the gradient in the vapour increases very much, and this is the main cause why

* E. Marx, *Ann. der Physik* [4] ii. p. 768 (1900).

† S. G. Lusby, *Proc. Cambridge Phil. Soc.* vol. xvi. part 1, p. 26 (1911).

‡ S. G. Lusby, *Phil. Mag.* Nov. 1911, p. 775.

§ *Proceedings Cambridge Phil. Soc. loc. cit.* p. 30.

the values given by Lusby are so much smaller than are given by $\sqrt{\theta}$. But in the pure flame the gradient decreases, though not very much, so that taking the gradient just below the salt vapour, the velocity per $\frac{\text{volt}}{\text{cm.}}$ would be relatively much larger than that given. Lusby does not give sufficient data to enable me to calculate the velocity according to the views here put forward *, but it looks possible that the $\sqrt{\theta}$ law holds roughly throughout the range.

To explain the large values obtained for the mobility, Lusby assumes that the positive carrier is always an atom of hydrogen. This is quite untenable, as it has been shown here experimentally that the carriers are metallic (§ 7). Particular attention is called to the fact that this was established for two metals (Sr and Na) and to the rough quantitative tests. Of course, none of this criticism of Lusby's paper affects his results, that the velocity is the same for all metals, except at very low temperatures: this result agrees with Lenard's formula for the mobility of a carrier of atomic size (see p. 871). His criticism of Lenard's early results on the deviation of the coloured streak in the electric field, based on the fact that chloroform removes the colour from the streak without much altering the conductivity (Smithells, Dawson, and Wilson) does not seem to me relevant. When glowing electrodes are in the vapour the liberation of an electron from the atom takes place mainly at the electrodes, and it is probable that while chlorine prevents the impact of metal atom against metal atom in the vapour liberating an electron, it does not stop this effect at the electrodes, and thus, while prohibiting "ionization" in the body of the vapour, does not much affect the conductivity †.

A short time ago H. A. Wilson ‡ published a paper containing a theoretical treatment of the carriers in flames containing metallic vapours. He makes Lenard's assumption, also made here, that the carrier is only positive during a fraction, f , of the time. Through the further assumption that the velocity of the carrier is inversely proportional to the square root of the atomic weight, he obtains values of f , and he further obtains similar values from the conductivity relations of the salts. The values agree so badly, that it is hard to believe that they furnish a proof of the correctness of the hypothesis. Wilson comes to the conclusion that the

* The potential curves are all reduced to 100 volts scale.

† See Lenard, "Über die Elektrizitätsleitung und Lichtemission metallhaltiger Flammen," *Sitzungsberichte der Heidelberger Acad.* 1911.

‡ H. A. Wilson, *Phil. Mag.* June 1911, p. 711.

positive carriers are metal atoms, as my experiments have shown, so far as their accuracy allows. But as the observations of the brightness of the Sr lines produced by the Sr deposited on the platinum strip cannot be carried out very exactly, we can only assert with certainty, that the carriers cannot possibly consist of more than two atoms. We have very good grounds for assuming that the light emission is effected by single atoms, on which assumption Lenard has based his researches on the subject*. The results of experiments on the diffusion of sodium vapour in the flame also indicate this†. It is, however, not absolutely certain that the faster carriers are centres of light emission: they are present in such relatively small numbers that they could not be expected to be visible.

§ 10. Conclusions.

(1) The positive carrier in a flame containing metal vapours is of metallic nature, very probably the metal atom.

(2) The positive carrier has two different definite velocities of migration in the electric field, according as it is present in the streak of metallic vapour or in the free flame: in both cases it alternates the positive with the neutral state. In the former case it is charged for about $\frac{1}{4.00}$ of the time, in the latter for $\frac{1}{6}$ of the time.

(3) For strontium the greater velocity of migration is $2.5 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$. There seems no reason to doubt the results of other experimenters, that the velocity is the same for different metals, which agrees with our theory. Hence this value probably gives the velocity of migration of an atom of any metal in the free flame.

(4) The presence of glowing platinum in the vapour causes the liberation of electrons from it in large quantities.

(5) There exist, besides the free electrons, negative carriers of the second kind which are metallic, in relatively small numbers. This gives an analogy with the canal rays.

This work was carried out in the Radiologisches Institut of the University of Heidelberg, to the Director of which, Professor P. Lenard, I am indebted for much help and encouragement. I also wish to express my thanks to Dr. Ramsauer for assistance and many valuable suggestions.

* P. Lenard, *Ann. der Physik* [4] xvii. p. 198 (1905).

† A. Becker, "Über die Diffusion leuchtender Metaldämpfe," *Heidelberger Acad.* 1911.