

reaction would take place between sulphuric acid, and an iodide, in the presence of a reducible substance, at a higher temperature.

Conclusions.

It would appear that the only evidence on which the assumption that gases of a permanent character, such as hydrogen, carbon monoxide, nitrogen, helium, and argon, exist in the free state in the mineral substances from which they are evolved on heating, rests on certain observations with regard to the cavities which can sometimes be detected by microscopic examination.

The cavities may be either apparently empty or they may contain liquid, and when the mineral is warmed the liquid disappears at a temperature which is a few degrees below the critical point of carbon dioxide or of some hydrocarbon. The fact that the critical temperature of the liquid is a little below the point corresponding to carbon dioxide, in the case of a mineral containing that substance, is not, however, of very great significance as pointing to the presence of a permanent gas. A small quantity of methane would produce the same result.*

Further, although it can be shown that *compact* minerals do enclose carbon dioxide and hydrocarbons, gases which can easily be liquefied, the analogy cannot be extended to gases such as hydrogen and helium in connection with minerals like chlorite, mica, and clèveite, which exhibit many cleavages.

On the other hand, there is, as I have endeavoured to show, a considerable amount of evidence in favour of the theory which I have put forward:—That in the *majority of cases* where a mineral substance evolves gas under the influence of heat, the gas is the product of the decomposition or interaction of its *non-gaseous* constituents at the moment of the experiment. The results of such experiments cannot, therefore, serve as basis for speculation as to origin and history of the substances in question.

“The Electrical Conductivity and Luminosity of Flames containing Vaporised Salts,” By ARTHUR SMITHELLS, H. M. DAWSON, and H. A. WILSON. Communicated by Sir H. E. ROSCOE, F.R.S. Received October 24,—Read November 17, 1898.

(Abstract.)

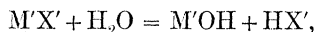
1. *Object of the Investigation.*

No general consensus of opinion appears to exist as to the mode by which the metal of an alkali salt is liberated when the salt is vaporised

* Kuenen, ‘Phil. Mag.’ 1897.

in a flame. By some the liberation is supposed to be effected thermally by chemical dissociation; others suppose that the salt is converted into hydrate or oxide, and then reduced by the flame gases. It is also noteworthy that, however the metal be liberated, and however oxidisable it may be, light is emitted from parts of the flame where oxidising gases are in abundance, and where even less oxidisable metals in the massive state are rapidly oxidised.

The primary object of the experiments described in this paper is to ascertain whether the luminosity imparted by vaporised salts to flames is related in a definite manner to the electrical conductivity of the salt vapours. The conductivity of vaporised salts in flames has been investigated by Arrhenius,* who concluded that it was of an electrolytic character. In the case of alkali salts, Arrhenius supposes that the salt vapour is acted upon by the large quantity of water vapour in the flame, in accordance with the following equation—



and that the metallic hydrate so formed undergoes partial electrolytic dissociation into the ions $\overset{+}{M}$ and $(\overset{-}{HO})$. 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 believe that electrolytes distributed in small concentration throughout a gas, would likewise be electrolytically dissociated,—a view to which his results as above stated, are conformable.

Since, according to the electrolytic dissociation theory of Arrhenius as applied to dilute solutions, the metallic ion in virtue of its electric charge can persist in an oxidising medium, it appeared that if the same theory were really applicable to salts vaporised in flames, it would afford an explanation both of the liberation of the element, and of its persistence in the midst of an oxidising atmosphere of flame gases.

Another consideration appeared to favour this hypothesis. According to Arrhenius, the conductivity of a salt vapour is proportional to the square root of its concentration in the flame, and according to Gouy† the luminosity of a flame coloured by an alkali salt also follows within certain limits, the same law.

The motive of the present authors was to test the above hypothesis, and incidentally to gain increased knowledge of the circumstances that govern the electrical conductivity of vaporised salts.

* 'Wied. Ann.,' vol. 42, p. 18, 1891.

† Gouy, 'Ann. Chim. Phys.,' vol. 18, p. 5, 1879.

2. *Apparatus.*

The apparatus employed consisted essentially of the arrangement used in other investigations of flame,* whereby the two cones that constitute the flame of a Bunsen burner, can be separated widely and maintained apart for any length of time. The gas and air supplies were regulated with great care, and the air supply was made to actuate a sprayer, whereby an extremely fine spray of any salt solution could be led into the flame. The devices used in regulating the gas and air supplies, and the precautions necessary in the construction and use of the sprayer, are described in the paper.

The electrode system which usually consisted of two coaxial cylinders of platinum-iridium alloy, was fixed symmetrically in the space between the two cones of the flame.

The source of electricity consisted of three accumulators, from which by means of a German-silver wire, 20 metres long, and two contact pieces, any E.M.F. up to 5·7 volts could be used. For higher E.M.F.'s Leclanché cells were used.

3. *Method of Working.*

After the apparatus had been adjusted, the current in either direction between the electrodes was measured by a Kelvin high resistance galvanometer for a series of E.M.F.'s. The constancy of the apparatus was tested at intervals during the progress of the experiments by measuring the conductivity due to a $\frac{1}{10}$ th normal solution of potassium bromide, and the results were satisfactory.

4. *Conductivity of the Free Flame.*

From the observed conductivity due to a salt, it was necessary to deduct the conductivity of the flame gases alone, and that of the water in the spray. This value, which is very small, was determined by measurements made when distilled water only was sprayed.

5. *Unipolar Conduction.*

Considerable unipolar effects were noticeable in the experiments, and measurements of these are given in the paper.

6. *Measurement of the Concentration of Salt-vapour in the Flame.*

It was not necessary for the purpose of the enquiry to determine the absolute amount of salt between the electrodes; but for the purpose of instituting some comparison with the results of Arrhenius, a rough

* Smithells, 'Phil. Mag.,' vol. 39, p. 122, 1895.

measurement of the amount of salt was attempted by a photometric method. It appeared that the amount of salt conveyed to the flame was about eighteen times as much as in the corresponding experiments of Arrhenius, so that it was possible to investigate the conductivity of salt vapours at greater concentrations than was done by Arrhenius.

7. *Relation between Current Strength and Electromotive Force.*

Experiments were made with a large number of salts, and with a difference of potential between the electrodes varying from 0.01 volt to 45 volts. The results show that with small E.M.F.'s up to 0.2 volt, Ohm's law is accurately obeyed. With greater E.M.F.'s the law is not obeyed, the deviation becoming greater in increasing proportion as the E.M.F. is increased.

The general relationship between current strength and E.M.F. was expressed by Arrhenius as follows :—

$$C = Af(E),$$

where C is current strength, E the E.M.F., and A a constant dependent on the solution sprayed. This expression is only valid for the present results within certain limits. With the more concentrated solutions it is not applicable.

Acting upon a suggestion of Professor J. J. Thomson, the authors have found an equation capable of expressing the relationship between C and E in a remarkably complete way. This equation is based upon the work of Thomson and Rutherford* on the passage of electricity through gases exposed to Röntgen rays, a phenomenon which has several points of external resemblance to that of conduction through flames. The equation is—

$$C = i + k_1 E,$$

where i bears the same relation to the E.M.F. as the current in X ray conductivity. Tables are given in the paper showing to what extent the above equation expresses the results obtained.

8. *Influence of Temperature on Conductivity.*

Experiments were made in which the electrodes were raised or lowered, so as to bring them into regions of different temperature. The temperature differences were measured by means of a platinum platinum-rhodium thermocouple. The results showed that the conducting power of the salt vapour increased very rapidly with increasing temperature, and that at temperatures not greatly below those which the vapour attains in flames, the conductivity would become inappreciable.

* 'Phil. Mag.,' vol. 42, p. 392, 1896.

9. *Relation of Conductivity to Concentration of Solution sprayed and to the Nature of the Salt.*

Results are given for solutions of the following substances :—

- a. Potassium salts :—Chloride, bromide, iodide, chlorate, nitrate, sulphate, carbonate, hydrate.
- b. Sodium salts :—Fluoride, chloride, bromide, iodide, nitrate, sulphate, carbonate, hydrate.
- c. Lithium salts :—Chloride, nitrate.
- d. Rubidium salts :—Chloride, nitrate.
- e. Cæsium salts :—Chloride, nitrate.
- f. Hydrogen salts :—Chloride, sulphate.

The concentration of the solution varied from $\frac{1}{500}$ th to $\frac{1}{2}$ normal. As an example of the range of work, it may be stated that potassium iodide was investigated with $\frac{1}{5}$, $\frac{1}{10}$, $\frac{1}{20}$, $\frac{1}{100}$, $\frac{1}{300}$ normal solutions, in each case measurements being made for E.M.F.'s of 5.6, 0.795, and 0.227 volts. The set of measurements was repeated more than once, as a rule, in order to avoid errors.

The results show that at small concentrations equivalent solutions of all salts of the same metal impart the same conducting power to the flame. At higher concentrations this equality no longer holds good; the oxy-salts show a greater conducting power than the haloid salts, the difference increasing with increasing E.M.F.

Numbers proportional to the molecular conductivity are calculated for the various salts, and it is shown (*a*) that in general the molecular conductivity of a salt increases with increasing dilution; (*b*) that the oxy-salts of all alkali metals behave differently from the haloid salts; and (*c*) that at all concentrations investigated, the conducting power of the oxy-salts of any one metal is the same. It also appears that with increasing concentration the molecular conductivity of the oxy-salts passes through a minimum value.

In the case of the haloid salts the equation $C = k\sqrt{q}$ (where C is the conducting power, q the concentration, and k a constant) holds good to a certain extent, but this is not at all the case with the oxy-salts.

The conductivity increases with increasing atomic weight of the metal, the increase being more rapid in the case of the oxy-salts than in that of the haloids.

10. *Conductivity of Flames containing Acids.*

The conductivity of acids in the flame is very small in comparison with that of alkali salts. Ammonium salts being decomposed in the flame, behave like their acid component. Sulphuric acid is doubtless also decomposed in the flame. The conductivity of hydrochloric acid

was measured with a view to subsequent experiments, and was found to be—with a half-normal solution—five or six times as great as that of the vastly more concentrated water vapour which existed in the flame.

11. Experiments with Decolorised Flames containing Salt-Vapours.

When chloroform vapour is passed into a flame containing a salt-vapour, the colour is suppressed, owing to the large amount of hydrochloric acid formed. The conductivity of flames in this condition was determined and compared as nearly as was possible with the conductivity of flames containing the same amount of vapour, but no chloroform. The salts of lithium, potassium, and caesium were used. It was found that the conductivity of the flames was not largely affected by the decolorisation. With small E.M.F.'s the conductivity was somewhat diminished, but with an E.M.F. of 5.6 volts an increase was always noticed.

12. Conductivity of Salts vaporised in the Flame of Cyanogen.

The view of Arrhenius is that salts are hydrolysed in flames by the water vapour present, and that the hydrate furnishes the ions. To gain some idea of the influence of water vapour, the cyanogen flame was chosen as a medium for the volatilisation of salts. Such a flame contains only the water coming from the sprayer. No differences were noticed in the behaviour of the several salts that would not have been found equally in a coal-gas flame.

The high general temperature reigning in a cyanogen flame causes a high degree of conductivity. A dry salt vaporised into a cyanogen flame from a platinum wire shows great conductivity, and thus it seems certain that the presence of water vapour in the flame is not necessary for the production of ions.

General Conclusions.

1. The authors conclude from their experiments, that the conductivity of vaporised salt is of an electrolytic character, but that there are features connected with it that distinguish it from electrolytic conduction in aqueous solution. Thus Ohm's law is only obeyed within certain limits, and the general relation between current strength and electromotive force can only be represented generally by a more complex expression.

2. The conductivities of different salts differ greatly, according to the electropositive constituent.

3. Among different salts of the same metal differences of conductivity

appear at the higher concentrations, but at low concentrations equivalent solutions have equal conductivity.

4. The conductivity of the haloid salts as a group is distinct from that of the oxy-salts.

5. The conductivity of the haloid salts of a metal among themselves increases with the increasing atomic weight of the halogen.

6. The conductivity of the oxy-salts of a metal is approximately equal, and approaches that of the hydrates.

7. The more easily oxidisable halogen salts are probably partly converted into oxide in the flame, so that their conductivity is composed of two parts.

8. The behaviour of the salts in flames supplied with chloroform vapour seems to establish the fact that the conductivity and the colour produced by the salt vapour are not due to a common cause.

The coloration of a flame by an alkali salt does not seem therefore to be connected with the ionisation of the salt. It must be attributed to the metal set free by a chemical process. This process consists probably in a reduction effected by the flame gases. An oxy-salt would, generally speaking, form in the first instance an oxide, which would then be reduced. In the case of haloid salts it seems also necessary to suppose that an oxide is intermediately formed, the metal then being liberated by reduction.

November 30, 1898.

Anniversary Meeting.

The LORD LISTER, F.R.C.S., D.C.L., President, in the Chair.

A full Report of the Anniversary Meeting, with the President's Address and Report of Council, will be found in the 'Year-book' for 1898-9.

The Account of the Appropriation of the Government Grant and of the Trust Funds will also be found in the 'Year-book.'