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THE DROP OF POTENTIAL AT THE CATHODE IN FLAMES.

1. A THESIS

Presented to the Department of Physics of The Rice Institute
in partial fulfillment of the requirements for the degree of
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by

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2. Boucher, E.P. The measurement of the resonance, radiation, and ionization potentials of several gases and vapors. (Reprinted from THE PHYSICAL REVIEW, n.s., v. XIX, no. 3, March, 1922)
3. Boucher, E.P. The mobility of negative ions in gasoline, hydrogen, and hydrogen-chlorine flames. (Reprinted from THE PHYSICAL REVIEW, pp. 807-819, v. 26, no. 6, December, 1925)

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7. A reprint from the Physical Review, entitled "The Mobility of Negative Ions in Gasoline, Hydrogen, and Hydrogen-chlorine Flames", by Paul Edward Boucher.	

ABSTRACT.

The theory as given by J.J.Thomson for the drop of potential at plane electrodes has been modified by allowing for recombination in the layer and a similar theory for cylindrical electrodes has been worked out. The equation for plane cathodes is $V_2 = \left(\frac{32\pi i}{75k_1} \right)^{\frac{1}{2}} x_2^{\frac{3}{2}}$, and for cylindrical cathodes is

$$V_2 = \left(\frac{2i}{3k_1(r_2^2 - r_0^2)} \right)^{\frac{1}{2}} \left[r_2^3 \log \left(\frac{r_2 + \sqrt{r_2^2 - r_0^2}}{r_0} \right) - \frac{r_2^3}{2} (r_2^2 - r_0^2)^{-\frac{1}{2}} - \frac{(r_2^2 - r_0^2)^{\frac{3}{2}}}{3} \right],$$

where V_2 = the potential drop across the sheath, i = the current density, x_2 = the sheath thickness at the plane cathode, r_0 = the radius of the cylindrical cathode, r_2 = the radius of the cylindrical sheath about the cathode, and k_1 = the velocity of the positive ions for a gradient of 1. volt per cm. The experimental results for platinum electrodes immersed in pure and NaCl flames agree well with the theoretical equations given. It is found that the drop in potential at the cathode occurs in a sheath of uniform thickness, which completely surrounds the electrode. By plotting the gas potential at various points in the flame against distance from the cathode it is possible to estimate the thickness of the sheath. Over 95% of the potential drop takes place across the sheath at the cathode provided it is of clean platinum. If the cathode is not clean electrons are emitted which partially neutralize the accumulation of positive ions and thus reduce the sheath thickness. By measuring V_2 , i , x_2 or r_0 and r_2 , and making

the proper substitutions in the above equations, the mobility k , of the positive ions is found to average 12.4 for a pure flame and 8.1 cms per sec. for one volt per cm for a NaCl flame.

A study of the characteristic current-voltage curve for a wire probe in a flame makes it possible to measure the voltage correction to be applied to the measured probe potential in order to obtain the true gas potential adjacent to the test probe. The correction is of the order of +1. volts.

It is found that the current density at the surface of the cylindrical sheath is constant for any given flame conditions, and size of cathode. Thus one can measure the current density existing in the small uniform gradient just outside the sheath. The current density at the sheath surface in a pure flame varies from 1. to 2.5 microamperes and for the NaCl flame from 5. to 11. microamperes.

1. INTRODUCTION.

When more ions of one kind than the other are present in a given space, an electrostatic effect occurs which modifies the potential distribution. The effect is well known in the conduction of electricity through gases at low pressures and in flames. In flames the velocity of the positive ion is much less than that of the negative ions which are mostly electrons, and as a consequence an accumulation of slow moving positive ions gathers about the cathode which produces a large cathode potential drop, especially in the case of clean platinum electrodes. These regions of large potential gradient near the electrodes were called by J.J. Thomson layers or sheaths.¹ Thomson has worked out a theory of the current between two parallel plane electrodes with uniformly ionized gas between them. His equation, $V = Ai + Bdi$,² where V = potential difference between the electrodes, A and B are constants, i = current, d = distance between the electrodes, has been successfully applied to the conduction of electricity in flames by H.A. Wilson.² The term Ai ² represents the drop of potential across the layer at the cathode, which is proportional to the square of the current.

³
In a paper on "Positive Ion Currents in the Positive Column of the Mercury Arc", Langmuir describes a sheath theory which successfully explains the flow of current in mercury vapor arcs. Under certain conditions the thickness of the positive

1. Thomson, "Conduction of Electricity Through Gases". Pg. 64.

2. Wilson, Phil. Mag. 10, 476, 1905.

3. Langmuir, Gen. El. Rev. 26, 731, 1923.

ion sheath can be measured, and the experimental values check well with those calculated from the space charge equation.

It is a well known fact that the potential of a gas as determined by the exploring electrode method will not be strictly correct when inequalities in the velocities of the plus and minus ions exist. For example, if the potential of the exploring electrode be gradually raised, electrons due to their higher velocity will reach the electrode even while the electrode potential is still negative with respect to the gas. It is thus possible for equal numbers of plus and minus ions to reach the electrode although its potential is still negative with respect to the adjacent gas. Under these conditions if one pair of quadrants of an electrometer is connected to a test electrode, and the other pair to either the cathode or anode in an ionized gas, the potential of the test electrode at any point between the cathode and anode will not be the same as that of the adjacent gas.

It occurred to the writer that a sheath theory might be applied to explain the flow of current between electrodes immersed in a flame. ¹ J.J. Thomson's theory for the conduction of electricity between two infinite parallel metal plates immersed in an ionized gas has been modified to fit the experimental conditions, and a corresponding theory developed for cylindrical electrodes. Successful experimental tests confirming the sheath theory for both plane and cylindrical cathodes have been carried

¹. Thomson, Loc. cit. Pg. 64.

out. The potentiometer method with a galvanometer as the indicating device was used to measure the potential gradient, from which the sheath thickness was deduced. By taking the current-voltage relation of the probe electrode it is possible to measure the correction to be applied to the probe potential in order to obtain the true gas potential.

2.THEORY.

It is well known that the potential gradient between two clean platinum electrodes in a flame is far from uniform. A large part of the potential drop occurs at the cathode and this has been called the cathode drop of potential. The writer has measured potential gradients in flames in which more than 95% of the potential drop occurs close to the cathode. The explanation offered for this large voltage drop is that the electrons or negative ions travel many times faster than the positive ions¹. The mobility k_1 for positive ions in a bunsen flame is about 1. to 2. cms per volt, while k_2 for the electrons varies from 2000. to 3000. cms per volt. Thus the electrons are immediately driven away from the cathode, while the positive ions because of their slow motion accumulate about the cathode, forming a positive space charge which limits the flow of current just as the space charge effect limits the electron current from a hot filament in a vacuum tube. Experiments described later show that for electrodes immersed in a flame a layer of positive ions of uniform thickness exists on both sides of a plane cathode and completely surrounds a cylindrical cathode. Likewise an electron sheath of comparatively small thickness exists about the anode.

For deriving an equation for the flow of current between infinite parallel plane electrodes in an ionized gas² Thomson supposes that the velocities of the ions are proportional to the electric intensity at any point, and also that near the positive

1.H.A.Wilson, Phil.Trans.,A,vol.192,1899.

2.Thomson, Loc.cit. Pg. 64.

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and negative plates there are layers in which recombination may be neglected.

First let us consider the case for large parallel plane electrodes. Experiment shows that electron emission may be neglected for clean platinum electrodes. Let n_1 and n_2 be the number of positive ions and electrons per unit volume at any point at a distance x measured from the anode surface. Let q be the number of positive ions or electrons produced in unit time per unit volume at this point. Let X = the electric intensity, k_1 = the velocity of the positive ions due to unit electric field, k_2 = the velocity of the electrons due to unit electric field, x_1 = the electron sheath thickness at the anode, x_2 = the positive ion sheath thickness at the cathode, α = the coefficient of recombination, e = the charge on an ion, and i = the current per square cm of electrode surface. The fundamental equations are (as given in Thomson's book "Conduction of Electricity Through Gases, Pg. 64)

$$\frac{dX}{dx} = 4\pi(n_1 - n_2)e \quad (1)$$

$$n_1 e k_1 X + n_2 e k_2 X = i \quad (2)$$

$$\frac{d(n_1 k_1 X)}{dx} = q - \alpha n_1 n_2 \quad (3)$$

$$\frac{d(n_2 k_2 X)}{dx} = -(q - \alpha n_1 n_2) \quad (4)$$

Differentiating Eq.(1) with respect to x and making use of Eqs.(3) and (4) we obtain

$$\frac{d^2 X^2}{dx^2} = 8\pi e (q - \alpha n_1 n_2) \left(\frac{1}{k_1} + \frac{1}{k_2} \right) \quad (5)$$

Thomson assumes that recombination is zero in the layer, but

perhaps a more satisfactory assumption for flame conditions may be arrived at as follows. At the anode surface where $x = 0$, all the current must be carried by electrons, and since the electric field drives all positive ions away from the anode surface, $n_1 = 0$ and hence $q - \alpha n_1 n_2 = q$. But at the sheath surface where the electric intensity is small compared with that inside, $n_1 = n_2$, and hence at $x = x_1$, $\frac{dX}{dx} = 0$ and therefore $q - \alpha n_1 n_2 = 0$. Equation (2) with $n_1 = n_2$ shows that the fraction of the current carried by either positive ions or electrons at the sheath surface is proportional to their respective mobilities. All the positive ions which carry current at the sheath surface are produced in the layer and hence the positive ion current increases from zero at $x = 0$ to $n_1 e k_1 X$ at $x = x_1$. The same considerations must hold at the cathode, where the current at the cathode surface must be carried entirely by positive ions, and the electron current in the opposite direction increases from zero at the cathode surface to $n_2 e k_2 X$ at the positive ion sheath surface. Furthermore the electrons which carry current at the sheath surface must be produced in this layer. We can therefore assume as an approximation consistent with the above that

$$q - \alpha n_1 n_2 = q \left(1 - \frac{x}{x_1} \right).$$

This gives $q - \alpha n_1 n_2 = q$ at $x = 0$, and $= 0$ at $x = x_1$. Thus recombination increases from zero at the electrode surface to its value at the sheath surface instead of being zero throughout the layer. Eq. (5) then becomes

$$\frac{d^2 X^2}{dx^2} = 8\pi e q \left(1 - \frac{x}{x_1} \right) \left(\frac{1}{k_1} + \frac{1}{k_2} \right).$$

We assume that the quantity q is constant for any given flame conditions, and so it can be removed from the above equation as follows. The number of the positive ions produced in the layer which carry the positive ion current at the sheath surface will be in accordance with our assumption equal to

$$\int_0^{X_0} (q - \alpha n_1 n_2) dx = \int_0^{X_0} q \left(1 - \frac{x}{X_0}\right) dx = n k_1 X_0,$$

where $n_1 = n_2$ and X_0 = the electric intensity in the uniform gradient and therefore at the sheath surface. Integrating this we obtain

$$\frac{q X_0}{2} = n k_1 X_0 = \frac{1 k_1}{e(k_1 + k_2)},$$

which is the number of positive ions which carry the current through unit area at the sheath surface. Then

$$8\pi e q = \frac{16\pi i k_1}{X_0(k_1 + k_2)}.$$

Making this substitution we have

$$\frac{d^2 X^2}{dx^2} = \frac{16\pi i}{k_2 X_0} \left(1 - \frac{x}{X_0}\right).$$

Integrating this with respect to x we get

$$\frac{dX^2}{dx} = \frac{16\pi i}{k_2 X_0} \left(x - \frac{x^2}{2X_0}\right) + C_1. \quad (6)$$

At $x = X_0$, we have $n_1 = n_2$, so that Eq. (1) becomes

$$\frac{dX^2}{dx} = 8\pi e(n_1 X - n_2 X) = 0.$$

Hence the constant becomes

$$C_1 = - \frac{16\pi i}{k_2 X_0} \left(\frac{X_0}{2}\right).$$

Replacing the constant C_1 in (6) with its value and integrating

we obtain $X^2 = \frac{16\pi i}{k_2 X_0} \left(\frac{x^2}{2} - \frac{x^3}{6X_0} - \frac{XX_0}{2}\right) + C_2.$

To determine C_2 we make use of the condition that at $x = x_1$, the electric intensity $X = X_0$, and

$$C_2 = X_0^2 + \frac{16\pi i}{k_2 x_1} \left(\frac{x_1^2}{6} \right).$$

Then substituting the value of C_2 and extracting the square root,

$$X = \sqrt{\frac{16\pi i}{6k_2 x_1} (x_1 - x)^3 + X_0^2} \quad (7)$$

The potential drop V_1 across the electron sheath is

$$\int_0^{x_1} X dx ;$$

Substituting the value of X given by Eq.(7), neglecting X_0 , since the electric intensity outside of the sheath is small compared to that inside, and integrating we have

$$V_1 = \sqrt{\frac{32\pi i}{75k_2}} x_1^{\frac{3}{2}}. \quad (8)$$

Solving for k_2 , the mobility of the electrons, we get

$$k_2 = \frac{32\pi i x_1^3}{75 V_1^2} \text{ cms per sec. per unit gradient in e.s.u. units.} \quad (9)$$

Dividing this by 300. will give k_2 in cms/sec. for one volt/cm.

Similarly the drop in potential across the positive ion sheath at the cathode is

$$V_2 = \sqrt{\frac{32\pi i}{75k_1}} x_2^{\frac{3}{2}} \quad (10)$$

and the mobility of the positive ions becomes

$$k_1 = \frac{32\pi i x_2^3}{75 V_2^2}. \quad (11)$$

Thus by measuring the current density, the thickness of and the potential drop across either sheath, we can calculate the velocities per unit gradient of either the positive ions or electrons.

The same assumptions used with plane electrodes can be applied to cylindrical electrodes. Let us consider the electron sheath about a long wire of small diameter as anode. With proper change of signs and symbols the theory will also apply to the positive ion sheath about the cathode. In addition to the symbols already defined, let r = distance measured normally from center of electrode, r_0 = radius of either anode or cathode, r_1 = radius of electron sheath about the anode, r_2 = radius of positive ion sheath about the cathode, and i = current per cm length of electrode.

The fundamental equations when transformed into cylindrical coordinates become

$$\frac{d(Xr)}{dr} = 4\pi er(n_1 - n_2) \quad (12)$$

$$2\pi rn_1 k_1 X e + 2\pi rn_2 k_2 X e = i \quad (13)$$

$$\frac{d(2\pi rn_1 k_1 X)}{dr} = (q - \alpha n_1 n_2) 2\pi r \quad (14)$$

$$\frac{d(2\pi rn_2 k_2 X)}{dr} = -(q - \alpha n_1 n_2) 2\pi r \quad (15)$$

Multiplying Eq.(12) by X , differentiating it with respect to r , and making use of Eqs.(14) and (15) we find that

$$\frac{d}{dr} \left(X \frac{d(Xr)}{dr} \right) = 4\pi er(q - \alpha n_1 n_2) \left(\frac{1}{k_1} + \frac{1}{k_2} \right). \quad (16)$$

As in the case of plane electrodes, the current at the anode surface must be carried entirely by electrons, so that $n_1 = 0$ at $r = r_0$, and $q - \alpha n_1 n_2 = q$. At the surface of the electron sheath where the electric intensity is small, $n_1 = n_2$, and therefore at $r = r_1$, we have $q - \alpha n_1 n_2 = 0$. A reasonable

assumption which fulfills these conditions is to let

$$q = \alpha n_1 n_2 = q \left(\frac{r_1^2 - r^2}{r_1^2 - r_0^2} \right).$$

Eq. (16) then becomes

$$\frac{d}{dr} \left(\frac{Xd(Xr)}{dr} \right) = 4\pi e q \left(\frac{r_1^2 - r^2}{r_1^2 - r_0^2} \right) \left(\frac{1}{k_1} + \frac{1}{k_2} \right) \quad (17)$$

We can remove the constant q by making use of the above assumption that the number of positive ions produced in the electron sheath available to carry current at the sheath surface will be

$$\int_{r_0}^{r_1} (q = \alpha n_1 n_2) 2\pi r dr = \int_{r_0}^{r_1} q \left(\frac{r_1^2 - r^2}{r_1^2 - r_0^2} \right) 2\pi r dr.$$

Integrating this and setting it equal to the number of positive ions passing through the sheath surface, we have

$$\frac{2\pi q}{r_1^2 - r_0^2} \left(\frac{r_1^4 - 2r_0^2 r_1^2 + r^4}{4} \right) = \frac{ik_1}{e(k_1 + k_2)}$$

$$\text{or } 4\pi q e = \frac{8k_1 i}{(k_1 + k_2) (r_1^2 - r_0^2)}.$$

Making this substituting, Eq. (17) becomes

$$\frac{d}{dr} \left(\frac{Xd(Xr)}{dr} \right) = \frac{8i}{k_2} \left(\frac{r_1^2 - r^2}{r_1^2 - r_0^2} \right).$$

Integrating this we have

$$\frac{Xd(Xr)}{dr} = \frac{8i}{k_2 (r_1^2 - r_0^2)} \left(\frac{r^2 r_1^2}{2} - \frac{r^4}{4} \right) + C_1.$$

To determine the constant C_1 , we know that $n_1 = n_2$ at $r = r_1$ and from Eq. (12) we get

$$\frac{Xd(Xr)}{dr} = 4\pi e r (n_1 X - n_2 X) = 0.$$

Therefore $C_1 = - \frac{8i}{k_2 (r_1^2 - r_0^2)} \left(\frac{r_1^4}{4} \right)$, and

$$\frac{d(Xr)^2}{dr} = \frac{16i}{k_2 (r_1^2 - r_0^2)} \left(\frac{r^3 r_1^2}{2} - \frac{r^5}{4} - \frac{r r_1^4}{4} \right).$$

Integrating this we find

$$(Xr)^2 = \frac{21 (3r^4 r_1^2 - r^6 - 3r^2 r_1^4)}{3k_2 (r_1^2 - r_0^2)^2} + C_2 .$$

At $r = r_1$, the electric intensity $X = X_0$, the value at the surface of the sheath.

$$\text{Therefore } C_2 = X_0^2 r_1^2 + \frac{21 r_1^6}{3k_2 (r_1^2 - r_0^2)^2} ,$$

and neglecting X_0 and taking the square root, we obtain

$$X = \sqrt{\frac{21}{3k_2 (r_1^2 - r_0^2)^2}} \frac{(r_1^2 - r^2)^{\frac{3}{2}}}{r} .$$

The potential drop V_1 across the cylindrical electron sheath is

$$\int_{r_0}^{r_1} X dr ,$$

and substituting the value of X and integrating between the limits r_1 and r_0 ,

$$V_1 = \sqrt{\frac{21}{3k_2 (r_1^2 - r_0^2)^2}} \left[r_1^3 \log \left(\frac{r_1 + \sqrt{r_1^2 - r_0^2}}{r_0} \right) - r_1^2 \sqrt{r_1^2 - r_0^2} - \frac{(r_1^2 - r_0^2)^{\frac{3}{2}}}{3} \right] \quad (18)$$

Solving for k_2 , the mobility of the electrons, we have

$$k_2 = \frac{21 \left[r_1^3 \log \left(\frac{r_1 + \sqrt{r_1^2 - r_0^2}}{r_0} \right) - r_1^2 \sqrt{r_1^2 - r_0^2} - \frac{(r_1^2 - r_0^2)^{\frac{3}{2}}}{3} \right]^2}{3 V_1^2 (r_1^2 - r_0^2)^2} \quad (19)$$

In a similar manner the drop in potential across the positive ion sheath about the cathode becomes

$$V_2 = \sqrt{\frac{21}{3k_1 (r_2^2 - r_0^2)^2}} \left[r_2^3 \log \left(\frac{r_2 + \sqrt{r_2^2 - r_0^2}}{r_0} \right) - r_2^2 \sqrt{r_2^2 - r_0^2} - \frac{(r_2^2 - r_0^2)^{\frac{3}{2}}}{3} \right] \quad (20)$$

and the mobility of the positive ion becomes

$$k_1 = \frac{21 \left[r_2^3 \log \left(\frac{r_2 + \sqrt{r_2^2 - r_0^2}}{r_0} \right) - r_2^2 \sqrt{r_2^2 - r_0^2} - \frac{(r_2^2 - r_0^2)^{\frac{3}{2}}}{3} \right]^2}{3 V_2^2 (r_2^2 - r_0^2)^2} \quad (21)$$

In the uniform gradient outside either sheath practically all the current is carried by the electrons and because of their high mobility only a small fraction of the applied voltage is

required to cause the current to flow. The experimental results described below agree well with the theoretical equations for the sheath at the cathode.

3. EXPERIMENTAL PROCEEDURE.

Those who have worked with flames are familiar with the difficulties in maintaining steady flame conditions for any length of time. Variations in gas pressure and quality of gas are the two prime causes of flame instability. In these experiments the city gas supply was found quite satisfactory so far as constant quality was concerned, in fact much superior to gasoline gas. A fairly constant gas pressure was maintained by connecting a gasometer in the gas line and placing sufficient weights on the movable drum to keep it stationary for any size flame. In this way any small variations in gas pressure were absorbed by the floating drum of the gasometer. The steadiness of the flame was frequently checked by noting the value of the current between two electrodes maintained at some constant potential difference. Any large variations in current were eliminated by slight adjustment of the control valves in the gas line. It was found that with these precautions the current variations could be limited to less than 5% for periods of two hours or more.

For the electrodes arranged one above the other, the vertical flame of a Meker burner was found suitable. For the horizontal arrangement of electrodes, a satisfactory burner was made by mounting a number of small quartz tubes, each about 3 mm inside diameter and 2.5 cm long, in holes drilled in a row along the length of a brass tube 2 cm in diameter. This burner will give a flame about 10. cm long, 1.4 cm thick,

and any height desirable. The electrodes were supported a short distance above the blue cones in the flame. Compressed air was admitted to produce a well oxidized flame, the cones being about 2 cms high. Solutions of various salts could be sprayed into the flame as desired by means of a Gouy sprayer connected in the air line.

In studying positive ions in a flame electron emission from the cathode must be eliminated so far as possible. At ordinary temperatures in a bunsen flame this is small for clean platinum. It was found that if clean platinum wires or foil were used for the cathode, so that the current was limited by the positive ion sheath about it, that it mattered little what the nature or size of the anode was. In case of the vertical flame the Meker burner was used as the anode.

Two clean platinum cylinders or plates were used as the electrodes in the horizontal flame. In the sheath theory for cylindrical electrodes the radius of the cylinder occurs in the formula for the flow of current. To test this equation for various cylinder diameters platinum wire of sizes No.26, 20, and 12 were procured. Cylinders of larger diameter were made of platinum foil. Thus the cylinder diameters tested ranged from .0406 cms to .60 cms, a maximum ratio of one to fifteen.

The method of taking data for the current-voltage curves was to connect the two electrodes in series with a galvanometer connected to an Ayrton shunt, and a slide wire rheostat of

3200. ohms resistance. A B battery of suitable voltage was connected across the high resistance, and thus by making one connection to the movable contact it was possible to vary the applied voltage in as small steps as desired. Suitable means were provided for reversing the direction of the applied voltage, this voltage being read by a Weston voltmeter.

The procedure for obtaining data by which the potential versus distance curves were plotted requires more detailed explanation. A diagram of the circuit used is shown in Fig.1. This shows the horizontal arrangement of electrodes. The exploring electrode, used for measuring the potential at various points between the two current electrodes, consisted of No.26 platinum wire. It is desirable to use a probe wire of as small radius as possible, but a smaller size will sag after a short time in a flame. The probe wire, welded to a piece of No.18 copper wire, was mounted on the movable carriage of a micrometer microscope, the microscope being removed. The screw of the micrometer scale was oriented so that its axis was parallel to the flow of current between the electrodes. Thus the position of the probe at any point with respect to the electrodes could be ascertained and the distance between the electrodes easily measured. The high resistance slide wire rheostat R in conjunction with the B battery formed a potentiometer device by means of which the probe could be maintained at any potential with respect to the cathode.

With the potential of the probe the same as that of

FIGURE I.

the cathode, $V_2 = 0$, positive ions will flow to it. As the probe is moved from the cathode to the anode the potential of the gas about it increases, and the probe current increases. By increasing V_2 , the potential of the probe with respect to the cathode, the probe current can be reduced to zero, at which point the probe would be at the same potential as the adjacent gas, if the velocities of the positive and negative ions were equal. In reality since the velocities are quite different, the voltage read when the galvanometer indicates zero probe current must have a small correction applied to it to give the true gas potential. This correction is of the order of one volt and must be determined by a preliminary measurement. This is more fully discussed in the Experimental Results. Thus the potential of the gas at various points between and outside the current electrodes can be quickly obtained, and by plotting probe voltage against distance from the anode we have a graph which shows how the gas potential varies as we go from one electrode to the other. If desired it is easy to obtain the potential gradient or electric intensity at any point from the graph.

The above method of obtaining potential gradient data affords a method of measuring the thickness of the positive ion sheath about the cathode. By means of the probe it is easy to show that the layer or sheath surrounds the cathode and furthermore that it consists almost entirely of positive ions and uncharged molecules and atoms.

In making measurements of potential inside the sheath,

one must be careful in noting the exact voltage at which the probe current is reduced to zero, for a further increase in voltage produces a very small increase in current, until the probe voltage becomes equal or greater than the potential at the edge of the sheath. When the probe voltage is greater than this, electrons can enter the sheath and if the probe is not too far inside the sheath surface the current will increase rapidly. If the probe is as much as a $\frac{1}{2}$ cm or more inside a thick sheath, its potential will have to be much greater than that of the sheath surface, for at lower potentials the electrons pulled into the sheath are lost by recombination before they reach the probe. This test shows that there are comparatively few free electrons or negative ions in the positive ion sheath especially near the cathode, and proves that the sheath exists not only theoretically but in reality.

As has already been stated the potential drop across the positive ion sheath is much greater than that outside it. So that to obtain data for testing the sheath theory we may choose that point on the potential versus distance graph where it begins to show a sharp change in curvature as the edge of the sheath. The sheath thickness is taken as the distance from the edge of the sheath to the center of the cathode. This distance can be measured to within 10% easily, but probably not much greater accuracy should be claimed because of the difficulty in choosing the point at which the density of positive ions increases appreciably over that of the electrons.

4. EXPERIMENTAL RESULTS.

In studying positive ions in a flame precautions must be taken that the platinum electrodes are clean. That it is necessary to reduce electron emission to a minimum may be seen from Fig.2. Curve No.1 is the characteristic current-voltage curve for a clean platinum electrode connected in series with a galvanometer, a variable potential and the burner as the other electrode. Curve No.2 represents the relation between current and voltage for a similar electrode covered with an oxide coat of burnt sealing wax. For positive potentials the current to these two electrodes, consisting of ^{electrons} ~~negative ions~~, is about the same. That is, the cathode drop at the burner limits the current in both cases. Electron emission cannot occur for positive potentials. The current becomes zero at about minus 1. volt for both clean and oxide coated electrodes, which shows that the energy of the emitted electrons due to the oxide coat is not sufficient to appreciably change the potential of the oxide coated electrode from that of the clean electrode for zero current. For negative potentials the current is much larger for the oxide coated electrode than the other. Oxide coated electrodes are well known as copious emitters of electrons, and in this case the larger part of the current consists in the emission of electrons which neutralize the cathode drop of potential. It is common practice where a uniform gradient through the flame is desired to coat the cathode with burnt

Every relative proximate formed have a single word as antecedent

FIGURE 2.

sealing wax or other oxide. Thus when a clean platinum electrode is made the cathode we have a comparatively small current to that when it is made the anode, provided the current is not limited by the other electrode. The thickness of the sheath of positive ions about the cathode to be described later on is a further proof that electron emission is negligible for clean platinum in a bunsen flame.

To test Thomson's theory for the flow of current in a flame, two parallel plane electrodes were supported 3. cms apart in the horizontal flame. Values of current were recorded for various applied voltages. Fig.3 shows two curves obtained by plotting current versus voltage, curve No.1 being for a pure flame, and No.2 for a NaCl flame. To determine the constants A and B in the equation $V = Ai^2 + Bi$, several pairs of values were scaled from the graphs which substituted for V and i gave a set of simultaneous equations from which A and B were solved. The various values of A and B thus obtained agreed well among themselves. Taking the average of the values of A and B, the equations which approximately represent curves No.s 1 and 2 are $V = 85.6 i^2 - 12.5 i$ and $V = 15.7 i^2 + 5.22 i$. Thomson's theory does not take into consideration that the layer about the cathode in a flame exists on both sides of the plane surface. This introduces no difficulty however for since the layers on both sides are of the same thickness, we may imagine the electrode to have twice the area with the layer on one side only.

FIGURE 3.

Next let us make use of the sheath theory to give a physical explanation of the flow of current to a clean platinum probe wire in a bunsen flame. Starting with a cylindrical wire charged to a potential of -5. volts (see Fig.2), there will be a layer about the electrode from which many of the electrons, because of their high mobility, will be removed as fast as produced, thus leaving in the layer an excess of positive ions; so that we may say that the electrode is surrounded by a cylindrical sheath of positive ions. The potential drop across this sheath is the well known cathode drop, and experiments show that it is a large fraction of the total drop between the electrodes. Inside the sheath the state of affairs is such that enough positive ions are produced to carry all the current at the cathode surface, and enough electrons are produced to carry practically all the current at the sheath surface. The number of positive ions entering the sheath from the outside will be small compared with the electrons passing out, because of their comparatively small mobility. As the negative potential of the probe wire is reduced the current and the sheath thickness both decrease. The electrons in a flame have velocities, due to the flame temperature, corresponding to about 1. volt, as can easily be shown by means of an electrometer and a pair of electrodes. So that when the negative potential is reduced to about -1. volt, the electric field will not be strong enough to remove all electrons. As a consequence recombination with the positive ions increases and even some of the faster electrons may reach the

cathode against the electric field, thus causing the positive ion sheath to decrease more rapidly in size, and we get a more rapid change in curvature of the graph. When equal numbers of plus and minus ions reach the cathode, the galvanometer indicates zero current although the electrode is still negative with respect to the adjacent flame gases and the burner used as anode. A further decrease in negative potential causes the current to reverse direction because of the excess of electrons over positive ions which reach the cathode against the electric field. If a Maxwellian distribution of velocities exists among the electrons, then the electron current may be represented by the ¹ equation

$$I = N_0 e \sqrt{\frac{eV}{3m}} \epsilon^{\frac{-3(V_0 - V)}{2V}}$$

I = current density, N_0 = electrons per unit volume, e = charge on one ion, V = average velocity of electrons expressed in corresponding volts, $V_0 - V$ = potential drop across the sheath, $\bar{V}$ = electron velocity in volts, and ϵ = Napierian base of logarithms. Above the zero current axis the positive ions in the sheath which reach the cathode are outnumbered by the faster electrons striking it and the current through the galvanometer reverses direction. If $\log I$ is plotted against $V_0 - V$ it should give a straight line. In Fig. 4 two graphs are shown in which current versus potential are plotted on logarithmic paper. Curve No.1 is for a NaCl flame and No.2 for a pure flame. Changes in curvature in the curves are easily seen below the x axis where the electrons not removed by the electric field

FIGURE 4.

are combining with the positive ions or actually reaching the cathode against the electric field. "Kinks" or "breaks" in the curves are seen on the y axis where the potential difference between the electrodes is zero. It will be noted that the curves between the changes of curvature and the "breaks" are practically straight lines. The positive ion sheath continues to decrease in size until the electrode potential is zero. Any small positive potential will cause the growth of an electron sheath about the electrode in place of the positive ion sheath. Since the mobility of the electrons is much greater than that of the positive ions, we may expect the rate of growth of the two sheaths to be different, and therefore a "break" in the log I versus V curve is to be expected when the positive sheath disappears and the electron sheath begins to grow. The "breaks" occur at zero volts and it seems reasonable to suppose that at this point the electrode and the adjacent flame gases are at the same potential, as a slight increase in potential will repel all positive ions for, since their velocities are small, they cannot move against an appreciable electric field.

In curve No.1 the current is zero for a potential of -.41 volts, and for a pure flame, curve No.2, at -.75 volts. In other words an insulated electrode immersed in a flame will acquire a negative potential just sufficient to reflect all negative ions having an average velocity corresponding to this potential. Note that the electrode takes up a higher negative potential in a pure flame than in a NaCl flame, the reason being that there are more available plus ions in the latter to

neutralize the high speed electrons. In reading the potential of a gas by the probe and electrometer method when the probe current is zero, it is evident that a correction of $+.4$ to $+1$. volt should be applied to give the true potential of the adjacent gas. This of course will depend on the gas mixture admitted to the burner and the locations of the electrodes in the flame. In these experiments it was found more convenient to determine the potential at which the galvanometer current to the probe was zero and then when desirable apply the proper correction. It will be seen later that the potential as determined by this method inside a positive ion sheath requires no correction.

According to the theory the density n_2 of the electrons increases from zero at the cathode surface to the normal value at the sheath surface. The flow of current to the probe for various potentials applied between it and the cathode throws light on this question. In Fig. 5 are shown curves which give the relation between probe current and voltage applied to it for various positions inside a sheath of constant thickness. The potential difference between the current electrodes was maintained constant at 88.6 volts. D = the distance of probe from the cathode. Curve No. 1 shows the current-voltage relation for the probe placed .1 cm from the plane cathode. With the probe potential with respect to the cathode equal to zero, the adjacent gas is at a positive potential and a flow of positive ions to the probe takes place. As the potential of the probe increases the positive ion current decreases until at +18. volts the

FIGURE 5.

probe current becomes zero. This is taken as the true potential of the gas at a point distant .1 cm from the cathode. It seems reasonable that the correction of $+.75$ volts for a pure flame ought not to be applied to obtain the correct gas potential, because there are not sufficient free electrons present in the sheath to appreciably change the probe potential. A further increase of probe potential gives a small increase in electron current which approaches a saturation value at 80. volts. This current remains constant up to 140. volts. The reason for this is that although the probe potential is larger than the potential drop across the sheath, yet the probe can only gather the few electrons produced in a limited region adjacent to it and any additional electrons that may be pulled into the sheath from the outside will be lost by recombining with the positive ions before they reach the probe. This indicates that the strong electric field plays the important part in rapidly removing the electrons from the positive ion sheath, and that the electron density near the cathode surface is small compared with the positive ion density. In curve No.3 the probe current becomes zero at 67.5 volts and this is the potential of the flame at a point .5 cm distant from the cathode. A further increase of probe potential gives a small increase in current until the potential attains 90. volts, at which potential electrons from outside the sheath begin to reach the probe and the current increases rapidly. Curve No.6 shows the condition existing at the edge of the sheath which is 1. cm from the cathode. The probe current becomes zero at 88.5 volts, and a fraction of a

volt above this is sufficient to produce a large increase in electron current to the probe. This is what one would expect at the edge of the sheath for the probe is in a region where there are equal densities of positive ions and electrons.

Thus we see that the electron density increases from zero at the cathode surface to $n_2 = n_1$ at the sheath surface. It is proper at the edge of the sheath to apply the correction of $+.75$ volts to the probe potential to obtain the true gas potential because the probe is now exposed to a large number of electrons having average velocities corresponding to $.75$ volts. The true potential of the gas at this point would therefore be $88.5 + .75 = 89.25$ volts. In plotting the potential vs distance data this correction has been neglected because it is much less than the sum of the other experimental errors.

In the vertical flame the sheath is thicker above the cathode than below. Some measurements showed that the sheath was as much as 50% thicker above than below the electrode, the reason being that the positive ions are carried up by the motion of the flame gases. It was found that better results in testing the sheath theory were obtained by using data obtained with the horizontal arrangement of electrodes.

Fig. 6 shows the results of plotting two sets of data for plane electrodes, one set for a pure flame and the other for a NaCl flame. The current electrodes were 3. cms apart. The voltage between the current electrodes was kept constant while the data for each curve was obtained. The points plotted are the voltages as read from the voltmeter V_2 when the probe-cathode

FIGURE 6.

current was just zero. The cathode is indicated by the heavy vertical line. For the highest voltage applied to the current electrodes the potential has been plotted for points on both sides of the cathode. This proves the existence of the positive ion sheath on both sides of the cathode and furthermore that in a horizontal arrangement of electrodes the sheath has the same thickness on either side. For example in the case of the pure flame the sheath thickness measured from the cathode towards the anode is 1.03 cms and the opposite direction 1.0 cms. For the NaCl flame, x_2 (= sheath thickness) equals .80 and .78 cms for the same cathode at a higher potential difference. The spraying of NaCl into the flame increases the density of positive and negative ions which causes a 30 to 50% decrease in sheath thickness. It will be noted that the change in curvature of the potential vs distance curve at the edge of the sheath is quite abrupt, indicating that the velocities of the positive ions and the electrons are very different. Outside the sheath, the curve is almost horizontal which means that the potential gradient from the edge of the sheath to the anode is small.

The method of measuring was not sensitive enough to measure accurately the potential drop and the electron sheath thickness at the anode. According to the theory, $k_1^2/k_2^2 = V_1/V_2$, and if $k_1 = 10$. cms per sec. for one volt per cm for positive ions, $k_2 = 3000$. cms per sec. for one volt per cm for electrons, $V_2 = 88$. volts = the potential drop across the positive ion sheath, then $V_1 = .00098$ volts = the potential drop across the electron sheath.

It is impossible with the present apparatus to measure such a small potential drop, but assuming the above values of V_1 and k_2 , and the corresponding value of $i = .693 \times 10^{-7}$ amperes per sq. cm, and substituting these values in c.g.s. units in the equation

$$x_1 = \sqrt{\frac{75k_2 V_1^2}{32 \pi i}},$$

$x_1 = .003$ cms = the electron sheath thickness. This is too small a distance to be even approximately measured with the probe used, but certainly the electron sheath thickness for this particular observation was less than the diameter of the probe which was .04 cms.

A summary of the data obtained in connection with Fig. 6 is given in Table 1. The sheath voltage drop and the sheath thickness were both taken from the graphs. The meaning of the symbols are as follows; V_2 = potential drop across the positive ion sheath, I = total current in amperes between the electrodes, i = current in amperes per sq. cm of cathode surface, and $k_1 = \frac{32 \pi i x_1^2}{75 V_2^2}$ = velocity in cms/ sec. for one volt/ cm. The effective area of the cathode (both sides) = 5.46 sq. cms.

That the equation given in the Theory for the positive ion sheath about the cathode satisfies the experimental results is shown by the good agreement between the values of k_1 . The largest deviation from the mean for the pure flame is 9.7% and for the NaCl flame 5.6%, and this seems quite satisfactory when it is remembered that the largest experimental error, that occurring in the measurement of the sheath thickness, is probably not much less than 5% and may be as much as 10% for small values of x_2 . The edge correction has also been neglected. The values of k_1 obtained will be discussed after presenting the results for

cylindrical electrodes.

TABLE 1.

Flame	V_2 (volts)	I (amp.)	i (amp.)	x_2 (cms)	k_1
Pure	10.4	1.19×10^{-7}	$.218 \times 10^{-7}$	.37	12.3
	22.1	1.75 "	.32 "	.53	11.8
	44.4	2.64 "	.485 "	.77	13.5
	65.9	3.10 "	.567 "	.92	12.3
	87.7	3.79 "	.693 "	1.03	11.9
NaCl	12.8	2.58×10^{-7}	$.471 \times 10^{-7}$	.27	5.32
	22.6	3.46 "	.633 "	.36	6.96
	44.9	5.11 "	.936 "	.50	7.0
	88.9	7.26 "	1.33 "	.71	7.33
	110.9	8.25 "	1.51 "	.80	7.55

The results for cylindrical electrodes are of perhaps greater interest, for the equations which represent the relations existing between current and volts involves not only the sheath radius but the radius of the electrode. The potential gradient curves for cathodes of radii .02, .103, and .30 cms, for various applied voltages in pure and NaCl flames are shown in Figs. 7 and 6. Here again the potentials for points on opposite sides of the cylinders are plotted for the largest value of potential difference used. The middle point of the cylindrical cathode and therefore of the sheath is indicated by the short vertical arrow, and at the bottom the cross-section to scale of each cylinder is shown. It will be noted that the agreement of the sheath radii as measured on either side of the various electrodes are well within the limits of experimental error claimed. The spraying of NaCl into the flame increases the current and decreases the sheath radius over that in the pure flame for the same applied voltages.

Tables 2 and 3 give the results in tabulated form for the pure and NaCl flames respectively. The meaning of the symbols are as follows; V_2 = voltage drop across the positive ion sheath, I = the total current in amperes, i = the current in amperes per cm length of the cathode, r_0 = the cathode radius in cms, r_2 = the positive ion sheath radius in cms, and k_1 = velocity per volt per cm of the positive ion as given by Eq.(21) in the theory. The effective length of the cylinder was 1.5 cms.

CYLINDRICAL ELECTRODES IN PURE FLAME.

FIGURE 7.

CYLINDRICAL ELECTRODES IN NaCl FLAME.

FIGURE 8.

TABLE 2. (Pure Flame)

V_2 (volts)	I (amp.)	i (amp.)	r_2 (cms)	r (cms)	$\frac{r_2}{r_0}$	k_1
22.6	$.76 \times 10^{-7}$	$.505 \times 10^{-7}$	.27	.02	13.5	17.1
44.7	1.06 "	.703 "	.37	.02	18.5	15.1
66.5	1.35 "	.90 "	.46	.02	23.0	16.3
88.6	1.62 "	1.08 "	.52	.02	26.0	15.3
Greatest deviation from the mean						= 7.2%
22.0	.594 "	.396 "	.465	.103	4.52	10.2
44.8	.89 "	.594 "	.655	.103	6.36	12.1
66.0	1.09 "	.725 "	.775	.103	7.52	11.9
88.1	1.42 "	.943 "	.84	.103	8.15	11.3
Greatest deviation from the mean						= 10.3%
22.3	1.45 "	.97 "	.67	.30	2.23	7.96
44.6	1.98 "	1.32 "	.87	.30	2.9	10.1
66.3	2.44 "	1.63 "	1.0	.30	3.33	10.7
88.5	2.97 "	1.98 "	1.15	.30	3.83	13.1
Greatest deviation from the mean						= 25.4%

TABLE 3. (NaCl Flame)

V_2 (Volts)	I (amp.)	i (amp.)	r_2 (cms)	r_0 (cms)	$\frac{r_1}{r_0}$	k_1
22.4	1.19×10^{-7}	$.79 \times 10^{-7}$	.21	.02	10.5	12.6
44.7	1.48 "	.99 "	.31	.02	15.5	12.8
67.0	2.19 "	1.45 "	.37	.02	18.5	13.8
89.0	2.74 "	1.82 "	.41	.02	20.5	13.2
Greatest deviation from the mean						= 5.3%
22.4	3.47 "	2.31 "	.278	.103	2.7	5.95
44.9	4.78 "	3.2 "	.368	.103	3.57	7.1
66.8	5.77 "	3.86 "	.433	.103	4.21	7.5
88.9	6.93 "	4.62 "	.493	.103	4.78	8.5
Greatest deviation from the mean						= 18.4%
22.4	5.78 "	3.86 "	.52	.30	1.73	6.3
45.0	8.57 "	5.71 "	.61	.30	2.03	6.6
67.1	9.9 "	6.60 "	.70	.30	2.33	7.5
89.2	11.9 "	7.92 "	.75	.30	2.5	7.3
Greatest deviation from the mean						= 10.4%

The agreement between the values of k_1 as given for each diameter of cathode is quite satisfactory when one remembers that the accumulated experimental error can hardly be less than 10%. The greatest deviation in k_1 from the mean is given for each size of cathode tested. It will be noted that the ratios of sheath radius to cathode radius vary from 1.73 to 26. The values of k_1 obtained by using cylindrical electrodes agree well with those obtained by using plane electrodes. In the case of cylinders the values of k_1 for both pure and NaCl flames decrease with increase of electrode radius. The gas adjacent to an electrode of .1 or .3 cm radius is cooler than near one of .02 cms radius. From kinetic theory we have $k_1 = e\lambda/mV$, where e/m is the ratio of the elementary charge to mass of an ion, λ is the mean free path, and V is the mean velocity of agitation. Thus k_1 varies directly with λ and inversely with V , and since λ varies directly with the absolute temperature and V varies directly with the square of the absolute temperature, k_1 varies directly with the square root of the absolute temperature and therefore should be less for a sheath about a large cool electrode than about a small hot one. It will also be observed that the values of k_1 as given for plane electrodes in both pure and NaCl flames are in all cases less than the corresponding values for the cylindrical cathode of .02 cms radius, and about the same in value for the two larger radii used. One would expect the cooling effect on the adjacent flame gases by the plane electrode to be greater than for the small wire of .02 cms radius and about the same for the other two cylinders used.

At the surface of the sheath there are equal numbers of plus and minus ions and the current is carried mainly by electrons leaving the sheath. An examination of the graphs shows that the potential gradient just outside the sheath surface is about the same no matter what the size of the sheath or the voltage drop across it. This suggests that the number of positive ions entering and electrons leaving the sheath surface per square cm is constant for all sizes of sheath and therefore the total current to the cathode for any applied voltage should be equal to the current passing through the sheath surface per square cm multiplied by the total sheath surface area. That is the total surface area of the sheath about a cylindrical cathode varies directly with the total current. Table 4 gives data which bears out this supposition. The first, second, and third columns give I the total current flowing to the cathode, r_2 the positive ion sheath radius, and r_0 the cathode radius. The fourth column gives the total sheath surface area including the ends of the cylinders. In the fifth column is given the ratio of I to total sheath surface area, which is the current density. The agreement between the various values of the ratio of I to sheath area is excellent for cylindrical electrodes, which shows that the total current I to the cathode is equal to the current per square cm of the sheath surface multiplied by the total sheath surface area.

The same calculations were repeated for the plane electrodes. But extreme values of the ratio of I to sheath area

TABLE 4. (Pure Flame)

I (Amp.)	r_2 (cms)	r_0 (cms)	Surface area (Sq. cms)	I/Surface area or current density
$.76 \times 10^{-7}$	.27	.02	3.009	2.52×10^{-6} amp.
1.06 "	.37	.02	4.36	2.42 "
1.35 "	.46	.02	5.67	2.39 "
1.62 "	.52	.02	6.61	2.44 "
.59 "	.465	.103	5.75	1.03 "
.89 "	.655	.103	8.87	1.01 "
1.09 "	.775	.103	11.09	.98 "
1.42 "	.84	.103	12.34	1.15 "
1.45 "	.67	.30	9.18	1.58 "
1.98 "	.87	.30	12.98	1.53 "
2.44 "	1.0	.30	15.75	1.55 "
2.97 "	1.15	.30	19.20	1.55 "

(NaCl Flame)

1.19 "	.21	.02	2.26	5.27×10^{-6} amp.
1.49 "	.31	.02	3.52	4.21 "
2.18 "	.37	.02	4.35	5.01 "
2.74 "	.41	.02	4.93	5.56 "
3.47 "	.278	.103	3.12	11.1 "
4.78 "	.368	.103	4.28	11.1 "
5.77 "	.433	.103	5.29	10.9 "
6.93 "	.493	.103	6.19	11.2 "
5.78 "	.52	.30	6.6	8.75 "
8.57 "	.61	.30	8.09	10.6 "
9.9 "	.70	.30	9.68	10.2 "
11.9 "	.75	.30	10.62	11.2 "

vary about 45%, so the agreement is not so good. This can be accounted for as follows. It was assumed that the sheath about a plane electrode was of boxlike form and the surface area of the box was computed. It is probable however that the sheath about a plane electrode, where the sheath thickness is comparable in size with the electrode dimensions, assumes an ellipsoidal form and hence it is difficult to calculate even approximately the surface area.

The average of the value of k_1 for the pure flame using cylindrical electrodes is 12.6 and for the NaCl flame 9.1 cms per sec. per volt per cm. For the plane electrode $k_1 = 12.3$ for the pure flame and 7.2 for the NaCl flame. The agreement between the values of k_1 obtained while using either cylindrical or plane electrodes is excellent. No attempt has been made to allow for the edge correction in the case of plane electrodes and the end correction in the case of cylindrical electrodes. Unless the plane electrodes were quite large and the sheaths thin it is probable that from the experimental standpoint cylindrical electrodes would require the smaller correction and would give the most reliable results. Allowing for the edge and end corrections would give smaller values of current density and hence smaller values of k_1 .

It is interesting to compute the value of k_1 on the basis of the kinetic theory of gases. Let us take nitrogen as the gas which will give an average atomic weight of all the constituents in the flame. The data for the calculation of $k_1 = e\sqrt{mV}$ are as follows (in e.s.u.); $T = 2143^\circ$ absolute temperature = flame

temperature, $e = 4.774 \times 10^{-10}$ e.s.u., $\lambda = 8.6 \times 10^{-6} \times 2143/273 = 6.76 \times 10^{-5}$ cms = mean free path, $m = 14. \times 1.66 \times 10^{-24} = 23.2 \times 10^{-24}$ grams, $V = 4.53 \times 10^4 \times 2143/273 = 12.7 \times 10^4$ cms per sec., = mean velocity of agitation. Substituting in the equation,

$$k_1 = \frac{4.774 \times 10^{-10} \times 6.76 \times 10^{-5}}{23.2 \times 10^{-24} \times 12.7 \times 10^4} = 1.09 \times 10^4 \text{ cms per sec.}$$

for one e.s.u. of potential per cm. = 36. cms per sec. for one volt per cm. The theoretical value of $k_1 = 36.$ agrees roughly with the experimentally determined values. It is difficult to estimate the average atomic weight of the flame gases, and undoubtedly the temperature of the flame inside the sheath is much less than the value assumed.

The values of k_1 are not much larger than the best values of 1. to 2. cms obtained by other experimental methods. Electron emission from the cathode has been neglected in the theory, but any such emission occurring would tend to give larger values of current and hence larger values of k_1 . On the whole it seems probable that the formulae derived for the sheath theory and the experimental procedure used give as good values of k_1 , the mobility of the positive ion in a flame, as can be obtained by any other method.

In concluding I want to express my appreciation to Dr. H.A.Wilson for his interest in these experiments and especially for his constructive criticism of the theory.

November 15, 1927.
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5. BIBLIOGRAPHY.

- Child, Phys.Rev.,32,492,1911.
- Compton, Turner, & McCurdy, Phys.Rev.,24,1924.
- Gold, Proc.Roy.Soc.,79,43,1907.
- Langmuir, Gen.Elec.Rev.,p731,1923.
- Langmuir, Science,58,290,1923.
- Langmuir, Jour.Franklin Inst.,196,751,1923.
- Langmuir, Phys.Rev.,2,450,1913.
- Langmuir, Phys.Zeits.,15,348,1914.
- Langmuir, Phys.Rev.,21,419,1923.
- Langmuir & Blodgett, Phys.Rev.,24,1925.
- Lusby, Phil.Mag.,22,775,1911.
- Marx, Ann. d. Physik.,2,790,1900.
- McCurdy, Phil.Mag.,48,905,1924.
- Moreau, Annales de Chimie et de Phys.,p30,1903.
- Richardson, Proc.Roy.Soc.,91,524,1914-15.
- Rutherford, Phys.Rev.,13,321,1901.
- Saxer, Phys.Rev.,3,325,1914.
- Smith & Langmuir, Phys.Rev.25,735,1926.
- J.J.Thomson, Conduction of Electricity through Gases.
- Townsend, Electricity in Gases.
- Watt, Phys.Rev.,24,69,1925.
- H.A.Wilson, Phil.Trans.,A,p517,1899.
- Wilson, Phil.Mag.,10,476,1905.

Wilson, Phil.Mag., June, 1906.

Wilson, Phil.Trans., A, 208, 247, 1908.

Wilson, Phil.Mag., 21, 711, 1911.

Wilson, Phil.Trans., A^{539,}, 1915.

THE MEASUREMENT OF THE RESONANCE, RADIATION, AND IONIZATION POTENTIALS OF SEVERAL GASES AND VAPORS.

BY PAUL EDWARD BOUCHER.

SYNOPSIS.

Minimum Resonance, Radiation and Ionization Potentials for Various Gases.—A special vacuum tube was used which embodied a modification of K. T. Compton's variable-area electrode by being so designed that either a gauze or a plate electrode could be slid into the position of the fourth electrode. The resonance potentials were obtained from the difference in voltage between successive peaks of the resonance curves; the ionization potentials from Lenard current-voltage curves corrected as to zero by the resonance curves; the relative importance of radiation and ionization at various voltages from the ratio of the Lenard currents obtained with the plate, to the corresponding currents obtained with the gauze electrode having only one fourth the area. The critical potentials in volts, accurate to about 0.1 volt except for toluene, are as follows:

Gas.	Resonance Potential.	Radiation Predominant.	Ionization Potential.
Hydrogen.....	10.1	10.1 to 13.6	13.6; 15.6
Nitrogen.....	8.4	8.4 to 15.8	15.8
Oxygen.....	8.0	None detected	14.0
Ether (C ₄ H ₁₀ O).....	6.6	8.1 to 10.1	13.6
Benzene (C ₆ H ₆).....	6.0	None detected	9.6
Toluene (C ₇ H ₈).....	6.2 ± 0.2	" "	8.5 ± 0.5
Xylene (C ₈ H ₁₀).....	6.5	" "	10.0
Chloroform (CHCl ₃).....	6.5	" "	11.5

The results for the resonance potentials for H₂, N₂ and O₂ agree with those obtained by Foote and Mohler, but the values for the corresponding ionization potentials are about 1 volt higher than theirs. The fact that no radiation was detected in the case of O₂ and of all the vapors except ether is rather remarkable; but it may be due to the method used.

A. INTRODUCTION.

A CONSIDERABLE amount of research has been carried out on the radiation and ionization potentials of various gases and vapors. The problem has been attacked in several ways but the results are not

in such good agreement as could be desired. The Bohr theory has been applied only to the hydrogen and helium atoms with much success. As time goes on we may expect extensions of this or other theories to other elements and even to compounds. The development of a satisfactory theory rests upon the accuracy with which the radiation, resonance, and ionization potentials can be determined. In this paper the writer describes methods and gives the results in which the critical potentials of several simple gases and compounds have been measured.

Some preliminary work was carried out, in which several ionization tubes of various designs were constructed and tested. Only the final form of the apparatus will be described here.

B. APPARATUS.

The problem of distinguishing between radiation and ionization is one of some difficulty. Davis and Goucher¹ have used a modification of the Lenard method in which they reversed the direction of the retarding field between two of the electrodes. A photoelectric effect due to radiation would give a current the direction of which would depend only on the direction of the retarding field, while a positive ion current due to ionization would be obtained with the retarding field in one particular direction. Other observers using the same method have not obtained consistent results.

K. T. Compton in the *Philosophical Magazine* for November, 1920, describes a three-electrode tube, having a variable area receiving electrode. This electrode consists of a cylinder closed at one end with a piece of foil and at the other with a piece of fine gauze. Either end could be turned towards the cathode, and thus the area exposed to radiation could be changed and a consequent variation in photoelectric current proportional to the area exposed might be expected. If the effect were one of ionization then a variation in the electrode area would not change the current.

The principle of a variable area electrode was employed, though the design was entirely different from that of Compton's. Fig. 1 will give an idea as to its construction. It was a four-electrode tube, though most of the time it was used as a three-electrode tube, two of the electrodes being connected together. The filament *A*, the platinum cylinder *B*, and the gauze *C* were mounted on the glass stopper *T*. This large glass stopper was fitted to the main part of the tube by a very fine ground glass joint. A small amount of grease was placed around the lower part of the joint, but several days would elapse before the grease could be

¹ *PHYSICAL REVIEW*, Vol. 10, No. 2, August, 1917, p. 101.

noticed working its way towards the vacuum. During the latter part of the work, the grease was entirely removed and the joint was sealed in with a mixture of beeswax and rosin. The ground joint was 8 cms. from the cathode, so that it did not become appreciably warm. Because of the large size of the opening, the entire assembly of the electrodes, *A*, *B*, and *C*, could be removed at will for alteration or repair.

Fig. 1.

The cathode *A* was a piece of platinum foil 1 cm. in length, cut narrow at the center, so that the central portion became much hotter than the ends, thus furnishing the larger portion of the supply of electrons and hence approximating to an equipotential source. It was coated with lime and baryta by giving it several coats of sealing wax and heating it at a high temperature in air before being placed in the tube.

The platinum cylinder was 2 cms. long, 2.5 cms. in diameter, and closed at one end except for a circular opening 0.5 cm. in diameter. The cylinder was thus slipped over the cathode so that the small hole was about 3 mms. directly above the cathode. A fine gauze placed over the small hole was found to improve the operation of the tube.

A small glass stem furnished both the support and the means of insulation for the fine gauze electrode *C*. This electrode was placed 6 mms. distant from the cylinder.

The innovation, the electrode of variable area *DD'*, consisted of a platinum foil disk of 3 cms. diameter, and a very coarse gauze disk of the same diameter. These were connected by a stiff wire 5 cms. long, and the whole was suspended from a glass sleeve. A glass rod fixed permanently in the tube, formed the track upon which the glass sleeve could be moved back and forth. A small piece of soft iron, enclosed in glass, was sealed to the movable electrode at *E*. Thus by means of an electromagnet outside the tube, the electrode could be moved so that either the solid disk or the coarse gauze was directly above the electrode *C*. It was

thought by placing these parts of the electrode 5 cms. apart, that while one disk was directly above *C*, the other would be too far away to receive any appreciable effect either due to radiation or ionization. The meshes of the coarse gauze were about 6 mms. square. The total effective area of one side that would be exposed to radiation was 7 square cms. for the solid disc, and 1.87 square cms. for the gauze. Thus the ratio of their effective areas was about 3.78. So that if the current received were entirely due to radiation incident on the electrode, it would be almost 4 times larger for the solid disc than for the gauze. A fine coil of platinum wire formed the flexible lead to the outside of the tube. All parts were made of platinum, so that before being connected to the pump, the entire tube was washed several times in nitric acid, rinsed in ammonia and distilled water and then dried in an electric oven.

C. METHODS EMPLOYED.

Three methods of operation were employed with tube No. 4. Figure 2 shows the connections which were essentially the same for the three methods. The cathode *A* was heated by four 7-volt Edison storage batteries.

Fig. 2.

This number was found to be advisable in order to obtain steady electron currents, because from 4 to 6 amperes of current were required to raise the cathode to the desired temperature. This source of current was found to be fairly constant. During most of the work, a piece of fine gauze was stretched across the small hole in the cylinder *B*. In the preliminary tryout of the tube, the cylinder was removed, but the results were very unsatisfactory and it was replaced. *C* is the fine gauze and *DD'* is

the movable electrode by which the area exposed to radiation could be varied. *B* and *C* were connected together most of the time.

The methods employed are called the Lenard, the ratio, and the resonance methods. The Lenard and the ratio methods were used simultaneously, that is, data by which ratio curves were plotted, were obtained from the Lenard readings. Battery *P* furnished the accelerating potential V_a , which was applied between the cathode and *BC*. For the Lenard method battery *Q* furnished the retarding potential V_r , which was applied between the variable area electrode *DD'* and *BC*. This potential was always larger than the highest value of the accelerating

potential used, usually about 30 volts. Thus BC was charged plus with respect to A , and electrons from the cathode would move to BC . Some would pass through the gauze covered opening into the space BC , where they would travel at a constant velocity, since the electric field in BC was zero. Those electrons which did not collide with atoms or molecules in BC and possessing sufficient velocity would pass through the fine gauze C into the space CD . Here however the large retarding potential V_r would prevent any electrons reaching D . Let us suppose that the electrons have attained a velocity V_a sufficient for them to cause the atoms they collide with to give off radiation. Then some of this radiation will fall on the movable electrode DD' , and due to what is called the photoelectric effect, electrons will be emitted from DD' and due to V_r will pass from DD' to BC , and we will have a current measured by the high sensitivity galvanometer G_2 . This special Leeds and Northrup high sensitivity galvanometer had a sensitivity of 5×10^{-11} amperes per mm. deflection. Now the value of the radiation current will depend on the area of the electrode exposed to radiation. Since the ratio of the area of the solid disc to the coarse gauze is about 3.8 we should expect the current to the disc to be almost four times that to the coarse gauze, provided the effect is purely one of radiation. On the other hand if the velocity of the electrons is sufficient to produce ionization by collision, then the positive ions formed will go to the electrode DD' , and we will have a current indication on the galvanometer in the same direction as for radiation effects. However if we vary the area of the electrode DD' , there will be no change in the value of the current since the ionization does not depend on the area of the electrode exposed. Thus we have a means for distinguishing between radiation and ionization. The procedure in obtaining the necessary data for the ratio test was to take first a reading of the Lenard current with the disc end of the movable electrode above C , then by means of an electromagnet move the gauze end above C , and again read the current value, the accelerating and retarding potentials meanwhile remaining constant. This procedure was continued for each value of accelerating potential applied. Dividing the current value to the disc by the current value to the coarse gauze we obtain the ratios of the currents for the various V_a 's applied. And we can conclude, at least with our present knowledge of the subject of photoelectric and ionization effects, that if the ratio approaches 4 in value, the effect is entirely due to radiation; if it becomes 1, then it is due to ionization, while if the ratio has some intermediate value between 1 and 4 both ionization and radiation are present.

The only change necessary to obtain resonance currents is to make the

retarding potential V , small, say 1 to 5 volts, instead of 30 volts as in the Lenard method. The collisions between electrons and the atoms of some gases appear to be elastic up to a certain velocity. Beyond this point, the collisions become inelastic, that is the colliding electrons give up their energy to the atoms or molecules, which in turn is used to remove one of the atom's electrons from its stable position to an unstable one, and thus radiation of frequency π is produced when the electron falls back into its stable position. Thus when inelastic collisions take place the colliding electrons lose their velocity. If the retarding potential is small and the accelerating potential is increased from zero, the electrons will acquire a velocity which will enable them to reach the electrode DD' against the retarding potential. When inelastic collisions take place, however, some of the electrons lose their velocity and these are unable to reach DD' against the retarding potential and a consequent decrease in electron current takes place. But as the increase in the accelerating potential is continued these electrons again increase in velocity and the electron current begins to increase in value once more. This increase continues, as the potential goes up, until the electrons have acquired a velocity such that inelastic collisions again take place, and we have a second decrease in current. As many as four resonance points in a current voltage curve have been obtained.

It is found that the gas pressure at which resonance curves may be obtained is limited in range. The best resonance curves are obtained between gas pressures of about 0.1 mm. to 2 or 3 mms. No doubt the distance between the electrodes is a factor in obtaining resonance curves, though just how it would affect the critical pressure is not known. The resonance potential may thus be accurately found by taking the difference in accelerating potential between two consecutive resonance points. It should be remembered that an atom or molecule does not necessarily give off radiation at its resonance potential.

The initial correction due to several factors, the initial velocity of the electrons, the contact difference of potential between the cathode and the receiving electrodes, the potential drop along the filament, may be obtained from the resonance curves. In most cases the potential at which the first resonance peak is obtained, is not equal to the difference between two resonance peaks. For any gas the difference between two resonance peaks is found to be always the same no matter what conditions prevailed. The writer found considerable variation in the applied potential difference at which the first resonance peak occurs. Mohler and Foote¹ have published some work on the "Ionization and Resonance

¹ Scientific Papers of the Bureau of Standards, No. 400.

Potentials of some Non-metallic Elements," in which they obtained the first resonance peaks with applied accelerating potentials of smaller value than the resonance potentials as read from the difference of two succeeding resonance peaks. In practically all the work reported in this paper, the initial applied accelerating potentials for the first resonance peaks were either equal to or greater than the resonance potentials. The explanation of this is not clear. It may perhaps be due to contact difference of potential in the cathode itself. We need not know the magnitude of the corrections in order to obtain the proper correction for the Lenard curves. This correction was obtained by taking the difference between the resonance potential and the applied potential at which the first resonance peak begins, and adding or subtracting it as the case may be to the ionization and radiation potentials obtained by the Lenard method.

The general procedure for obtaining the radiation and ionization potentials of any gas was as follows: The tube was first heated to about 300° C. in an electric heater, and the cathode was also heated to a high temperature to help free the electrodes and glass from occluded gas. Liquid air was placed on the trap and the pump was started. This treatment was continued for several hours with a new tube, and was always repeated for an hour or more before each day's work was begun. After such treatment the Gaede pump would give vacuums of the order of 10^{-4} mms. The gas to be tested was then admitted to the desired pressure, and by means of a Geissler tube and an Adam Hilger direct-reading spectroscope, the purity of the gas was tested. If not satisfactory it was pumped out and refilled. Readings were never recorded until the currents became constant in value. After a set of readings was taken, several potentials were rechecked and if the current values varied more than a few mms. deflection on the galvanometer the data were rejected. For any gas pressure data for the resonance curves were first taken and then that for the Lenard and ratio curves.

For admitting the vapors, a bulb connected to a three-way stopcock was sealed on close to the electrode tube. A little of the liquid was poured into the bulb, then it was frozen by liquid air, and all the gas was pumped out above the frozen liquid. The stopcock was then closed, the liquid air removed, and the pure vapor could be admitted as desired. Some difficulty was experienced in admitting the proper amount of vapor. Due to the sudden expansion of the vapor on entering the vacuum, some would condense on the walls of the tube, and considerable time would be required to obtain the desired pressure. It was found however that by first getting a large electron current in vacuum and then just admitting

enough vapor to cause this current to decrease, that the desired pressures could be obtained much more quickly.

D. EXPERIMENTAL RESULTS.

The experimental results obtained in measuring the radiation and ionization potentials of several gases and vapors will now be described in the order performed.

1. Hydrogen.

Hydrogen for this test was prepared by the action of caustic potash on aluminum. It was found very convenient to store the gas in a tank under water pressure, so that if any leakage should take place, it would be only loss of hydrogen. A calcium chloride tube was inserted between the storage tank and the ionization apparatus. This tube could be exhausted before admitting hydrogen. The apparatus was always washed out several times with the gas in question before adjusting the

Fig. 3.

pressure for a test. Liquid air was always kept on the trap during these tests. The purity of the gas was tested by examining its spectrum.

Some characteristic curves obtained with hydrogen gas are shown in Fig. 3. Curves 4 and 5 are resonance curves, obtained at the same pressure, but at different filament temperatures. Curves 4a, 6a, and 7a

are Lenard curves obtained at the same pressure but at different filament temperatures. These are the current values measured to the disc of the movable electrode while obtaining the two sets of data from which the corresponding ratio curves were plotted.

The resonance curves give these results:

Curve.	1st Res. Pt.	2d Res. Pt.	Difference.	Correction.
4.....	11.5	21.6	10.1	$10.1 - 11.5 = -1.4$
5.....	12.0	22.0	10.0	$10.0 - 12.0 = -2.0$

Curve 4 gives a break at 17 volts, and adding the correction (-1.4 volts) to this gives $17.0 - 1.4 = 15.6$ volts, which is the ionization potential as determined from the resonance curves. Lenard curves 4a and 7a both have sharp increases in current at 17.0 volts. Referring to the ratio curves this is evidently the potential where strong ionization predominates. Applying the correction we have $17.0 - 1.4 = 15.6$ volts for the ionization potential of hydrogen. Curve 6a gives a resonance potential at $11.6 - 1.4 = 10.2$ volts. Thus it will be seen that the resonance and ionization potentials obtained by the three methods check very well indeed. The break in the resonance curves due to ionization at 15.6 volts was not obtained in all curves. The ionization at this potential evidently prevents the second resonance peak from being as high and sharp as the first. This can be readily explained by the fact that when ionization sets in both plus and minus ions are formed. Remembering that the resonance currents consist simply of electrons possessing sufficient velocity to go against the small retarding potential applied between the movable electrode and BC, it will be readily seen that any sudden introduction of positive ions would tend to diminish the electron current, for the positive ions would be attracted by the retarding field to the movable electrode. If the effect were strong enough we might get a complete reversal of current. This has been obtained with some of the vapors worked with and will be referred to again.

The ratio curves deserve further consideration. Radiation and some ionization appear to exist at 10.2 volts. As the accelerating potential is increased the effect becomes principally one of radiation though some ionization is no doubt present. Ionization begins to increase at about 15.0 volts on the ratio curves. Adding the correction (-1.4) to 15.0 gives 13.6 volts as the potential at which ionization begins to supercede radiation. At this potential the ratio begins to decrease rapidly from 4 until it reaches a value of almost 1.0 at $17.0 - 1.4 = 15.6$ volts.

Final Results.

Radiation and some ionization was found at.....	10.1 $\pm$ 0.1 volts.
Radiation predominates between.....	10.1 to 13.6 volts.
Ionization begins to increase at.....	13.6 volts.
Strong ionization begins at.....	15.6 volts.

It is interesting to compare these values with those given by the Bohr theory for hydrogen.

Bohr's theory gives:

Resonance potential.....	10.16 volts.
Ionization potential of the atom.....	13.54 volts.
Ionization potential of the molecule.....	16.26 volts.

There is good agreement between the radiation and resonance potentials, and the first ionization potentials. But the strong ionization found at 15.6 volts does not check quite so well with 16.26 volts as predicted by Bohr's theory. Compton and Olmstead,¹ who first used the ratio method, give 10.8 volts for the resonance potential, 13.4 volts an additional critical velocity, and 15.9 volts the point where intense ionization sets in. The latter two values check fairly well with those found, but there is considerable difference between 10.8 and 10.1 volts.

2. Nitrogen.

Nitrogen gas was prepared by heating a solution of ammonium chloride and sodium nitrite in a hot water bath. It was passed through a red hot copper coil and collected against pressure in a storage tank. As before an air tight connection through a calcium chloride tube was used for admitting the gas into the apparatus. Phosphorus pentoxide and liquid air removed the other impurities. The spectrum checked well with that given by Georges Salet in his "Analyse Spectrale."

Some trouble was experienced at first due to what has been called by some writers, polarization effects. Difficulties of this nature have been reported by other observers for various gases. The nature of the trouble seems to be obscure. The character of the resonance and Lenard curves was not affected, but some of the first ratio curves showed that the gauze apparently received more current than the disc. This is difficult to account for, unless the disc was exposed a long time to a freshly coated filament, and some kind of an insulating layer was deposited on it. However this trouble was eliminated by removing the filament base, recoating the filament, and heating all platinum parts to a white heat with a gas flame. The electrodes were replaced and the movable electrode was bombarded by electrons from the hot cathode by applying a potential difference of 50 volts. This trouble was never repeated in the subsequent work.

¹ PHYSICAL REVIEW, Vol. 17, No. 1, Jan., 1921, p. 45.

Fig. 4 shows the type of results obtained. Curve 3 shows three distinct resonance points. In some of the curves four resonance points were obtained. This curve gives a resonance potential between the first two peaks of 8.4 volts. Subtracting from this value the value at which the first resonance point begins, gives an initial correction of -3.2 volts, which as explained before takes care of all corrections. The Lenard curve 3a, at the same pressure (0.4 mms.), gives the first indication of current at 11.5 volts, and a sharp change in slope due to ionization at 19.0 volts. Adding the correction, -3.2 volts, gives 8.3 volts for the resonance potential and 15.8 volts for the ionization potential.

Fig. 4.

Curve 3r shows the ratio of the plate to the gauze current. This ratio is greater than 1 up to 19 volts, where it suddenly drops to a value of 1. It however indicates some ionization as well as radiation before the ionization potential is reached.

Curve 1 shows the arcing potential. It gives a resonance potential of about 8.5 volts and a consequent initial correction of -3.5 volts. Adding this to the observed potential at which arcing sets in, 20.5 volts, gives the arcing potential as 17.0 volts. The retarding potential used for this curve was only 5 volts, yet here we have an interesting case in which the increase of the accelerating potential from 20.5 to 21.0 volts gives a complete reversal of current, the galvanometer indicating a large positive current instead of an electron current. The magnitude of the

current was too large to measure on the scale. An intense bluish glow was observed when this break in the current curve took place. By using lower pressures and smaller retarding potentials, curves of type 3 were obtained without arcing setting in.

Using the frequency corresponding to the wave-length, $= 1492.8 \text{ \AA.}$ of the isolated doublet in the nitrogen spectrum, observed by Lyman,¹ in the quantum relation, $Ve = h\nu$, we obtain $V = 8.27$ volts. The potential, 8.3 volts, obtained agrees fairly well with this calculated radiation potential. The limiting spectral line corresponding to the ionization potential of nitrogen has not been identified. With the ionization potential of nitrogen equal to 15.8 volts, this limiting spectral line should have a wave-length equal to 782.0 Angstrom units.

Final Results.

Resonance potential of nitrogen.....	8.4 ± 0.1 volts.
Radiation predominates between.....	8.4 and 15.8 volts.
Ionization potential of nitrogen.....	15.8 volts.

3. *Oxygen.*

An oxone generator was used to generate the oxygen gas, which was said to be 99.4 per cent. pure. It was collected in the storage tank and admitted into the apparatus through a calcium chloride tube. Sometimes the spectrum would show a red line corresponding with that of hydrogen, but this would soon disappear with a hot cathode. Figure 5

Fig. 5.

¹Lyman, The Spectroscopy of the Extreme Ultraviolet, p. 113.

shows resonance, Lenard and ratio curves. The best resonance curves were obtained between pressures of 0.5 and 0.1 mm. Three resonance peaks were easily obtained. Curves 1 and 5 give resonance peaks starting at 8, 16, and 24 volts. The true resonance potential is then 8 volts, and there is no initial correction to apply to the corresponding Lenard and ratio curves. Hence the Lenard curves, 1*a* and 5*a*, give the ionization potential as 14.0 volts. It will be noted that no indication of current was found before 14.0 volts. It was sometimes thought that an indication of current could be detected at 13.7 volts, but this is not certain. The increase at 14 volts however was very definite. There is no indication of another ionization potential in the Lenard curves at a higher potential. Mohler and Foote¹ found resonance at 7.9 volts, ionization at 15.5 volts, but no Lenard indication of current before 15.5 volts. The resonance potential checks with that found in this investigation, but there is a difference of 1.5 volts in the ionization potentials. Hughes and Dixon² obtained what they called an ionizing potential at 9.2 volts for oxygen. They also state that the curve rises slowly from the axis for several volts, then begins to increase more rapidly. So that it is possible that there is a radiation or ionization effect before 14 volts which is too feeble to be detected in the Lenard method by the galvanometer used. The ratio curves give a value of 1.0 for all accelerating potentials, which means that the current is principally due to ionization from 14 volts on.

Curve 6 was taken immediately after Curve 5. The shift in the position of the curve was caused by reversing the direction of the heating current through the cathode. With Curve 5 the negative end of the accelerating potential was applied to the plus side of the cathode, and reversing the heating current for Curve 6, was the same as applying the accelerating potential to the negative side of the cathode. The resonance peaks of Curve 6 occur at accelerating potentials of about 1.2 volts greater value than those for Curve 5, and this was found to be equal to the potential drop along the filament due to the heating current. Hence we see that the accelerating potentials as read from the voltmeter for Curve 5 are about 0.6 volt less and those for Curve 6 are about 0.6 volt greater than they would have been if there was no potential drop along the filament.

Curve 6 gives 8.0 volts for the resonance potential, and an initial correction of about $8.0 - 9.0 = -1.0$ volt, which added to the corresponding Lenard Curve 6*a*, gives 14.0 volts for the ionization potential, which agrees with the values obtained from the other curves.

¹ Bureau of Standards Publications, No. 400, Oct. 14, 1920.

² PHYSICAL REVIEW, Vol. 10, No. 5, 1917, p. 502.

Final Results.

Resonance potential of oxygen.....	8.0 volts.
Radiation was not detected at any potential.	
Ionization potential of oxygen.....	14.0 volts.

4. Ether ($C_4H_{10}O$).

Ethyl ether, prepared by Squib for anaesthesia purposes, was poured into the special bulb for admitting the vapors. With the ether frozen by liquid air, the gas above it could be pumped out to a pressure of less than .00075 mm. Then by closing the three way stopcock to the bulb and removing the liquid air, the vapor could be admitted as desired. Pressures between 0.2 and 0.6 mm. gave the best results.

Figure 6 shows some typical curves. Curves 1 and 2 give resonance

Fig. 6.

Fig. 7.

potentials of 6.6 and 6.7 volts respectively. The initial correction is -1.4 volts. Beyond the second resonance point the current decreases rapidly, passes the zero axis and increases in the opposite direction. This effect is supposed to be due to two causes; one a large production of positive ions by ionization by collision, and the other, a decomposition or a chemical action of some kind taking place. It was found that the electron currents were steady in value until the second resonance point was passed. At this point the current would slowly decrease even with a constant accelerating potential, a phenomenon which indicates that some other effect besides ionization by collision is present. It may be

in ether, a compound consisting of carbon, hydrogen, and oxygen, that some kind of decomposition takes place when the molecules collide with electrons having a velocity equivalent to the accelerating potential at which the second resonance peak is produced.

The Lenard Curve 2*a* starts at 9.5 volts, and adding the corresponding correction of -1.4 volts, gives 8.1 volts as the potential at which current is first indicated. Perhaps a more sensitive current measuring device would have indicated a current at the first resonance potential, 6.6 volts. There is a large increase in current at $11.5 - 1.4 = 10.1$ volts. Curve 2*c* was taken at a lower cathode temperature and it shows a rapid increase at about the second resonance point, $15.0 - 1.4 = 13.6$ volts. It is interesting, too, that at large values of accelerating potential, the Lenard currents also decrease with time.

The ratio curves indicate both radiation and ionization up to about 11.5 volts. From here the ratio decreases to a value of 1.0 at 12.5 volts. It is noteworthy that, since oxygen and hydrogen are both constituents of ether, the first indication of the Lenard current, 8.1 volts, agrees with the resonance potential of oxygen, and the increase at 10.1 volts is very close to the resonance potential of hydrogen. Of course additional information will be required before we can determine just what part of the ether molecule is affected when radiation or ionization is produced.

Final Results.

Resonance potential of ether.....	6.6 $\pm$ 0.1 volts.
Radiation and ionization were found at.....	8.1 volts.
Ionization predominates at.....	10.1 volts.
Strong ionization was found at.....	13.6 volts.

5. *Benzene (Benzol) (C₆H₆).*

The benzene used was guaranteed to be of the highest purity and crystallizable by Merck and Co. The benzene vapor gave less trouble than ether. Very little time was required to obtain steady currents.

Fig. 7 gives typical curves for benzene vapor. No difficulty was experienced in obtaining four resonance peaks. It was found that with retarding potentials of 3 volts or more, only two resonance peaks could be obtained, for the electron current beyond the second resonance peak would decrease to zero value and increase in the opposite direction as in the case of ether. The first indications of resonance in Curve 6 are at applied accelerating potentials of 6, 12, 18, and 24 volts, which gives the resonance potential as 6.0 volts with no initial correction to be applied to the corresponding Lenard curves. Curve 9, obtained at a higher vapor pressure, gives first indications of resonance at 5, 11, and 17 volts

and thus a resonance potential of 6.0 volts and an initial correction of $6.0 - 5.0 = + 1.0$ volt.

The corresponding Lenard curves, 6a and 9a, start at 9.7 and 8.5 volts respectively. Curve 6a needs no correction, while Curve 9a has an initial correction of + 1.0 volts to be added to 8.5 volts thus making it 9.5 volts. The Lenard curves give no further indication of a critical potential above 9.5 volts. The value of the ratio curves is approximately one at all accelerating potentials, which shows the effect is due principally to ionization.

Before taking the data for Curve 11, the cathode was removed and examined. It was found to be covered with a deposit of carbon, sootlike in appearance. A black deposit of this nature was never noticed while working with hydrogen, nitrogen, or oxygen. Subsequent removals of the cathode while working with xylene have also shown a black deposit. This deposit seems to give a fairly large supply of electrons. The cathode was then recoated with sealing wax and replaced. The curves taken immediately afterwards like Curve 11 required a larger applied initial accelerating potential to produce the first resonance peak than did Curve 9, which was taken at approximately the same gas pressure before the cathode was recoated. So that it would appear that an oxide coated filament requires a larger potential to separate the electrons from it than one with a carbon deposit. Subsequent removals and recoating of the cathode tend to substantiate this statement. Curve 11 gives resonance at 7, 13, and 19 volts and consequently a resonance potential of 6.0 volts, with an initial correction of $6.0 - 7.0 = - 1.0$ volt. The Lenard Curve 11a starts at 10.5 volts and adding the correction gives 9.5 volts as the ionization potential.

Final Results.

Resonance potential of benzene.....	6.0 volts.
Radiation was not detected at any potential.	
Ionization potential of benzene.....	9.6 ± 0.1 volts.

6. Xylene (C_8H_{10}).

Xylene vapor gave similar results to that of benzene. The currents were steady except at accelerating potentials of about 20 volts or more. At these higher potentials both the resonance and the Lenard currents exhibited decreases in value while at a constant accelerating potential. This indicates that some other effect besides ionization is present at these higher potentials.

Fig. 8 gives samples of the curves obtained with xylene vapor. In Curve 5 resonance begins to set in at accelerating potentials of 8.0, 14.5,

and 21.0 volts. This gives 6.5 volts as the resonance potential with an initial correction of -1.5 volts. Curve 2 shows only two resonance

Fig. 8.

Fig. 9.

peaks beginning at 6.5 and 13.0 volts. The difference gives 6.5 volts as the resonance potential and no initial correction to apply to the corresponding Lenard and ratio curves.

Lenard Curve 5a begins at an accelerating potential of 11.5 volts and adding the proper initial correction, -1.5 volts, gives 10.0 volts as the ionization potential. Curve 2a with no initial correction needed, also gives 10.0 volts for the ionization potential.

The ratio curves with a constant value of one, give no indication of radiation at any accelerating potential.

Final Results.

Resonance potential of xylene.....	6.5 volts.
Radiation was not detected at any potential.	
Ionization potential of xylene.....	10.0 volts.

7. Toluene (C_7H_8).

Some trouble was experienced while working with toluene vapor. The ionization tube had developed a leak, which necessitated the rebuilding of the glass stopper electrode assembly. With vapor present, a large initial accelerating potential of 5 to 6 volts was required to obtain a measurable electron current against a retarding potential of 1 or 2 volts.

The currents were steady until the first resonance peak was passed. Then they were somewhat erratic in their variations at a constant accelerating potential. Sometimes the current deflection would increase a few mms., then decrease a few mms., but always finally coming to rest at a definite position. It was impossible at any vapor pressure to obtain three resonance peaks, though curve 7 gives some indication of a third resonance peak at about 20 volts.

Some characteristic curves of toluene vapor are shown in Fig. 9. Curve 7 indicates resonance setting in at 8.5 and 14.5 volts, which gives a resonance potential of 6.0 volts with an initial correction of -2.5 volts. Curve 4 gives 6.5 volts for the resonance potential with an initial correction of $6.5 - 9.5 = -3.0$ volts.

Lenard Curve 4a starts at 11.5 volts and applying the proper correction gives 8.5 volts for the ionization potential. Curve 7a also gives $11.0 - 2.5 = 8.5$ volts.

The ratio curves give no indication of radiation. In fact, except for the large initial correction, toluene vapor behaves in a manner similar to that of benzene and xylene. These three belong to the benzene group, and therefore might be expected to give similar results.

Final Results.

Resonance potential of toluene.....	6.25 $\pm$ 0.25 volts.
Radiation was not detected at any potential.	
Ionization potential of toluene.....	8.5 $\pm$ 0.5 volts.

8. *Chloroform (CHCl₃).*

Commercially pure chloroform was used during this test. The filament had been freshly coated before admitting the vapor. After working several hours the filament was examined and no traces of carbon deposit could be detected. The electron currents obtained in chloroform vapor were always steady and apparently no decomposition of the vapor took place.

Fig. 10 shows some typical chloroform curves. Curve 2 gives a resonance potential of 6.5 volts with a correction of $+1.0$ volt, and likewise Curve 4 gives a resonance potential of 6.5 volts with a correction of $+1.5$ volts.

The Lenard Curves 2a and 4a give respectively 10.5 and 10.0 volts, both of which with the proper corrections, give 11.5 volts as the ionizing potential at which the Lenard current is first detected.

The ratio test gave a value of one for all accelerating potentials, showing that radiation was not present in a measurable quantity.

Fig. 10.

Final Results.

Resonance potential of chloroform.....	6.5 volts.
Radiation was not detected at any potential.	
Ionization potential of chloroform.....	11.5 volts.

The resonance potentials of hydrogen, nitrogen, and oxygen agree well with those obtained by Foote and Mohler,¹ who used the same method. The ionization potentials of these three gases as found in this investigation using the Lenard method, are respectively about one volt lower than those given by Foote and Mohler. This discrepancy may possibly be attributed to the method of making initial corrections, a difference in galvanometer sensitivity, and the design of the tube.

The indication of radiation in hydrogen as given by the ratio curves agrees well with that given by the ratio curves of Compton and Olmstead.² Strong radiation was found to predominate between the resonance and ionization potentials of nitrogen, while no radiation was detected in oxygen.

¹ Scientific Papers of the Bureau of Standards, No. 400.

² PHYSICAL REVIEW, Vol. 17, No. 1, Jan., 1921, p. 45.

E. CONCLUSION.

Table of Results. (In volts.)

Gas or Vapor.	Resonance Potential.	Radiation Predominates.	Ionization Potential.
Hydrogen— H_2	10.1 ± 0.1	10.1 to 13.6	13.6
Nitrogen— N_2	8.4 ± 0.1	8.4 to 15.8	15.6
Oxygen— O_2	8.0	No radiation detected.	15.8
Ether— $C_4H_{10}O$	6.6 ± 0.1	8.1 to 10.1	14.0
Benzene— C_6H_6	6.0	No radiation detected.	13.6
Toluene— C_7H_8	6.2 ± 0.25	No radiation detected.	9.6 ± 0.1
Xylene— C_8H_{10}	6.5	No radiation detected.	8.5 ± 0.5
Chloroform— $CHCl_3$	6.5	No radiation detected.	10.0
		No radiation detected.	11.5

So far as is known the critical potentials of the vapors used have not been heretofore determined. The resonance potentials for the vapors have about the same values, all lying between 6 and 7 volts. The ionization potentials also occur at a limited range of accelerating potential lying between 8 and 10 volts. Radiation was detected only in the case of ether. If it is present in the other vapors it is too small to be detected by the method used.

It should be noted that the results of this investigation indicate that in many cases inelastic collisions between the electrons and atoms take place without a measurable quantity of radiation being given off. Either this is due to a lack of sensibility in the detecting device, the method of measurement used, or the energy absorbed by the atom from the colliding electron is dissipated in some unknown manner.

Hughes and Dixon¹ found the ionization potentials of acetylene C_2H_2 , methane CH_4 , ethylene C_2H_4 , and ethane C_2H_6 , to be between 9.5 and 10.0 volts, which is of the same order as the ionization potentials of the vapors measured in this investigation. So that the hydrocarbons so far measured have approximately the same ionization potential.

The ionization potentials of the compounds are less than those of the simple elements of which they are composed. At least they are less than those of hydrogen and oxygen, the ionization potential of the carbon molecule not being known. This result might be expected from a consideration of the theory of the structure of the molecule. For

¹ PHYSICAL REVIEW, Vol. 10, No. 5, Nov., 1917, p. 495.

instance in a molecule containing a large number of electrons, the repulsive forces of neighboring electrons acting on any one electron will weaken the attractive force between it and the positive nucleus. So that such a molecule could be caused to give up one of its electrons with a smaller input of energy than a molecule containing say, only one or two electrons. No definite conclusions can as yet be drawn as to what part of the molecule is ionized. The loss of an electron by a molecule may mean a rearrangement of the remaining electrons about the nucleus, or it may mean the loss of an electron from one particular atom in the molecule.

In concluding the writer wishes to express his thanks to Dr. H. A. Wilson, under whose direction this investigation was carried out.

THE RICE INSTITUTE,
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THE MOBILITY OF NEGATIVE IONS IN GASOLINE, HYDROGEN, AND HYDROGEN-CHLORINE FLAMES

By PAUL E. BOUCHER

ABSTRACT

The Hall effect method of measuring the mobility of the negative ions was used, the horizontal or vertical flame being placed in a field of 4000 to 5000 gauss. The Pt cathode was coated with sealing wax. The temperature was varied by control of the air or oxygen intake and was measured, relatively, by a Pt-Pt-Rh couple. In a hydrogen flame the mobility increases with temperature somewhat for potential gradients over 25 volts/cm, but in a gasoline vapor flame the mobility decreases markedly. The addition of Cl, Br, CHCl, CCl, NH₄Cl or I (in alcohol) to the hydrogen and gasoline flame decreases the mobility, the effect being greatest for Cl and being progressively less for the other substances in the order given. In the hydrogen-chlorine flame values as low as 52 cm/sec. per volt/cm were obtained. Addition of NaCl, Na₂CO₃ or KCl increases the mobility somewhat. The highest value obtained is 5600 for hydrogen flame with NaCl sprayed in, about 30 percent higher than for a similarly sprayed gasoline flame. In explanation of these variations it is suggested that when certain substances, particularly the halogens, are added to the flame, the negative ion which is normally a free electron for the greater part of its life, tends to be attached to form a cluster so that the average period during which it is a free electron is decreased and hence the mobility also. Temperature changes and potential changes probably affect the mobility by influencing the formation of these clusters.

INTRODUCTION

ALL measurements made on the ordinary bunsen flame agree in that the mobility of the negative ion is a thousand or more times greater than that of the positive ion. Some of the early measurements for the negative ion gave a mobility of 1000 cm per sec. per volt per cm. E. Gold¹ obtained two values of 8000 and 12900. H. A. Wilson² found an average value of 2450 using the Hall effect method. J. S. Watt,³ using the Hall effect method, found the mobility to vary from 2700 to 1600 for potential gradients of 1 to 32 volts per cm. His results also indicate that the mobility is slightly less for salted flames than for free flames. H. A. Wilson and A. B. Bryan,⁴ using an alternating current method of measurement at a constant frequency, found mobilities ranging from 6000 to 19300 for potential gradients from 64 to 9.4 volts per cm. By varying the frequency

¹ E. Gold, Proc. Roy. Soc. A, **79**, 43 (1906).

² H. A. Wilson, Phys. Rev. **3**, 375 (1914).

³ J. S. Watt, Phys. Rev. **25**, 69 (1925).

⁴ H. A. Wilson and A. B. Bryan, Phys. Rev. **23**, 195 (1924).

from 10×10^5 to 4×10^6 , keeping the gradient and concentration approximately constant, they were able to vary the mobility from 24000 to 8800. They found by varying any one of three factors, potential gradient, frequency of applied potential, or concentration, that the mobility of the negative ions could be made to vary through a wide range.

The character of a flame has been found by others to be profoundly influenced by the addition of chlorine or some of its compounds. Tufts⁵ found that the introduction of chloroform into a salted flame decreased the conductivity and also the intensity of the light emitted. Wilson⁶ has suggested that when HCl is fed into a flame it may possibly condense on negative ions and diminish their velocity. J. Franck and P. Pringsheim⁷ found in the hydrogen-chlorine flame that the anode fall of potential was greater than the cathode fall of potential, and from a comparison of the conductivities of the salted flame and the hydrogen-chlorine flame, concluded that free electrons could not exist in the latter flame and therefore that the negative carrier consists of an atom or a cluster of atoms. Their results seemed to indicate that the mobility of the positive ion was greater than that of the negative ion in the hydrogen-chlorine flame. S. Kalandyk⁸ concludes from measurements of the conductivity of flames, that the mobility of the negative ion is greater in the oxy-salted flames and the mobility of the positive ion is greater in the hydrogen-chlorine flame.

The successful development of methods by which very steady hydrogen and gasoline vapor flames can be maintained made it seem desirable to investigate the various factors which appear to influence the mobility of the negative ion. In particular, the effect of temperature and the chemical nature of the flame has been studied. The following types of flame were used in this investigation: air-hydrogen, oxygen-hydrogen air-gasoline vapor, oxygen-gasoline vapor, hydrogen-chlorine. These flames were modified by varying the proportions of the constituent gases and by the introduction of the following chemicals: CCl_4 , CHCl_3 , I, Br, Cl, NaCl, Na_2CO_3 , NH_4Cl , and KCl.

EXPERIMENTAL PROCEDURE

The Hall effect method as described in detail by Wilson² was used. The burner was placed between the pole-pieces of a Weiss electromagnet. The pole-pieces were 10 cm in diameter and 5 cm apart. Magnetic fields

⁵ F. Tufts, *Phys. Zeits.* **5**, 76 (1904).

⁶ H. A. Wilson, *Phil. Trans.* **A216**, 63 (1916).

⁷ J. Franck and P. Pringsheim, *Deutsch. Phys. Gesell. Verh.* **13**, 328 (1911).

⁸ S. Kalandyk, *Journ. de Phys.* **5**, 345 (1924).

of 4000 to 5000 gauss were used. A very steady gasoline or hydrogen flame was obtained by passing the gas into a gasometer then through an oxy-acetylene blow-pipe to the burner. The needle valves of the blow-pipe gave a very fine adjustment of both gas and air or chlorine.

Experiments were carried out on both vertical and horizontal flames. In the former the electrodes are placed one above the other; in the latter, which is a broad flat flame, the electrodes are arranged to conduct the current horizontally. For the vertical hydrogen flame a special copper tip was used on the blow-pipe. This gave a flame about 2 to 3 cm in diameter and from 1 to 20 cm in length as desired. The bore of the copper tip was about 3 mm in diameter at the outlet and 4 mm at the intake end. This conical bore prevented backfiring and steadied the flame. Two horizontal burners were made, one for gasoline vapor and one for hydrogen. These burners differ from previous types in that the number of quartz tubes used per unit length was increased by using tubing of a small diameter; thus the cones in the flame were small and close together. For the gasoline burner, 17 quartz tubes, each 2.5 cm long and having an inside diameter of 2.5 mm, were mounted on a brass tube of about 1.5 cm inside diameter. The centers of the tubes were placed about 0.5 cm apart, thus making the burner about 8.5 cm long.

This burner could not be used for hydrogen, for the addition of a small amount of air would cause the flame to blow back and burn inside. It was found however by taking small quartz tubing of about 3 mm inside diameter and heating one end in an oxy-hydrogen flame until it contracted to a diameter of about 2 mm, that considerable air could be added to the hydrogen flame before it blew back inside the burner. The horizontal burner was not so easy to control as the vertical blow-pipe, so that most of the work with hydrogen was done using the blow-pipe.

Gouy sprayers were used to mix various salts with the air. In the case of chloroform, carbon tetrachloride, and bromine, a double air path was used. By means of pinch-cocks the air could be made to pass over the liquid carrying the vapor with it, or by the other path air alone entered the burner.

The hydrogen and chlorine were obtained in the usual commercial tanks, and by suitable pressure regulators, any desired amount of each could be admitted to the flame. A motor driven blower, acting through a pipe line opening over the flame, was used to pump the HCl gas outdoors. Even then it was necessary to wear a gas mask while working with the hydrogen-chlorine flame.

The electrodes consisted of platinum wire, with small cross wires on the end. The negative electrode was kept coated with sealing wax and

the resulting oxides served to reduce the negative fall of potential and produce a uniform gradient in the flame. The potential difference was applied by means of a 300 volt battery connected in series with a galvanometer. The Hall effect angle was measured by means of two platinum probes mounted on the ends of two copper wires which were insulated from each other and supported by two coaxial quartz tubes. This probe assembly extended into the flame through a hole drilled in one of the pole-pieces of the magnet. The copper leads on the outside were connected to an electrometer having a sensitivity of about 5 cm per volt. The galvanometer and electrometer circuits were kept entirely insulated from the ground.

There is no simple method by which the absolute temperature of a flame can be quickly determined, and since relative values serve almost as well in the present case, a platinum-platinum-rhodium thermocouple was adopted. This thermocouple was placed near one of the electrodes in such a position as not to affect the current. In a well oxidized blue gasoline flame the couple gave a temperature of 1200°C. The actual temperature⁹ of such a flame is about 1870°C. In all cases the temperature as given by the couple has been used in this paper. The thermocouple was very useful in maintaining constant flame conditions. Flames of the same character at a given temperature could be consistently reproduced from day to day.

THEORY

The mobility of the positive and negative ions in a horizontal flame may be expressed by the following formula;¹⁰ $k_1 - k_2 = (1 - dR/R) Y/XH$, where k_1 = mobility of positive ions, k_2 = mobility of negative ions, X = horizontal electric field, Y = vertical electric field due to the Hall effect, H = magnetic field, and dR/R = magneto-resistance effect, or fractional increase of resistance of the flame when the magnetic field is on.

Since k_1 is small compared with k_2 , and $Y/X = \tan \theta$, where θ is the angle through which the probes must be rotated to bring the electrometer deflection back to zero when the magnetic field is on, the formula becomes, neglecting the resistance term, $k_2 = -10^8 \tan \theta / H$ cm/sec. per volt per cm. In all measurements of the angle θ , the necessary data for computing the potential gradient and the temperature were recorded at the same time. The magneto-resistance term dR/R was omitted in the formula, for the correction amounted to not more than 4 percent about the magnitude of the experimental error.

⁹ Hodgman and Lange, *Handbook of Chemistry and Physics*, p. 526.

¹⁰ C. W. Heaps, *Phys. Rev.* **24**, 652 (1924).

The simple type of theory indicates that the mobility of negative ions in a gas should vary with the square root of the absolute temperature if the mass remains constant. By varying the temperature it was thought that some confirmation of this conclusion might be found. The data, however, do not agree with this theory, hence there must be other factors entering which the simple type of theory does not contemplate. It seems probable that the mass of the ion is a function of the temperature. Above the flame where the temperature was 475°C, Saxer¹¹ found the mobility

Fig. 1. Mobility of negative ions in the horizontal gasoline flame as a function of potential gradient for various flame temperatures.

of the negative ions to be only 4.30, a value comparable with that of the positive ions. In the hot part of the flame the mobility may be several thousand, so it appears that high temperatures may tend to break up cluster ions, decreasing their average mass and thus increasing k_2 .

EXPERIMENTAL RESULTS

A. Temperature variation. By the addition of air and oxygen the temperature of the gasoline and hydrogen flames was varied and measurements of the mobility and potential gradient made. Fig. 1 shows graph-

¹¹ A. H. Saxer, Phys. Rev. 3, 325 (1914).

ically the effect of varying the temperature of the horizontal gasoline flame. Each curve represents measurements taken at a constant temperature. Curve 1 was obtained with a well oxidized blue flame, the temperature of the thermocouple being 1240°C. Oxygen was added to raise the temperature to 1400°C and data for Curve 2 were taken. The mobility for large gradients decreased. The Curves 3, 4, and 5 at the lower temperatures, were obtained by reducing the air supply. The upper part of the flame for these curves was luminous, though the electrodes were kept in the blue part of the flame. If the electrodes are placed in the luminous part, carbon collects rapidly on the electrodes and measurements are not reliable. For large gradients it will be noted that the mobility was varied from 2300 to 4000 by adding various amounts of air and oxygen.

In the horizontal hydrogen flame the mobility varied from 3500 to 2600 for a variation of potential gradient from 3 to 20 volts per cm. The temperature could not be changed much, and k_2 was practically constant for the temperatures used. Two sets of data chosen at random from that taken with the vertical hydrogen flame are given in Table I.

TABLE I
Typical results for vertical hydrogen flame

Temp.	Battery e.m.f. (volts)	Current (10 ⁻³ amp.)	X (volts/cm)	k_2
1215°C	20	24	4.1	4170
	40	44	9.3	4310
	80	75	20.4	4600
	130	90	32.2	3420
	170	110	44.1	3900
1370	20	30	4.2	4170
	40	59	8.8	4120
	80	105	19.5	4520
	130	170	33.8	5340
	170	190	42.2	5100

For low values of X the value of k_2 is about the same for both temperatures, but for large gradients the value of k_2 is larger at the higher temperature. All data taken show the same variation, so that the mobility for large gradients in the hydrogen flame undoubtedly increases with temperature.

B. *The effect of chloroform and carbon tetrachloride.* A two way air path was connected so that when desired the air furnished to the vertical hydrogen flame could be made to pass over liquid chloroform. A constant voltage of 80 was applied to the flame, the electrodes being one above the other, and the mobility was measured for various proportions of hydrogen,

air, and chloroform. At a thermocouple temperature of 1410°C (the electrodes were near the melting point and the hydrogen flame was probably around 2000°C), the value of k_2 for the free flame was 4800. Then as the chloroform path was opened, k_2 dropped to 4380, and finally with all the air passing over chloroform, k_2 was 3250. Then on lowering the temperature from 1410°C to 1190°C, by reducing the amount of hydrogen, leaving air and chloroform the same, k_2 dropped to 1625. The Hall effect angle for other potential gradients, with the air passing over liquid chloroform, varied from 3.2° to 4.8°, corresponding to values of k_2 ranging from 1230 to 1875.

The effect of the chloroform on the gasoline flame was even more striking, for here the Hall effect angle of 10.5° for the free blue flame dropped to 1.1° for a magnetic field of 5000 gauss. These angles correspond to a change of k_2 from 3690 to 384.

Another compound of chlorine, carbon tetrachloride, was mixed with the air-hydrogen flame. Table II shows the effect of varying the temperature of the flame while the amount of CCl_4 added remained constant.

TABLE II
Results for air-hydrogen flame with CCl_4 added

Temp.	X (volts/cm)	Angle	H (gauss)	k_2
1180°C	2.48	2.85°	4500	1110
	9.85	2.85	4500	1110
	20.6	3.3	4480	1285
	39.0	3.75	4500	1450
	46.0	4.15	4500	1610
1350	2.35	5.35	4480	2090
	8.7	6.35	4480	2490
	17.3	7.2	4400	2870
	35.0	9.1	4400	3640
1180	45.0	4.55	4400	1800

The temperature was varied by adjusting the hydrogen needle valve, the amount of air and CCl_4 remaining approximately constant. By changing the temperature of the thermocouple from 1180°C to 1350°C the mobility of the negative ion was practically doubled. When the temperature was again reduced to 1180°C k_2 dropped to 1800, a somewhat higher value than in the first instance. The lack of agreement is probably due to the rate of introduction of CCl_4 decreasing with time.

Hydrochloric acid gas is formed in the flame by the breaking up of chloroform and carbon tetrachloride. Any salt or oxide coating placed on the electrodes is removed in the flame in a few minutes. The electrodes

are so well cleaned that when subsequently used in the free hydrogen flame, with considerable applied potential, the current is so small that measurements of the gradient and Hall effect angle cannot be made. Most of the potential drop occurs very near the cathode if the latter is free of lime or salts.

C. *The effect of iodine and bromine.* Since compounds of chlorine cause such marked decreases in k_2 in the flame, it was thought that iodine and bromine, being also electronegative and having other properties similar to chlorine, might decrease k_2 . Iodine exists in a crystalline form at ordinary temperatures and is therefore more difficult to add to the flame, than chloroform. The data for Table III were obtained by first spraying alcohol into the flame, and then a solution of iodine crystals in alcohol.

TABLE III

Results for hydrogen flame when alcohol and solution of iodine in alcohol is added

Spray	Temp.	Battery e.m.f. (volts)	Current (10^{-7} amp.)	X (volts/cm)	k_2
Alcohol	1330°C	20	40	5.1	4580
		40	101	9.7	4880
		100	175	24.6	4550
		190	200	46.0	5360
		275	250	75.0	5690
Alcohol and iodine	1340	20	20	4.9	3810
		40	57	9.1	4660
		100	72	22.6	4380
		190	83	69.7	4680
		275	130	82.0	4000

With the addition of the iodine to the alcohol the current for the same applied voltage was decreased to one half and k_2 shows a definite decrease for all values of potential gradient. The quantity of iodine added to the flame in this experiment was probably small compared with the amount of chloroform added in the previous experiment. It is possible that larger proportions of iodine to air would cause a decrease in k_2 comparable with that produced by chloroform.

Liquid bromine was placed in one air path and added to the hydrogen flame. Bromine boils at 58.7°C and being quite volatile its vapor mixed readily with the passing air. The flame became bluish in color with a faint trace of yellow, and the oxide coat on the cathode disappeared as a deep red vapor. The Hall effect angle decreased from 10° to less than 1° for a field of 4800 gauss, which is the largest decrease in angle produced by any of the substances except chlorine gas. The corresponding decrease in k_2 is from 3700 to 360.

D. *The effect of NaCl, Na₂CO₃, NH₄Cl, and KCl.* The effect on k_2 produced by the addition of the chlorine compounds already described made it seem worth while to test other compounds of chlorine. For this purpose normal solutions of sodium chloride and sodium carbonate were sprayed into the hydrogen flame under the same conditions and compared. Table IV shows some of the data obtained at constant temperature.

TABLE IV

Results for hydrogen flame into which normal solutions of NaCl and Na₂CO₃ are sprayed

Salt	Temp.	X (volts/cm)	Angle	k_2
NaCl	1290°C	2.1	14.9°	5610
		2.9	13.9	5180
		5.1	13.9	5330
		10.1	13.5	5210
Na ₂ CO ₃	1290°	2.2	13.3	5190
		3.4	13.6	5200
		7.2	13.8	5400
		10.1	13.6	5380

The values of k_2 for NaCl and Na₂CO₃ in the hydrogen flame are practically the same.¹² Thus Cl introduced in the form of NaCl has no more effect on the mobility than CO₃ introduced as Na₂CO₃. The above data show that the value of k_2 for the salted vertical hydrogen flame is about 20 percent higher than for the free hydrogen flame at the same temperature.

A normal solution of potassium chloride sprayed into the hydrogen flame gave a mobility practically the same as was obtained with sodium chloride.

A concentrated solution of ammonium chloride was sprayed into the flame. The oxide coated cathode gave off a red vapor just as when chloroform was added. No doubt considerable HCl was formed in the flame since NH₄Cl dissociates into ammonia and hydrochloric acid at a temperature of 337.8°C. Values of k_2 were obtained varying from 3400 to 1770. The NH₄Cl thus produces a diminution of mobility which is quite appreciable.

E. *Distilled water and NaCl solution in the gasoline flame.* Some measurements were made on the gasoline flame, first spraying distilled water and then a solution of NaCl into the flame. The results for the small quartz tube burner were similar to those obtained by Watt,³ who

¹² H. A. Wilson has reached this same conclusion in the case of a gasoline vapor flame, loc. cit.³

used a large burner, large electrodes, and a larger current. The value of k_2 varied from about 3000 to 2000 and decreased with the increase in potential gradient, as he found to be the case. Contrary to his results, k_2 for small gradients at least was slightly higher for the salted flame than for the one containing distilled water. This behavior is similar to that in the case of the hydrogen flame, where k_2 is higher for the salted than for the free flame.

F. The effect of chlorine gas using the hydrogen flame. At ordinary pressures and temperatures chlorine may be fed directly to the hydrogen flame, using the blow-pipe, without air being added. The hydrogen-chlorine flame is characterized by a blue greenish color and a high temperature, equal to that of the air-hydrogen flame. Any salts on the electrodes are rapidly removed. The current through the flame was of the same order as that in an air-hydrogen flame with the cathode coated with oxides. The electrometer reading was much steadier than in the air-hydrogen flame.

Other writers working with the hydrogen-chlorine flame, have concluded that the positive ions have a greater mobility than the negative ions. The theory of the Hall effect indicates that if the mobility k_1 of the positive ions equals k_2 for the negative ions, the Hall effect will be zero, and if the positive ions have a greater mobility than the negative ions, the Hall effect changes sign.

Chlorine was added until the temperature of the flame was almost sufficient to melt the electrodes, but in no case could a reversal in the Hall effect angle be detected. Samples of values obtained for the angle and for k_2 are shown in Table V.

TABLE V
Results for hydrogen-chlorine flame

Angle	H	k_2
1.65°	5000 gauss	576
0.15	4975	52
0.6	4975	210
0.25	4650	94
0.3	4650	113
0.25	4650	94
0.2	4650	70

The smallest angle measured was 0.15°. Although the experiments were repeated on several days, there was no doubt about the direction of rotation of the Hall effect angle; it always indicated a greater mobility of the negative than of the positive ion.

Next some measurements were made on the potential gradient at different parts of the flame. Kalendyk⁶ found a larger potential gradient at the anode than at the cathode for the hydrogen-chlorine flame.

The flame and the current electrodes were arranged so that they could be moved vertically, the potential probes being fixed through the pole-pieces of the magnet. In all trials the potential gradient was found to be greater at the anode, which was the lower electrode. But a large drop of potential at the anode indicates that the positive ions have a greater velocity than the negative ions. By the Hall effect method, however, k_2 was always greater than k_1 . Then it was thought that the velocity of the flame gases might have some influence on the potential drop, so the potential gradient was measured with the upper electrode as the anode. Again a much larger drop in potential was found near the lower electrode, now the cathode. These tests were repeated several times on different days and always agreed. The conclusion to be drawn is that k_2 is greater than k_1 in the hydrogen-chlorine flame but that the actual velocity of the positive ions may be greater than that of the negative ions. The velocity of the flame gases is an important factor to consider. For a quartz tube burner the velocity is about 200 cm per sec. The velocity for the blow-pipe burner used was certainly very much greater than this, so that when plenty of chlorine is used in the flame the velocity given to the negative ions by the flame motion is greater than the velocity given by the electric field, unless the latter is quite large.

The large potential drop at the lower electrode no matter whether it is made the anode or cathode is therefore explained as follows. If the lower electrode is the anode then the positive ions are carried up both by the flame and by the electric field while the negative ions must move down against the flame motion. Thus the positive ions have their velocity increased and the negative ions have theirs decreased, the resultant velocity of the positive ions is greater than that of the negative ions, and a negative space charge is set up around the anode. The anode fall of potential is in this case greater than the cathode fall. The Hall effect angle indicates that under these conditions the mobility of the negative ions is not much greater than that of the positive ions.

If the upper electrode is now made the anode, the positive ions must move down against the flame motion and the negative carriers will move up with the flame gases. Thus the negative ions have a greater velocity than the positive ions, which in this case are retarded by the gas motion. This condition results in a larger potential drop at the cathode than at the anode.

The effect of chlorine on the gasoline flame is similar to that of chloroform. If no air is mixed with the gasoline vapor the flame becomes luminous. On adding chlorine gas, the flame remains luminous, k_2 is small, and measurements are difficult since carbon collects rapidly on the electrodes.

CONCLUSIONS

The effect of flame temperature on the mobility of the negative ion cannot be predicted by the simple formula of kinetic theory. As the temperature of a gasoline vapor flame is raised by the addition of oxygen the mobility of the ion decreases. If hydrogen is burned instead of gasoline vapor the mobility increases with temperature, at least in a strong electric field. It appears probable that the negative ion during its life is a free electron part of the time and a charged atom or cluster of atoms the rest of the time. The mobility will diminish as the fraction of the ion's life as a free electron diminishes. A high temperature should be unfavorable to the existence of ionic clusters, so one would expect the mobility to increase with temperature. However, to increase a flame temperature the character of the flame must be changed and possibly constituents appear which have a tendency to attach the free electrons. In this way the diminution of mobility of the negative ion in the gasoline flame may be explained.

The experiments show clearly that feeding Cl, Br, and I into a flame diminishes the mobility of the negative ion. Franck and Pringsheim maintain that in a hydrogen-chlorine flame the negative ion is practically never a free electron. The present experiments indicate that Br and I behave like Cl in the hydrogen flame, and that the electron is quickly attached to atoms of the introduced halogen, or possibly to combinations of the halogen with hydrogen. When the temperature of the H_2 -air- CCl_4 flame was raised by varying only the H_2 constituent the mobility of the negative ion increased. In this case the higher temperature evidently tended to prevent the attachment of Cl or of HCl to the electron.

If Cl is fed into the flame as NaCl or KCl it does not appear to slow up the negative ion. However, when introduced as NH_4Cl , CCl_4 , or $CHCl_3$ its effect is decidedly evident. The latter compounds are easily broken up so that a Cl or possibly HCl molecule is free to attach an electron. The breaking up of the salts of the metals does not appear to be extensive enough to produce constituents which can attach electrons, or possibly an electron is produced for each atom of metallic salt which is broken up. In the latter case the negative ions would be a mixture of free electrons and ionic clusters.

These experiments do not corroborate the conclusion of Franck and Pringsheim that the mobility of the negative ion in the hydrogen-chlorine flame is less than that of the positive ion. The presence of a potential drop at the anode larger than that at the cathode may be caused by the high velocity of the flame gases, even though the mobility of the negative ion is greater than that of the positive ion.

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