

XLII. On the electrical conductivity of flames containing salt vapours for rapidly alternating currents

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These results relate to two gases only ; but so far as they go they show :—(i.) That the range varies inversely as the pressure, which result might have been anticipated ; (ii.) that the total number of ions set free in a gas is independent of the pressure, but is different in different gases. The total ionization is greater in ethyl chloride than in air. This is a contrary result to that which we obtained during our experiments on absorption. We were unaware at that time of the enormous force required to saturate the complex gas.

Finally, the following experiments may be briefly described:—

We have tried the effect of reversing the field on the relation between current and potential, and found a result which was practically negative. We have found a similar result when the α particles were not shot straight across the ionization chamber in the direction of the lines of force, but in a slanting direction. These experiments were made in the endeavour to find whether there was any relation between the direction in which electrons were projected and the direction of the applied field. We have also tried to alter the range in air by using different potential gradients, with the idea that it might be possible to obtain ions from an atom traversed by a slower α particle, if only enough electric force were applied. But the result was the same, no matter whether the force was 20 volts to the cm. or 2000 ; and a variation of $\cdot 2$ mm. could hardly have escaped detection.

During the progress of this work, one of us (R. D. Klee-man) left Australia for England. We wish to acknowledge with gratitude the assistance of Mr. H. J. Priest, B.Sc., in completing the observations.

XLII. *On the Electrical Conductivity of Flames containing Salt Vapours for Rapidly Alternating Currents.* By H. A. WILSON, M.A., D.Sc., M.Sc., Professor of Physics, King's College, London, Fellow of Trinity College, Cambridge, and E. GOLD, B.A., Hutchinson Student, St. John's College, Cambridge*.

THE following paper contains an account of a series of experiments on the electrical conductivity of a Bunsen flame containing various alkali salt vapours, the currents used being alternating ones with frequencies varying from $7\cdot 14 \times 10^4$ to $6\cdot 2 \times 10^6$ per second.

The conductivity was measured between two platinum electrodes immersed in the flame, and the variation of the

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conductivity with the amount of salt present in the flame and with the nature of the salt was investigated. The variation of the conductivity with the frequency of alternation, the maximum electromotive force, and the distance between the electrodes was also examined. The results obtained enable a comparison to be made between the conductivities of the various alkali salt vapours for alternating currents and their conductivities for steady currents as previously determined*.

It appears that the relative conductivities for rapidly alternating currents are nearly proportional to the square roots of the corresponding conductivities for steady currents.

The flame is found to behave for very rapidly alternating currents more like a dielectric of high specific inductive capacity than like a conducting medium; and it is shown that this result is in accordance with the ionic theory.

The rest of the paper is divided into the following sections:—

- (1) Description of apparatus used.
- (2) Variation of the conductivity with the concentration and nature of the salt vapour.
- (3) Variation of the conductivity with the maximum P.D., the frequency, and the distance between the electrodes.
- (4) Theory of the conductivity for rapidly alternating currents.
- (5) Summary of results.

(1) *Description of Apparatus used.*

To produce a steady flame containing a definite amount of salt vapour, an apparatus similar to those described in the two papers referred to above was used. The principal parts of the apparatus are shown in fig. 1.

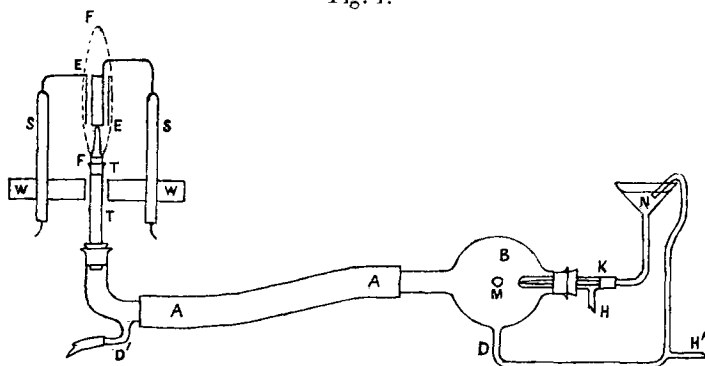
A mixture of coal-gas and air containing spray of a salt solution was burnt from a glass tube TT tipped with a short thin copper tube 1 cm. in diameter.

The mixture was formed in a glass bulb B, from which it passed through a wide tube AA to the burner. In the bulb and AA the coarser spray settled, and was allowed to escape through the tubes D and D'. The spray was produced by a

* "The Electrical Conductivity and Luminosity of Flames containing Vaporised Salts," by A. Smithells, H. M. Dawson, and H. A. Wilson, Phil. Trans. A 193. 1899. "On the Electrical Conductivity of Flames containing Salt Vapours," by H. A. Wilson, Phil. Trans. A 192. 1899.

Gouy sprayer K, worked by compressed air, which was supplied by a rotary blower worked by a $\frac{1}{2}$ -H.P. motor. The compressed air entered at H, and the salt solution at N.

Fig. 1.



- | | |
|----------------------------|-------------------------------|
| FF. Flame. | B. Sprayer-bulb. |
| EE. Electrodes. | K. Sprayer. |
| SS. Glass tubes. | N. Solution-tube and funnel. |
| WW. Wood block. | HH'. Compressed-air tubes. |
| TT. Flame-tube. | M. Gas tube. |
| AA. Wide indiarubber tube. | DD'. Solution-overflow tubes. |

The pressure of the air-supply was indicated by a water-manometer, and was always kept at the same value, about 80 cms. of water. The salt solution was contained in a large funnel, and its level always kept a constant height above the sprayer-nozzle. The amount of gas entering the bulb was measured by a water-meter, and its pressure kept constant by means of a regulator; it did not vary appreciably.

The gas and air supplies were so adjusted that a "non-luminous" flame having a sharply-defined inner cone was obtained. This flame was very steady in appearance, and could be maintained constant for any length of time required.

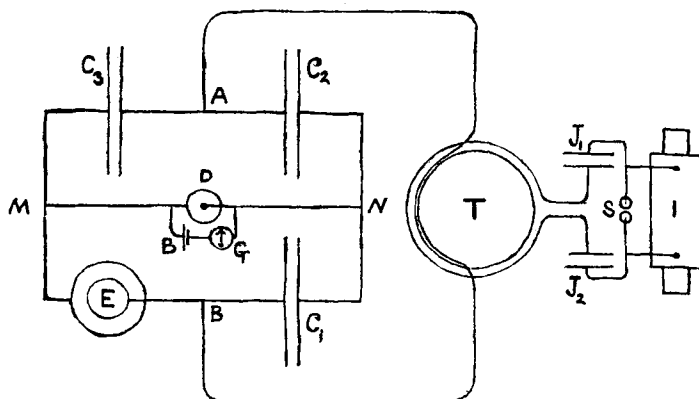
The electrodes used in most of the experiments consisted of two concentric cylinders made of thin platinum, of the following dimensions:—

Diameter of outside cylinder . .	2.4 cms.
Height " " . .	5.0 "
Diameter of inside cylinder . .	1.2 "
Height " " . .	5.2 "

They were supported symmetrically about the axis of the flame at such a height that the inner cone of the flame just reached up to the level of the lower ends of the cylinders.

The conductivity between the electrodes was determined by means of a Wheatstone-bridge arrangement, of which the electrodes formed one arm, and the other three arms consisted of small air-condensers, the capacity of one of which was adjustable. The arrangement is shown in fig. 2.

Fig. 2.



- | | |
|---|--|
| E. Flame-Electrodes. | G. Galvanometer. |
| C ₁ C ₂ . Air-condensers. | T. Tesla Coil. |
| C ₃ . Adjustable Air-condenser. | J ₁ J ₂ . Leyden jars. |
| D. Detector. | S. Spark-gap. |
| B. Cell. | I. Induction-coil. |

An induction-coil, I, charged up two Leyden-jars, J₁ J₂, and these discharged at a spark-gap S. The outside coatings of the jars were connected through the primary of a Tesla coil, T. The primary of this coil consisted of 33 turns wound into a spiral, 29 cms. long and 19.2 cms. in diameter, on a large glass cylinder. The secondary coil had three turns, and was placed inside the glass cylinder, halfway up it. It was connected to the bridge arrangement at A and B, as shown.

An "electrolytic detector," D, was connected to the points M and N of the bridge. This detector consisted of two platinum electrodes dipping into 20 per cent. sulphuric acid. One electrode was a platinum cylinder 3 cms. in diameter and 4 cms. high, while the other was a platinum wire $\frac{1}{1000}$ inch in diameter sealed into a glass tube and cut off close to the surface of the glass. The large electrode was contained in a test-tube, which it just fitted; and the glass tube carrying the small electrode was supported by a cork fitting the test-tube. The small electrode was just below the surface of the acid at the middle of the tube. The two electrodes were connected to a silver-chloride cell B and a

moving-coil galvanometer G. The cell B gave about one volt and served to polarize the electrodes. When an alternating P.D. was produced between M and N, the detector was depolarized and a current passed through the galvanometer. The deflexion of the galvanometer-coil was read by means of an incandescent lamp and a scale, a current of 10^{-9} ampere giving a deflexion of one scale-division.

The condensers C_1 , C_2 each consisted of two parallel circular disks 10 cms. in diameter, supported on ebonite rods. The distance between the disks of C_1 was 0.15 cm. and of C_2 0.75 cm., in most of the experiments. The condenser C_3 consisted of two brass disks 10 cms. in diameter, whose distance apart could be adjusted and measured by means of an accurate micrometer-screw.

To determine the conductivity between the flame-electrodes, the rapidly alternating P.D. produced by the Tesla coil was applied at A and B (fig. 2), and the condenser C_3 was adjusted until the deflexion of the galvanometer was a minimum. On starting the alternating current, the galvanometer deflexion increased to a maximum value and then fell off slowly. The alternating current was always kept on for 15 secs. and the maximum deflexion noted, and then after an interval of 15 secs. the current was turned on again and so on. During the intervals the condenser was adjusted, and the deflexions corresponding to a series of positions of the adjustable condenser-disk were thus obtained. A curve was then drawn on squared paper showing the relation between the galvanometer deflexion and the condenser-screw reading, and so the screw reading for which the deflexion was a minimum was obtained. The observations at each position of the condenser-disk were repeated several times and the mean taken; the series of observations was also repeated first in one direction and then in the other, while various intermediate positions were also tried so as to make as certain as possible that the correct relation between the deflexion and the condenser distance was obtained. These precautions were very necessary because the apparatus was sometimes irregular in its action. No great difficulty was experienced in keeping the flame sufficiently constant during the experiments, but it was not easy to keep the alternating current constant. This was due partly to variations taking place at the spark-gap and partly to irregularity in the action of the induction-coil interrupter. The spark-gap finally adopted consisted of two platinum spheres kept in an atmosphere of hydrogen. In most of the experiments the length of the gap was about 0.2 cm.

Several different kinds of interrupters were tried, but finally the ordinary App's platinum contact-breaker was used. The platinum contacts were always carefully filed smooth before starting an experiment and a 10-inch coil was used with a four-volt battery, the contact-breaker being adjusted so that the coil gave only a short spark when not connected to the Leyden jars. In this way the apparatus was made to work sufficiently steadily to obtain fairly satisfactory observations. The distance between the condenser-plates corresponding to the minimum galvanometer-deflexion could be obtained within about 5 per cent. of its value. It was only after a long series of attempts extending over nearly a year that the apparatus was got to work well enough to obtain reliable results, and numerous modifications were tried before the form above described was finally adopted.

To compare the conductivities due to different salts, the increase in the apparent capacity of the flame-electrodes consequent on introducing each salt was calculated in terms of the capacities of the three condensers.

With a bridge arrangement each arm of which is a capacity with negligible self-induction, the condition for a balance is $C_1 C_3 = C_2 C_4$, a condition independent of the frequency. It was found that when the ratio $\frac{C_2}{C_1}$ was altered, then C_3 changed approximately proportionally, so that it appeared justifiable to apply the equation $C_1 C_3 = C_2 C_4$. Let d_1 be the distance between the plates of the adjustable condenser at the minimum for the flame free from salt, and d_2 for the flame containing salt. The capacity of the adjustable condenser in the first case is $\frac{A}{4\pi d_1} + D$, where D is a quantity nearly independent of d_1 and A the area of each condenser-plate [Clerk Maxwell, 'Electricity and Magnetism,' art. 202].

We have therefore

$$C_1 \left[\frac{A}{4\pi d_1} + D \right] = C_2 C_4,$$

where C_4 is the apparent capacity of the flame-electrodes with the flame free from salt. Also if C_4' is the apparent capacity with salt in the flame we have

$$C_1 \left(\frac{A}{4\pi d_2} + D \right) = C_2 C_4'.$$

Hence
$$\frac{C_1 A}{4\pi} \left(\frac{1}{d_2} - \frac{1}{d_1} \right) = C_2 (C_4' - C_4);$$

so that the change, in the apparent capacity, due to the introduction of the salt is given by the equation

$$C_4' - C_4 = \frac{C_1 A}{C_2 4\pi} \left(\frac{1}{d_2} - \frac{1}{d_1} \right).$$

In the experiments we have made, the self-inductions of the arms of the bridge could be neglected in comparison with the capacities without appreciable error.

It was found possible with the bridge arrangement described to obtain an approximate balance. That is, the minimum galvanometer-current was always small compared with the currents when the adjustable condenser-plate was far from the position which gave the minimum deflexion. This showed that the arm of the bridge containing the flame behaved like a capacity simply, or like a capacity and self-induction in series. If the flame had behaved like a capacity and resistance in parallel, then a balance could not have been obtained. The current through the flame with a given maximum P.D. and frequency is proportional to the apparent capacity, so that it is reasonable to regard the apparent capacity as a measure of the conductivity of the flame for the rapidly alternating currents employed.

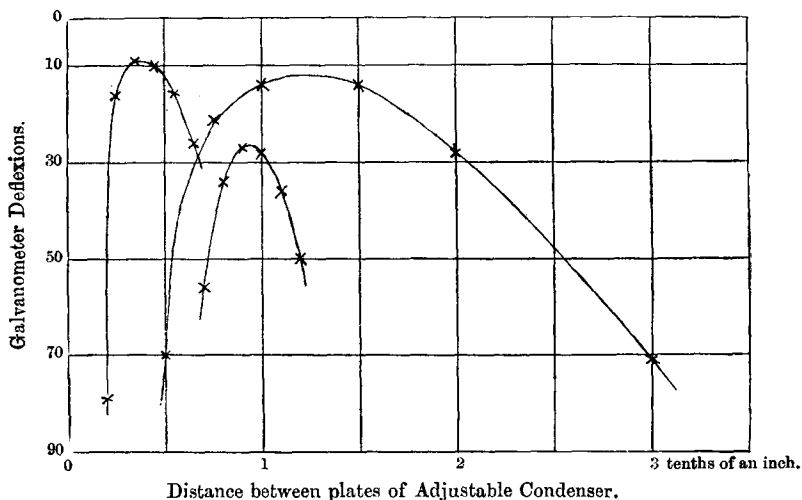
To obtain relative values of the apparent capacities, it is therefore sufficient to calculate $\frac{1}{d_2} - \frac{1}{d_1}$ for each salt solution sprayed. Since the absolute amount of salt in the flame could be only roughly estimated, it was useless to attempt to obtain exact values for the absolute apparent capacities; so that it was unnecessary to know the ratio $\frac{C_1}{C_2}$ exactly.

The value of d_1 , the minimum position for the flame free from salt, was about half the value obtained with no flame. Consequently $\frac{1}{d_1}$ corresponds to twice the capacity of the flame-electrodes with air as dielectric. The capacity in this case was 3.6 cms., and $\frac{C_1}{C_2}$ was very nearly $\frac{1}{5}$ in most of the experiments described below.

(2) Variations of the apparent Capacity with the Concentration and Nature of the Salt Vapour.

The salt solutions sprayed were made up with distilled water and pure salts carefully dried. We shall first give a few examples of the curves obtained, showing the relation between the distance apart of the condenser-plates and the galvanometer deflexion, from which curves the position of the minima were deduced. Fig. 3 shows several such curves. The sharpness of the minimum was usually greater

Fig. 3.

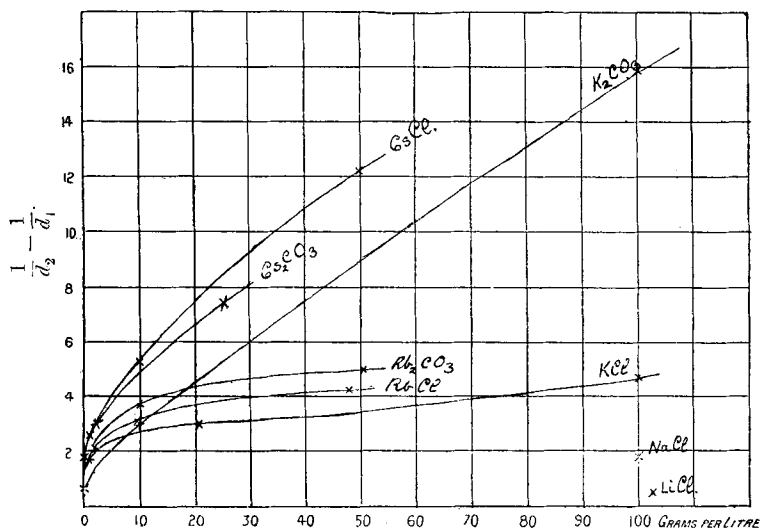


when the conductivity was large and the distance therefore small, than when the converse was the case. The accuracy with which the minimum could be found was consequently nearly the same for large as for small conductivities.

During the course of the experiments the ratio of the two condensers, C_1, C_2 , was changed on one or two occasions. When this had been done, some of the observations made before the change were repeated, and the factors required to reduce all the results to the same standard so determined. The following table contains the results obtained, the number of alternations per second being 3.2×10^5 , and $d_1 = 3.33$ tenths of an inch.

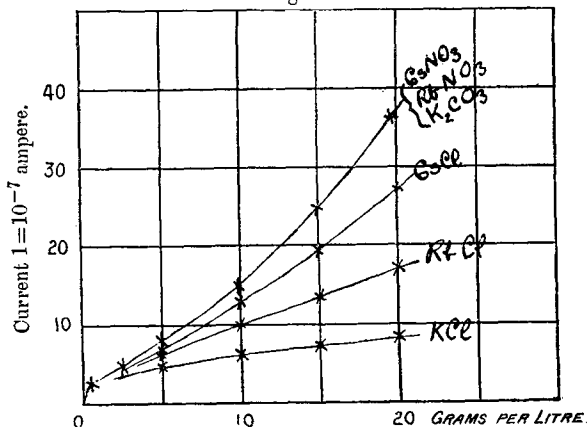
Salt.	Grams per litre.	d_2 (in tenths of an inch).	$\frac{1}{d_2} - \frac{1}{d_1}$.
CsCl	50	0.08	12.2
"	10	0.18	5.26
"	1	0.34	2.64
"	0.333	0.48	1.78
"	0.1	1.10	0.61
Cs ₂ CO ₃	25.5	0.13	7.40
"	2.55	0.30	3.03
"	0.26	0.59	1.40
"	0.026	1.90	0.23
RbCl	48.1	0.22	4.24
"	9.6	0.29	3.15
"	1.92	0.41	2.14
Rb ₂ CO ₃	50.4	0.19	4.96
"	10	0.25	3.70
"	1	0.50	1.70
K ₂ CO ₃	100	0.062	15.8
"	10	0.297	3.07
KCl	100	0.20	4.70
"	20.8	0.30	3.03
"	1	0.50	1.70
NaCl	100	0.47	1.83
LiCl	102.5	1.3	0.47

Fig. 4.



In fig. 4 the above values of $\frac{1}{d_2} - \frac{1}{d_1}$, and the corresponding strengths of the solutions, are shown graphically for each salt. Fig. 5 shows the steady currents due to an E.M.F. of 0.227 volt, taken from the papers referred to above.

Fig. 5.



The amount of salt entering the flame in the present experiments was nearly the same as in the older experiments.

The following table gives the values of $\frac{1}{d_2} - \frac{1}{d_1}$ for decimal solutions obtained from the curves in fig. 4, and also the steady currents due to 0.227 volt.

Salt.	$\frac{1}{d_2} - \frac{1}{d_1}$ (k)	Salt.	Steady Current (1 = 10 ⁻⁷ ampere). (k')	Ratios.	$\frac{\sqrt{k'}}{k}$.
CsCl.....	6.7	CsCl.....	22.2	3.3	0.70
$\frac{1}{2}$ C ₂ CO ₃ ...	5.9	CsNO ₃	36.6	6.2	1.03
$\frac{1}{2}$ Rb ₂ CO ₃ ...	3.7	RbNO ₃	25.9	7	1.37
RbCl	3.2	RbCl	11.3	3.5	1.05
$\frac{1}{2}$ K ₂ CO ₃	2.9	$\frac{1}{2}$ K ₂ CO ₃	11.2	3.9	1.15
KCl	2.6	KCl	5.75	2.2	0.92

The fifth column contains the ratios of the numbers expressing the conductivities for steady currents to the values of $\frac{1}{d_2} - \frac{1}{d_1}$. In the previous work the conductivities of caesium and rubidium carbonates were not measured; so the values for nitrates are given, since the conductivities of all oxy-salts of the same metal were found to be nearly equal for

494 Prof. Wilson and Mr. Gold : *Electrical Conductivity of steady currents.* It will be seen that, roughly speaking, the relative conductivity for steady currents varies in a similar way to the conductivity for rapidly alternating currents as represented by $\frac{1}{\bar{a}_2} - \frac{1}{\bar{a}_1}$.

The last column contains the square root of the conductivity for steady currents divided by $\frac{1}{\bar{a}_2} - \frac{1}{\bar{a}_1}$. The numbers in this column do not vary much, showing that the conductivity for rapidly alternating currents varies, roughly speaking, as the square root of the conductivity for steady currents.

The conductivities of KCl and RbCl were found to vary nearly as the square root of the concentration in the case of steady currents ; so that we should expect them to vary as the fourth root of the concentration for rapidly alternating currents. The following table shows that this is nearly the case.

Salt.	Grams per litre. (C)	$\frac{1}{\bar{a}_2} - \frac{1}{\bar{a}_1}$ (k)	$k/\sqrt[4]{C}$.
RbCl.....	48.1	4.24	1.6
„	9.6	3.15	1.79
„	1.92	2.14	1.81
KCl	100	4.70	1.49
„	20.8	3.03	1.42
„	1.0	1.70	1.70

Considering the large variation in C the values of $k/\sqrt[4]{C}$ are surprisingly constant for these two salts.

The following table shows the relative variation of the conductivity CsCl for steady and alternating currents. The numbers are taken from figs. 4 and 5.

	Grams per litre.	$\frac{1}{\bar{a}_2} - \frac{1}{\bar{a}_1}$ (k)	Steady Current. (k')	$\sqrt{k'/k}$.
CsCl	20	7.3	26	0.70
„	15	6.4	19.5	0.69
„	10	5.3	13	0.68
„	5	4.1	7.4	0.66
„	1	2.6	3.0	0.67

It is clear from these results that $\frac{1}{d_2} - \frac{1}{d_1}$ varies nearly as the square root of the steady current due to a small P.D.

(3) *The Variation of the Conductivity with the Potential-Difference and Number of Alternations per Second.*

The variation of the conductivity of the flame as measured by $\frac{1}{d_2} - \frac{1}{d_1}$, with the maximum P.D. applied to the bridge arrangement, was effected by varying the length of the spark-gap in the primary circuit of the Tesla coil. The spark passed between two platinum spheres in air at the ordinary pressure. The following table gives the results obtained when spraying a solution of CsCl containing one gram per litre :—

Spark-length.	P.D. (E.S. Units at gap.)	d_2 .	$\frac{1}{d_2} - \frac{1}{d_1}$ (k).	$k\sqrt{\text{P.D.}}$
0.0055 cms.	2.60	0.23	4.05	6.55
0.011 "	3.6	0.42	2.08	3.95
0.017 "	4.7	0.43	2.03	4.4
0.028 "	6.4	0.48	1.78	4.5
0.044 "	8.8	0.50	1.70	5.0
0.10 "	16	0.53	1.59	6.3
0.20 "	27.8	0.60	1.37	7.2

The last column contains the products of $\frac{1}{d_2} - \frac{1}{d_1}$ and the square root of the corresponding potential-difference as estimated from the spark-length in the primary circuit of the Tesla coil. The numbers in this column vary between 4 and 7, while the P.D. varies by a factor of 11. Taking into account the roughness of the method used to estimate the P.D. and the large change made in it, we may conclude that $\frac{1}{d_2} - \frac{1}{d_1}$ probably varies approximately inversely as the square root of the maximum P.D. applied.

The effect of varying the number of alternations per second was tried by altering the capacity in the primary circuit of the Tesla coil. A solution containing one gram of CsCl per litre was sprayed. The following table gives the results obtained :—

Capacity.	Self-Induction.	Alternations per second.	d_2 .	$\frac{1}{d_2} - \frac{1}{d_1}$.
33000 cms.	136500 cms.	7.14×10^4	0.4	2.1
6400 „	„	1.62×10^5	0.4	2.1
1600 „	„	3.24×10^5	0.34	2.6
150 „	„	10.8×10^5	0.30	3.0
150 „	4100 cms.	6.2×10^6	0.30	3.0

It will be seen that the value of $\frac{1}{d_2} - \frac{1}{d_1}$ varies as the number of alternations per second is changed. Unfortunately it was not found possible to obtain the variation of d_2 with the frequency very exactly; and all that can be said is that changing the frequency from 7.14×10^4 to 6.2×10^6 per second does not change $\frac{1}{d_2} - \frac{1}{d_1}$ by more than 25 per cent. of its mean value.

If we suppose that $\frac{1}{d_2} - \frac{1}{d_1}$ varies as n^x , where n is the frequency, then the results just given show that x lies between $+0.05$ and -0.05 .

For a pure capacity $x=0$, and for a pure self-induction $x=-1$; so that it appears that the flame behaves nearly like a pure capacity. That it does not include much conductivity in parallel with the capacity is shown by the fact that it could be nearly balanced by three condensers. In the section below, on the theory of conductivity, it is shown that these conclusions from the experiments might have been anticipated.

To obtain the apparent specific inductive capacity of a salt vapour, it is only necessary to multiply the numbers for $\frac{1}{d_2} - \frac{1}{d_1}$ given above by $2d_1=6.66$ and add on unity. The apparent specific inductive capacities so obtained vary from about 100 for the strongest solution of K_2CO_3 sprayed to about 4 for the solution of $LiCl$ *.

Some experiments were made to find out how the conductivity varied with the distance between the electrodes.

* These values of the apparent specific inductive capacity have of course no relation to the true specific inductive capacity, which must be nearly unity.

Two parallel vertical platinum disks each 1.5 cms. in diameter were used, and it was found that $\frac{1}{d_2} - \frac{1}{d_1}$ was independent of the distance between them when this was less than 3 or 4 millimetres.

When they were 10 millimetres apart $\frac{1}{d_2} - \frac{1}{d_1}$ was about double its value between 0 and 4 mms. This increase in the apparent capacity is no doubt due to the fact that the cross-section of flame acted on by the P.D. is greater when the distance between the electrodes is comparable with their diameter.

We may therefore conclude that $\frac{1}{d_2} - \frac{1}{d_1}$ would be independent of the distance between the electrodes if they were very large. This is in agreement with the results for constant P.D.'s, for which the current is independent of the distance between the electrodes when they are near together.

(4) *Theory of the Conductivity of Ionized Gases for rapidly alternating Currents.*

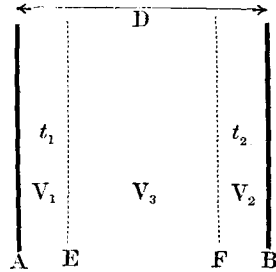
It will be convenient now to describe an approximate theory of the conductivity of ionized gases for rapidly alternating currents—a theory which affords an explanation of the experimental results obtained in this investigation.

Suppose a large parallel plate-condenser filled with a uniformly ionized gas, and let the distance between the plates be D cms. Let the potential-difference between the plates be given by the formula $V = V_0 \sin pt$, and let the number of positive or negative ions per c.c. be n , each ion carrying a charge $\pm e$. In a Bunsen flame the velocity of the negative ions is about $1000 \frac{\text{cms.}}{\text{sec.}}$ for one volt per cm., while the velocity of the positive ions under the same potential gradient is only about $60 \frac{\text{cms.}}{\text{sec.}}$ Moreover, the mass of the positive ions is probably very large compared with that of the negative ions. Consequently, in a rapidly alternating electric field the amplitude of vibration of the negative ions will be large compared with that of the positive ions. As a first approximation, therefore, we shall assume that the positive ions do not move at all, so that all the current is carried by the negative ions. We shall also suppose that all the negative ions move in the same way with the same velocity, so that the number of negative per c.c.

remains n except within a distance d of each electrode, d being twice the amplitude of vibration of the negative ions. It is easy to see that on these assumptions the negative ions will practically all be contained in a slab of thickness $D-d$, which will vibrate between the plates so as just not to touch either of them. For if a new negative ion is formed outside the slab, it will almost immediately strike the electrode near it; whereas a new negative ion formed in the slab cannot reach either electrode except by diffusion, which we shall neglect. Thus we may regard the whole space between the plates as filled with positive electricity of density $+ne$, and the vibrating slab of thickness $D-d$ as containing also negative electricity of density $-ne$. Thus inside the slab the total density is zero and outside is $+ne$.

Let X denote the electric intensity between the plates at a distance x from one of them. Then, inside the slab $\frac{dX}{dx}=0$, and outside $\frac{dX}{dx}=4\pi ne$.

Let A and B be the two plates, and let the slab be represented by the space between the two dotted lines E, F . Let $AB=D$, $AE=t_1$, $FB=t_2$, and suppose the potential of A kept zero while that of $B=V$. Let the rise of potential in AE be V_1 , in EF be V_3 , and in FB be V_2 . In EF $\frac{dX}{dx}=0$ so that X is constant. Let its value be X_0 . Then



$$V_3 = -X_0(D-d),$$

where $d=t_1+t_2$. In AE we have

$$\frac{d^2V}{dx^2} = -4\pi\rho,$$

where $\rho=ne$. From this we get

$$\frac{dV}{dx} = -4\pi\rho x + C \quad \text{and} \quad V = -2\pi\rho x^2 + Cx + D,$$

where C and D are constants to be determined. When $x=0$

$$V = D = 0,$$

and when $x=t_1$

$$\frac{dV}{dx} = -4\pi\rho t_1 + C = X_0.$$

Hence

$$V_1 = 2\pi\rho t_1^2 - X_0 t_1.$$

In the same way in FB we have

$$V = -2\pi\rho x^2 + C'x + D'.$$

When $x = D - t_2$

$$\frac{dV}{dx} = -X_0 \quad \text{and} \quad V = V_1 + V_3;$$

so that we get for V at $x = D$,

$$V = -X_0D + 2\pi\rho(t_1^2 - t_2^2).$$

Now $t_1 + t_2 = d$, so that

$$V = -X_0D + 2\pi\rho d(2t_1 - d). \quad \dots \quad (1)$$

The force acting on a negative ion is $-X_0e - A \frac{dt_1}{dt}$, where A is a constant representing the viscous resistance to motion with unit velocity. Let m be the mass of a negative ion; then its equation of motion is

$$-X_0e = m \frac{d^2t_1}{dt^2} + A \frac{dt_1}{dt}. \quad \dots \quad (2)$$

The current-density inside the slab is given by the equation

$$i = -\rho \frac{dt_1}{dt} + \frac{K}{4\pi} \frac{dX_0}{dt},$$

where K is the specific inductive capacity of the medium between the plates in the absence of ions. Thus K is unity, and

$$i = -\rho \frac{dt_1}{dt} + \frac{1}{4\pi} \frac{dX_0}{dt}. \quad \dots \quad (3)$$

Now in a flame containing a salt vapour the fall of potential nearly all takes place near the electrodes, so that X_0 is probably very small, even when rapidly alternating currents are used. Consequently, since ρ is large, $\frac{1}{4\pi} \frac{dX_0}{dt}$ may be neglected in comparison with $-\rho \frac{dt_1}{dt}$. Hence (3) becomes $i = -\rho \frac{dt_1}{dt}$ approximately. Substituting in (1) the value of X_0 got from (2) we get

$$V = V_0 \sin pt = D \left(\frac{m}{e} \frac{d^2t_1}{dt^2} + \frac{A}{e} \frac{dt_1}{dt} \right) + 2\pi\rho d(2t_1 - d).$$

This gives

$$V_0 p \cos pt = \frac{mD}{e} \frac{d^3t_1}{dt^3} + \frac{AD}{e} \frac{d^2t_1}{dt^2} + 4\pi\rho d \frac{dt_1}{dt}.$$

But $\frac{dt_1}{dt} = -\frac{i}{\rho}$. Hence

$$-V_0 p \cos pt = \frac{mD}{e\rho} \frac{d^2i}{dt^2} + \frac{AD}{e} \frac{di}{dt} + 4\pi di. \quad \dots (4)$$

The solution of this equation is

$$i = \frac{-\frac{e\rho}{mD} V_0 \sin(pt - \alpha)}{\left\{ \left(1 - \frac{4\pi d e \rho}{p^2 m D}\right)^2 p^2 + \frac{A^2}{m^2} \right\}^{\frac{1}{2}}}, \quad \dots (5)$$

where

$$\tan \alpha = \frac{-\left(1 - \frac{4\pi d e \rho}{p^2 m D}\right) pm}{A}.$$

If a P.D. $V = V_0 \sin pt$ is applied to a condenser of capacity C , the current is given by the equation $i = CV_0 p \cos pt$. For the flame, if A and m are both negligible (5) becomes

$$i = -\frac{V_0 p \cos pt}{4\pi d},$$

so that the apparent capacity is $\frac{1}{4\pi d}$ per unit area. Now $\frac{d}{2}$ is the amplitude of vibration of the negative ions so that $d\rho$ must be the amount of electricity flowing during a half-vibration.

Let $i = -\frac{dQ}{dt}$ so that $Q = \frac{V_0}{4\pi d} \sin pt$.

Then we have, integrating from 0 to π ,

$$d\rho = \frac{V_0}{2\pi d} \quad \text{or} \quad d = \sqrt{\frac{V_0}{2\pi\rho}},$$

so that the apparent capacity per unit area is

$$\frac{1}{4\pi d} = \sqrt{\frac{\rho}{8\pi V_0}}.$$

If $\rho = 0$ this makes the capacity zero, whereas it should be $\frac{1}{4\pi D}$. This is due to the omission of $\frac{1}{4\pi} \frac{dX}{dt}$, which would not be negligible if ρ were very small. If, however, we take $\sqrt{\rho/8\pi V_0}$ to be not the apparent capacity but the increase in the apparent capacity due to the presence of the ions, then no error will be made even if ρ be small. The quantity $\frac{1}{d_2} - \frac{1}{d_1}$ which has been determined is proportional, as we have seen, to the increase in the apparent

capacity when salt is added to the flame. In what follows we shall speak of $\frac{1}{d_2} - \frac{1}{d_1}$ as the apparent capacity.

Thus we should expect the apparent capacity per unit area to vary as the square root of the number of ions per c.c., and inversely as the square root of the maximum P.D. applied, but to be independent of the distance between the electrodes. The experimental results are in surprisingly good agreement with these conclusions. Thus we have seen that the apparent capacity is nearly independent of the number of alternations per sec., and varies as the square root of the steady current conductivity. For small E.M.F.'s the conductivity for steady currents is proportional to the number of ions per c.c. and to the velocity of the ions. But it has been shown* that all alkali-salts in flames give ions having the same velocity, so that the conductivity for steady currents should vary nearly as the number of ions per c.c. present. Hence the observed apparent capacity varies nearly as the square root of the number of ions present. The apparent capacity was also independent of the distance between the electrodes, provided this was small compared with their diameters. Further, we have seen that the apparent capacity varies roughly inversely as the square root of the maximum P.D., measured by the length of the spark-gap in the primary coil of the Tesla transformer. It appears, therefore, that the expression $\sqrt{\rho/8\pi V_0}$ does represent approximately the observed variations of the apparent capacity of the electrodes in the flame containing salt vapour.

This expression has been obtained by neglecting the mass of the ions and the resistance to their motion through the flame-gases, so that it appears that the amount of alternating current through the flame is determined merely by the density of the layer of positive charge left in the gas near the electrodes when the negative ions move under the action of the applied field.

If a steady P.D. V is applied to two electrodes immersed in an ionized gas, and if the positive ions cannot move, it is easy to see that a current will only pass for the short time required for the accumulation of positive charge near the negative electrode to become sufficient to make the electric force near the positive electrode zero. Thus the two electrodes will behave like a condenser when the P.D. is applied. When a rapidly alternating P.D. is applied it is easy to see that even if the positive ions can move, provided their velocity is small

* H. A. Wilson, Phil. Trans. A. 1899.

compared with that of the negative ions, the arrangement will behave like a condenser if the number of ions per c.c. is very large and the mass of the negative ions very small.

Denoting the apparent capacity per unit area by C , we

$$\text{have } C = \sqrt{\frac{\rho}{8\pi V_0}} = \frac{K}{4\pi D},$$

where K is the apparent specific inductive capacity. Consequently $\rho = \frac{V_0 K^2}{2\pi D^2}$. The length of the spark-gap used in the experiments on the variation of the apparent capacity with the concentration and nature of the salt was about 2 mms. in hydrogen gas at atmospheric pressure. The Tesla coil had 33 turns in its primary coil and 3 turns in its secondary, so that V_0 was about 400 volts or 1.2 E.S. units. D was 0.6 cms., so that for the strongest K_2CO_3 solution sprayed, for which $K = 100$ (p. 496), we have

$$\rho = \frac{1.2 \times 10000}{2 \times 3.1 \times 0.6^2} = 5400 \text{ E.S. units.}$$

The charge on one ion is 3×10^{-10} E.S. units, so that the number of ions per c.c. was

$$\frac{5400}{3 \times 10^{-10}} = 18 \times 10^{12}.$$

The amount of salt entering the flame was determined by finding the loss of weight of a bead of sodium-chloride placed in an equal Bunsen flame, so that the light emitted by this flame was equal to that emitted by the flame when a solution of NaCl containing 10 grams per litre was sprayed. In this way it was found that 0.53 milligram entered the flame per minute. Consequently the amount of K_2CO_3 entering the flame per minute with the strongest solution was 5.3 milligrams. The velocity of the flame-gases was about 200 cms. per second, and the diameter of the flame about 3 cms., so that the amount of salt per c.c. in the flame was about

$$\frac{5.3}{200 \times \pi (1.5)^2 \times 60} = 7 \times 10^{-5} \text{ milligram.}$$

Hence, taking the mass of an atom of hydrogen as 10^{-24} gram, the number of salt molecules per c.c. was about

$$\frac{7 \times 10^{-8}}{138 \times 10^{-24}} = 5 \times 10^{14}.$$

It thus appears that about one molecule in 30 molecules of K_2CO_3 was ionized in the flame. For most of the other salt solutions sprayed the proportion of the molecules ionized in the flame comes out less than one in 30.

In the paper on the conductivity of flames for steady currents, referred to above, numbers are given which are proportional to the molecular conductivity of all the salts tried, so that it is not necessary here to discuss further the variation of the conductivity with the nature and concentration of the salt vapour.

Let q be the number of ions produced per c.c. per sec. in the flame and n the number present per c.c. Then $q = \alpha n^2$, where α is a constant which has been shown by Langevin to be equal to $f \cdot 4\pi e(k_1 + k_2)$, where f is a proper fraction, and k_1, k_2 are the ionic velocities due to unit electric intensity. For the flame we have $k_2 = 1000 \frac{\text{cms.}}{\text{sec.}}$ for one volt per cm., or $3 \times 10^5 \frac{\text{cms.}}{\text{sec.}}$ for one E.S. unit of electric intensity. Hence

$$\alpha = 4\pi \cdot f \cdot 3 \times 10^{-10} \times 3 \times 10^5 = 1 \cdot 1 \times 10^{-3} f.$$

Now for the strongest K_2CO_3 solution sprayed $n = 1 \cdot 8 \times 10^{13}$, hence

$$q = f 1 \cdot 1 \times 10^{-3} \times 1 \cdot 8^2 \times 10^{26} = 4 \times 10^{23} f.$$

The number of salt molecules per c.c. is about 5×10^{14} ; so that it appears that each salt molecule is ionized and recombines about $10^9 f$ times per second. The value of f under ordinary conditions is about 0.2. Probably in the flame it is less, say 0.1. Taking the temperature of the flame-gases to be 2000°C. , we get for the number of collisions made by a salt molecule per second in the flame rather less than 5×10^8 . So it appears that the K_2CO_3 molecules are ionized once for every 5 collisions with another molecule. It is therefore probable that the cause of the ionization of salt vapours in flames is the shock of molecular collision.

The current which could be carried by the 5×10^{14} ions produced per c.c. is about 60 amperes, which is enormously greater than the observed currents per c.c. of flame between the electrodes. This result agrees with the conclusion* that the observed steady currents through flames containing salt vapours are very far from the saturation value. Since each salt molecule is ionized many times per second, the salt would all be carried to the electrodes as ions if the current were sufficiently great. If we suppose that the electrodes absorb the ions which reach them, then the maximum possible current would be equal to that required to electrolyse the same amount of salt in a solution. This has been previously found to be the case for alkali salts vaporised in a current of air †.

* H. A. Wilson, *Phil. Mag.* October 1905.

† H. A. Wilson, *Phil. Mag.* August 1902.

Equation (5) may be written

$$i = \frac{-pe\rho V_0 \sin(pt - \alpha)}{\{(mDp^2 - 4\pi de\rho)^2 + A^2 D^2\}^{\frac{1}{2}}}$$

It is easy to show that the term $A^2 D^2$ is negligible compared with $(mDp^2 - 4\pi de\rho)^2$. We have $D = 0.6$ cm. and $Xe = Av$, where X = electric intensity and v = velocity of negative ions due to X . If $X = 1$ E.S. unit, $v = 3 \times 10^5 \frac{\text{cms.}}{\text{sec.}}$; so that $D^2 \cdot A^2$ is equal to $\frac{0.6 \times 9 \times 10^{-20}}{9 \times 10^{10}} = 3 \times 10^{-29}$.

In $(mDp^2 - 4\pi de\rho)^2$ the term $4\pi de\rho$ is about 6×10^{-9} for $e = 3 \times 10^{-10}$, and $4\pi d\rho$ is about 20. Also when p is say 10^6 , mDp^2 must be small compared with $4\pi de\rho$, because, as we have seen, changing p does not much affect the apparent capacity. Hence $(mDp^2 - 4\pi de\rho)^2$ is of the order 10^{-18} .

The expression for i becomes therefore on putting $\alpha = -90^\circ$,

$$i = \frac{pe\rho V_0 \cos pt}{4\pi de\rho - mDp^2}$$

Hence the apparent capacity per unit area is

$$C = \frac{e\rho}{4\pi de\rho - mDp^2}$$

Therefore if C_1 and C_2 are values of C corresponding to values p_1, p_2 of p , we have

$$4\pi d\rho - \frac{m}{e} Dp_1^2 = \frac{\rho}{C_1},$$

$$4\pi d\rho - \frac{m}{e} Dp_2^2 = \frac{\rho}{C_2};$$

$$\therefore D \cdot \frac{m}{e} \cdot (p_2^2 - p_1^2) = \rho \left(\frac{1}{C_1} - \frac{1}{C_2} \right).$$

Also approximately $\rho = 8\pi V_0 C^2$ when p is small enough for mDp^2 to be small compared with $4\pi de\rho$, so that

$$\frac{e}{m} = \frac{D(p_2^2 - p_1^2)}{8\pi V_0 \left(\frac{1}{C_2} - \frac{1}{C_1} \right) \times C^2}$$

If C_1 nearly = C_2 we can put $C^2 = C_1 C_2$, and get

$$\frac{e}{m} = \frac{D(p_2^2 - p_1^2)}{8\pi V_0 (C_2 - C_1)}$$

Thus if the variation of C with p were known with sufficient accuracy, $\frac{e}{m}$ for the negative ions could be calculated. It is hoped that further experiments will enable this to be done for the negative ions of different salts.

Summary of Results.

(1) For rapidly alternating currents a flame containing an alkali-salt vapour behaves like an insulating medium having a high specific inductive capacity.

(2) The conductivity of different alkali-salt vapours in a flame for rapidly alternating currents as measured by the apparent capacity of platinum electrodes immersed in the flame varies as the square root of the conductivity of the same salt vapours for steady currents. This result confirms the view that the negative ions from all salts have the same velocity.

(3) The apparent capacity varies nearly inversely as the square root of the maximum applied P.D.

(4) The apparent capacity is nearly independent of the number of alternations per second.

(5) The apparent capacity is nearly independent of the distance between the electrodes.

(6) The results (1) to (5) are in agreement with the ionic theory of the conductivity of the flame for rapidly alternating currents when the velocity of the positive ions and the inertia and viscous resistance to the motion of the negative ions are neglected in comparison with the effects due to the number of ions per c.c.

(7) The apparent capacity per sq. cm. area of the electrodes is equal, according to the theory just mentioned, to $\sqrt{ne/8\pi V_0}$, where n is the number of positive ions per c.c., e the charge on one ion, and V_0 the maximum applied P.D.

(8) Not more than one molecule in 30 salt molecules is ionized at any instant in the flame, but each molecule is probably ionized and recombines several million times per second.

(9) The steady currents observed through salt vapours in flames are very far from the maximum possible currents corresponding to the number of ions produced per second.

XLIII. *The Electrical Conductivity of Metallic Oxides.* By F. HORTON, D.Sc., B.A., Fellow of St. John's College, Cambridge*.

THE theory of electrolytic dissociation has furnished a simple explanation of conductivity, in electrolytes, by assuming that the current is carried as a stream of electric charges by the ions into which a certain proportion of the molecules of an electrolyte are dissociated. Conduction in

* Communicated by Prof. J. J. Thomson.