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THE PHENOMENA OF IONIZATION IN FLAME
GASES AND VAPORS.¹

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INTRODUCTION.

IN a previous paper on the phenomena of ionization in flames² the writer described a new method for studying the phenomena of electrical conduction through flame gases and vapors. The old method, employed by Sv. Arrhenius,³ H. A. Wilson⁴ and most other investigators of the electrical conductivity of flames, was to introduce into the flame under investigation clean platinum electrodes which became heated to incandescence by the flame. The conductivities of the flame gases and vapors between the electrodes were then compared by comparing the currents which a given impressed electromotive force would send through the flame.

All investigators found that under the above conditions the current increased less rapidly than the impressed electromotive force, and according to some, seemed to approach a saturation value. It was also found that for a given impressed electromotive force the current depended very largely upon the temperature of the electrodes, particularly that of the cathode, and was practically inde-

¹ A preliminary account of some of the work described in the present paper was given in the *PHYSICAL REVIEW*, Vol. XX., p. 186.

² *Phys. Zeitschr.*, Band 5, Heft 3, pp. 76-81.

³ *Wied. Ann.*, XLII., 1891.

⁴ *Phil. Trans. A.*, Vol. CXCII., 1899.

pendent of the distance apart of the electrodes. This led some investigators¹ to advance the hypothesis that the ionization to which the conductivity of the flame was due, took place almost entirely at the surface of the glowing electrodes, and that throughout the volume of the flame there was little or no ionization.²

It was pointed out by the writer in the paper above referred to, that the total resistance encountered in the flame (R) may be considered in three parts, the resistance in the neighborhood of the cathode (R_k), the resistance in the neighborhood of the anode (R_a), and the resistance of the remainder of the flame between the electrodes (R_f) giving the equation $R = R_k + R_a + R_f$, and that if R_k or R_a were large in comparison with R_f , a variation in the distance apart of the electrodes would not change appreciably the value of R . Furthermore, it was shown that since R_k and R_a are functions of the conditions at the electrodes and of the current flowing between them, the above mentioned relations between current, electromotive force, and temperature of the electrodes, could be explained without denying the existence of a very considerable volume ionization throughout the flame.

The device employed by the writer for studying the electrical conductivity of flame gases and vapors has for its objects:

I. The reduction of the electrode resistances R_k and R_a to an order of magnitude equal to or smaller than that of the flame resistance R_f .

II. The maintenance of uniform conditions around the electrodes while the conditions throughout the conducting flame are being varied, as for example, by the introduction of the vapors of various salts.

III. The entire elimination of the electrode resistances, by determining the resistance, or conductivity, of a given section of the connecting flame from measurements of the current through that section and of the potential difference between the two faces of the section.

¹ H. A. Wilson, *ibid.*; J. J. Thomson, *Conduction of Electricity through Gases*, London, 1903, pp. 172 and 199.

² This view has been abandoned by H. A. Wilson in a recent paper, *Phil. Mag.*, Vol. 10, No. 58, pp. 476-485, in which he takes the view of a volume ionization throughout the flame.

The first of these objects was accomplished by the employment of platinum electrodes (P, P , Fig. 1) coated with calcium oxide and heated in separate electrode flames. Such incandescent electrodes of calcium oxide have been shown by Whenelt¹ to possess the property of offering a very slight resistance to the passage of an electric current to or from a conducting gas. The resistance of the electrode flames was made very small by supplying the burners

Fig. 1.

E, E , Fig. 1, with a mixture of gas and of air which had been blown through an atomizer containing a strong solution of potassium nitrate, the vapor of this salt being known to impart a very high degree of conductivity to the flame containing it. The flame under investigation was used as a connecting flame between the two electrode flames, and its resistance was made as great as possible by using, as a burner, a long narrow slot (0.1 cm. by 21 cm.) cut in a block of soapstone (B , Fig. 1). This burner gave a very broad, thin flame having a relatively large resistance.

¹ Ann. der Phys., Band 4, Heft 14, p. 425, 1904.

The second object was accomplished by having the supply of gas and air for the connecting burner independent of the supply for the electrode burners, so that the conditions in the connecting flame could be altered without in any way changing the conditions around the electrodes. The gas and air supplied to the connecting flame were both passed through suitable meters so that the volume of either consumed per minute could readily be measured. The type of meter used consisted of a small circular opening in a thin, metal diaphragm so mounted that the difference of pressure on the two sides of the diaphragm, when a current of gas or air was flowing through the opening, could be accurately measured by an inclined *U*-tube manometer containing xylene. A schematic diagram of one of these meters is shown in *M*, Fig. 8. Each meter was calibrated by connecting it in series with a standard gas meter, and the values of the manometer readings were determined in cubic feet per minute when gas or air was blown through. The conditions in the connecting flame could thus not only be varied independently of the electrode flames, but the volumes of gas, air, or spray supplied to the burner could readily be measured.

To accomplish the third object, the current through the flame was measured by connecting in series with the electrodes (*PP*, Fig. 1), a galvanometer of the d'Arsonval type, sensitive to about 10^{-8} amperes and provided with a universal shunt. The electromotive force employed was furnished by a battery of dry cells, and could be varied between about 1.5 and 200 volts. The difference of potential between the two faces of any section of the connecting flame was determined by inserting two fine, platinum wires (*pp*, Fig. 1) near the tip of the inner blue cone, and at a distance apart equal to the breadth of the section under investigation. The wires were connected respectively to the needle and to the middle point of the series of batteries used to impress a fixed difference of potential between the quadrants. Under these conditions the deflections of the electrometer needle were directly proportional to the difference of potential between the wires *pp* for all values of the potential to be measured.

The difference of potential between the wires *pp* was shown by the following experiments to be a true measure of the difference of

potential between the corresponding points in the flame. The introduction into, or withdrawal from the flame, of the electrometer wires, was found to produce no change in the current through the flame of as much as one per cent. of its value. The difference of potential across a breadth of 6 cm. of the connecting flame was measured by means of the electrometer wires in three steps of 2 cm. each, and again in a single step of 6 cm. the two measurements were found to agree within the errors of the readings. A further test of the correctness of the potential difference obtained by the use of the electrometer wires was made by measuring with them the potential difference across the connecting flame and also the difference of potential between either electrode plate and one of the electrometer wires inserted at the boundary between the electrode flame and the connecting flame. The sum of the three differences was found to be equal to the electromotive force impressed at the electrodes.

Measurements of the potential difference between the cathode plate and the flame around it under various conditions showed that this difference increased much more rapidly than the current between the electrodes, and it was found that by using a long connecting flame, a small impressed electromotive force (one or two volts) and a saturated solution of KNO_3 in the atomizer supplying the electrode flames the resistances at the electrodes could be made so small in comparison with the resistance of the connecting flame that they could be neglected without introducing any appreciable error. Under these conditions the conductivity of the connecting flame could be taken as directly proportional to the current for a given impressed electromotive force. In some cases it was found more convenient to determine relative conductivities in this way than by the use of the electrometer wires. A comparison of the two methods, however, showed that in all cases they gave the same results.

In this paper the term "conductivity of a given section of the connecting flame" will be used to designate the quotient obtained by dividing the current through the flame by the potential difference between the two faces of the section. Since the connecting flame was not rectangular in shape, but was more or less irregular

in its upper boundary, the lines of current flow and the equipotential lines in the connecting sheet of flame are not straight but are slightly curved, and therefore the "given section" above referred to is not a rectangular section. As, however, the measurements, were all relative, the shape of the section was unimportant so long as it remained the same. Furthermore, it was found that the size and shape of the upper portions of the flame had little or no influence on the total conductivity, as over 90 per cent. of the current was carried by the lower portions of the flame quite near the slot of the burner.

The experiments described in this paper have been made with flames consuming ordinary illuminating gas. The measurements are mostly relative, and the paper is more in the nature of a qualitative investigation into the source of ionization in flame gases and vapors than a quantitative study of the same. The writer hopes soon to be able to make a more quantitative study of the phenomena. The measurements already made have, however, led to a number of very important general relations which are given in the following sections.

I. A SATURATION CURRENT NOT POSSIBLE IN THE COMBUSTION CONES OF THE ORDINARY BUNSEN FLAME.

Some experiments were undertaken by the author in connection with Dr. J. Stark¹ for the purpose of ascertaining whether a saturation current could be obtained between two platinum wire electrodes, either clean or coated, with CaO placed very close together in the Bunsen flame. The results showed conclusively that no trace of a saturation current could be obtained under these conditions, but that for impressed electromotive forces of over 100 volts, the current increased more rapidly than the electromotive force. Under these conditions it was not possible to determine the relation between current and potential gradient in the flame, since the gradient could not be considered as uniform between the electrodes.

Later some experiments were undertaken by the author, in which the long connecting flame was used between the two electrode

¹ Phys. Zeitschr., Band 5, Heft 9, pp. 248-257.

flames. Various electromotive forces, up to 8,000 volts, were impressed at the electrodes, and the potential gradient and corresponding current in the connecting flame were measured as described in the introduction, the electrometer wires being placed in the inner blue cone of the flame and about 4 cm. apart. For

Fig. 2.

potential gradients ranging between 0.1 and 50 volts per cm., the current was found to increase directly as the potential gradient, the relation being a simple linear one. For gradients between 100 and 400 volts per cm., the current was found to increase more rapidly than the potential gradient. The results are shown in the curve, Fig. 2. When the impressed electromotive force was still farther increased, there were unmistakable evidences of ionization by impact, such as a sudden increase in the current, a decrease in the potential gradient and a marked increase in the temperature of the electrodes and of pieces of mica or platinum that might be placed in the connecting flame.

Experiments were also tried in which the electrode flames and the electrometer wires were placed in the outer blue cone of the connecting flame instead of in contact with the inner blue cone. The results, however, were similar to the above, showing that within

the combustion cones of the flame it is not possible to obtain a saturation current. Within these regions the rate of production of ions is so great that ionization by impact is produced before the potential gradient is great enough to remove the ions as fast as formed.

II. ELECTRICAL CONDUCTIVITY OF THE DIFFERENT CONES OF THE BUNSEN FLAME.

For the purpose of studying the electrical conductivity of the different parts of the Bunsen flame, a separable cone burner was constructed by placing over the slot in a soapstone burner similar to *B*, Fig. 1, a rectangular chimney of soapstone 1 cm. wide on the inside and 9 cm. high. Through small holes in the ends of the chimney, copper wires were inserted carrying thin platinum foil electrodes coated with CaO. The electrometer wires were inserted through small holes in one side of the chimney, about 4 cm. apart and directly between the electrodes. The holes were so spaced that the electrodes and the electrometer wires could be placed in either of the following positions: (1) In the inner blue cone, (2) in the space about a centimeter above the inner blue cone, (3) in the space just below the outer blue cone, (4) above the chimney in the outer blue cone.

In each of the above positions the electrometer wires were placed 4 cm. apart and directly between the electrodes, which were ordinarily kept about 8 cm. apart. The currents and the corresponding potential differences between the electrometer wires were measured in each of the above positions for a number of different impressed electromotive forces. The following are representative of the results obtained:

Position 1. — With a potential gradient of 12 volts per cm., the current was 2.7×10^{-4} amperes, and increasing the gradient increased the current in the same proportion.

Position 2. — A potential gradient of 9 volts per cm. gave a current of 4.5×10^{-7} amperes, and doubling the potential gradient increased the current to only 6.0×10^{-7} amperes.

Position 3. — A potential gradient of 10 volts per cm. gave a current of 3.5×10^{-8} amperes, and doubling the potential gradient did not appreciably increase the current.

Position 4. — A potential gradient of 9 volts per cm. gave a current of 2.1×10^{-6} amperes, and increasing the potential gradient increased the current proportionately.

On comparing the specific conductivities of the different parts of the flame from the above data, it should be kept in mind that the cross-sections of the blue cones carrying the currents in positions 1 and 4 were much smaller than the cross-sections of the intermediate gases carrying the currents in positions 2 and 3. The difference in specific conductivity between the blue cones and the intermediate gases is, therefore, even greater than would appear from the above data. From these data it appears that the specific conductivity of the gases in the inner blue cone of the Bunsen flame is about 1,000 times greater than the specific conductivity of the gases in the region just above the blue cone, and about 10,000 times greater than the specific conductivity of the same gases after ascending some 7 or 8 cm. above the lower cone. The measurements also show the specific conductivity of the inner cone to be about 100 times that of the outer cone.

While the measurements in the combustion cones showed no indication of a saturation current, the measurements made in the region between the two cones showed unmistakably the possibility of such in this region.

These measurements would seem to show that in the Bunsen flame, the source of the ionization is the chemical process of combustion taking place in the two cones of the flame, and that between and outside of these cones we have recombinations of the ions produced in the cones. Therefore the number of free ions per c.c. in the ascending gas diminishes rapidly as the gas is carried away from the regions of combustion.

In the case of the ordinary luminous gas flame where no air is mixed with the gas before it reaches the burner, it was found that the conductivity of the upper luminous portion of the flame was very small in comparison with the conductivity of the colorless, or faintly blue, lower portion. This was shown by introducing a sheet of mica across the flame so as to cut in two the upper luminous portion, when it was found that the current was not appreciably diminished. If, however, the mica were lowered so as to cut into

the lower non-luminous portion, the current was decreased and became zero when the mica sheet touched the burner. This shows that the chemical reactions taking place in the lower non-luminous portions of the ordinary gas flame are the ones chiefly productive of ionization, and that the consumption of the carbon particles in the upper luminous portions of the flame is accompanied by a relatively small amount of ionization.

III. RELATION BETWEEN THE CHARACTER OF COMBUSTION IN A GAS FLAME AND ITS ELECTRICAL CONDUCTIVITY.

The next experiments were for the purpose of comparing the electrical conductivities of flames consuming the same quantity of illuminating gas per minute, but having mixed with the gas various quantities of air or carbon-dioxide, so as to change the character and appearance of the flame. The burner used was the long, slot burner *B*, Fig. 1. Measurements of the conductivity of the ordinary, luminous type of gas flame and of the Bunsen type of flame consuming the same volume of gas per minute showed that the Bunsen flame possessed from one and a half to two times the conductivity of the luminous flame. When the volume of gas supplied to the burner was kept constant, and gradually increasing amounts of air mixed with it before feeding it to the burner, the character of the flame changed gradually from the luminous to the Bunsen type. In this transition five rather distinct types of flame could be recognized by the eye. The diagrams in Fig. 3 show roughly the

Fig. 3.

appearance of cross-sections of the different types. The ordinary, luminous type of flame is shown in *A*, no air being mixed with the gas before it was fed to the burner. The addition of air caused the flame to become shorter and change gradually to the type represented in *B*, which showed some rudiments of an inner blue cone,

and that portion of the carbon luminosity immediately above the inner cone seemed to be more luminous and of a less reddish hue than the rest. When the volume of air added was about equal to the volume of gas, the carbon luminosity had disappeared, with the exception of a faintly luminous cap to the rather feeble inner blue cone, type *C*. The further addition of air destroyed this luminous cap, and when the volume of air was something over twice the volume of gas, a cross-section of the flame had much the appearance shown in *D*. The inner blue cone seemed to have no well developed cap. The further addition of air caused the flame to assume the Bunsen type, *E*, and on continuing to increase the supply of air, the only effect was to cause the combustion cones to contract around the mouth of the burner.

Measurements were made of the conductivity of a given section of the above flame as gradually increasing amounts of air were added to a constant supply of gas of 0.18 cu. ft. per minute. The relation between conductivity and rate of supply of air is given

Fig. 4. Supply of Gas Constant at 0.18 cu. ft. per minute.

in the curve, Fig. 4. The measurements showed that the change in the character of the flame from type *A* to type *C* was accompanied by an increase in its conductivity, while the change from type *C* to *D* caused a decrease in conductivity. After the full development of the inner blue cone, the further addition of air caused the conductivity to increase to a maximum and then to decrease again, but rather slowly, as the velocity of efflux of the gases from the burner becomes greater and the combustion cones smaller.

A close relation between the character of the combustion taking place in a flame and its electrical conductivity was to be expected after the experiments described in section II., which showed that the

process of ionization was practically confined to the combustion regions of the flame, and was dependent on the type of combustion taking place in those regions. The number of free ions per cubic centimeter in any combustion region depends, however, in all probability, not only on the character of the chemical reactions taking place in that region, but also on the temperature and possibly the dilution of the gas in the region of combustion. Some such assumption would seem to be demanded for the explanation of the following phenomena :

When gradually increasing amounts of CO_2 instead of air were mixed with a fixed volume of the illuminating gas before delivery to the burner, the effect was to decrease the carbon luminosity and give a flame consisting of a single, thin, blue combustion sheet on either side of the burner slot. Measurements on the conductivity of the flame showed, however, no marked variation in conductivity until enough CO_2 had been added to destroy all the carbon luminosity, when the further addition of CO_2 caused a gradual decrease in the conductivity. The decrease was approximately proportional to the increase in the rate of supply of CO_2 .

IV. RELATION OF FLAME CONDUCTIVITY TO RATE OF CONSUMPTION OF GAS.

Measurements were next made for the purpose of determining the relation between the conductivity of a given section of the connecting flame and the rate of consumption of gas by the flame. For flames of ordinary illuminating gas unmixed with air (type *A*, Fig. 2), and consuming over a few hundredths of a cu. ft. of gas per minute, the relation between conductivity and rate of consumption of gas was found to be a linear one, although, for rates of consumption of over 0.15 cu. ft. per minute, with the burner used, the flame became very smoky. A typical set of readings is given in Fig. 5.

The conductivity of a shorter section of the connecting flame was measured for rates of gas consumption ranging from 0.01 cu. ft. to 0.16 cu. ft. per minute. For rates of consumption less than a few hundredths of a cu. ft. per minute, with the burner used, the flame consisted of a single blue cone with no carbon luminosity.

Fig. 5.

The character of the flame changed to the ordinary luminous type as the rate of supply of gas was increased. The relation between

Fig. 6.

the rate of consumption of gas and the electrical conductivity of the flame is shown by the curve in Fig. 6. It was found that at first,

for the non-luminous flame, the conductivity increased quite rapidly with the rate of supply of gas. As the carbon luminosity became more pronounced the conductivity increased less rapidly, and finally, after the development of a flame of type *A*, Fig. 2, the relation between conductivity and rate of gas consumption became practically a linear one.

Other experiments were made in which air was mixed with the illuminating gas before feeding it to the burner, and as the supply of gas was increased, the supply of air was increased in the same proportion, so as to keep the ratio of air to gas a constant. This gave the same type of flame for all rates of supply of gas. Under these conditions measurements were made of the conductivity of the connecting flame for various rates of consumption of gas and for different ratios of gas to air. The result of a typical set of readings is

Fig. 7.

given in Fig. 7, the volume of air being equal to the volume of gas. So long as the character of the flame was kept the same and the ratio of gas to air remained constant, the electrical conductivity of the flame was found to increase directly with the rate of consumption of gas by the flame.

The above simple relation between the electrical conductivity and the rate of supply of gas to a flame is readily explained if we assume that for a given type of combustion the number of free ions per

cubic centimeter within the region of combustion remains constant. Increasing the rate of supply of gas to the burner would cause a proportional increase in the cross section of the combustion zone, and the electrical conductivity would increase directly as the area of this cross section.

V. CONDUCTIVITY IMPARTED TO A FLAME BY SALT VAPOR.

Investigations on the conductivity imparted to a gas flame by the introduction of spray from a solution of salt were carried on by means of the apparatus shown in Fig. 8. The spray from the solu-

Fig. 8.

tion under investigation was obtained by passing a current of air or illuminating gas through an atomizer (*A*) containing the solution. The spray from the atomizer was led into a settling bottle (*B*) where the larger drops carried over from the atomizer were deposited. The spray was then conveyed through a T-tube to a meter (*M*) and thence to a Y-tube where it could be mixed with definite volumes of air or gas before being delivered to the burner. The diaphragm in *M* could readily be changed, and by means of the pinch-cock *C*, the flow of spray could be so regulated that for any size of opening in the diaphragm the difference in pressure on the two sides could be kept constant without changing the pressure on the atomizer. Under these conditions it was found that the flow through the diaphragm was directly proportional to the area of the opening. This device afforded two means of varying in a measurable manner the quantity of salt introduced into the flame: (1) Keep-

ing the opening in the diaphragm and the difference in pressure between the two sides the same, the concentration of the solution in the atomizer could be varied; (2) keeping the same solution in the atomizer, the size of the opening in the diaphragm in M could be altered and varying quantities of the spray admitted to the flame.

The conductivity imparted to the flame by the salt spray was determined by subtracting from the total conductivity determined in the usual way, the conductivity of the flame when consuming an equal amount of gas and of air which had been blown through the atomizer when it contained water in place of the salt solution. Whether the air was saturated with water vapor or dry seemed to make no difference in the conductivity of the flame.

Preliminary measurements showed that the conductivity imparted to the connecting flame by the introduction of salt spray varied greatly according to the character of the flame. Measurements of the relative conductivities imparted to a flame by different quantities of salt spray were also found to be quite different for the different types of flame. It therefore seemed desirable to investigate more carefully the effect that variations in the character of the flame would have on the salt conductivity imparted to the flame by a given amount of spray.

Experiments were undertaken for the purpose of determining the effect on the salt conductivity of gradually increasing the supply of gas to the burner while keeping the rate of supply of air and of salt spray constant. Increasing the supply of gas caused the flame to change gradually from a forced Bunsen flame of type E to a flame of type B , very rich in carbon luminosity. The rate of supply of air and spray from the atomizer through the meter (M , Fig. 8) was kept constant at 0.23 cu. ft. per minute. Measurements were made of the salt conductivity imparted to the flame by the spray from a solution of NaCl as increasing quantities of gas were mixed with the spray. The measurements were repeated when solutions of different concentrations were placed in the atomizer, the rate of supply of air and spray being kept constant at 0.23 cu. ft. per minute. The results are shown in the curves in Fig. 9. An examination of the curves shows that the salt conductivity increases at first very rapidly with the increase of gas. It reaches a maximum

when the rate of supply of gas is about equal to the rate of supply of air through the atomizer, giving a flame of type *C*. The salt conductivity then decreases, but very slowly, as the rate of supply

Fig. 9.

of gas is increased. A change in the concentration of the salt solution in the atomizer does not change the general character of the above relation.

Other experiments were tried in which the salt spray was introduced into the flame by blowing the gas itself through the atomizer. The supply of gas and spray from the atomizer was kept constant and gradually increasing amounts of gas supplied to the burner by a separate tube. Under these conditions the salt conductivity imparted to the flame remained almost constant, although the cross-section of the flame, due to the addition of the gas, was increased several times.

Other measurements of the salt conductivity imparted to the flame were made when the rate of supply of spray was kept constant and the rate of supply of gas and of air both increased in such a way as to keep the total volume of air equal to the volume of gas supplied. Under these conditions it was found that the salt conductivity increased directly with the rate of supply of air and gas for all solutions of moderate concentration. When a very concentrated solution of NaCl was placed in the atomizer, the salt conductivity

imparted to the flame seemed to increase somewhat less rapidly than the rate of supply of air and gas. The results of measurements made with three different concentrations of salt solution in the

Fig. 10.

atomizer are given in the curves of Fig. 10, the volume of air was kept equal to the volume of gas supplied.

In the next experiments the illuminating gas itself was blown through the atomizer, and the rate of supply of gas and spray to the burner was kept constant at 0.17 cu. ft. per minute. The conductivity of the flame was then measured, as gradually increasing amounts of air were mixed with the gas and spray before delivery to the burner. Under these conditions the character of the flame changed from a flame of type *A* through the intermediate types to a forced Bunsen flame of type *E*. The measurements of the gas conductivity when pure water was placed in the atomizer are given

Fig. 11.

in the curve in Fig. 11. The measurements of the salt conductivity imparted to the same flame when solutions of NaCl of different concentrations were placed in the atomizer are given in the curves of Fig. 12. An examination of the figures shows that the mixture of

Fig. 12.

air and gas which gives the maximum conductivity to the pure flame gives also the maximum of salt conductivity. The addition of air to a flame of type *A* containing salt spray causes the salt conductivity to increase at first with the quantity of air added. This increase continues until the rate of supply of air is about equal to the rate of supply of gas, when the farther addition of air causes a less rapid increase in the salt conductivity until enough air has been added to give a flame of type *E*. Continuing the addition of air causes a more rapid increase in the salt conductivity which finally reaches a maximum when the volume of air is between three and four times the volume of gas. The ratio between this maximum of salt conductivity and the conductivity imparted by the same quantity of salt to the flame of type *A* when no air was mixed with the gas, was found to be quite different when different concentrations of the salt solution were used in the atomizer. The following are the ratios obtained :

Number of Grams of NaCl Dissolved in 200 cc. of H ₂ O.	Ratio of Maximum Salt Conductivity Im- parted to a Flame of Type <i>E</i> to the Conduc- tivity Imparted to a Flame of Type <i>A</i> Con- suming the Same Quantity of Gas.
20	2.9
1.6	5.7
.8	6.8

These numbers show that the variation in the salt conductivity due to a variation in the character of the flame, on the addition of air, is much greater when the quantity of salt in the flame is small than when it is large. The increased quantity of salt ions in the flame seems to diminish in some way the effects of the changes tending to bring about an increase in ionization.

Experiments were also made in which gradually increasing amounts of pure oxygen instead of air were added to a fixed rate of supply of gas and spray. The results were of a similar character to those obtained by the use of air.

Another set of measurements was made in which gradually increasing amounts of CO₂ in place of air were added to the fixed rate of supply of gas and spray from the atomizer. For very dilute solutions of NaCl in the atomizer, the addition of CO₂ caused no change in the salt conductivity imparted to the flame until enough CO₂ had been added to destroy the carbon luminosity, when the farther addition of CO₂ caused a decrease in the conductivity. For the more concentrated solutions in the atomizer the salt conductivity seemed to decrease with the first addition of CO₂. The results of measurements made with three different concentrations of salt solution are given in the curves of Fig. 13. The rate of supply of gas and spray was kept constant at about 0.17 cu. ft. per minute.

Experiments were made with the separable cone burner described in Section II., when a large quantity of spray from a saturated solution of NaCl was mixed with the air and gas before delivery to the burner. Measurements of the current and potential gradient were made in the positions 1, 2, and 4 (see Section II.), with the following results:

Position 1.—With a potential gradient of 7 volts per cm. the current was 7.5×10^{-4} amperes.

Position 2.—A potential gradient of 0.7 volt per cm. gave a current of 7.5×10^{-6} amperes.

Position 4. — A potential gradient of 10 volts per cm. gave a current of 75×10^{-6} amperes.

In all these positions an increase in the potential gradient was accompanied by a proportional increase in the current. If, from the

Fig. 13.

total conductivity of the different cones given above, we subtract the conductivity due to the flame gases given in Section II., we shall have numbers expressing, approximately, the salt conductivity imparted to the different cones of the flame. In this way it was found that the conductivity imparted to the inner blue cone by the salt spray was about ten times the conductivity imparted by the spray to the region just above the inner cone, and about two hundred times the conductivity imparted to the outer blue cone. The difference between the salt conductivity of the inner blue cone and the conductivity in the region between the two cones is seen to be very much less than for the flame gases themselves. (See results given in Section II.)

It seems difficult, if not impossible, to account for the phenomena described in this section on the assumption that the ionization of the salt spray in the flame is due simply to the high temperature of the flame. The temperature at a given point in the region of combustion in a flame of type *A* can certainly not decrease with the increase in the supply of gas to the flame. There would there-

fore be no good reason for assuming that the rate of production of salt ions per cu. cm. in this region of combustion would be diminished by increasing the supply of gas if the ionization were due simply to the temperature. Increasing the supply of gas would however, increase the cross-section of the combustion zone, so that one would naturally expect an increase in the total salt conductivity imparted to a flame of type *A* on the addition of gas. The experiments showed that the salt conductivity remained practically a constant for widely varying rates of supply of gas. When, however, a flame of type *C* was obtained by mixing air with the gas, the salt conductivity did increase in almost direct proportion to the amounts of gas and air added (see Fig. 10). Furthermore, the addition of air to a flame of type *A*, the rate of supply of spray and gas being kept constant, was shown to cause an increase in the salt conductivity (see first parts of curves in Fig. 12).

The above seems to warrant the conclusion that in order to have the salt spray ionized in the flame one must have not only the high temperature of the flame, but also the mixture of the spray with oxygen. Other conditions remaining the same, the salt conductivity imparted to a flame by the introduction of salt spray can be increased by the addition of air or oxygen.¹

VI. RELATION BETWEEN SALT CONDUCTIVITY AND THE RATE OF SUPPLY OF SALT TO THE FLAME.

Experiments were next undertaken for the purpose of determining the effect on the salt conductivity of increasing the rate of supply of spray to a flame of type *B* consuming gas at a fixed rate. Three methods were tried for varying the rate of supply of spray.

1. The diaphragm in the meter *M*, Fig. 8, was changed and the pinch-cock *C* so adjusted that for different openings in the diaphragm the difference in pressure on the two sides remained constant. Under these conditions the rate of supply of spray to the burner could be increased by increasing the rate of supply of air in the same proportion. The constant rate of supply of gas to the burner was large enough to give a flame of type *B* for even the largest amount of air and spray. Under these conditions it was

¹ Some further results are given in the PHYSICAL REVIEW, Vol. XXII., page 113. On page 114, the 16th line from the top, instead of $Na = 6$, it should read $Na = 3$.

found that with rather concentrated solutions of NaCl in the atomizer, the salt conductivity imparted to the flame increased directly with the volume of spray supplied to the flame. With very dilute solutions, however, the salt conductivity seemed to increase a little more rapidly than the rate of supply of air and spray. The

Fig. 14.

results of measurements made with two solutions of very different concentrations are given in the curves of Fig. 14.

2. In the above method of varying the supply of spray to the flame, the proportion of air to gas was also varied. To avoid this, a second method of varying the rate of supply of spray was tried in which, by means of an independent supply of air, the quantity of spray delivered to the flame could be varied without changing the proportion of air to gas.

3. A second method of accomplishing the same result would be to vary the concentration of the salt solution in the atomizer, keeping other conditions the same. Both of these methods were tried, and the results are given in the following table. The flame in both cases was of the type *B* having the volume of air less than the volume of gas.

The numbers in the first vertical column of the table are proportional to the salt conductivities imparted to the flame by the spray from a very concentrated solution of NaCl (40 g. in 200 c.c.),

when the area of the opening in the diaphragm was respectively 1, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the area of the largest opening used. The numbers in the other vertical columns are proportional to the salt conductivities when solutions of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the concentration of the above were used in the atomizer. The numbers in the horizontal rows of the table, therefore, are proportional to the salt conductivities imparted to the flame by spray from the different solutions when the area of the opening in the diaphragm remained the same.

Concentration of Salt Solution.

		Concentration of Salt Solution.					Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Concentration of the Solution.
		1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{24}$	
Area of Diaphragm Opening.	1	94	77	60	43	25	3.8
	$\frac{1}{2}$	73	55	41	28	16	4.6
	$\frac{1}{4}$	53	41	29	20	11	4.8
	$\frac{1}{8}$	34	26	18	12	6	5.7
	$\frac{1}{24}$	16	12	9	6	2.5	6.4
Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Diaphragm Opening.		5.9	6.4	6.7	7.2	10.0	

The numbers representing the conductivities imparted to the flame by small quantities of the salt vapor are liable to a larger percentage of error than the numbers representing the larger conductivities. They were obtained, like the other numbers, by subtracting from the total flame conductivity the conductivity of the flame when water was placed in the atomizer instead of the salt solution. For small quantities of salt in the flame, however, the total conductivity was of the same order of magnitude as the conductivity of the flame with water in the atomizer, and since it was found difficult to maintain absolutely uniform conditions in the flame, these

small differences are liable to a possible error of as much as 25 per cent. for the very smallest conductivities.

In the vertical column to the right of the table are given the ratios between the salt conductivities imparted to the flame by a given volume of spray from the concentrated and from the most dilute solution. In the row of figures below the table are given the ratios between the salt conductivities imparted to the flame by the largest and the smallest volumes of spray from the solutions of different concentrations. An inspection of these ratios shows that as the total quantity of salt in the flame is decreased, the same percentage variation of the quantity causes a much larger percentage variation in the salt conductivity imparted to the flame. In other words, increasing the quantity of salt in the flame seems to retard the process of ionization.

A further inspection of the ratios shows that for certain rates of supply of the salt spray to the flame, the conductivity varies approximately as the square root of the rate of supply, but that for larger rates the variation is less rapid than the square root law would give, and for smaller rates it is more rapid. A number of measurements were made of the salt conductivity imparted to a flame of type *B* when a very dilute salt solution was used in the atomizer — about $\frac{1}{700}$ concentrated. They showed that under these conditions the conductivity was almost directly proportional to the rate of supply of the spray.

The experiments of this section give additional evidence in favor of the conclusion arrived at in the last section. The linear relation between salt conductivity and rate of supply of salt spray when the rate of supply of air was increased proportionately (see Fig. 14) shows that the presence of oxygen plays as important a rôle in the phenomena of ionization of the salt spray as the high temperature of the flame.

When the rate of supply of gas and air was kept constant and the rate of supply of salt spray was increased, the experiments showed that for extremely small rates of supply of the spray, the salt conductivity increased in almost direct proportion to the rate of supply of the spray. As the quantity of the salt in the flame became larger, however, the conductivity was found to increase much

less rapidly than the rate of supply of salt. This would seem to be due to a decrease in the proportion of oxygen to salt spray, owing to which, a smaller proportion of the spray is ionized.

VII. RELATION BETWEEN LUMINOSITY AND CONDUCTIVITY IMPARTED TO A FLAME BY THE VAPOR OF A SALT.

In a previous paper¹ the writer described some experiments on the relation between the luminosity and the conductivity imparted to a flame of the Bunsen type by the vapor of NaCl or of LiCl, when the luminosity was varied by the introduction of the vapor of chloroform, and it was shown that the relation was practically a direct one, the vapor of the chloroform reducing the conductivity in the same proportion as it reduced the luminosity.

The relation between luminosity and conductivity has also been determined when the luminosity was varied by varying the amount of spray introduced into the flame, either by changing the concentration of the solution in the atomizer or by changing the size of the opening in the diaphragm in *M*, Fig. 8. The sodium luminosity of a section of a low thin flame of the Bunsen type was determined by forming an image of the section on the slit of one of the spectroscopes of a Brace spectrophotometer, the filament of an incandescent lamp being used before the other slit for comparison. The conductivity of the same section of the flame was determined in the usual way by inserting the electrometer wires about 1 cm. apart and one on either side of the section. A number of simultaneous measurements of the conductivity and luminosity imparted to the flame by the vapors of either sodium or lithium chloride showed that varying the quantity of vapor in the flame by changing either the concentration of the solution in the atomizer or the size of the opening in the diaphragm in *M*, Fig. 8, or both, caused the luminosity to vary in the same proportion as the conductivity. In all these measurements the salt conductivity and luminosity were determined by subtracting from the total, the conductivity or luminosity due to the flame when water was placed in the atomizer. The measurements shown in Fig. 15, for NaCl, are representative of the results obtained.

¹ Phys. Zeitschr., Band 5, Heft 6, pp. 157-159.

A number of other measurements were made when a sheet of mica, which was found to be quite free from sodium, was inserted

Fig. 15.

across the flame so that the lower edge of the mica was about 1 cm. above the burner. The electrometer wires were placed about half

Fig. 16.

a centimeter apart, one on either side of the mica, and just above the burner. An image of the section of the flame between the lower

edge of the mica and the burner was formed on the slit of the spectro-scope. Simultaneous measurements of the luminosity and conductivity imparted by the salt vapor to this section were made when the character of the flame was varied by varying the supply of air and gas, and keeping the rate of supply of spray to the flame constant. The relation between luminosity and conductivity, under these conditions, was also found to be a simple, linear one. A representative set of measurements for LiCl is given in Fig. 16. The conductivity measurements for the lithium salts are liable to a larger percentage error than those for sodium, owing to the smaller conductivity imparted by lithium salts to the flame.

The foregoing results show that when the luminosity imparted to a gas flame by the vapor of either sodium or lithium chloride is varied by varying the rate of supply of salt or by varying the character of the flame, the electrical conductivity imparted to the flame by the salt vapor is varied in the same proportion.

The relation between the electrical conductivity and the luminosity imparted to a flame by the spray from a solution of CaCl_2 did not seem to be so simple a one as for the salts of lithium and sodium. Owing to the relatively small conductivity imparted to the flame by the salts of calcium the measurements are liable to a larger percentage error and no very satisfactory results have as yet been obtained.

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