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III. *The Electrical Conductivity and Luminosity of Flames containing Vaporised Salts.*

By Arthur Smithells, H. M. Dawson, *and* H. A. Wilson, *The Yorkshire College, Leeds.*

Communicated by Sir H. E. Roscoe, *F.R.S.*

THE colour imparted to flames by the salts of an alkali metal is generally considered to be due to the metal existing in the state of incandescent vapour, but there does not appear to be any settled opinion as to the process by which the metal is set free from its salts. It is frequently assumed that the high temperature reigning in the flame dissociates the salt. There is, however, little, if any, independent evidence in favour of this view. Another explanation ascribes the liberation of metal to chemical decomposition. Thus, in the case of sodium chloride introduced into the flame of a Bunsen burner consuming coal-gas, it would be supposed that in the first instance the water vapour present would act in accordance with the following equation :—

$$NaCl + H_2O = NaHO + HCl.$$
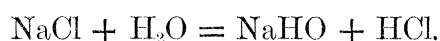
The sodium hydrate (or possibly oxide) so produced would then be deprived of its oxygen by reducing gases (hydrogen, hydrocarbon, carbon monoxide) existing in the flame. A somewhat similar explanation would have to be applied to the flames of hydrogen, carbon monoxide, and cyanogen, though, in the case of the last two gases, the steps of the processes are still more hypothetical.

It is a noteworthy fact that the coloration of flames by alkali salts extends up to, and even beyond, the outer margin of the visible region of combustion, where the flame gases are usually considered to be fully oxidised and where free atmospheric oxygen exists. In such parts of a flame metals, much less oxidisable than the alkali metals, are rapidly oxidised when in the massive state. A copper wire, for example, becomes incrusted with oxide in a region where yellow light is abundantly emitted from a salted flame. A superoxygenated oxy-hydrogen flame is also coloured yellow by salt.

In discussing these facts* one of us was led to consider whether an alternative explanation might not be sought from some conclusions, derived by Professor Arrhenius, from a study of the electrical conductivity of salt vapours in flames.†

* 'Philosophical Magazine' (V.), vol. 37, 245, 1894.
† 'Wied, Ann.,' vol. 42, 18, 1891.

N 9.9.99

From the analogy stated to exist between dilute solutions of solids and matter in the gaseous state, and from his own theory that in dilute solutions electrolytes are in greater or less degree dissociated into their ions, Arrhenius was led to suppose that the vapour of electrolytes distributed in small concentration throughout a gas would likewise be electrolytically dissociated.   He considers his experimental results to harmonise with this view.   He supposes that when an alkali salt is introduced into a coal-gas flame the large excess of water vapour present converts the salt into a hydroxide, in accordance with the following equation :—

$$M'X' + H_2O = M'OH + HX'.$$

The hydroxide is then supposed to dissociate to a certain extent into its ions.

Now, according to the electrolytic theory of solution, a free ion may, in virtue of its electric charge, be characterised by properties totally different from those pertaining to the ordinary chemical atom.   Thus, in a dilute solution of sodium chloride, sodium ions may persist in presence of water.   If we accept the results and views of Arrhenius, we might suppose that in a flame coloured by an alkali salt, the metal is liberated as an ion, and as such may persist in a strongly oxidising medium of flame gases.   Such an explanation would avoid the difficulties attending the more usually adopted views.

Another consideration appeared to favour the hypothesis suggested to us by the results of Arrhenius.   According to him the conductivity of a salt vapour is proportional to the square root of its concentration in the flame.   Now Gouy has shown ('Ann. Chim. Phys.,' 18, 5, 1879), that the luminosity of a flame coloured by an alkali salt is also within certain limits nearly proportional to the square root of its concentration in the flame.

The parallelism of these numerical relationships would obviously find a simple explanation in the event of the luminosity and electrical conductivity being both dependent on the presence of free ions.

The importance of these deductions as affecting spectrum analysis decided us to undertake an experimental investigation of the subject, and we were the more inclined to this from the belief that we had at hand an apparatus capable of giving accurate results.   Besides this, a close examination of the results of Arrhenius revealed some apparent discrepancies that detract from the weight of his conclusions.[*]

The apparatus that we designed to employ was that used in other investigations of flame (Smithells, ' Phil. Mag.' (V.), 39, 123 (1895)).   This apparatus permits of the wide separation of the two cones that constitute the non-luminous flame of a Bunsen burner, and it was thought that the interconal space which, in the apparatus, is quite shielded from draughts, would afford a particularly favourable means of

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[*] In his paper (*loc. cit.*) on p. 33, Arrhenius, dealing with the relation of conductivity to electromotive force, gives a set of galvanometer readings for an electromotive force of ·2 Daniell.   Later in the paper, on p. 36, when dealing with the relation of electromotive force to concentration, another set of readings,

obtaining constant conditions during the experiments. In other respects it was proposed to use arrangements similar to those of ARRHENIUS.

Preliminary experiments with the apparatus showed at once that numerous precautions were necessary to secure constant results, and it was only after many months of trial and the accumulation and rejection of series of measurements that the apparatus was finally brought into a reliable working condition.

The experiments have been confined to salts of the alkali metals. The relative conductivities of flames into which the salts were projected were determined and the experiments were designed to show :

I. The relation between conductivity and electromotive force.
II. The relation between the conductivity and the amount of salt present.
III. The relation between the conductivities of equivalent quantities of various salts of the same metal.
IV. The comparative conductivity of equivalent quantities of the salts of different metals.
V. The behaviour of the same salts in different flames.

From these results, conclusions are drawn respecting the primary object of the investigation, which was to discover whether the coloration of flames, and their electrical conductivity when containing vaporised salts, are due to a common cause.

Description of Apparatus and Method of Working.

The apparatus employed in this investigation consisted essentially of an arrangement for producing a Bunsen flame with separated cones, into which salt solutions could be introduced as a fine spray along with the mixed coal-gas and air. A pair

also for an electromotive force of ·2 Daniell, is given. The following are extracts from the two sets of readings :—

	Normal NaCl.	$\frac{N}{4}$ RbCl.	$\frac{N}{16}$ CsCl.	Normal LiCl.	Normal NaÃc.
From Table 1	25·8	215	152	5·4	30·0
„ Table 2	41·0	161	121	8·1	30·2
Per cent. difference . .	59	− 26	− 20	50	0·6

The fact that the readings are not identical is not important, as ARRHENIUS expressly states that his electrodes suffered change in course of the investigation; but it will be observed that the differences are quite capricious. Thus the second reading for sodium chloride is 60 per cent. greater than the first, whilst for rubidium chloride the second reading is 25 per cent. less than the first. We are unable to conjecture any satisfactory explanation of these discrepancies.

of electrodes was placed between the cones, and the electric currents between them measured under various E.M.F.s.

It was found that any unsteadiness of the flame produced considerable and irregular deflections of the galvanometer which prevented the current from being measured in a satisfactory manner. The steadiness of the flame could be judged readily by observing the lower cone, which, in consequence of the large amount of air mixed with the gas (about 5 vols. air to 1 of coal-gas) in order to produce separation of the cones, was very sharply defined. This cone in our earlier experiments could be seen to oscillate up and down and from side to side.

With a view to reducing this oscillation to a minimum, so as to obtain a steady galvanometer deflection, care was taken to regulate the quantity and pressure of the gas and air supplies with as much nicety as possible. This greatly diminished the oscillations, and a further great improvement was effected by admitting the gas close to the nozzle of the sprayer, so as to produce a more perfect admixture.

With the arrangements finally adopted, it was found that the values obtained for any particular solution remained approximately constant during the whole period covered by our experiments.

The air was supplied under high pressure by means of a Westinghouse air-pump, the amount of air used being but a small fraction of what the pump could supply. The air was filtered through a long cotton-wool plug, P (fig. 1), and a first adjustment of the supply was afforded by a tap close to a small mercury manometer, M. The excess of air thus diverted blew off through a tube dipping 160 centims. below the surface of water contained in the cylinder, C. The air to be used was next passed into an iron drum, D, of 500 litres capacity, in order to damp down any pulsations of pressure.

The coal-gas was regulated by admission into a large gas holder, G, whence it passed through a micrometer screw tap, S, to the flame tube.

The adjustment of the sprayer is a matter of great importance, as the constancy of its action determines mainly the accuracy of the experiments. To obtain constant action it is necessary to work the sprayer with a much greater air supply than is just sufficient to actuate it, otherwise small variations in the pressure produce considerable changes in the amount of spray produced. Besides this, a strong air supply, producing a large amount of spray, permits the use of more dilute solutions than would otherwise be necessary. The difficulty of obtaining reliable results increases rapidly as the concentration of the solutions is increased.

The arrangement of the sprayer finally adopted is shown in fig. 2. The outer tube, O, was blown like a test-tube, with a hole 2 millims. in diameter. The inner tube, I, which was made narrow, so as to leave as much free space as possible, was joined to a wider tube, and, after exact adjustment, this was cemented to the outer tube. The sprayer was fitted into a large paraffined cork, C, which closed the end of the tubulated

Fig. 1.
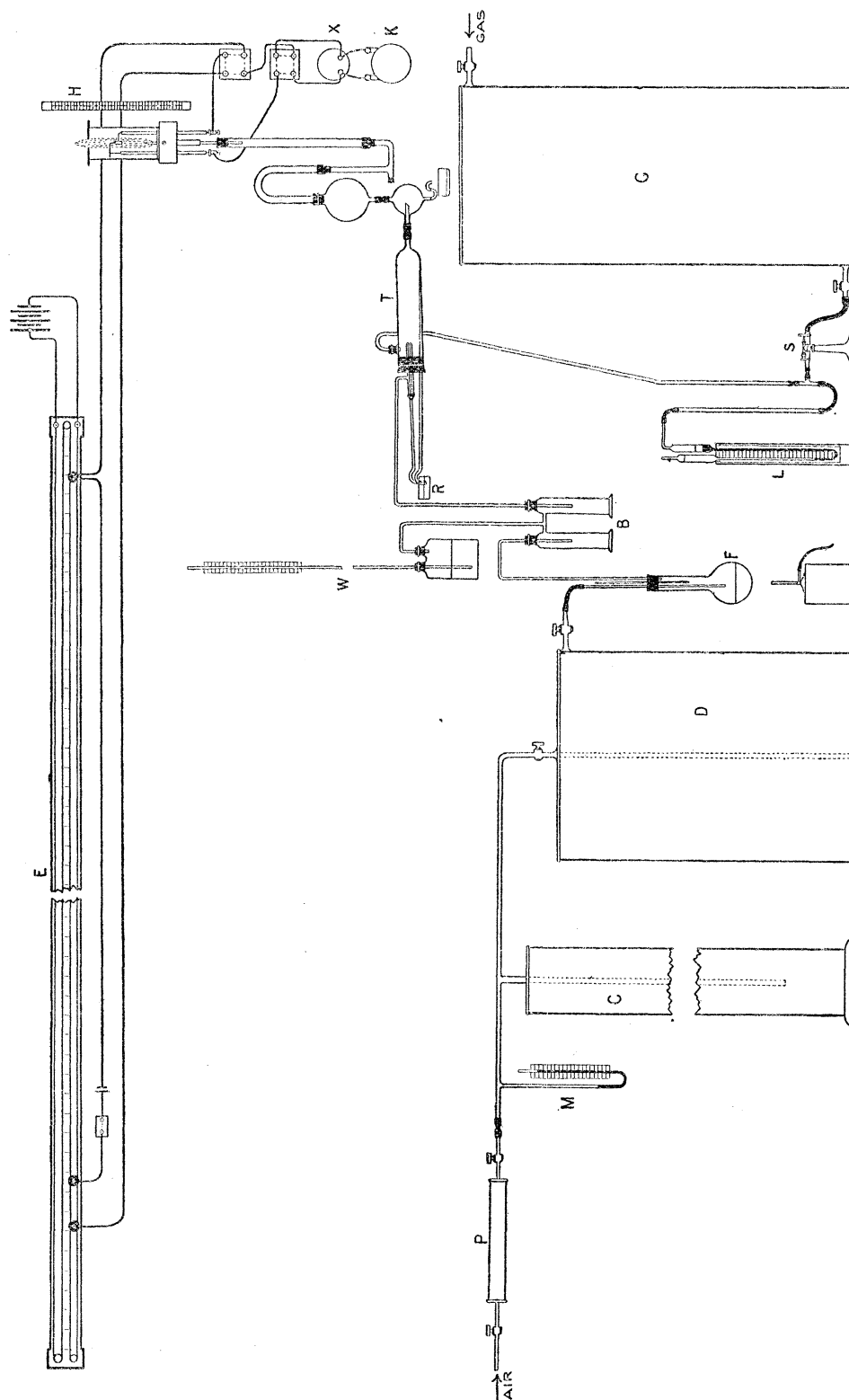
glass cylinder, and in this most of the coarse spray was deposited, running back into the reservoir of solution.

The solution in the reservoir, R, was always adjusted to a constant level, which was about 1 centim. below the nozzle of the sprayer.

The air supply from the iron drum, D (fig. 1), was passed through a flask, F, half
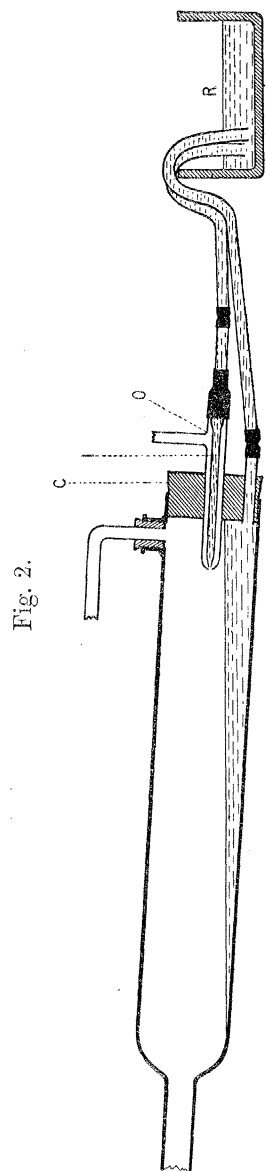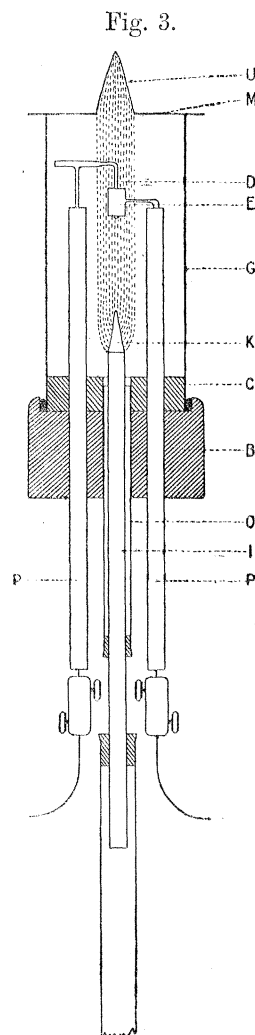

Fig. 2.

Fig. 3.

full of water, which, being gently warmed, served to saturate the air with moisture. Any excess of moisture was condensed in the long tube and in two empty bottles, B. A water manometer, W, was connected to a branch between these bottles, and the air supply regulated so that this indicated 118·5 centims., the variations not exceeding 1 or 2 millims.

The gas pressure was measured by a multiplying differential manometer, L, contain-

ing two immiscible liquids of nearly equal specific gravity. A pressure of 1 centim. of water corresponded to a motion of 10 centims. in the surface of separation. The pressure actually employed produced a motion of the surface of separation of 18·65 centims. A constriction was made in the gas supply tube just before it joined the air, so that the pressure should be great enough to be measured with accuracy. The variation in the gas pressure during the experiments did not exceed ·25 per cent.

It was found advisable to pass the mixture of gas, air, and spray through a considerable length of apparatus, in order to allow only very fine spray to get to the flame, and to allow time for the thorough mixing of gas and air, on which the steadiness of the flame so greatly depends. The arrangement of this part of the apparatus is obvious from fig. 1.

The cone-separating apparatus and electrodes are shown in fig. 3. The gaseous mixture and spray pass up through the central tube, I, made of thin brass. On this tube the upper part of the apparatus could be slid up or down, so as to bring the electrodes to any desired height above the mouth of the tube. The hard wood block, B, was provided with three screws for centring the tube. A wider brass tube, O, was fixed into the block, and was provided at the lower end with a cork, through which the inner tube could slide.

A large cork, C, was cemented on to the wooden block in order to keep the glass cylinder, G, in position. The lower edge of the cylinder fitted into a groove in the block and was trapped with mercury.

A mica plate, M, kept in position by brass clips and pierced in the centre by a hole 2·2 centims. in diameter, was placed on the top of the glass cylinder. The electrodes were supported by two rigid porcelain tubes, P, fixed into the wood block by a packing of fusible metal. The electrodes consisted of two concentric cylinders of platinum iridium alloy. The outside cylinder, E, was supported by a wire of the same material, ·5 millim. in diameter, thickened after a distance of 1·5 centims. to 2 millims., and bent at right angles so that it reached for 3 centims. down the porcelain tube, where it was joined to a platinum wire. By means of a cross-piece fitting into a V-shaped groove at the top of the porcelain tube, this attachment of the electrode was kept in a fixed position. The inner electrode cylinder, D, was supported in a similar way. The lower end of this cylinder was provided with conical cap so as to avoid the formation of eddies in the gas stream.

The dimensions of the electrodes were—

Height of cylinders . . . . 1·575 centims.
Inside diameter of outer cylinder. . . . . ·875 centim.
Outside diameter of inner cylinder . . . . ·450 ,,

The electrodes were set up so as to be concentric and co-axial with the flame, so that a symmetrical region of flame gases was included.

In our preliminary experiments we tried electrodes consisting of platinum foil

suspended by stretched platinum wires, according to the plan of ARRHENIUS. We found them unsatisfactory owing to the slackening of the wires after heating. We also tried thicker platinum plates attached to thin platinum rods and supported by porcelain tubes. We believe, however, that our final arrangement was preferable in point of rigidity and in including a symmetrical zone of gases for measurement.

A vertical millimetre scale, H (fig. 1), fixed behind the glass cylinder, enabled the height of the electrodes and of the inner cone of flame, K, to be read by means of a cathetometer telescope.

The source of electricity used by us consisted usually of three accumulators. A German silver wire, 1·5 millims. in diameter and 20 metres long, carefully calibrated, was stretched four times along a bench over a millimetre scale, E. By making contact with two heavy three-legged contact-pieces at two points, any E.M.F. up to 5·7 volts could be taken off this wire.

The current in the circuit through the flame was measured by a Kelvin astatic reflecting galvanometer, K, of 5600 ohms resistance, provided with a shunt box, X. In every case in taking a reading the current through the galvanometer was reversed and the mean deflection taken. The sensibility of the galvanometer, as we used it, was about $2·85 \times 10^{-9}$ ampere for one scale division. All connecting wires were supported on glass rods fixed in paraffin blocks.

The E.M.F. given by the stretched wire was compared on all occasions with that given by a standard Clark element, and the sensibility of the galvanometer was repeatedly determined.

In some earlier experiments higher E.M.F.s were obtained by means of Leclanché cells up to thirty in number.

In the following pages the measurement of current strength is always given, except where otherwise specified, in terms of 10^{-7} ampere unit.

Method of making an Experiment.

In beginning an experiment the tubulated cylinder, T (fig. 1), was removed, and, together with the sprayer, washed well with distilled water and dried by a current of air.

The cylinder was then replaced and the reservoir, R, filled with the solution to be investigated.

Any salt which in a previous experiment had deposited on the flame tube was removed, and the cylinder, G (fig. 2), and mica plate washed and dried. The gas was then turned on and, after an interval, lighted above the mica plate. Air was next supplied until the sprayer came into action, when the level in the reservoir, R, was adjusted. When the flame had become non-luminous the mica plate was removed, so that the whole flame descended and burnt at the mouth of the flame tube. As soon as the air had reached the right pressure the mica plate was replaced, whereupon the outer cone, U (fig. 3), of the Bunsen flame rose and burned above the mica.

When distilled water is sprayed the two cones of flame are blue in colour; the inner one is extremely thin and bright. The cones are free from the reddish tints (due to dust) seen in an ordinary Bunsen burner. The interconal space (dotted in fig. 3) emits no light.

When a salt solution is sprayed the characteristic radiation appears at the surface of the inner cone and extends over the dotted region shown in fig. 3, forming an approximately cylindrical column 3 centims. in diameter, in which the electrodes are symmetrically immersed. The electrodes become bright red, the inner one being rather brighter than the outer one is on the outside.

After about ten minutes spraying the measurements were commenced. The highest E.M.F. was usually applied first and lower ones substituted successively. At the end of a series the earlier observations were repeated.

The current was measured, and then reversed and measured again, and as the current was also taken in both directions through the galvanometer, four readings were obtained, and of these the average was taken.

During an experiment one observer watched the manometers on the air and gas supply, whilst the other took the galvanometer readings.

In working with strong solutions great care is necessary to keep the air in the right hygrometric state. If it is not moist enough, salt crystals deposit on the nozzle of the sprayer and impede the air supply; whilst if it is too moist, drops of water are deposited, with the same effect.

In our earlier experiments with sprayers, in which the outer tube was conical at the end, much trouble came from these sources; the trouble was much less with the form of sprayer described above.

To gauge the constancy of the apparatus we employed a $\frac{1}{10}$ normal solution of potassium bromide. The following readings for an E.M.F. of 5·6 volts, taken at intervals during three months, will give an idea of degree of constancy attained :—

21·1, 21·3, 20·7, 21·8, 21·6, 22·9, 22·1, 21·7 : Mean 21·4.

Other solutions were used, from time to time, as a control. When abnormal values were obtained, an examination of the apparatus always disclosed some slight remediable defect.

Conductivity of the Free Flame.

To obtain the true conducting power of a vaporised salt it is necessary, in every case, to make a correction in order to eliminate that portion of the observed conductivity which is due to the flame gases. For this purpose we made, in the first instance, a series of observations on the conductivity of the flame, with the addition only of the spray of distilled water.

In making these experiments, it was found necessary to change the distilled water at frequent intervals, otherwise the apparent conductivity steadily increased owing, it

would appear, to solution of the glass. The quantity dissolved is, of course, small, but still quite sufficient to make itself felt. The conductivity of the flame gases alone, is, it must be remembered, extremely small in comparison with that of a flame containing the spray of $\frac{1}{1000}$ normal solution of a potassium salt.*

The following table gives the conductivity of the flame gases with distilled water spray for several electromotive forces :—

E.M.F. in volts . .	5·66	2·52	1·09	·803	·521	·230.
Current	·547	·313	·226	·177	·118	·056.

These results are plotted in Curve V, p. 110, the ordinates being multiplied by 10.

The above values were checked from time to time during our work. The agreement was always well within the limits of accuracy required, and consequently we have used these values in all cases to represent the conductivity of the free flame, subtracting them from the gross readings given by salt solutions to obtain the conductivity of the salt vapour itself.

ARRHENIUS, in his experiments on this subject, noticed an increased conductivity of the free flame immediately after a salt solution had been sprayed. He attributed it to a deposition of salt on the electrodes, the deposit remaining on the electrodes for some time after the spray of salt solution had been stopped. The effect in question was not important in the case of salts of the alkali metals on account of their ready volatility.

In our experiments we noticed this effect, but we believe that in our apparatus with the salts used by us it was fully accounted for by the fact that after the spray of salt had been replaced by one of water, salt spray lingered for some time in the apparatus between the sprayer and the flame tube. We noticed that the flame remained coloured below the electrodes, and that as the colour faded the galvanometer deflection fell steadily to the normal value. We have therefore used the normal value as the true correction. Even if our explanation of the higher value, found immediately after stopping the salt spray, is incomplete, the arbitrariness in our case of taking any other value than the normal one as the correction, would forbid us attempting further refinement, where, as a matter of fact, the difference involved could not seriously affect our final results.

Unipolar Conduction.

It has long been known that unipolar conduction is shown to a marked extent in the case of flame gases, that is to say the current passes from one electrode to the other more easily in one direction than in the reverse direction. The following table

---

* SCHALLER has shown ('Zeit. Phys. Chem.,' 25, 497, 1898) that pure water acts so rapidly on glass vessels as to forbid their use in conductivity experiments, but that with salt solutions, even of very small concentration, the solvent action is not sufficient to introduce sensible error.

gives the results obtained by us in an early series of experiments, where the electrodes consisted of two platinum plates equal in size and placed as symmetrically as possible in the flame. A $\frac{1}{16}$ normal solution of KCl was used in these experiments :—

E.M.F. in volts.	Galvanometer deflection.	Galvanometer deflection (current reversed).
43·5	+ 39·7	− 48·8
29·0	+ 33·2	− 41·0
14·5	+ 24·7	− 29·3
7·3	+ 19·4	− 23·0
2·9	+ 15·1	− 16·9
1·5	+ 12·8	− 14·2

With the cylindrical electrodes used in our later experiments the electrode surfaces are of different size, and with these the unipolar effect is much greater. The following is a table for $\frac{1}{20}$ normal KCl solution :—

E.M.F. in volts.	Galvanometer deflection.	Galvanometer deflection (current reversed).
5·74	+ 81·3	− 22·5
2·56	+ 69·5	− 18·7
·815	+ 52·8	− 14·1
·378	+ 35·2	− 11·1
·116	+ 12·1	− 3·0

These results are plotted in Curve I.

Curve I.
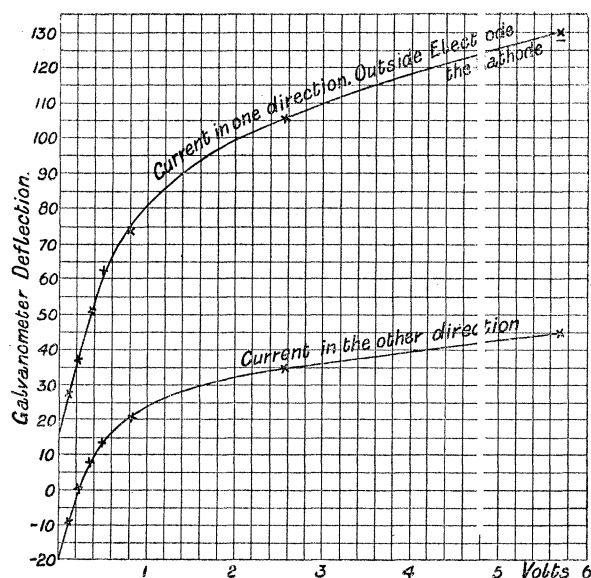
Unipolar conduction $\left(\frac{N}{20} KNO_3 \text{ solution sprayed}\right)$.

We do not propose to enter into a discussion of the cause of this unipolar conduction, which has already been the subject of frequent, but not very fruitful, research. If it be due to the assymmetry of the electrode system, either in regard to their size or position in the flame, and if it be connected with the well-known influence of ultra-violet light or of a high temperature in facilitating the discharge of negative electricity, the circumstances of our experiments offer no obstacle to such an explanation. But they do not throw any fresh light on the phenomenon, and it is outside the scope of our enquiries to discuss it.

Concentration of Salt Vapour in the Flame.

To obtain an estimate of the quantity of salt vapour entering the flame in our experiments, we adopted the method used by ARRHENIUS.

The cone separating apparatus was removed, and the flame obtained at the orifice of the tube I (fig. 3). A bead of sodium sulphate was held in the flame for a measured interval of time, during which the light intensity was compared photo-metrically with that of a standard candle. The loss in weight of the bead was determined. By spraying a sodium sulphate solution of suitable strength in our apparatus, a flame of light intensity equal to that containing the bead was obtained.

The following numbers give the results. They afford, at the same time, a confirmation of the statement of GOUY, that above a certain limit the light intensity of a flame coloured by the vapour of an alkali salt varies approximately as the square root of the amount of salt introduced.

Experiment 1. Loss of weight of bead per minute, ·00161 gram. Intensity of light, 1·56.

Experiment 2. Loss of weight of bead per minute, ·00325 gram. Intensity of light, 2·00.

Experiment 3. Solution sprayed $\frac{1}{2}$ normal sodium sulphate. Intensity of light, 1·53.

Experiment 4. Solution sprayed $\frac{1}{5}$ normal sodium sulphate. Intensity of light, ·95.

From Experiments 1 and 2 we have—

      Ratio of light intensities . . . . 1·3

      Square root of ratio of concentrations . . . . . 1·4

From Experiments 3 and 4—

      Ratio of light intensities . . . . 1·6

      Square root of ratio of concentrations . . . . . 1·6

The amount of salt supplied to the flame per minute by the half normal sodium sulphate solution may therefore be taken as ·0016 gram, and as a rough approxima-

tion we may conclude that the number of gram molecules supplied to the flame per minute is*

$$\frac{\cdot0016}{71} \times 2 = 4\cdot5 \times 10^{-5}.$$

It is important to note that we were able to investigate the conductivity of salt vapours at much greater concentrations in the flame than was done by ARRHENIUS, and, as will appear in what follows, the results at high concentrations are very different from those obtained at the lower ones.

Curve II.
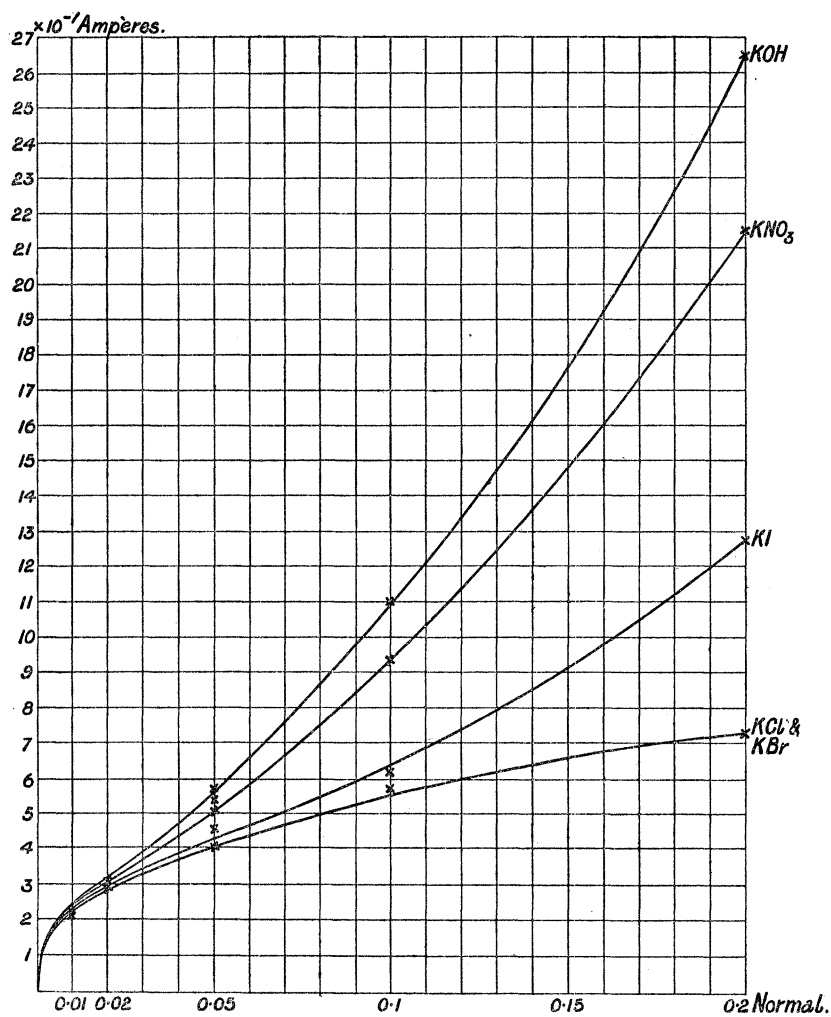
Variation of current with concentration of solution.   E.M.F., ·227 volt.

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* This estimate, which has no pretensions to exactness, was made chiefly in order to inform us how our experiments compared with those of ARRHENIUS in respect to the concentration of salt in the flame.   In his experiments a normal solution sent into the flame ·26 × 10⁻⁵ gram molecule of salt per minute.   In our apparatus an $\frac{1}{18}$ normal solution would yield this amount of salt.   We confirmed this result by comparison of the conductivity numbers for salt solutions.

Relation of Conductivity to Concentration of Solution and to the Nature of the Salt.

Experiments with solutions of the various salts in different concentrations show that the relation between conductivity and concentration of salt vapour in the flame is not of a very simple nature.

Marked differences of conductivity are shown by salts according to their electro-positive constituent, and under certain conditions, also, according to their electro-negative constituent.

Curve III.
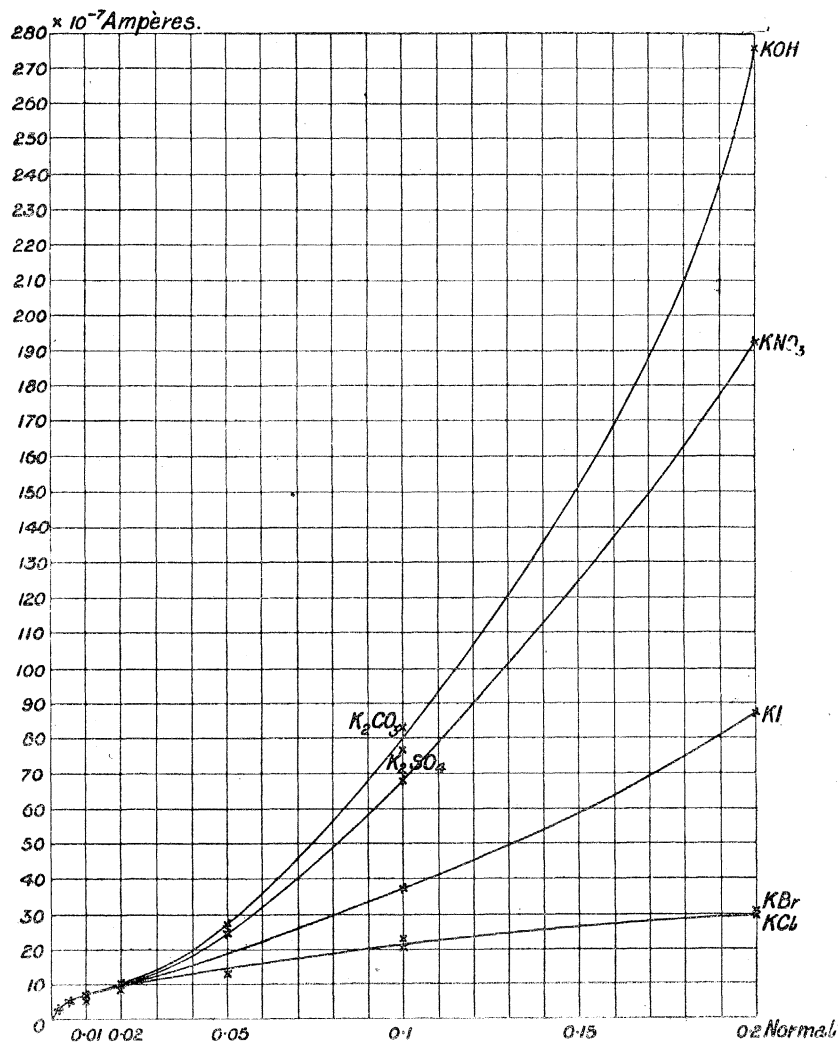
Variation of current with concentration of solution.   E.M.F., 5·60 volts.

Curves II, III, and IV show clearly the variation of conducting power with concentration, the ordinates and abscissæ being respectively current strength and concentration.

Curve IV.
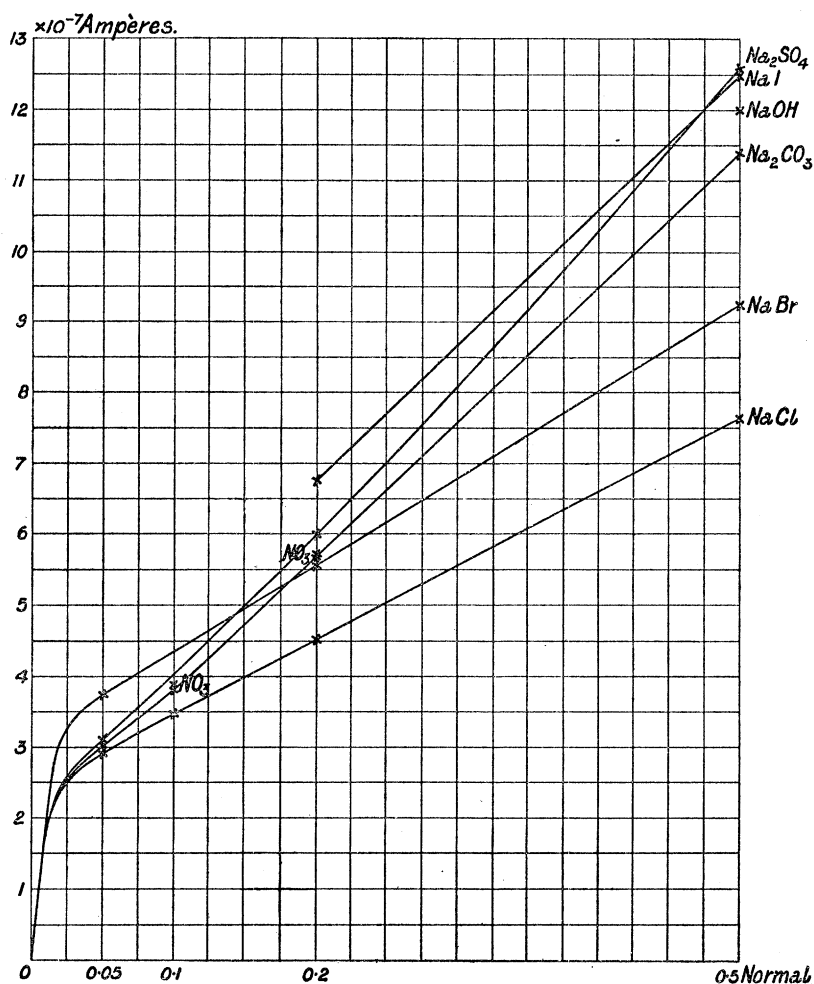
Variation of current with concentration of solution.   E.M.F., 5·60 volts.

In the following table the experimental numbers are given for three different electromotive forces.   In all cases the numbers have been corrected for the conducting power of the free flame.

Concentration of solution.	E.M.F.	KCl.	KBr.	KClO₃.	KI.	KNO₃.	$\frac{N}{2}$ K₂SO₄.	$\frac{N}{2}$ K₂CO₃.	KOH.
·2 normal	5·60	31·9	31·4	30·5	86·5	193	...	...	276
	·795	18·9	20·1	16·8	43·2	70·8	...	...	82·6
	·227	7·34	7·32	6·62	12·8	21·6	...	...	26·6
·1	5·60	21·0	21·4	...	37·8	68·3	83·3	76·4	
	·795	13·4	12·4	...	21·3	29·3	33·4	35·4	
	·227	5·75	5·74	...	6·2	9·35	11·0	11·2	
·05	5·60	14·1	14·7	12·9	22·8	24·5	27·5	27·6	24·1
	·795	9·23	10·3	8·35	12·8	13·2	13·8	14·2	12·8
	·227	4·0	4·13	3·81	4·6	5·1	5·71	5·43	5·4
·02	5·60	8·93	...	...	...	10·2			
	·795	6·09	...	...	...	6·63			
	·227	2·97	...	...	...	3·15			
·01	5·60	6·02	6·97	6·77	6·99	7·06	6·33	6·00	6·1
	·795	4·27	4·90	4·69	4·78	4·84	4·56	4·30	4·05
	·227	2·17	2·23	2·31	1·97	2·47	2·30	2·20	1·86
·005	5·60	5·47	...	...	...	5·27			
·002	...	...	4·03	...	3·89	...	...	3·73	
			2·80	...	2·73	...	...	2·59	
			1·50	...	1·24	...	...	1·45	

Concentration of solution.	E.M.F.	NaF.	NaCl.	NaBr.	NaI.	NaNO₃.	$\frac{N}{2}$ Na₂SO₄.	$\frac{N}{2}$ Na₂CO₃.	NaOH.
·5 normal	5·60	8·98	7·66	9·24	12·5	...	12·6	11·4	12·0
	·795	4·78	5·37	5·38	5·83	...	6·64	6·60	6·20
	·227	2·00	2·07	2·11	2·21	...	2·49	2·45	2·61
·2	5·60	4·03	4·54	5·56	6·72	5·73	5·99	5·67	
	·795	2·65	3·14	3·32	3·36	3·77	3·75	3·64	
	·227	1·39	1·42	1·41	1·39	1·85	1·61	1·71	
·1	5·60	...	3·49	...	...	3·88	...	3·78	
	·795	...	2·45	...	...	2·67	...	2·65	
	·227	...	1·15	...	...	1·30	...	1·30	
·05	5·60	2·91	2·95	3·76	...	...	3·09	3·02	3·00
	·795	2·08	2·21	2·50	...	...	2·16	2·12	2·07
	·227	·98	1·05	·97	...	....	·96	·97	·98

Concentration of solution.	E.M.F.	LiCl.	LiNO₃.	RbCl.	RbNO₃.	CsCl.	CsNO₃.	HCl.
·5 normal	5·60	1·88	2·28	...	...	...	...	1·08
	·795	1·09	1·59					
	·227	·56	·89	...	...	...	...	·35
·1	5·60	1·29	1·47	41·4	213·0	123	303	
	·795	·87	·99	26·4	82·4	60·5	115	
	·227	·41	·53	11·3	25·9	22·2	36·6	
·02	5·60	...	...	14·8	19·4	17·6	20·1	
	·795	...	...	9·65	11·6	11·7	13·1	
	·227	...	...	4·71	5·14	5·9	6·2	
·004	5·60	...	...	6·46	5·44	7·98	7·86	
	·795	...	...	4·51	4·18	5·70	5·51	
	·227	...	...	2·41	2·26	3·02	2·97	

The foregoing tables show—

I. That at small concentrations equivalent solutions of all salts of the same metal impart the same conducting power to the flame.

II. That at higher concentrations the equality mentioned in I no longer holds good, the oxysalts showing a greater conducting power than the haloid salts. This difference increases with increasing concentration, and with increasing electromotive force.

A clearer conception of the relations which hold is obtained by expressing the conducting power in terms of molecular conductivities. It is impossible to give absolute molecular conductivities, as this would require an exact knowledge of the concentration of salt vapour between the electrodes and of the capacity of the electrode system. In the following table the numbers, which are proportional to the molecular conductivities, have been obtained by dividing the numbers of the preceding table by the concentration of the solution, taking $\frac{1}{10}$ normal solutions as of unit concentration.

The values all refer to an E.M.F. of ·227 volt. At this E.M.F. Ohm's law is obeyed with close approximation in our experiments, so that the conditions correspond in this respect with those of conduction in aqueous solution, from which the idea of molecular conductivity is drawn.

Concentration of solution.	KCl.	KBr.	KClO₃.	KI.	KNO₃.	$\frac{N}{2}$ K₂SO₄.	$\frac{N}{2}$ K₂CO₃.	KOH.
·2	3·67	3·66	3·31	6·4	10·8	...	...	13·3
·1	5·75	5·74	...	6·2	9·35	11·0	11·2	
·05	8·0	8·26	7·62	9·2	10·2	11·42	10·86	10·8
·02	14·8	...	...	...	15·7			
·01	21·7	22·3	23·1	19·7	24·7	23·0	22·0	18·6
·002	...	75·0	...	67·0	...	...	72·5	

Concentration of solution.	NaF.	NaCl.	NaBr.	NaI.	NaNO₃.	$\frac{N}{2}$ Na₂SO₄.	$\frac{N}{2}$ Na₂CO₃.	NaOH.
·5	·40	·41	·42	·44	...	·50	·49	·52
·2	·69	·71	·72	·70	·92	·80	·85	
·1	...	1·15	...	...	1·30	...	1·30	
·05	1·96	2·10	...	...	...	1·92	1·94	1·96

Concentration of solution.	LiCl.	LiNO₃.	RbCl.	RbNO₃.	CsCl.	CsNO₃.	HCl.
·5	·11	·18	...	...	...	...	·07
·1	·41	·53	11·3	25·9	22·2	36·6	
·02	...	...	23·5	25·7	29·5	31·0	
·004	...	...	60·2	56·3	75·5	74·2	

The following conclusions may be drawn from the above tables :—

I. In general, the molecular conductivity of a salt increases with increasing dilution.

II. The oxysalts of all alkali metals behave differently to the haloid salts.*

III. At all concentrations investigated, the conducting power of the oxysalts of any one metal is approximately the same.

With regard to the halogen salts, it appears that potassium iodide occupies an intermediate position, forming a transition member from the haloids to the oxysalts. Sodium bromide and iodide would appear to occupy a similar position among the sodium salts.

It appears also that with increasing concentration the molecular conductivity of the oxysalts attains a minimum value. This is very evident with the oxysalts of potassium, and recognisable in those of rubidium and cæsium, the minimum values being 11, 26, and 34 in the respective cases.

* Potassium chlorate, being converted by the flame into the chloride, is an exception to this statement.

No minimum is observable in the case of the sodium or lithium salts, nor in the case of the chlorides of cæsium, rubidium, and potassium, and the bromide of potassium. It is probable, however, that in the case of these salts a minimum value of the molecular conductivity would be found, if higher concentrations could be investigated, for this is distinctly observable in the case of potassium iodide. It will also be seen that with the oxysalts of potassium the minimum is only attained at higher concentrations than in the case of the oxysalts of rubidium and cæsium.

The intermediate character of iodide of potassium is once more evident, for the minimum value of the molecular conductivity is about 6, whilst that for the bromide and chloride must be considerably less, and that for the oxysalts is 11.

In the case of the haloid salts the variation of conducting power with concentration may be approximately expressed by the equation

$$c = k \sqrt{q},$$

when c is conductivity, q the concentration, and k a constant.

This is shown for NaCl and KCl in the following tables:—

	KCl.					NaCl.			
	E.M.F. 5·6 volts.		E.M.F. ·227 volt.			E.M.F. 5·6 volts.		E.M.F. ·227 volt.	
Concentration of solution.	Found.	Calculated.	Found.	Calculated.	Concentration of solution.	Found.	Calculated.	Found.	Calculated.
·2	31·9	(31·9)	7·34	(7·34)	·5	7·66	(7·66)	2·07	(2·07)
·1	21·0	22·6	5·75	5·20	·2	4·54	4·84	1·42	1·31
·05	14·1	15·9	4·00	3·67	·1	3·49	3·42	1·15	·93
·02	8·93	10·1	2·97	2·32	·05	2·95	2·42	1·05	
·01	6·02	7·1	2·17	1·65					
·005	5·47	5·0							
·002	4·03	3·2							

The agreement which here is by no means complete cannot be recognised at all in the oxysalts except at low concentrations. In this respect our results differ from those of ARRHENIUS, who gives the relation $c = k \sqrt{q}$ as one of general applicability. The chief cause of the difference in our results lies doubtless in the fact already mentioned, that, with a solution of given concentration, much more salt was carried into the flame in our experiments than in those of ARRHENIUS.

It is of interest to determine the variation of conducting power from metal to metal of the series of salts investigated. This is most satisfactorily done by making use of concentrations at which the individualities of the several salts of one metal have disappeared. On account of the relatively bad conducting power of the lithium and

sodium salts, experiments at great dilutions were not attempted with them. The greatest dilution at which all salts were examined was $\frac{1}{10}$ normal, and, although at this concentration the various salts of each metal do not conduct equally well, we may take the chloride as representing the haloid salts and the nitrate as representing the oxysalts. The following table gives the comparison :—

	Chlorides.			Nitrates.		
E.M.F.	5·60	·795	·227	5·60	·795	·227
Cæsium	123	60·5	22·2	303	115	36·6
Rubidium . . .	41·4	26·4	11·3	213	82·4	25·9
Potassium . . .	21·0	13·4	5·75	68·4	29·3	9·35
Sodium	3·49	2·45	1·15	3·88	2·67	1·32
Lithium	1·29	·87	·41	1·47	·99	·53
Hydrogen . . .	·75	...	·27			

It is evident that the conductivity increases with increasing atomic weight of the metal, and that the increase is more rapid in the case of the oxysalts than in that of the haloids.

Influence of Temperature on Conductivity.

In the form of apparatus used by us a column of hot gases ascends from the lower cone of combustion to the upper one, the temperature rapidly decreasing. By altering the relative position of the electrodes and the mouth of the flame tube the electrodes could be brought into regions of different temperature. We do not attempt in the present enquiry to deal fully with the relation between the temperature of salt vapours and their conductivity, but have contented ourselves with making a few experiments, so as to gain an idea of the general order of the relationship.

By means of two millimetre scales etched on opposite sides of the glass cylinder, G (fig. 3), the distance between the tip of the inner cone and the lower edge of the electrodes (which in these experiments were square plates of platinum) was adjusted to 5, 15, and 25 millims. in the respective cases.

To measure the temperature, a platinum platinum-rhodium thermo-couple was placed first 2 millims. above, then 2 millims. below the electrodes in the axis of the flame, and the mean of the galvanometer readings taken to represent the temperature of the vapour between the electrodes. The solution sprayed in all cases was $\frac{1}{4}$ normal sodium carbonate.

The following table contains the results; the observations were repeated in the order given, so as to control their accuracy :—

	Height of lower edge of electrodes above tip of inner cone.	Position of thermo-couple.	Temperature deflection.	Conductivity.
(1)	·5 millims.	2 millims. above	256	235
	·5 ,,	2 ,, below	375	215
(2)	25 ,,	2 ,, above	237	85
	25 ,,	2 ,, below	311·5	80
(3)	15 ,,	2 ,, above	250	135
	15 ,,	2 ,, below	334	125
(4)	25 ,,	2 ,, above	240	86
	25 ,,	2 ,, below	314	80
(5)	5 ,,	2 ,, above	259	235
	5 ,,	2 ,, below	376	215

It will be seen from the above table that the temperature registered by the thermo-couple, when below the electrodes, is much higher than when above. The numbers representing the conducting power are otherwise, a slightly lower reading being obtained when the thermo-couple was below the electrodes. This is, of course, due to the cooling effect of the thermo-couple, which in the lower position was immersed in the gases before they reached the electrodes.

It should be stated that the cylindrical column of interconal gases and salt vapour was not appreciably altered by changes in position of the flame tube, so that the quantity of salt vapour between the electrodes was sensibly the same in all cases.

The end result of the above experiments may be expressed as follows :—

Temperature of vapour.	Conducting power.
316·5	225
292	130
275·6	82·7

These readings are on an arbitrary scale, but they show very clearly that the conducting power increases rapidly with increasing temperature, and that at temperatures not greatly below those which the vapour attains in flames the conductivity would become inappreciable. It may be stated that the temperature intervals in the above table correspond approximately to 140 and 95 Centigrade degrees.
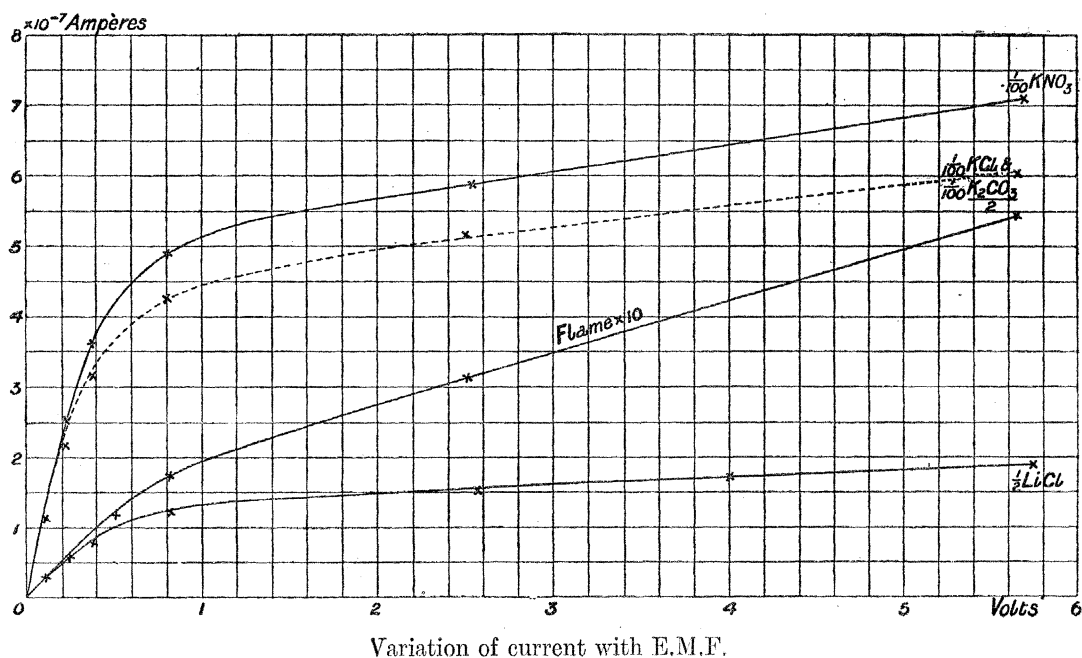
Relation between Current Strength and Electromotive Force.

Experiments on the relation between current strength and electromotive force were carried out with a large number of salts, and with a difference of potential between
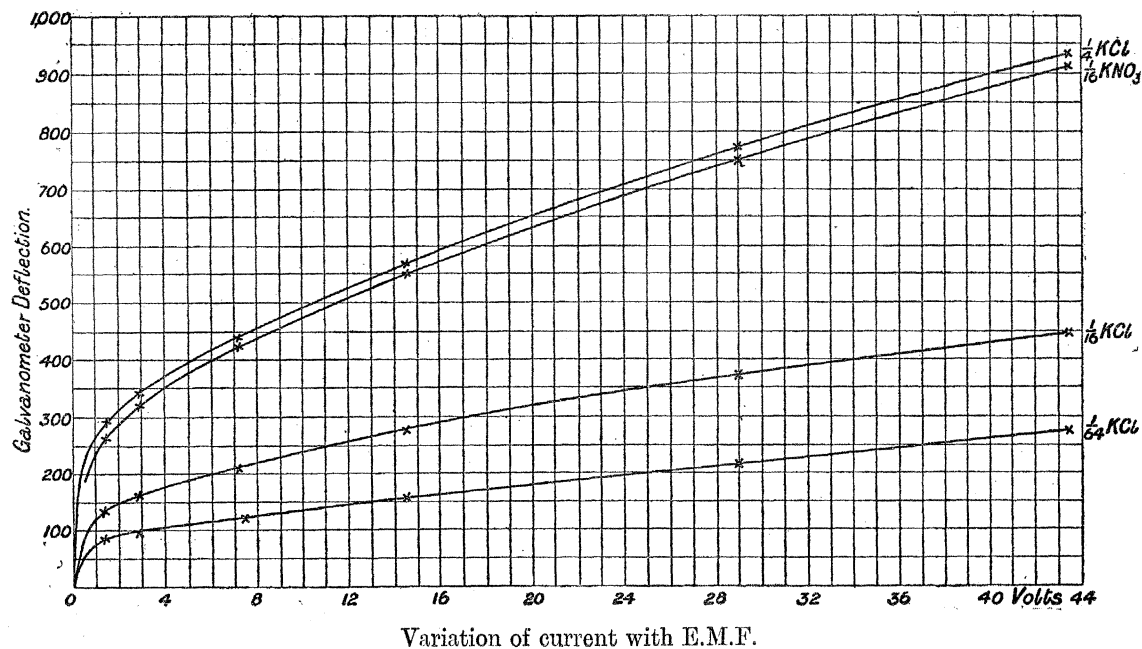
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the electrodes, which varied from ·01 volt to 45 volts.   The results show that with small electromotive forces up to ·2 volt, Ohm's law is accurately obeyed.   With greater electromotive forces the law is not obeyed, and the deviations increase with increasing electromotive force.   The results are plotted on the Curves V to IX.
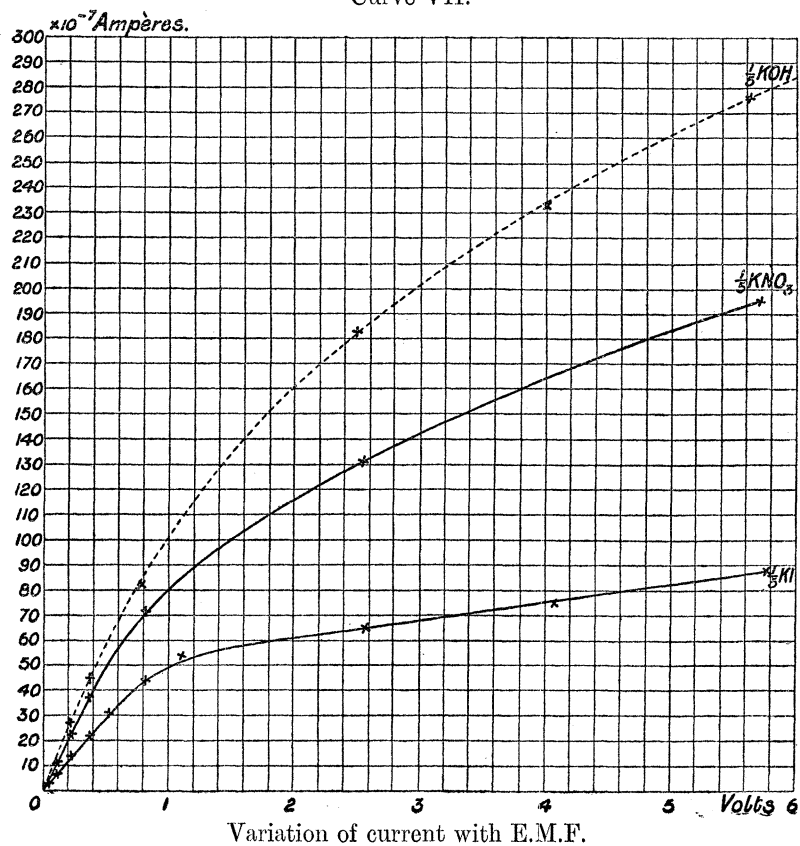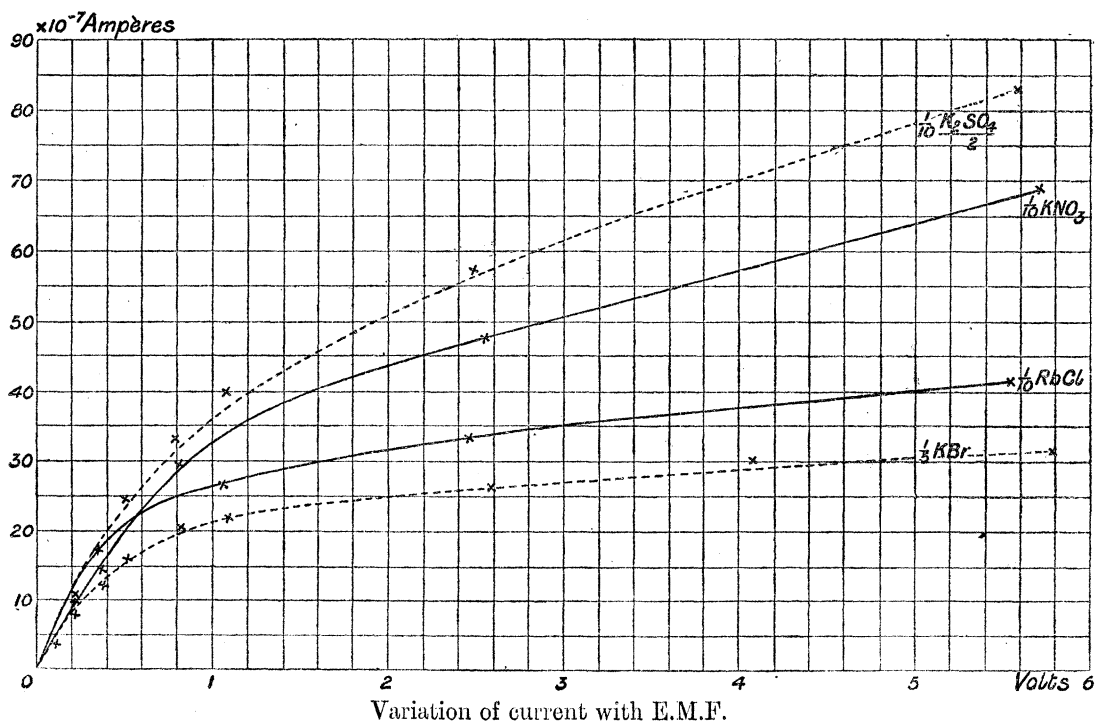
Curve V.

Variation of current with E.M.F.

Curve VI.

Variation of current with E.M.F.

Curve VII.

Variation of current with E.M.F.

Curve VIII.

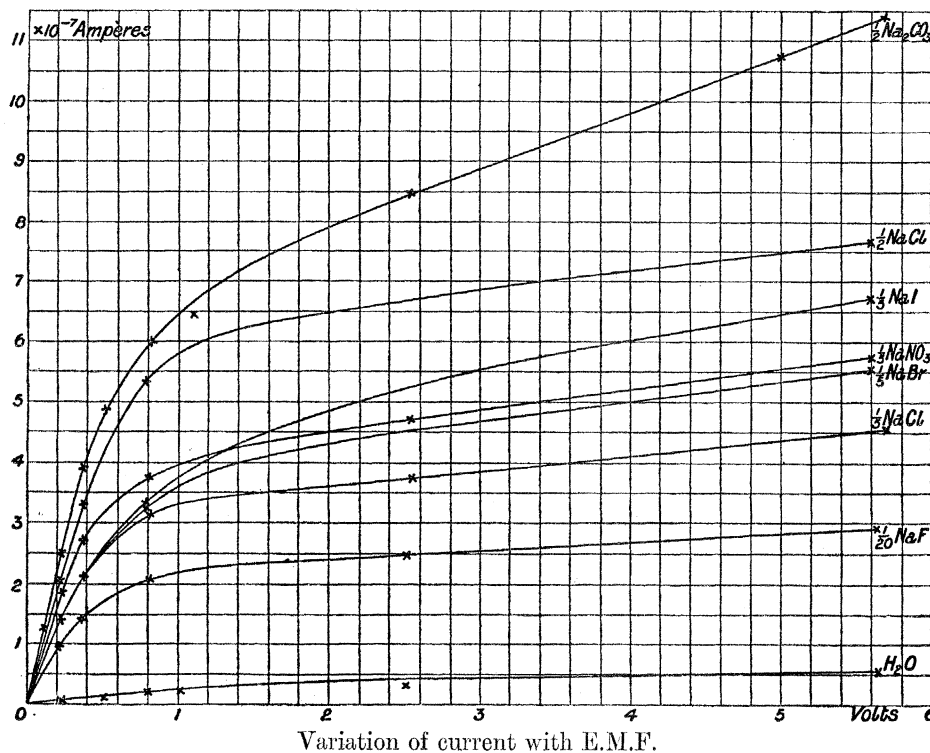Variation of current with E.M.F.

Curve IX.

Variation of current with E.M.F.

The following two tables sufficiently indicate the degree to which Ohm's law is obeyed by vaporised salts :—

E.M.F.	Ratio.	$\frac{N}{64}$ KBr.		$\frac{N}{64}$ K$_2$SO$_4$.		$\frac{N}{16}$ KCl.		$\frac{N}{16}$ KBr.	
		Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.
volt.									
·1	10	30·2	9·90	27·3	9·92	53·1	10·03	50·7	10·15
·08	8	23·9	7·84	21·0	8·00	42·1	7·94	40·6	8·12
·06	6	18·2	5·97	16·65	6·06	32·0	6·04	30·6	6·10
·04	4	12·0	3·93	10·95	3·98	21·05	3·96	20·25	4·05
·02	2	6·1	2·00	5·45	1·98	10·65	2·01	10·15	2·03
·01	1	3·05	1·00	2·75	1·00	5·3	1·00	5·0	1·00

E.M.F.	Ratio.	$\frac{N}{64}$ KI.		$\frac{N}{4}$ KCl.		$\frac{N}{16}$ KNO$_3$.	
		Deflection.	Ratio.	Deflection.	Ratio.	Deflection.	Ratio.
volts.							
44·5	3708	305	85·9	935	118	611	129
1·5	126	87·2	24·5	290	36·7	188	39·6
·12	10	24·7	9·77	78·5	9·94	47·5	10
·012	1	3·55	1	7·9	1	4·75	1

Our results are in harmony with those of ARRHENIUS in so far as they show that Ohm's law is only valid at low electromotive forces in the case of vaporised salts.

To express the general relationship between current strength and electromotive force, ARRHENIUS gives the equation $C = Af(E)$, where C = current strength, E = electromotive force, and A = a constant dependent on the solution sprayed. He found that for any electromotive force (E), $f(E)$ was the same for solutions of different salts and of different concentrations.

The validity of this equation is also confirmed by our observations up to a certain point, but with more concentrated solutions marked divergence is apparent. This will be evident from the following table.

The $\frac{1}{100}$ normal solutions of potassium salts which we investigated all gave approximately the same current for any one electromotive force. We have, therefore, used these to calculate some values of $f(E)$. Taking $f(E) = 1$ when $E = 5$ volts, we get from the numbers for $\frac{1}{100}$ normal KCl and $\frac{1}{100}$ normal K_2CO_3 solutions the following values :—

E.	$f(E).$
volts.	
2	·850
1	·760
·7	·709
·5	·638
·2	·332

From these values of $f(E)$ we calculate the current which should be found in the case of a series of salts, and the numbers so obtained are inserted in a table side by side with those indicating the currents actually measured :—

E.M.F.	$\frac{N}{100}$ KNO$_3$.		$\frac{N}{5}$ KOH.		$\frac{N}{5}$ KBr.		$\frac{N}{2}$ Na$_2$CO$_3$.		$\frac{N}{5}$ NaCl.	
	Ob-served.	Calcu-lated.	Ob-served.	Calcu-lated.	Ob-served.	Calcu-lated.	Ob-served.	Calcu-lated.	Ob-served.	Calcu-lated.
2	5·64	5·80	15·8	22·2	2·47	2·62	7·86	9·12	3·62	3·73
1	5·07	5·18	9·85	19·8	2·16	2·34	6·38	8·16	3·28	3·33
·7	4·70	4·84	7·60	18·5	1·90	2·18	5·65	7·61	3·00	3·11
·5	4·22	4·35	3·60	16·6	1·53	1·96	4·73	6·84	2·63	2·80
·2	2·25	2·26	2·31	8·65	·64	1·02	2·30	3·56	1·30	1·46

It is evident from the foregoing table that the formula $C = Af(E)$ does not express the relation existing between current strength and electromotive force over the series of observations made by us.

We are indebted to Professor J. J. THOMSON for a suggestion which has led us to

an equation capable of expressing the relationship in question in a remarkably complete way.   In a paper published by Professor THOMSON and Mr. RUTHERFORD in the 'Phil. Mag.' ((V.) vol. 42, p. 392 (1896)), an account is given of the passage of electricity through gases exposed to Röntgen rays.   According to the authors, the current through a gas exposed to Röntgen radiation between two parallel plates increases more and more slowly as the potential difference between the plates is increased, until finally a maximum current is obtained which remains constant under all further increase of potential difference.   The electromotive force corresponding to the attainment of this state is called a saturating E.M.F.   Assuming that the conductivity of Röntgenised gas is due to the presence of free ions, and that the rate of disappearance of these ions by recombination to form neutral molecules is proportional to the square of the concentration of the ions, THOMSON and RUTHERFORD give the following formula, $I - i = A \frac{i^2}{E^2}$, where I is the maximum current for a saturating E.M.F., i is the current strength for any electromotive force E, and A a constant.

Röntgenised gases and the gases of a flame exhibit a noteworthy similarity in their behaviour.   Thus both rapidly lose their power of conducting electricity when they pass from the source where they have acquired this power.   Both also lose their conductivity when passed between a pair of electrodes maintained at different potentials. (GIESE, 'Wied. Ann.,' vol. 17, p. 517, 1882.)   That the conductivity in both cases may be due to ions has been suggested by previous investigators.

A glance at the curves in which THOMSON and RUTHERFORD plot the relation between current strength and electromotive force, will show that there is a general resemblance to the Curves I to V, by which our own results are plotted.   The current through the flame, however, continues to increase even when a large E.M.F. is applied, whilst that through a Röntgenised gas reaches an almost constant value.

For potentials above one volt our curves are almost rectilinear, so that the relationship between current and E.M.F. may, for E.M.F.s above 1 volt, be expressed by the equation

$$c = I + k_1 E \qquad \qquad (1)$$

that is to say, the current strength may be represented as composed of two parts, one being a constant quantity and the other a quantity proportional to the E.M.F.   This equation, however, does not give us the value of the current for small E.M.F.s.

If we represent the relation between the current and E.M.F. at all E.M.F.s by the equation

$$c = i + k_1 E,$$

then i is a variable which at high E.M.F. attains a constant value I exactly as the current through a Röntgenised gas attains a constant value.

From the analogy of the flame conductivity to that of Röntgenised gases, we

assume that the equation used by THOMSON and RUTHERFORD to represent the relation between the current and the E.M.F. in their experiments should also represent the relation between i and the E.M.F. in our experiments.

Accordingly, then, the equations

$$c = i + k_1 E \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$I - i = k_2 \frac{i^2}{E^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

should represent the value of the current strength at all E.M.F.s in our experiments. In the case of Röntgenised gases $k_1 = 0$, or is very small, so that $c = i$.

In the following tables the observed currents for various salts are compared with those calculated by means of equations (2) and (3), and curves calculated by means of these equations, using in each case the values given below for k_1, k_2 and I, are dotted in the curve diagrams V, VII, and VIII. The points marked near them show the experimentally determined currents.

$\dfrac{N}{100}$ KCl and $\dfrac{N}{2}$ K$_2$CO$_3$.

$I = 4\cdot50 \times 10^{-7}$.
$k_1 = \cdot278 \times 10^{-7}$.
$k_2 = \cdot020 \times 10^{+7}$.

E.M.F.	Current (calculated).	Current (from curve in Diagram IV).
volts.	amperes.	amperes.
·076	$1\cdot02 \times 10^{-7}$	$\cdot80 \times 10^{-7}$
·179	2·05 ,,	1·83 ,,
·346	3·10 ,,	3·10 ,,
·80	4·22 ,,	4·30 ,,
1·09	4·50 ,,	4·53 ,,
2·00	4·96 ,,	5·00 ,,
5·00	5·87 ,,	5·90 ,,

$\dfrac{N}{10}\dfrac{K_2SO_4}{2}$.

$I = 4\cdot23 \times 10^{-6}$.
$k_1 = \cdot74 \times 10^{-6}$.
$k_2 = \cdot148 \times 10^{+6}$.

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
·10	$\cdot574 \times 10^{-6}$	$\cdot55 \times 10^{-6}$
·214	1·16 ,,	1·12 ,,
·516	2·38 ,,	2·50 ,,
1·04	3·77 ,,	3·90 ,,
3·20	6·36 ,,	6·40 ,,
5·00	7·83 ,,	7·87 ,,

$\dfrac{N}{5}$ KOH.
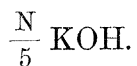
$$I = 16.9 \times 10^{-3}.$$
$$k_1 = 2.10 \times 10^{-6}.$$
$$k_2 = .141 \times 10^{+6}.$$

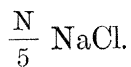| E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.085	1.07×10^{-6}	$.96 \times 10^{-6}$
.184	2.28 ,,	2.13 ,,
.407	4.75 ,,	4.80 ,,
.666	7.30 ,,	7.30 ,,
1.18	11.3 ,,	11.1 ,,
2.00	16.1 ,,	15.8 ,,
4.08	23.6 ,,	23.6 ,,
5.97	28.4 ,,	28.2 ,,

$\dfrac{N}{5}$ KBr.

$$I = 2.41 \times 10^{-6}.$$
$$k_1 = .135 \times 10^{-6}.$$
$$k_2 = .158 \times 10^{+6}.$$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.213	$.73 \times 10^{-6}$	$.70 \times 10^{-6}$
.335	1.05 ,,	1.07 ,,
.625	1.59 ,,	1.73 ,,
.802	1.81 ,,	2.00 ,,
1.25	2.17 ,,	2.23 ,,
1.91	2.46 ,,	2.45 ,,
2.76	2.67 ,,	2.69 ,,
3.50	2.81 ,,	2.85 ,,
4.50	3.00 ,,	3.02 ,,
6.00	3.21 ,,	3.20 ,,

$\dfrac{N}{5}$ NaCl.

$$I = 3.10 \times 10^{-7}.$$
$$k_1 = .258 \times 10^{-7}.$$
$$k_2 = .030 \times 10^{+7}.$$

E.M.F.	Current (calculated).	Current (from experimental curve).
volts.	amperes.	amperes.
.12	1.03×10^{-7}	$.80 \times 10^{-7}$
.33	2.08 ,,	2.00 ,,
.40	2.30 ,,	2.30 ,,
.74	2.89 ,,	3.05 ,,
1.12	3.19 ,,	3.30 ,,
2.00	3.55 ,,	3.60 ,,
3.00	3.85 ,,	3.88 ,,
5.00	4.39 ,,	4.40 ,,

The agreement of the calculated and observed values in the above tables shows that the relation between the current and E.M.F. in our experiments can be represented with considerable accuracy by the formula in question.

In order to show that i gradually attains a maximum value in our experiments as the E.M.F. is increased, the calculated values of i are inserted in a separate column of the foregoing tables.

In the case of $\frac{1}{100}$ normal KCl, $\frac{1}{100}$ normal K_2CO_3, $\frac{1}{10}$ normal K_2SO_4, and $\frac{1}{5}$ NaCl, it will be seen that i has almost reached its maximum value, that is, it has become nearly equal to I at an E.M.F. of 5 volts.
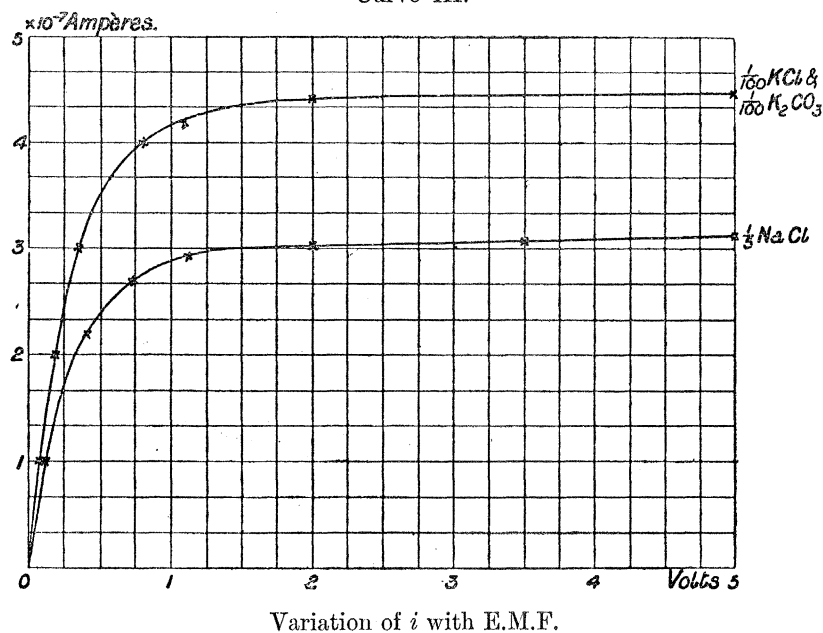
In the case of $\frac{1}{5}$ KBr, this is the case at 6 volts, whilst in the case of $\frac{1}{5}$ KOH the maximum value is not quite reached at 6 volts.

The values of i are plotted in Curves X and XI. As was to be expected, the form of these curves is perfectly similar to those given by THOMSON and RUTHERFORD.

Curve X.
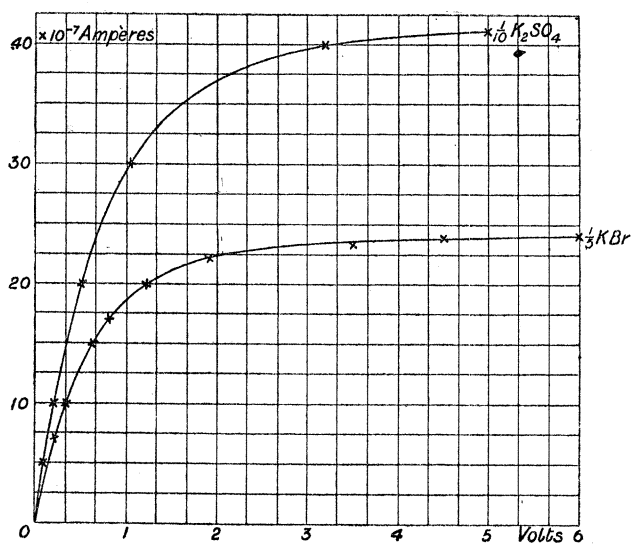
Variation of i with E.M.F.

Curve XI.

Variation of i with E.M.F.

We will conclude this section by showing what relation must hold between the constants I, k_1, and k_2, in order that the equation used by ARRHENIUS (see *ante*, p. 113), $C = Af(E)$, where $f(E)$ has the same value for all solutions, may hold good.

Solving $I - i = k_2 \dfrac{i^2}{E^2}$ for i, we get

$$i = - \frac{E^2}{2k_2} \pm \frac{E}{2} \sqrt{\frac{E^2}{2k_2^2} + \frac{4I}{k_2}}.$$

Now $C = i + k_1E$.

Substituting the above value for i, we have

$$C = E \left\{ k_1 - \frac{(E - \sqrt{4Ik_2 + E^2})}{2k_2} \right\}$$

$$= IE \left\{ \frac{k_1}{I} - \frac{(E - \sqrt{4Ik_2 + E^2})}{2Ik_2} \right\}.$$

From this it follows that if Ik_2 and $\dfrac{k_1}{I}$ have the same values for all solutions, then $f(E)$ in the equation of ARRHENIUS, $C = Af(E)$, will be of the same form for all solutions.

According to THOMSON and RUTHERFORD (*loc. cit.*), k_2 should be a constant for any one substance, whatever the concentration.

The following table contains some values of the quantities I, k_1, k_2, $\dfrac{k_1}{I}$, and Ik_2 for various solutions :—

Solution.*	$I \times 10^{+7}$.	$k_1 \times 10^{+7}$.	$k_2 \times 10^{-7}$.	$\dfrac{k_1}{I}$.	Ik_2.
$\frac{1}{5}$ KOH	169	21	·0141	·124	2·38
$\frac{1}{5}$ KI	46·0	7·1	·0140	·154	·645
$\frac{1}{10}$ K$_2$SO$_4$	42·3	7·4	·0148	·175	·626
$\frac{1}{5}$ KBr	24·1	1·35	·0158	·056	·381
$\frac{1}{20}$ K$_2$CO$_3$	14·5	2·4	·0143	·166	·207
$\frac{1}{50}$ KNO$_3$	6·66	·713	·0144	·107	·096
$\frac{1}{50}$ KCl	6·38	·55	·0144	·086	·092
$\frac{1}{100}$ KNO$_3$	4·83	·395	·0154	·082	·075
$\frac{1}{100}$ KCl	4·50	·278	·0200	·062	·090
$\frac{1}{2}$ Na$_2$CO$_3$	6·11	·927	·0301	·152	·184
$\frac{1}{2}$ NaCl	5·5	·383	·0296	·0696	·163
$\frac{1}{5}$ NaCl	3·1	·258	·0300	·083	·093
$\frac{1}{20}$ NaF	2·12	·147	·044	·0694	·093
$\frac{1}{10}$ RbNO$_3$	120	18·6	·00910	·155	1·09
$\frac{1}{10}$ RbCl	25·2	2·56	·00915	·102	·23
$\frac{1}{50}$ RbCl	10·8	1·04	·0124	·104	·134
$\frac{1}{250}$ RbCl	4·70	·412	·0228	·088	·107
$\frac{1}{10}$ CsNO$_3$	148	27·8	·0066	·188	·976
$\frac{1}{10}$ CsCl	53·5	6·43	·00682	·120	·365
$\frac{1}{50}$ CsCl	12·0	1·09	·0072	·091	·087
$\frac{1}{250}$ CsCl	5·91	·465	·0122	·0786	·072
$\frac{1}{2}$ LiCl	1·24	·114	·083	·092	·102
$\frac{1}{10}$ LiCl	·83	·0825	·128	·099	·106

It is clear from the above numbers that $\dfrac{k_1}{I}$ varies considerably, according to the solution sprayed. Nevertheless, the values for the more dilute solutions do not differ much from ·08.

k_2 has nearly equal values for the salts of each metal, except for values of I less than about 5×10^{-7} ampere. Below this, k_2 increases as I diminishes, so that Ik_2 is nearly constant.

We have thus the following values of $k_2 \times 10^{-7}$ when I is greater than 5×10^{-7}.

* The concentration is given in terms of a normal solution.

Cæsium	Salts	.	.	.	·0066
Rubidium	,,		.	.	·0091
Potassium	,,		.	.	·0144
Sodium	,,		.	.	·0300
Lithium	,,		.	.	·08

When I is below 5×10^{-7}, then Ik_2 has nearly the same value for all solutions, viz., $Ik_2 = \cdot09$.

It thus appears that both $\dfrac{k_1}{I}$ and Ik_2 are nearly of the same value for all solutions, provided I is less than 5×10^{-7}, so that for dilute solutions ARRHENIUS's equation $C = Af(E)$ holds good. When, however, I is greater than this, k_2 becomes constant, so that Ik_2 increases proportionally to I, and $f(E)$ changes in form.

This increase in Ik_2 corresponds to a decrease in the slope of the beginning of the curves, so that as the concentration of the solution is increased, the curves bend over more and more gradually towards the axis of E.M.F.

In Curve XII the variation of k_2 with the atomic weight of the metal is shown.

The points fall nearly on the curve, $Mk_2 = \cdot7$ (M = Atomic Weight) which is drawn.

Curve XII.

Variation of k_2 with Atomic Weight.
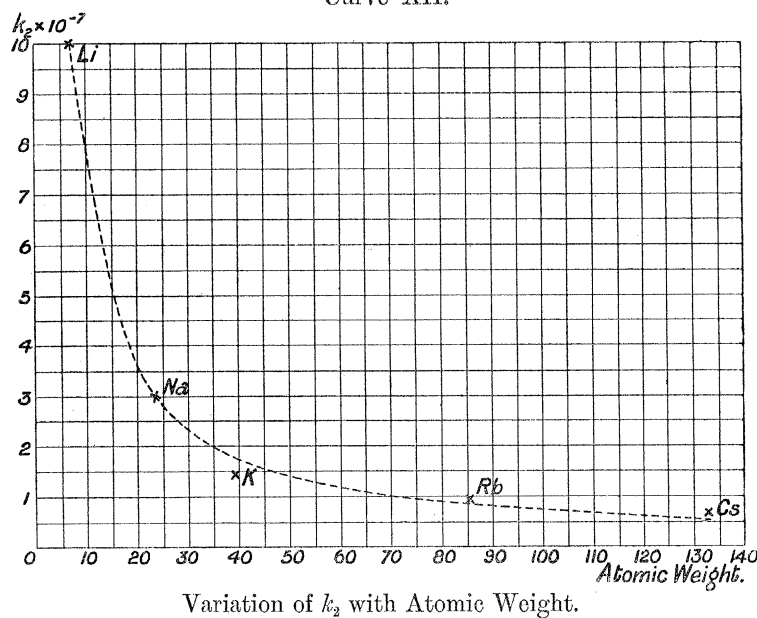
Conductivity of Flames containing Acids.

Since the majority of acids are decomposed at the temperatures employed in our experiments, our investigation of the effect of acids on the conductivity of the flame was limited to hydrochloric and sulphuric acids.

It has already been shown that the free flame has a measurable though small conductivity, and, for the sake of comparison, the numbers obtained on p. 98 are appended to those obtained by spraying half normal solutions of HCl and H_2SO_4.

E.M.F.	Distilled water.	$\frac{N}{2}$ HCl.	$\frac{N}{2}$ H_2SO_4.
5·60 ·227	·54 ·055	1·46 ·396	·510 ·105

The conductivity of the acids is thus very small in comparison with that of the alkali salts.*

We also investigated the conductivity of ammonium chloride, and found it to be almost the same as that of an equivalent solution of hydrochloric acid. This is readily explained by the dissociation of the salt into HCl and NH_3 at the temperature of the experiment.

The following values, corrected for the conductivity of the free flame, were obtained :—

| E.M.F.	$\frac{N}{2}$ NH_2Cl.	$\frac{N}{2}$ HCl.	$\frac{N}{2}$ H_2SO_4.
volts. 5·6 ·227	1·03 ·321	·92 ·341	− ·03 ·05

In the flame the H_2SO_4 is no doubt largely decomposed, yielding sulphur dioxide, whilst the hydrochloric acid is more stable. This accounts for the greater conductivity of the hydrochloric acid.

It is possible that in these cases, where the conductivity is small, dust particles entering with the air may have an appreciable effect. It is impossible to estimate this effect; we sought to reduce it as far as possible by filtering the air through cotton wool. If we consider it to have been insignificant, it is possible to make a comparison of the conducting power of water and hydrochloric acid in the flame. The quantity of water vapour in the flame with a spray of distilled water was many hundred times, probably many thousand times, the quantity of hydrochloric acid in the flame when a half normal solution was sprayed. The numbers given above show that the conductivity of the hydrochloric acid is at least two or three times that due to the water vapour alone.

Experiments with Decolorized Flames containing Salt Vapours.

The introduction of chloroform vapour into a flame coloured by the vapour of a lithium salt completely destroys the coloration (SMITHELLS, 'Phil. Mag.,' (V), 39, 122, 1895). The chloroform affords a convenient means of supplying an abundance of

hydrochloric acid along with combustible carbon, and the first action in the flame may be expressed by the equation :

$$CHCl_3 + H_2O = CO + 3HCl.$$
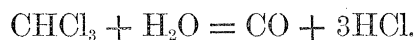
Experiments were made with flames containing chloroform vapour together with salt spray, in order to discover if any relation existed between the conditions requisite for coloration and those which determine conductivity.

In order to introduce the chloroform at any moment into the flame without disturbance of the experimental conditions, the apparatus was so arranged that by means of a three-way tap the gas supply could be passed through one or other of two similar U-tubes placed "in parallel," one containing a little water and the other an equal volume of chloroform. The flame remained steady when the change was made from one course to the other, and by use of a thermo-couple we found that the temperature in the neighbourhood of the electrodes likewise was not sensibly affected.

The following table gives a comparison of the conductivity of the flame containing lithium salts in the coloured and colourless states :—

	$\frac{N}{2}$ LiCl.		$\frac{N}{10}$ LiNO$_3$.	
E.M.F.	5·60	·227	5·60	·227
Current strength :				
Coloured flame	2·14	·547	2·01	5·87
Colourless „	2·44	·251	4·50	5·39

The above figures show that the conducting power is not destroyed when the flame is decolorized. It appears that the influence of the introduction of chloroform on the conductivity, such as it is, varies with the E.M.F. employed. At 5·6 the conductivity is uniformly increased when chloroform is added, whilst at ·227 volt a diminution is observed in both cases.

If the conductivity of the flame alone (that is, without salt) and of the flame with chloroform alone be subtracted from the above numbers, we obtain the following values for the salt alone :—

	5·6 volts.	·227 volt.
$\frac{N}{2}$ LCl :		
Coloured flame . . .	1·7	·50
Decolorized flame . .	1·5	·17
$\frac{N}{10}$ LiNO$_3$:		
Coloured flame . . .	1·5	·52
Decolorized flame . .	3·0	·41

As the lithium salts have but a small conductivity in the flame, it was thought possible that the alteration of conductivity above tabulated might depend on the large excess of hydrochloric acid in the flame. The experiments were therefore extended to the salts of cæsium and potassium, which have so high a conductivity as to preclude the possibility just suggested.

In the following table the results are given in scale deflections :—

E.M.F. in volts . . .	5·60	1·08	·227	·028
CsCl solution :				
Coloured flame	850	740	264	33
Decolorized flame . . .	1410	700	212	26
KCl solution :				
Coloured flame	55	...	105	
Decolorized flame . . .	78	...	93	

The above figures show that just as in the case of lithium salts, the conductivity of flames containing the salts of cæsium and potassium does not disappear on removal of the colour by means of chloroform, and the influence of the E.M.F. on the changes of conductivity that are noticed is the same in form as in the case of the lithium salts. It appears that at a certain E.M.F. the addition of chloroform would produce no effect in the conductivity. For the cæsium chloride solution used it follows from the table that this E.M.F would be about 1·1 volt.

Conductivity of Salts vaporised in the Flame of Cyanogen.

It has already been stated in the introduction that the equal conductivity of various salts of the same metal was attributed by ARRHENIUS to the conversion of each salt into hydrate by the large excess of water vapour present.

It appeared of interest to investigate the behaviour of salts in a gaseous medium containing only a small percentage of water vapour, and for this purpose we chose the flame of cyanogen. To avoid the presence of water altogether is impracticable, if the salt has to be sprayed; but if we suppose that in a coal-gas flame any considerable proportion of the hydrogen has been burned before it reached the neighbourhood of the electrodes, the quantity of water vapour in such a flame will be very great compared with that of a cyanogen flame, in which the only water is that introduced by the sprayer (partly as drops and partly as water vapour). As we estimated this difference in the amount of water to be something like 10 to 1, we thought it probable that, if the hypothesis of ARRHENIUS were correct, marked

differences of conductivity should be observable when salts in suitably concentrated solution were sprayed in the flames of coal-gas and cyanogen. For this purpose $\frac{1}{50}$ normal solutions of potassium salts were employed. In a coal-gas flame solutions of this concentration conduct equally well, but in a cyanogen flame, where no water is produced by combustion, such solutions should act like the more concentrated solutions in a coal-gas flame, that is to say, their individual conductivities should become apparent.

In carrying out the experiments the limited amount of cyanogen available* at one time necessitated some alterations in the apparatus. The vessels for the collection of coarse spray were removed, and the flame tube connected directly to the tubulated cylinder, into which the sprayer projected. The flame was not separated into its two cones, and just enough air used to keep the sprayer steadily in action. The amount of salt entering the flame was not greatly different from what it was with the apparatus in its ordinary form.

The following results were obtained with an E.M.F. of 5·55 volts :—

Experiment No. 1.		Experiment No. 2.	
Solution.	Conductivity.	Solution.	Conductivity.
$\frac{N}{50}$ KCl	167·0	$\frac{N}{50}$ KBr	199·0
$\frac{N}{50}$ K$_2$SO$_4$	177·0	$\frac{N}{50}$ KNO$_3$	205·0
Distilled water	6·4	Distilled water	5·7

After each of the above experiments a measurement was carried out with a coal-gas flame under exactly the same conditions of pressure. This gave the following numbers :—

Experiment No. 1.		Experiment No. 2.	
Solution.	Conductivity.	Solution.	Conductivity.
$\frac{N}{50}$ K$_2$SO$_4$	19·4	$\frac{N}{50}$ KBr	21·8

Subtracting the conductivity of the flame without salt, and correcting for a slight variation in the condition between the two cyanogen experiments, we have the following values :—

* One cubic foot stored over mercury in an iron gas-holder.

$\dfrac{N}{50}$ KCl. 161,

„ KBr 163,

„ KNO$_3$ 169,

„ K$_2$SO$_4$ . . . . 171.

The conductivities of the four salts are almost equal at the concentration used; the two haloid salts have somewhat less values than the two oxysalts.

It appears, therefore, that the smaller quantity of water in the cyanogen flame has not had a marked effect in bringing out the individual conductivities of the salts. It would, however, be unsafe to draw any positive conclusion as to the cause of conductivity from these experiments. We were deterred from prosecuting the enquiry further, because of the non-comparable character of the two flames in respect of temperature, a factor which has so great an influence on conductivity.

It will be noticed that the conductivity of salts in a cyanogen flame is about ten times that which they have in a coal-gas flame. The cyanogen flame without salt also conducted about ten times as well as the coal-gas flame without salt. We found that a cyanogen flame, into which a bead of salt was introduced by means of a platinum wire, showed a very high degree of conductivity. This was largely due to the very rapid rate at which the bead was vaporised; it shows at the same time that high conductivity may occur in the absence of hydroxides.

Consideration of Results.

We have not given, and do not think it necessary to give, an account of all previous investigations on the electrical conductivity of flame gases.* In recent times the conductivity of salt vapours has been investigated by WIEDEMANN and EBERT ('Wied. Ann.,' 35, 209, 1888), J. J. THOMSON ('Phil. Mag.,' (V), 29, 356 and 441), and by ARRHENIUS (*loc. cit.*), with a view to determining its character, whether electrolytic or otherwise. WIEDEMANN and EBERT, working with high electromotive force and comparatively cool electrodes, came to the conclusion that the discharge through flames was of a disruptive character, and facilitated in different degrees by the vapours of different salts. THOMSON, using a highly heated porcelain tube, provided with platinum electrodes, considered his results to indicate an electrolytic conduction. The conclusions of ARRHENIUS, as has already been stated, are entirely in favour of the view that the conduction of salt vapours is electrolytic in character.

Our own results do not seem to admit of any other explanation than that the conduction of salt vapours is electrolytic in character. At the same time the features presented by the conduction in the case of salt vapours do not correspond in every particular to those of the conduction of salts when dissolved in liquid solvents. In

* A good summary is given by HEMPTINNE ('Zeitschf. f. Phys. Chem.,' 12, 244, 1893).

the case of salt vapours, the high temperatures at which alone the conductivity can be examined, the correspondingly greater mobility of the molecules or ions, as well as the enormous reduction in the density and viscosity of the medium, and in the concentration of the salt, give ample ground for expecting characteristics in the phenomena of conduction very different from those which occur with liquid electrolytes at ordinary temperatures, although in both cases the conduction may be of a truly electrolytic character.

To take first of all the relation between current strength and electromotive force, we have in the case of liquid electrolytes, provided polarisation of the electrodes is avoided, a strict applicability of Ohm's law. In the case of salt vapours this law only applies for low electromotive forces. This was found both by ARRHENIUS and ourselves. ARRHENIUS, from theoretical considerations, believes that Ohm's law should hold also for higher electromotive forces, and he concludes that the divergence from it must be regarded as only apparent. This, however, leaves the divergence entirely unexplained.

For an expression capable of representing the relationship between current strength and electromotive force we were led, as already stated, to a formula derived by Professor J. J. THOMSON and Mr. RUTHERFORD from their study of the conductivity of gases subjected to Röntgen rays. In a gas exposed to Röntgen rays a steady supply of ions is supposed to be generated and the resulting concentration of ions is then determined by the fact that the rate at which they combine is proportional to the square of the number present, assuming equal numbers of positive and negative ions to be distributed throughout the gas. In a flame containing salt vapour it may be supposed that a steady supply of ionising salt is carried up between the electrodes, so that the conditions would be, to this extent, analogous in the two cases.

In applying the formula to our results we have had to recognise a feature distinguishing the behaviour of salt vapours from that of Röntgenised gases, namely, the fact that the current strength continues to rise slowly even at high E.M.F.s. The explanation of this difference does not seem to be difficult.* It would be accounted for by the increased electrostatic field either bringing in ions from the neighbourhood of the electrodes or increasing the rate of ionisation between them.

We have now to consider our results in reference to the question of the state in which the salts exist in the flame, and give rise to the conductivity. It could hardly be expected, *prima facie*, that the salts would all be vaporised without change, for even those among them that are most stable under ordinary conditions are likely to undergo some change of composition at the very high temperature reigning in the flame, and in the presence of various flame gases. The liability to change is indeed so great, and, at the same time, the precise character and extent of the change so little

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* A kind of convective conduction, proportional to the E.M.F. which ARRHENIUS recognised in his experiments on alkaline earth metals, cannot here be in question. We have referred to this subject in another connection on p. 98.

known from independent evidence, that great caution is necessary before declaring that the results of such experiments as we have undertaken establish any one possible view.

The most important generalisations derivable from our study of the relation between current strength and concentration of different sets of salts of different metals are first, that the conductivities differ always according to the metal; secondly, that among salts of the same metal differences of conductivities evident at high concentrations disappear when the dilution is greater; and thirdly, that the conductivity of haloid salts is different from the conductivity of oxysalts.

We will give the explanation of these general facts, which appears to be most in conformity with our results, and most compatible with chemical evidence.

The fact that the conductivity of haloid salts at higher concentrations is approximately proportional to the square root of the concentration is consistent with the presence of a binary electrolyte, and as we have found that the conductivity of chlorides is maintained when the presence of a large quantity of chloroform in the flame forbids us to suppose that the chlorides are chemically altered, we conclude that the binary electrolyte in question is the haloid salt itself.

Again, the approximately equal conductivity of the oxysalts of any one metal which approaches that of the hydrates, indicates that in the flame they are changed into the same electrolysable substance, which we conclude is the hydroxide or oxide.

At the same time, whilst we recognise the haloid salts as being present to a considerable extent undecomposed in the flame, and acting as electrolytes, the fact that at high dilution the haloid salts and oxysalts alike of any one metal have the same conducting power, makes it probable that under these circumstances the haloid salts have also been converted into hydroxides, thus giving a common dissociating body.

The fact that potassium iodide at higher concentrations has a greater conductivity than potassium chloride, or bromide, is compatible with the greater readiness with which this salt is acted upon by oxidising agents. Whilst the chloride and bromide preserve their individuality, the iodide is largely converted into the oxide, which has a higher conductivity.

Coming lastly to the question whether the luminosity in flames coloured by salt vapours is connected with their electrical conductivity, we think our observations on flames containing chloroform give a definite decision in the negative.

The addition of chloroform to a flame produces hydrochloric acid. Now the conductivity of a flame containing either chloroform or hydrochloric acid, but no salt, is shown by our experiments (see p. 121) to be extremely small. Since in a flame containing an alkaline chloride the conductivity depends on the ionisation of this salt, the increased concentration of the chlorine ions due to the introduction of chloroform is so small that the degree of ionisation is not materially reduced and the conductivity therefore is not greatly affected.

The coloration of the flame is, however, entirely destroyed by the addition of chloroform.

We can say, therefore, that hydrochloric acid prevents the occurrence in the flame of the substance on which the emission of light depends, and that this substance is not merely the metal existing as an ion.

Thus the question which originally impelled us to our experiments is answered. Since it is answered in the negative, some other explanation of the luminosity of salt vapours must be sought, and we fall back upon the alternatives which have already been discussed by one of us on a previous occasion ('Phil. Mag.,' (V), 37, 245 (1894)).

It seems clear that the coloration of a flame containing vaporised sodium chloride is dependent upon the presence of the vapour of the metal in the non-ionic state, and the explanation of this, most conformable to our experiments, is that a very small proportion of the chloride is first converted into oxide by oxidising gases in the flame and the oxide then reduced by reducing gases in the flame. The presence of hydrochloric acid prevents the formation of oxide and hence prevents also the liberation of the metal. Whether the metal vapour glows solely in consequence of its high temperature, or because of vibrations imparted to its atoms during chemical change, is a question which our experiments were not designed to answer.