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On the Electrical Conductivity of Air and Salt Vapours

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X. *On the Electrical Conductivity of Air and Salt Vapours.*

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THE experiments described in this paper were undertaken with the object of obtaining information on the variation of the conductivity of air and of salt vapours with change of temperature, and on the maximum current which a definite amount of salt in the form of vapour can carry. They are a continuation of the two researches[*] on the same subject published in 1899.

In the paper "On the Electrical Conductivity and Luminosity of Flames" some observations on the variation of the conductivity with the temperature at different heights in the flame are given. They indicate a rapid increase in the conductivity with rise of temperature.

The method employed in the experiments now to be described was the following:— A current of air containing a small amount of a salt solution in suspension in the form of spray was passed through a platinum tube heated in a gas furnace; this tube served as one electrode, and the other was fixed along its axis. The temperature of the tube was measured by means of a platinum platinum-rhodium thermo-couple, and the amount of salt passing through the tube was estimated by collecting the spray in a glass-wool plug. From the temperature variation of the conductivity the energy required to produce the ionization can be calculated, and this compared with the energy required to ionize bodies in solutions.

Since the publication of the researches just referred to several papers[†] on the conductivity of salt vapours in flames by Dr. E. MARX have appeared. The first of these is concerned mainly with the fall of potential between the electrodes, and the

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[*] HAROLD A. WILSON, "On the Electrical Conductivity of Flames containing Salt Vapours," 'Phil. Trans.,' A, vol. 192, 1899. A. SMITHELLS, H. M. DAWSON, and H. A. WILSON, "The Electrical Conductivity and Luminosity of Flames containing Vaporised Salts," 'Phil. Trans.,' A, vol. 193, 1899.

[†] VON ERICH MARX, "Ueber den Potentialfall und die Dissociation in Flammengasen," 'Gesellschaft der Wissenschaften zu Göttingen,' 1900, Heft 1; 'Annalen der Physik,' 1900, No. 8. "Ueber das Hall'sche Phänomen in Flammengasen,' 'Annalen der Physik,' 1900, No. 8.

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results obtained are in good agreement with those described in my paper, and show with greater detail the changes in the potential fall due to changes in the temperature of the electrodes. Cooling the positive electrode diminishes the fall of potential close to the negative electrode. This effect is easily explained, as Dr. MARX points out, on the assumption that the ionization occurs mainly on the surface of the hot platinum, and that cooling the platinum diminishes the amount of this ionization. The negative drop is due to the presence of positive ions in the gas near the negative electrode, and cooling the positive electrode diminishes the supply of positive ions, and consequently also the negative drop. In my paper, referred to above, I described this effect and explained it in this way. Dr. MARX has also used his results on the fall of potential to make an estimate of the velocities of the ions in the flame. The calculation is based on the investigation given by Professor J. J. THOMSON* of the distribution of potential between the electrodes when all the ionization is uniformly distributed throughout the volume of the gas, as in the case of the conductivity of air due to Röntgen rays when aluminium electrodes are used.

In the theory given by Professor THOMSON the space between the electrodes, when the current is far from its saturation value, is considered to be divided into three parts by planes parallel to the electrodes. In the middle region the intensity (X_0) is constant, so that the numbers of positive and negative ions present are equal, and the ionization is equal to the recombination. The value of the current density is given by $\iota = X_0 ne\,(k_1 + k_2)$, where n is the number of positive or negative ions present in unit volume, e the charge carried by an ion, k_1 and k_2 the velocities of the positive and negative ions respectively due to unit intensity.

In the regions near the electrodes, whose thicknesses will be denoted by λ_1 and λ_2 no recombination is supposed to take place, so that if the middle region is taken away the distance between the electrodes becomes $\lambda_1 + \lambda_2$, and then the current density has the saturation value for this distance, viz., $qe\,(\lambda_1 + \lambda_2)$, where q is the number of ions produced in unit time in unit volume of the gas.

Dr. MARX's determination of the velocities of the ions in the flame depends therefore on the assumption that the ionization occurs uniformly throughout the space between the electrodes which, according to my experiments (*loc. cit.*), is not even approximately the case in flames containing salt vapours. In his first paper Dr. MARX agreed with the conclusion that nearly all the ionization occurs on the electrodes, and brought forward fresh evidence in favour of its truth, and at the same time applied Professor THOMSON's theory to calculate the velocities of the ions.

In his paper in WIEDEMANN's 'Annalen,' Dr. MARX again describes the same experiments, but comes to the conclusion that at any rate when the E.M.F. is small, the surface ionization is not large compared with the volume ionization, so that when

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* "On the Theory of the Conduction of Electricity through Gases by Charged Ions," 'Phil Mag., March, 1899.

the E.M.F. is small it is allowable to apply Professor THOMSON's theory to flames. It is consequently necessary to consider the arguments brought forward by Dr. MARX in favour of his view.

His main reason for concluding that the ionization is nearly uniformly distributed is the existence of a point of inflexion in some of the curves showing the fall of potential between the electrodes, which, as he points out, can only occur theoretically when there is some volume ionization.

It is easy to calculate the variation of the electric intensity between two electrodes when only surface ionization occurs and a saturating P.D. is applied. We have then

$$dX/dx = 4\pi(n_1 - n_2)e \quad \ldots \ldots \quad (1),$$

$$(d/dx)(k_1 n_1 X) = 0 \quad \ldots \ldots \quad (2),$$

$$(d/dx)(k_2 n_2 X) = 0 \quad \ldots \ldots \quad (3),$$

$$(k_1 n_1 + k_2 n_2) Xe = \iota \quad \ldots \ldots \quad (4).$$

If q_1 is the number of positive ions coming in unit time from unit area of the positive, electrode (2) gives

$$k_1 n_1 X = q_1 ,$$

and in the same way

$$k_2 n_2 X = q_2 .$$

Hence substituting in (1)

$$\frac{dX}{dx} = 4\pi\left(\frac{q_1}{k_1 X} - \frac{q_2}{k_2 X}\right)$$

or

$$2X\frac{dX}{dx} = 8\pi\left(\frac{q_1}{k_1} - \frac{q_2}{k_2}\right).$$

Integrating we get

$$X^2 = 8\pi\left(\frac{q_1}{k_1} - \frac{q_2}{k_2}\right)x + C.$$

If we measure x from a point where the intensity is X_0, then $X_0^2 = C$, so that

$$X^2 - X_0^2 = 8\pi\left(\frac{q_1}{k_1} - \frac{q_2}{k_2}\right)x .$$

Therefore in this case the intensity should increase regularly from one electrode to the other unless $q_1/k_1 = q_2/k_2$, in which case $X = X_0$ everywhere.

The fall of potential in the flame when the upper electrode is negative is like that indicated by the above calculation ('Phil. Trans.,' A, vol. 192, 1899, p. 508), and so agrees with the view that the ionization nearly all occurs on the electrodes.

In Dr. MARX's experiments the upper electrode appears to have always been positively charged, in which case, as I have shown, the curves show a rapid fall of potential near both the electrodes with a nearly uniform intensity in the intervening space, and this form of curve is obtained even when very large voltages are applied.

Thus even when a very large P.D. is applied the observed curves show that the electric intensity between the plates is very small, almost zero in some cases, so that there is no reason to suppose that there is no recombination occurring between the electrodes when this form of curve is obtained; in fact, a saturating P.D. has not really been applied, so that MARX's argument breaks down. The presence of surface ionization has much the same effect as an increase in the distance between the electrodes, and consequently protects the intervening region from the applied P.D., so that it does not get saturated.

When the current is reversed so that the upper electrode is negative the supply of negative ions is greatly diminished owing to the comparatively low temperature of the upper electrode. Consequently, since the current is mainly carried by the negative ions it becomes easier to saturate the intervening space and the potential fall curve changes accordingly.

I think, therefore, that the observed potential fall curves are not inconsistent with the view that most of the ionization occurs close to the surfaces of the glowing electrodes.

The remainder of the present paper is divided into the following sections:—

(1) Description of the apparatus used.
(2) Variation of the current with the E.M.F.
(3) Variation of the current through air with the temperature.
(4) Variation of the current through salt vapours with the temperature.
(5) Summary of results.

1. *Description of the Apparatus used.*

The apparatus used is shown in fig. 1.

It consisted of a platinum tube TT, 25 centims. long and 0·75 centim. in diameter. having a narrow tube T′ joined on at one end, and a flange FF, 6 centims. in diameter, joined on at the other. This tube was supported horizontally in a FLETCHER's tube furnace, the fire-clay blocks of which are shown by the dotted lines.

The flange served to keep the furnace gases from the open end of the tube. An electrode, EE, consisting of a platinum tube, 12 centims. long and 0·3 centim. in diameter, was supported on an adjustable insulated stand, along the axis of the tube TT. The end of this electrode was closed by a conical platinum cap which was about 9 centims. down the tube TT.

At T′ the platinum tube was sealed on to a glass tube through which the air charged with spray entered. The spray was produced by a Gouy sprayer, S, which projected the spray into a glass bulb, G, about 8 centims. in diameter, from which the air and spray were led through an inverted U-tube in which the coarser spray settled.

The solution was contained in a reservoir R. The level of the surface of the solution being 30 centims. above the nozzle of the sprayer. The greater part of the spray settled in the bulb and first half of the U-tube, and was returned to R through a tube, DD, up which the liquid was forced by air introduced by the tube K.

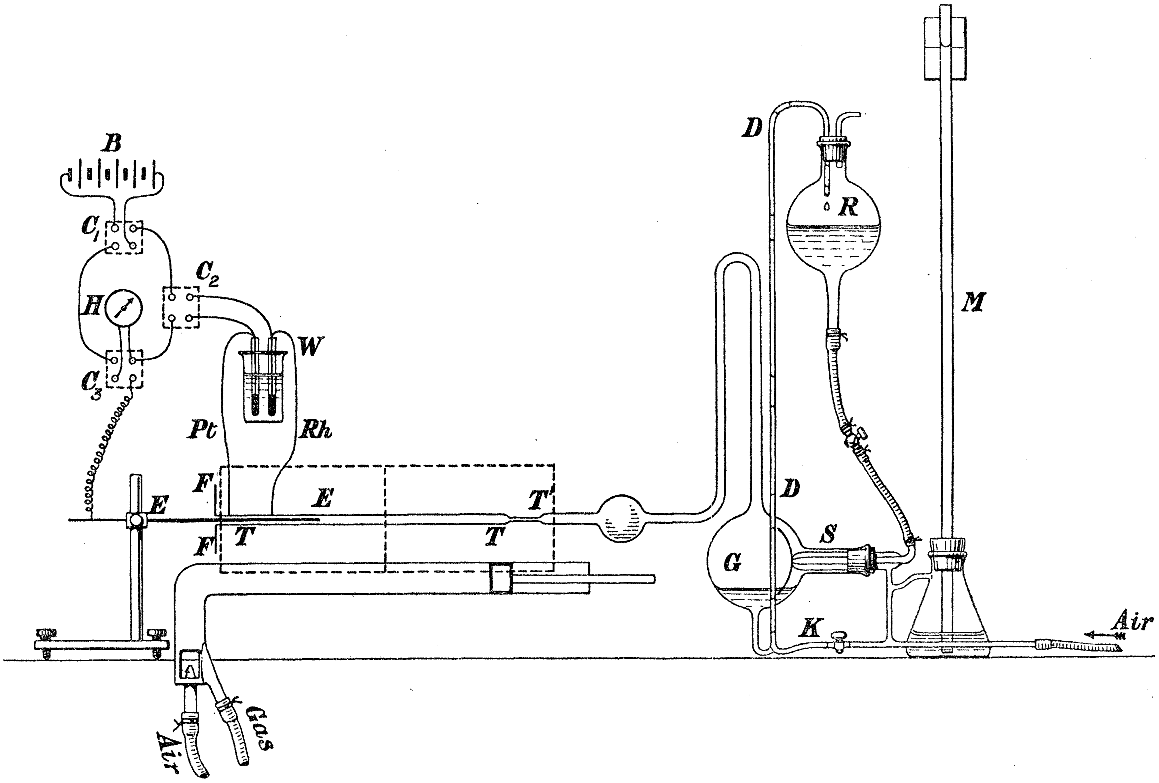

Fig. 1.—TT Platinum tube. EE Electrode. S Sprayer. R Reservoir of salt solution. M Air manometer. W Water bath. Pt, Rh Thermo-couple wires. H Galvanometer. B Battery. C_1 C_2 C_3 Commutators.

The supply of compressed air used was obtained by means of two water injector pumps similar to the one used in the previous work on the conductivity of flames. Some of the air was allowed to escape by bubbling through mercury which served to keep its pressure nearly constant, and the rest was passed through a large carboy to smooth out small oscillations in the pressure. The air pressure at the sprayer was measured by means of the water manometer, M, and was kept constant at 50 centims. This arrangement gave enough air to work the sprayer and also the furnace except at temperatures above about 1100° C., when the air supply to the furnace was supplemented by oxygen from a cylinder by means of which a temperature of 1400° C. could be obtained.

The temperature of the tube was measured by means of a platinum platinum-rhodium thermo-couple, which was simply connected directly to an Ayrton-Mather dead-beat galvanometer of about 500 ohms resistance. The platinum wire served to support the tube, and the Pt/Rh wire was fused on to the tube at a point on its upper surface, so that the tube itself formed one of the elements of the couple. The couple was standardised by determining the galvanometer deflection corresponding to the melting point of K_2SO_4, which melts, according to HEYCOCK and NEVILLE, at 1066° C. The K_2SO_4 was introduced into the tube on a small platinum spatula, and the temperature gradually increased until it was seen to melt, and the corresponding deflection noted. Then by maintaining the tube at a series of constant temperatures near the melting point, and finding when the K_2SO_4 melted, it was possible to obtain two temperatures very near together, at one of which the K_2SO_4 melted and at the other remained solid. The mean of the two galvanometer deflections was taken as corresponding to 1066°, and the temperature corresponding to any other deflection was first calculated on the assumption that the deflection was proportional to the difference between the temperatures of the two junctions. The "platinum temperatures" thus obtained have been corrected to the centigrade scale by means of the table of corrections given by CALLENDAR ('Phil. Mag.,' Dec., 1899, p. 534).

This method of getting the temperatures was quite sufficiently accurate for the purposes of the present investigation, for which it was useless to aim at a greater accuracy than 5° or 10°, and, according to CALLENDAR, the corrections are much more accurate than this near 1000°, while even at 300° the error is not more than 10°.

The Pt and Pt/Rh wires dipped into mercury cups kept in a water bath at a known temperature, from which copper wires led to the galvanometer.

The gas supplied to the furnace was kept at a constant pressure by means of a gasometer, and the air and oxygen supply tube was provided with a water manometer by means of which the pressure of the supply could be maintained constant if necessary, for any length of time. In this way the tube could be maintained constantly at any desired temperature within 5° without difficulty.

The current through the air and salt between the electrode EE and the tube T, due to various potential differences between them, was measured by the galvanometer used to measure the temperature. By means of commutators the connections with the galvanometer could be immediately changed from the thermo-couple to the conductivity apparatus. The difference of potential was supplied by a battery of small secondary cells.

2. *Variation of the Current with the E.M.F.*

Before making observations on the variation of the current with the temperature at constant E.M.F., some observations were made on the variation of the current with the E.M.F. at constant temperature.

The results obtained at a temperature of 1080° C. for air alone, without salt and no air current passing along the tube, are shown graphically in diagram No. 1.

When the outside tube was negatively charged the current soon attained an almost constant value as the E.M.F. was increased, but when the outside tube was the positive electrode the current continued to increase rapidly with the E.M.F., and was much greater than the current in the reverse direction, except with very small E.M.F.'s.

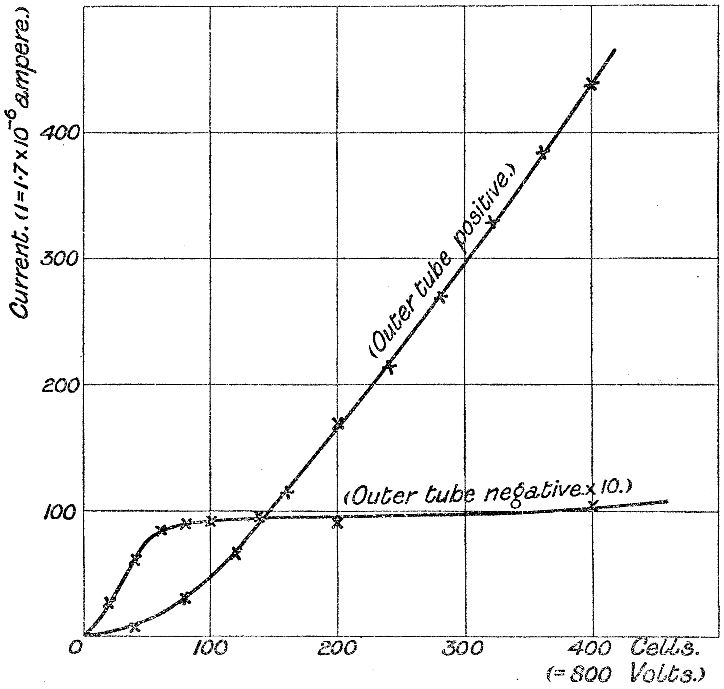

Diagram No. 1.

When no air current was passed through the tube the inner electrode was much colder than the outside tube, especially near the flange, owing to its losing heat by conduction along the tube supporting it. This difference of temperature between the two electrodes enables the great difference between the two currents to be explained in the same way as the similar differences observed in flames can be explained.

It was shown by GUTHRIE ('Phil. Mag.,' vol. 46, p. 257, 1873), that a red hot metal can retain a negative but not a positive charge in air. This is the reverse of what occurs in a flame where a negative charge leaks away much more rapidly than a positive one. Consequently when the hotter tube is positive the current is greater than when it is negative.

The electric intensity is of course greater at the inner tube than it would be if both electrodes had the same area, and it is possible that this circumstance helps to exaggerate the difference between the two currents.

An experiment was therefore tried, using a wire 1 millim. in diameter instead of the inner tube. The results are shown graphically in diagram No. 2.

The general character of the curves is the same as before, but the two currents at any E.M.F. are much smaller.

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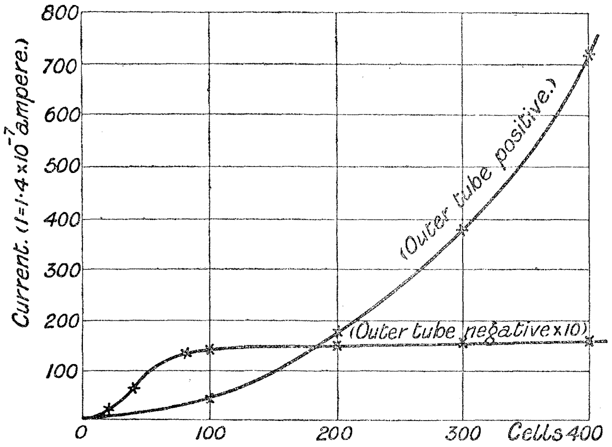

Diagram No. 2.

The effect of cooling the inner tube by blowing a current of air through it was also tried. A small hole was bored at the point of the conical cap to allow the air to escape. The results obtained are shown in diagram No. 3.

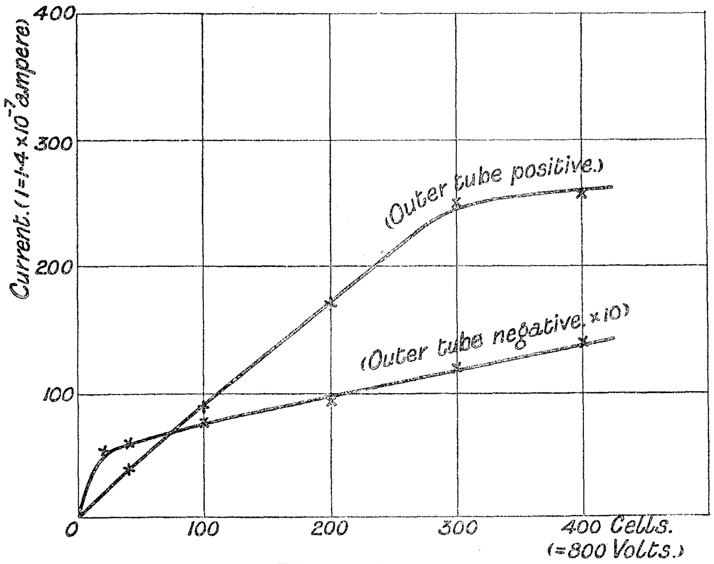

Diagram No. 3.

Cooling the inner tube greatly diminished the current in both directions, and also caused the current, with the outer tube positive, to begin to show signs of attaining a saturation value.

A very peculiar phenomenon was noticed in all the above experiments. On first applying the E.M.F. the current was much greater than the steady value to which it soon settled down. This effect was always much more marked when no current had been passed for some time than immediately after breaking the circuit. Thus on first heating the tube in the morning to about 1100°, and putting on an E.M.F. of 400 volts, the current would be as much as ten times its final value, to which it would drop in about one minute. If after passing this current for 10 minutes, the circuit was broken for 10 seconds, then, on remaking it, the initial current would be perhaps 20 per cent. greater than the final steady value to which it would fall in a few seconds.

Long-continued heating of the tube to 1500° was found to diminish this effect, which, however, slowly reappeared, though not entirely, when the tube was cooled. It was also found that the steady currents observed through air fell off considerably as the platinum tubes became more and more aged through use.

This effect is presumably due to long-continued heating of the platinum. A similar effect was observed by ELSTER and GEITEL ('Wied. Ann.,' vol. 37, p. 315, 1889) in their experiments on the charge communicated to a neighbouring plate by an incandescent platinum wire in air. At first the plate gets a positive charge, but this diminishes with long-continued heating of the wire, and finally at low pressures actually changes sign and the plate then gets a negative charge. NAHRWOLD ('Wied. Ann.,' vol. 35, p. 107, 1888) ascribes the positive electrification first observed to the action of dust in the air, and regards the final communication of a negative charge as the normal effect.

It is clear that the falling off in the amount of conductivity as the tube gets aged is due to a change of some kind in the state of the platinum. Perhaps occluded gases are gradually expelled from it, though it seems very unlikely that the loss of a small quantity of gas should produce such a marked change in the amount of ionization as actually occurs. I think a change in the state of molecular aggregation of the platinum, due to long-continued heating, is the most probable cause of the falling off in the amount of ionization produced in the air close to it, though it is not easy to see why any such change should have this effect. Perhaps the porosity of the metal diminishes with long-continued heating, so that the effective surface of metal exposed to the gas is diminished.

The large current obtained for a short time on first applying the E.M.F. suggests the idea that the passage of the current produces some kind of polarisation of the electrodes, but on connecting the electrodes directly to the galvanometer immediately after applying a big E.M.F. for some time, no indication of a polarisation current could be detected. If the applied E.M.F. was suddenly reversed in direction, the current after reversing was for a short time greater than the steady value to which it soon settled down, but this effect was not greater than what would have been observed if the E.M.F. had merely been suddenly applied in the second direction without first applying it in the opposite direction.

The object of the investigation being to obtain information on the variation of the conductivity with temperature, the investigation of these peculiar effects was not proceeded with, but I hope before long to make experiments with a view to elucidate their real nature.

The values given for the observed currents through air throughout this paper are the steady values attained after the E.M.F. had been applied for a short time. In most cases it was only necessary to wait a few seconds before taking the reading. The current through salt vapours did not show any such peculiar changes,* and in the later experiments, after the tube was aged, was usually very large compared with that carried by the air at the same time. When the tube was nearly new the current, carried by the air at high temperatures, was sometimes of the same order of magnitude as that due to the salt. The actual numbers obtained in many cases are given below.

When a salt solution was being sprayed the variation of the current with the E.M.F. was of a much simpler character than with air alone.

The current due to the salt was usually greater when the outside tube was negative, but the character of the relation between the current and E.M.F. was about the same in either case.

Diagram No. 4 shows the current E.M.F. curves got while spraying a 1 per cent. KCl solution at 900°.

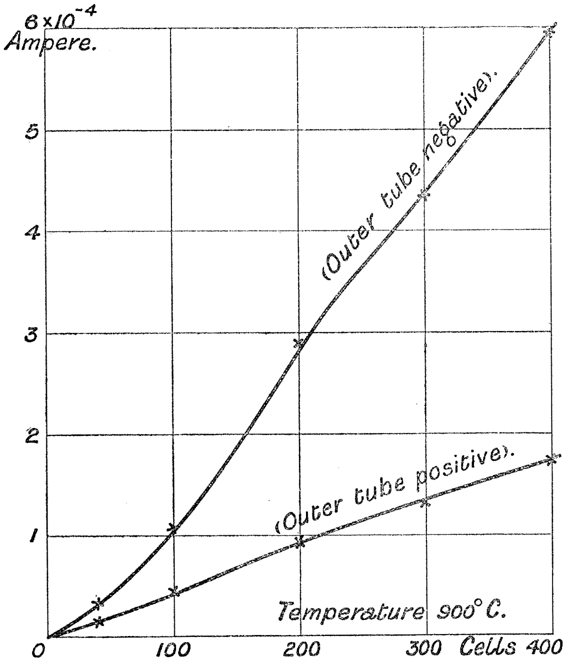

Diagram No. 4.

A comparison of the curves given below, showing the variation of the current at constant E.M.F. with the temperature for different E.M.F.'s, shows that as the temperature falls the E.M.F. at which approximate saturation is attained falls also, so that below 500° saturation is attained at about 100 volts.

The following table shows the way in which the relation of the current to the E.M.F. varies with the temperature. The numbers are for a 1 per cent. KI solution, and were taken from the curves given in Section 5 :—

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* *Note, added August* 8, 1901.—This applies to KI and KCl. Some salts do show the effect as well as air. See Appendix.

Current (1 = 10^{-5} ampere).

	500°.	700°.	900°.	1100°.	1300°.
40 volts	0·2	0·3	0·3	0·9	2·5
100 ,, ...	5·1	5·5	5·5	6·8	9·2
800 ,, ...	7·0	30·0	45·0	35·0	71·0

We see that for small E.M.F.'s the current increases very slowly at first, and then more rapidly. At higher E.M.F.'s it becomes nearly constant at 500°, whereas at 1300° it is nearly proportional to the E.M.F.

Diagram No. 5 shows the variation of the current with the E.M.F. for KI at 1200°.

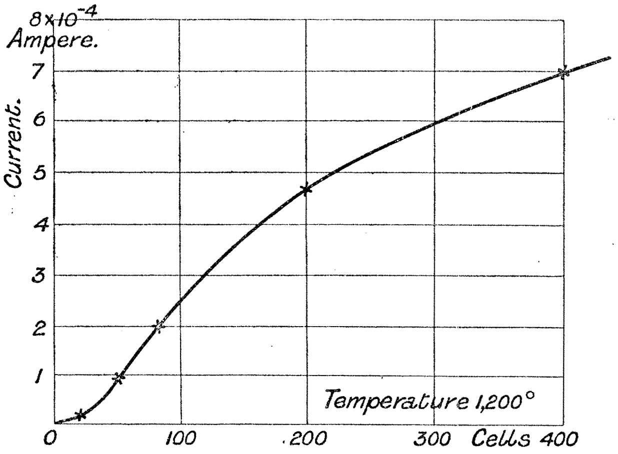

Diagram No. 5.

3. *Variation of the Current through Air with the Temperature.*

To determine the variation of the conductivity with the temperature at constant E.M.F., a series of measurements of the current due to a fixed number of cells at different temperatures was made. The value of the current was not read until it had become constant. A temperature reading was always taken both before and after the measurement of the current, and unless the two readings agreed the measurement was repeated. Usually no difficulty was experienced in keeping the temperature sufficiently constant, owing to the excellent working of the regulating arrangements on the gas and air supplies. The highest temperature was done first and the temperature then diminished by steps until the current became inappreciable, when the temperature was raised again and some of the observations repeated.

The usual current of air coming from the sprayer was always passed through the tube, since it served to keep the inner electrode at nearly the same temperature as the outer one. Measurements of this kind, using air alone, were made from time to time during the course of the investigation, and, as already mentioned, it was found that a marked falling off in the conductivity at any particular temperature occurred as the tube got aged.

The character of the relation between the current and temperature, however, was not sensibly affected by this ageing of the tube. The results of the first series of observations of this kind done are shown in diagram No. 6. The tube had then been used at intervals for about a fortnight.

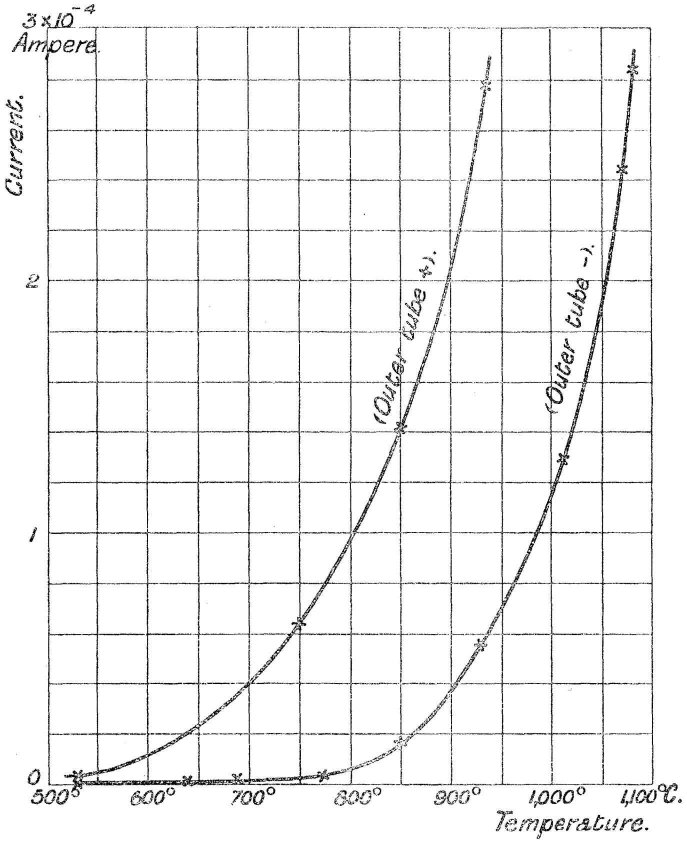

Diagram No. 6.

The gradual falling off in the conductivity is shown by the numbers in the following table, which give the values of the currents at several temperatures obtained on different dates :—

Current through Air in Amperes.

E.M.F. 800 volts.

Outer tube negative.

	Temperature 800°.	900°.	1000°.	1100°.
July 6 . . .	8×10^{-6}	40×10^{-6}	120×10^{-6}	400×10^{-6}
,, 10 . . .	2 ,,	11 ,,	50 ,,	140 ,,
,, 30 . . .	0·1 ,,	0·7 ,,	2·5 ,,	8 ,,

Diagram No. 7 shows the results obtained with an E.M.F. of 240 volts, the outer tube being the negative electrode. Date, July 29.

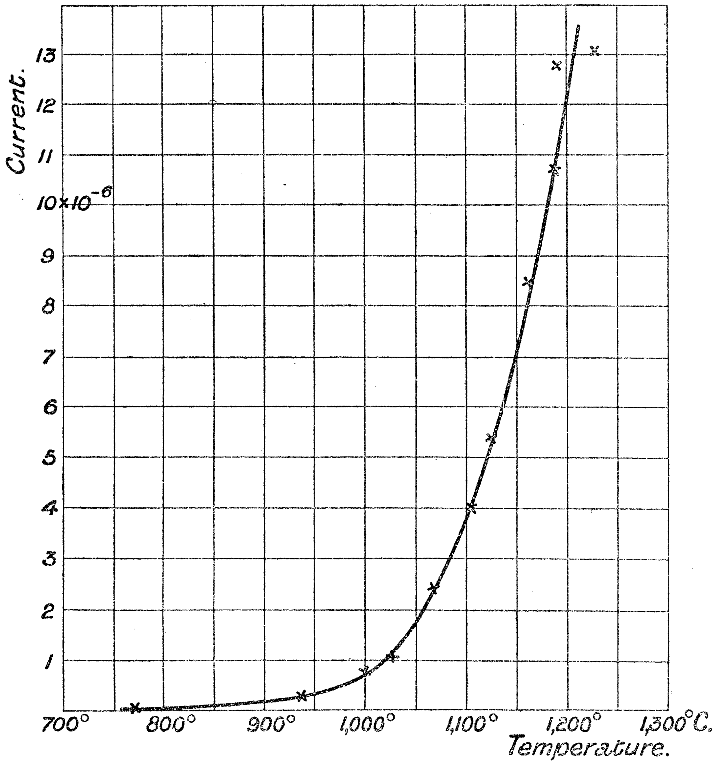

Diagram No 7.

Diagram No. 8 shows the results obtained, using 40 volts, on July 28.

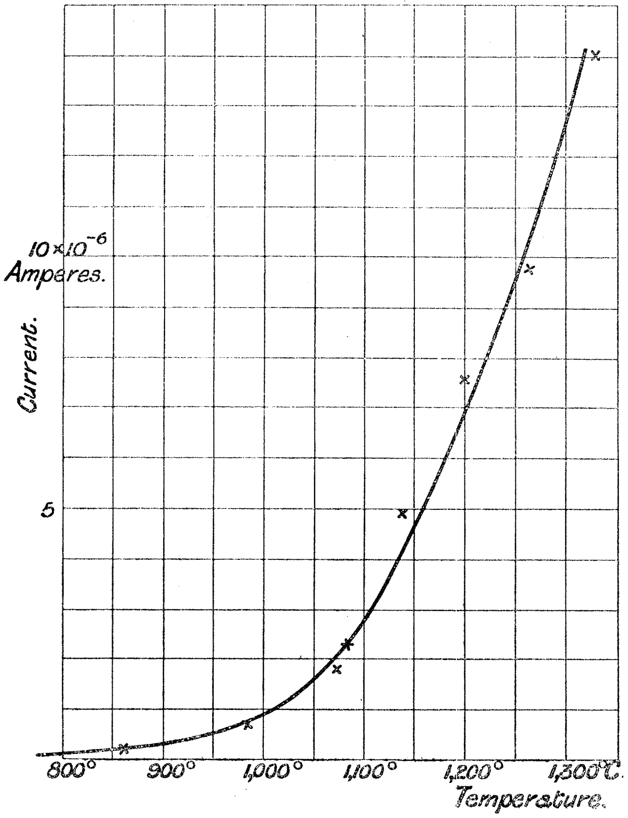

Diagram No. 8.

Diagram No. 9 shows the relation between the logarithms of the current and the absolute temperature, using values taken from diagram No. 7. The relation between the logarithms is roughly $\log C = 17{\cdot}17 \log \theta - 59{\cdot}3$, where C is the current and θ the absolute temperature.

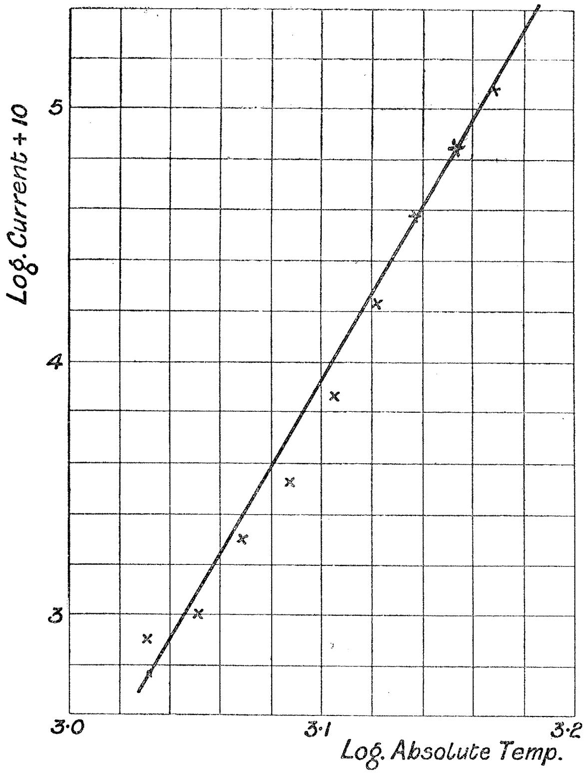

Diagram No. 9.

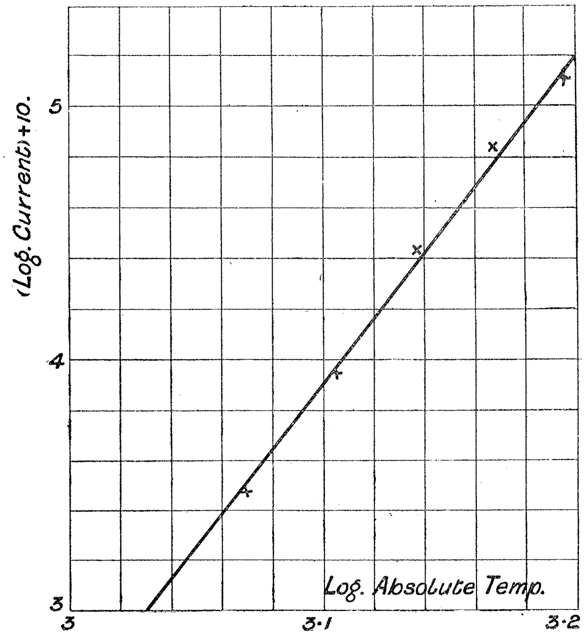

Diagram No. 10.

Diagram No. 10 shows the relation between the logs got from diagram No. 8. This gives $\log C = 12{\cdot}8 \log \theta - 45{\cdot}8$.

According to these formulæ some current should be obtained at any temperature, however low.

The above results show that the conductivity does not begin suddenly at a definite temperature, but always increases regularly with rise of temperature, so that the lowest temperature at which conductivity can be detected depends entirely on the sensitiveness of the galvanometer.

The calculation of the energy required to ionize the conducting gas from the variation of the conductivity with the temperature will now be considered.

The ionization practically all takes place in a thin layer close to the surface of the platinum, and the number of ions in this layer will depend on the rate at which they are formed and on their rate of recombination.

For the purpose of this calculation the rate of production of ions will be regarded as a function of the temperature and concentration of the gas in this layer. At any constant temperature, if C is the concentration of the gas and C′ that of the positive or negative ions supposed equal, we have

$$C = \alpha C'^2,$$

where α is a constant and it is assumed that one molecule of the gas dissociates into two ions. The case is evidently on these suppositions exactly analogous to, say, the dissociation of N_2O_4 into $2NO_2$, and the equation commonly employed to represent the variation of the dissociation with temperature in such cases can be employed. It is

$$\frac{q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \log\left\{\frac{x_1^2}{x_2^2} \cdot \frac{1 - x_2^2}{1 - x_1^2} \cdot \frac{T_2}{T_1}\right\},^*$$

where q is the heat developed when 1 gramme molecule of the gas is formed from the ions by recombination, and x is the fraction of the gas dissociated at the absolute temperature T. q is supposed expressed in calories and is taken as being constant between T_1 and T_2.

If x is small then approximately

$$\frac{q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \log \frac{x_1^2}{x_2^2} \cdot \frac{T_2}{T_1}.$$

The current when the potential gradient is small is equal to $A\,n\,(k_1 + k_2)$, where n is the number of positive or negative ions in the gas per unit volume of the layer, k_1 and k_2 the velocities of the positive and negative ions respectively, and A a constant. Now k_1 and k_2 vary with the temperature, probably being proportional

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[*] See 'Lectures on Physical Chemistry,' VAN'T HOFF, vol. 1.

to a small power of the absolute temperature such as the square root over small ranges of temperature.

Hence at temperatures near 1000° C., k_1 and k_2 may be taken as constant over small ranges of temperature without serious error, so that the current with a small E.M.F. is proportional to n, and n is proportional to x when x is small. Hence in the formula

$$\frac{q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \log \frac{x_1^2}{x_2^2} \cdot \frac{T_2}{T_1},$$

provided we take T_1 and T_2 very near together, we may replace $(x_1/x_2)^2$ by the square of the ratio of the two currents obtained at T_1 and T_2.

The following table gives values of q obtained from diagram No. 8 :—

$(T_1 - 273.)$	$(T_2 - 273.)$	C_1.	C_2.	q.
1000°	950°	0·9	0·5	71,000
1200°	1150°	7·0	4·7	64,000
1300°	1250°	12·6	9·6	49,000

Thus q for 1 gramme molecular weight of air is about 60,000 small calories between 1000° and 1300° C.

If we take the charges on the ions to be the same as in the electrolysis of solutions then we can obtain an estimate of the potential difference, through which the charge on an ion must fall to do enough work to ionize a molecule of air. To electrolyse 1 gramme molecular weight of any substance requires $9{\cdot}6 \times 10^4$ coulombs, consequently the required P.D. is

$$\frac{60{,}000 \times 42 \times 10^6}{9{\cdot}6 \times 10^4 \times 10^7} = 2{\cdot}6 \text{ volts.}$$

The energy set free in a solution when 1 gramme molecular weight of water is formed from its ions H and OH, is well known to be about 17,000 calories, and when ozone O_3 decomposes into oxygen 30,000 calories are set free. It is interesting to note that the energy in these two cases is of the same order of magnitude as the value just calculated for the energy necessary to ionize air.

Rutherford has determined the energy of the Röntgen rays absorbed by a given volume of air, and the number of ions produced in the same volume by the rays. From this he deduces the energy required to ionize one molecule of air at the ordinary temperature. His result expressed in volts multiplied by the charge on one ion is 170, which is 70 times greater than the value I have obtained at temperatures above 1000°.

It is probable that in Professor Rutherford's experiment the greater part of the Röntgen rays absorbed by the air is not used up in producing ions.

If we suppose that the energy required to ionize a molecule is due to the electric attraction between the two charges, then it is easy to calculate the distance between them in the molecule before it is ionized. We have, if e is the charge on one ion and r the distance required,

$$\frac{2 \cdot 6\, e}{300} = \frac{e^2}{r},$$

and according to J. J. THOMSON* $e = 6 \times 10^{-10}$ electrostatic unit, hence

$$r = 7 \times 10^{-8} \text{ centim.}$$

This is of the same order of magnitude as the radius of molecular action in liquids at the ordinary temperature.

Professor TOWNSEND† has shown that the potential difference through which the ionic charge must fall to have enough energy to ionize a molecule of air at the ordinary temperature is less than 5 volts, and probably greater than 1 volt. My result, 2·6 volts for air at temperatures above 1000° C., is therefore nearly the same as TOWNSEND'S, in spite of the great difference between the temperatures at which his and my experiments were carried out.

4. *Variation of the Current through Salt Vapours with the Temperature.*

In the earlier measurements made on the conductivity of salt vapours the conductivity of the air alone without salt at temperatures above 900° was not small

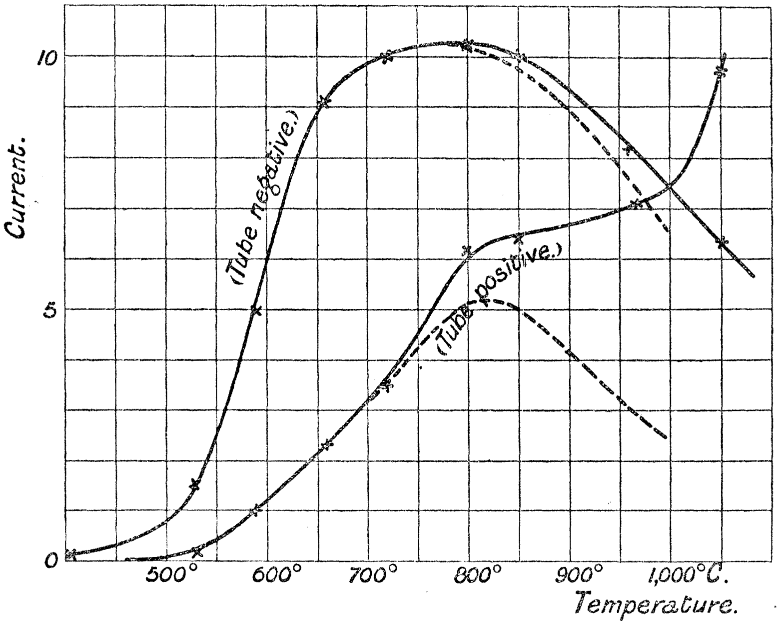

Diagram No. 11.

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* 'Phil. Mag.,' December, 1898.

† "The Conductivity produced in Gases by the Motion of Negatively Charged Ions," 'Phil. Mag.,' February, 1901.

compared with that of the salt, but as the tube got aged the conductivity of the air fell off to such an extent that it became quite small compared with that of the salt when solutions containing 10 grammes in a litre were sprayed.

Diagram No. 11 shows the variation of the current with the temperature when spraying a solution of KCl, done when the tube was nearly new.

The conductivity due to the KCl has a maximum value at about 800°. The current due to the salt is greater when the outer tube is negative, while the reverse holds good for air, so it is best to have the outer tube negative when measuring the conductivity of salt vapours. The dotted curves drawn were got by subtracting the current due to the air alone from the current due to both salt and air.

In all the measurements given below the outer tube was negative, and the conductivity of the air alone was negligible compared with that of the salt.

Diagrams Nos. 12, 13, and 14 show the variation of the current with the temperature when a solution of KI containing 10 grammes in a litre, was sprayed with E.M.F.'s of 800, 100, and 40 volts respectively.

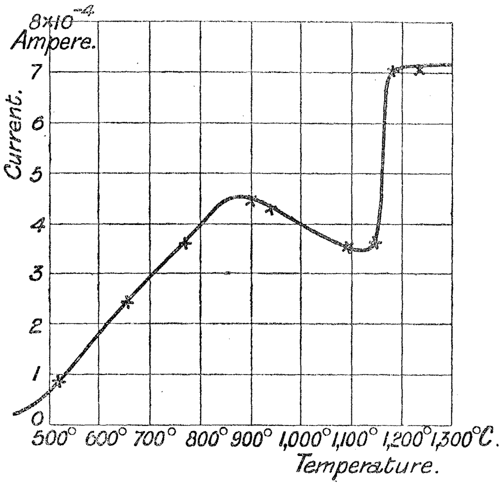

Diagram No. 12.

It is evident from these curves that the relation between the conductivity of salt vapours and the temperature is of a much less simple character than is the case for air alone.

As the temperature rises the conductivity at first increases rapidly and then attains a maximum value at about 900° C., above which it falls again until about 1150° C. is reached, when it suddenly begins to rise very rapidly. Above 1200° C. the current again becomes nearly independent of the temperature.

With an E.M.F. of 800 volts, the sudden rise at 1150° just doubles the current, which suggests that at this temperature some kind of dissociation occurs and doubles the number of ions available.

The amount of salt passing through the tube was determined by substituting for the platinum tube a large glass tube about 4 centims. in diameter and 50 centims. long, tightly packed with glass wool. The resulting increase in the air pressure in the bulb and U-tube was counterbalanced by increasing the pressure of the air supply to the sprayer and the air pressure above the solution in the reservoir by an equal amount.

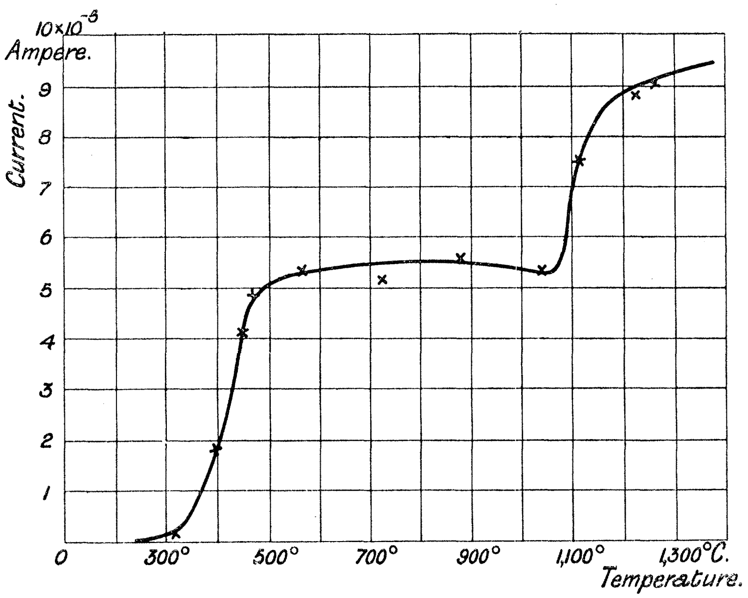

Diagram No. 13.

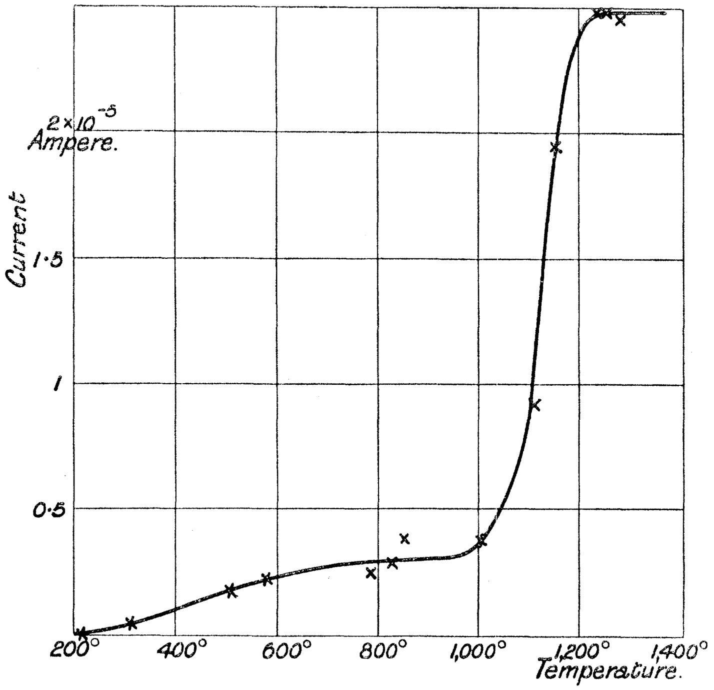

Diagram No. 14.

A solution containing 20 grammes of NaCl in a litre was sprayed for one hour, and the amount of NaCl in the plug determined by washing out with water and titrating against standard $AgNO_3$ solution. That the plug stopped all the spray was shown by passing the escaping air into a Bunsen flame when no coloration could be detected. With a shorter plug of glass-wool all the spray was not stopped. In this way it was found that 4·7 milligrammes of NaCl were stopped by the plug in one hour, this number being the mean of several concordant determinations.

In the later experiments a new sprayer was used, which sprayed 2·2 times as much salt as the old one. The ratio of the amounts of salt sprayed by the two sprayers was got by comparing the conductivities due to 1 per cent. KCl solutions when sprayed by the two sprayers under similar conditions at 1200°, and with an E.M.F. of 800 volts. Under these conditions the current is proportional to the electrochemical equivalent of the salt passing through the tube, as will be shown below. The amount of KI passing through the tube during the above measurements was therefore $1·46 \times 10^{-3}$ milligramme per second.

To electrolyse this amount of KI in a solution requires a current of

$$\frac{1·46 \times 10^{-3} \times 39}{166 \times 0·405} = 8·5 \times 10^{-4} \text{ ampere.}$$

The current obtained at 1400° with 800 volts was 7×10^{-4} ampere, which is therefore nearly equal to the current required to electrolyse the KI used in a solution.

It is probable that at high temperatures the KI is converted into KOH by the water vapour present. The reaction being

$$KI + H_2O = KOH + HI.$$

The view that all salts of the alkali metals are converted into hydrates at a high temperature in the presence of water vapour was used by ARRHENIUS to explain his results on the electric conductivity of flames, and this view is also in accord with the results of the investigation published in 1899, "On the Electric Conductivity and Luminosity of Flames containing Vaporised Salts."* According to this view the falling off in the current above 900° might be explained as being due to KOH being less ionized than KI at this temperature.

Thus up to about 900° the conductivity may be supposed entirely due to KI, but at this temperature KOH and HI begin to be formed, and conduct less well than KI, so that the current falls off. As the temperature rises, however, the KOH begins to dissociate into ions, so that at 1200° the current attains a maximum value when it is completely electrolysed.

The energy required to ionize a gramme molecular weight of KI can be calculated in the same way as was done for air by using the values of the current obtained at

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* 'Phil. Trans.,' A, vol. 193, 1899.

low temperatures* where the current is small compared with that required to completely electrolyse the salt. At 250° C. a current of 2×10^{-7} ampere was obtained with 40 volts, and at 300° a current of 4×10^{-7}. Hence the energy required to ionize 1 gramme molecule of KI is about 15,000 calories, or about one quarter that necessary to ionize a gramme molecule of air.

Diagram No. 15 shows the variation of the current with the temperature for K_2CO_3, a solution containing 10 grammes in a litre, being sprayed with an E.M.F. of 400 volts.

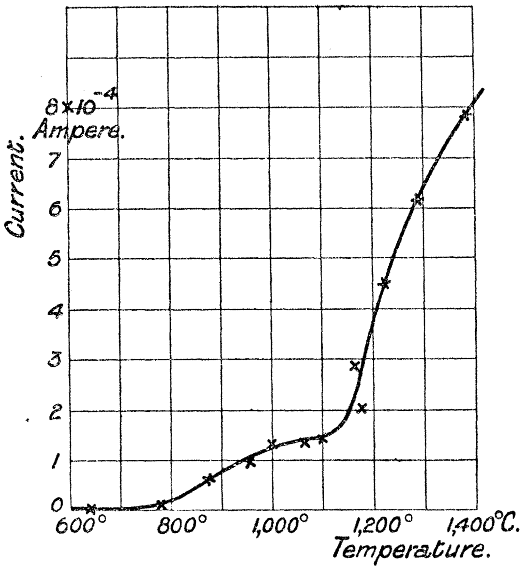

Diagram No. 15.

Diagram No. 16 shows the variation of the current with the temperature for KCl with an E.M.F. of 800 volts.

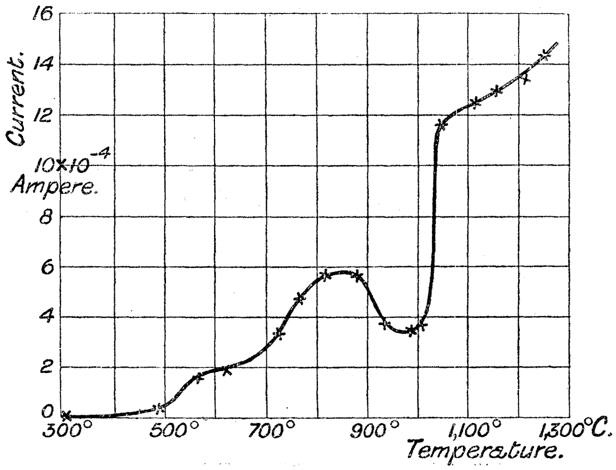

Diagram No. 16.

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* At high temperatures the per cent. of the salt ionized is not small, so that the method used for calculating the energy breaks down.

The following table gives the maximum currents observed with KI, KCl, and K_2CO_3, and the currents required to electrolyse the same amount of each in a solution :—

Salt.	Current.	Current calculated.	Ratio.
KI	7×10^{-4}	$8{\cdot}5 \times 10^{-4}$	0·82
KCl	15×10^{-4}	$18{\cdot}9 \times 10^{-4}$	0·80
K_2CO_3 . . .	16×10^{-4}	$20{\cdot}4 \times 10^{-4}$	0·79

It thus appears that the maximum amount of current carried by the vapours is nearly equal to the maximum amount the same bodies could carry in a state of solution.* This agreement must be regarded as considerable evidence in favour of the view that the ions are of the same nature in the two cases.

5. *Summary of Results.*

(1.) The variation of the current between platinum electrodes in air with the temperature may be expressed approximately by a formula of the type $A\theta^n$, where θ is the absolute temperature and A and n constants. The value of n was about 17 when the E.M.F. used was 240 volts, and 13 with 40 volts.

(2.) The energy required to ionize 1 gramme molecular weight of air is about 60,000 calories between 1000° and 1300°.

(3.) The current through a halogen salt vapour in presence of air and water reaches a maximum value near 900°, and then falls as the temperature rises. Near 1100° it again rises rapidly with the temperature.

(4.) The energy required to ionize 1 gramme molecular weight of KI is about 15,000 calories at about 300°.

(5.) The maximum current carried by a definite amount of salt vapour is nearly equal to the current required to electrolyse the same amount of salt in an aqueous solution.*

In conclusion, I wish to say that my best thanks are due to Professor J. J. THOMSON for much kindly interest and advice throughout the course of the work described in this paper.

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* For similar results with nineteen different alkali salts see Appendix.

APPENDIX.

Added August 9, 1901.

SINCE writing the above paper I have made measurements with a slightly modified apparatus on a number of other salts of the alkali metals. The modifications made in the apparatus were not important. A separate galvanometer was provided for the thermo-couple, so that the temperature and conductivity could be observed simultaneously, and the length of the platinum tube was increased by 12 centims. to further insure that the current of air should have time to take up the temperature of the tube. The sprayer nozzle had to be readjusted, which considerably increased the amount of salt passing through the tube. With these exceptions the apparatus was practically identical with that described above.

Measurements were made with salts of the alkali metals besides those of potassium, so far only used.

At temperatures approaching 1300° the current E.M.F. curves for most salts resemble that given above for KI at 1200°. Below 1100° the current is almost always greater when the outer tube is negative, as already pointed out. However, above this temperature it has been found that the two-current E.M.F. curves cross each other, so that the current is then the greater at high E.M.F.'s when the outer tube is positive.

The following table gives the currents observed when a 1 per cent. solution of CsCl was being sprayed at a temperature of 1340° C.

P.D. Volts.	Current (amperes). Outer tube −.	Current (amperes). Outer tube +.
1200	$8{\cdot}80 \times 10^{-4}$	$15{\cdot}10 \times 10^{-4}$
800	8·65 ,,	13·10 ,,
600	8·80 ,,	9·30 ,,
400	7·62 ,,	4·25 ,,
200	2·34 ,,	1·14 ,,
120	0·93 ,,	0·46 ,,
40	0·23 ,,	0·12 ,,

These results are typical of the behaviour of most alkali metal salts.

It was found that with many salts on first applying the P.D. the current was often abnormally great for a short time, and then settled down rapidly to a steady value, just as it does for air. KI, KCl, and other easily volatile salts only show this effect very slightly, so that as these salts were mainly used in the experiments described above, this effect was not observed with salts until after the above paper was written.

It seems just possible that this effect is due to salt vapour (or, in the case of air, some gas) condensing on the cooler parts of the tube, and to the application of the P.D. causing some of this condensed vapour to evaporate, so that until equilibrium is again restored the amount of salt passing between the electrodes is abnormally large.

The main object of these further experiments was to test the conclusion that the maximum or saturation current carried by the vapour is equal to that required to electrolyse the same amount of the salt in a solution.

Using solutions containing 10 grammes in a litre it was not found possible to saturate the vapour, except in a few cases when the saturation current was found to be approximately that required by the above-mentioned conclusion.

Experiments were therefore tried with solutions containing 1 gramme in a litre, in the hope that with a smaller quantity of salt it would be easier to approach the saturation current. This device proved entirely successful, and the saturation current was in every case nearly inversely proportional to the electro-chemical equivalent of the salt used. It was also verified that the saturation current for a particular salt was proportional to the concentration of the solution sprayed.

The following table gives the currents observed at about 1350° C. with 840 volts with solutions containing 10 grammes in a litre, the outer tube being positively charged in every case.

Salt.	Electro-chemical equivalent. (E.)	Galvanometer deflection. (C.) 1 = $5{\cdot}2 \times 10^{-6}$ amperes.	EC.	Remarks.
CsCl	168	290	$4{\cdot}9 \times 10^4$	Saturated.
RbI . . .	212	260	5·5 ,,	,,
Rb_2CO_3 . .	115	316	3·6 ,,	Not saturated.
KI	166	315	5·2 ,,	Saturated.
NaI . . .	150	315	4·7 ,,	Nearly saturated.
Na_2CO_3 . .	53	505	2·7 ,,	Not saturated.
LiI	134	330	4·4 ,,	,,
LiBr . . .	87	350	3·0 ,,	,,

With CsCl, RbI, KI, and NaI, which were all saturated, or nearly so, the product EC has nearly the same value, viz., $5{\cdot}1 \times 10^4$.

The following table gives the results obtained with solutions containing 1 gramme in a litre.

Salt.	Electro-chemical equivalent. (E.)	Galvanometer deflection. (C.) 1 = 5·2 × 10^{-6} ampere.	EC.
CsCl	168	31	5·2 × 10^3
Cs_2CO_3 . . .	163	31	5·1 ,,
RbI	212	24	5·1 ,,
RbCl	121	43	5·2 ,,
Rb_2CO_3 . . .	115	47	5·4 ,,
KI	166	32	5·3 ,,
KBr	119	41	4·9 ,,
KF	58	85	4·9 ,,
K_2CO_3 . . .	69	77	5·3 ,,
NaI	150	35	5·3 ,,
NaBr	103	47	4·9 ,,
NaCl	59	91	5·3 ,,
Na_2CO_3 . . .	53	91	4·8 ,,
LiI	134	39	5·2 ,,
LiBr	87	60	5·2 ,,
LiCl	43	120	5·2 ,,
Li_2CO_3 . . .	37	144	5·3 ,,
		Mean value . . .	5·14 × 10^3

It is clear from the above results that the saturation current is inversely proportional to the electro-chemical equivalent of the salt. The mean value of the product EC, 5·14 × 10^3, is also very approximately one-tenth of the value 5·1 × 10^4 obtained with solutions containing 10 grammes in a litre, which shows that the saturation current is proportional to the concentration of the solution sprayed.

The amount of salt passing through the tube was determined again by a modification of the method originally employed by ARRHENIUS to determine the amount of salt supplied by a sprayer to a flame.

A solution containing 40 grammes of lithium chloride per litre was sprayed and the air and spray mixed with coal-gas and the mixture then burnt from a brass tube, so as to form a Bunsen flame.

A Bunsen burner was adjusted so as to give another sensibly equal and similar flame, which was placed close beside the first. A weighed bead of fused LiCl was held in the axis of the second flame on a platinum wire loop, and its height in the flame adjusted till the tips of the two flames appeared equally brightly coloured.

Under these circumstances the rate of supply of salt to the two flames must be nearly the same, so that the loss of weight of the bead of LiCl measures the rate at which LiCl is supplied by the sprayer.

The loss of weight of the LiCl bead was found to be 7 milligrammes in 10 minutes in one experiment, and 6 milligrammes in 10 minutes in another experiment. This gives for the number of milligrammes of salt passing through the platinum tube per second when a solution containing 1 gramme in a litre is being sprayed—

$$\frac{6\cdot5}{600 \times 40} = 2\cdot7 \times 10^{-4}.$$

Taking the amount of hydrogen liberated in electrolysis by 1 ampere in 1 second as $1\cdot04 \times 10^{-5}$ gramme, we can now calculate a theoretical value for the product EC given in the above tables of results. For solutions of n grammes in a litre

$$\text{EC} = n\frac{2\cdot7 \times 10^{-4}}{1\cdot04 \times 10^{-2} \times 5\cdot2 \times 10^{-6}}$$

$$= 5n \times 10^{3}.$$

This agrees extremely well with the observed values of EC, viz.,

$$5\cdot1 \times 10^{4} \quad \text{when} \quad n = 10,$$
$$\text{and } 5\cdot14 \times 10^{3} \quad \text{when} \quad n = 1.$$

It is evident that these results prove that FARADAY's laws for the passage of electricity through liquids apply also to alkali salts in the state of vapour. This must be regarded as very conclusive evidence in favour of the theory that the passage of electricity through salt vapours is a process very analogous to the electrolysis of salt solutions.

In a dilute solution of such a salt as KCl each molecule of the salt is believed to dissociate into two ions, +K and −Cl. According to the corpuscular theory of electricity, if we denote a corpuscle by α then these ions are $\text{K} - \alpha$ and $\text{Cl} + \alpha$.

The results described in this paper prove that the amount of electricity which can be transported by salt in the form of vapour is equal to the amount required to electrolyse the same amount of salt in a solution.

This can be explained on the corpuscular theory in two ways, the first of which involves electrolysis of the salt, whereas the second does not. According to the first, the molecules of the salt vapour dissociate into ions, $\text{K} - \alpha$ and $\text{Cl} + \alpha$, exactly as in a solution. These ions then move to the electrodes and give up their charges, so becoming K and Cl, the K being at the negative electrode and the Cl at the positive electrode.

According to the other explanation a molecule of the salt vapour merely loses a corpuscle, thus forming two ions

$$\text{KCl} - \alpha \quad \text{and} \quad \alpha.$$

Then the KCl goes to the negative electrode and only corpuscles go to the positive electrode, so that no separation of the two constituent atoms of the molecule takes place.

The high velocity of the negative ions, compared with that of the positive ions, seems to favour the latter view, but the known cases in which separation of the elements of a compound by electrolysis in gases appears to take place, strongly support the view that the ions are similar to those existing in solutions.

The present experiments do not show what happens to the ions after they have discharged on the electrodes, except that apparently they do not participate any further in the transport of the electricity. It is hoped that future experiments will throw more light on this question.