

THE S I S:

"IONIZATION IN GASEOUS MEDIA DURING
COMBUSTION."

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NOTE.

Part 1 has been accepted for publication by the
Faraday Society.

Part 2 has been accepted for publication by the
Faraday Society.

Part 3 has been sent to the Chemical Society
for publication.

P A R T 1.

IONIZATION IN FLAMES OF VARIOUS ORGANIC SUBSTANCES.

1. Introduction.

The study of the phenomenon of detonation in internal combustion engines has recently given rise to many subsidiary problems of fundamental importance. It has been suggested by many writers that ionization is one of the chief causes of detonation, though no relation has yet been discovered between the former and the latter. Up till now attention has been devoted mainly to the study of ionization in gaseous explosions. The object of the present experiments was to determine the correlation, if any, between the degree of ionization of various substances in flames and the amount of detonation in an engine cylinder charged with fuels containing these substances.

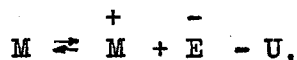
The range of investigation includes an experimental study of ionization in flames of hexane, ether, alcohol, coal gas, etc., and the effect of adding iron carbonyl, amyl nitrite, etc., - substances which alter the highest useful compression ratio (H.U.C.R.)¹ of a fuel.

All gases conduct electricity, but very delicate apparatus is required to show that some gases in their natural state possess this property even to a small extent. Unless ions have been produced by raising the temperature, by exposure to active rays, or by some other method, all gases are relatively good insulators.

One/

¹ The H.U.C.R. is the highest compression ratio which it is worth while to employ with a given fuel. If the compression is raised above this limit excessive detonation leading to pre-ignition and loss of power is obtained. For full information on this subject reference is made to the Aeronautical Research Committee publication, R. & M.No,1013, on Dopes and Detonation by Callendar, King, and Sims.

One of the oldest methods of obtaining gases in an ionised state is by producing flame. Giese,² by studying the electrical properties of gases coming from flames, discovered the theory which is now used to explain gaseous conductivity. The current passing between two electrodes at different potentials immersed in gaseous media is at present considered to be due to the movement of the electrons toward the anode and the positive ions towards the cathode. The mobility of the former is of a higher order than the latter, except possibly when the electrons become attached to neutral atoms. At higher temperatures the neutral atoms (M) gaseous elements dissociate into ions (M⁺) and electrons (E⁻) in the following manner:-



where U is the energy absorbed in the process.

Saha,³ assuming that the electron is a monatomic gas of atomic weight 1/1836 and the energy U to be the product of the ionization potential and the electronic charge, has recently developed a theory of thermal ionization of gaseous elements at high temperatures which has received confirmation by experiments with salt vapours in flames at particular temperatures by Noyes and Wilson,⁴ Barnes,⁵ and for variation in temperature by the writer⁶.

Garner and Saunders,⁷ by using an Einthoven galvanometer for measuring the percentage of ionization occurring in explosions of hydrogen and oxygen, found that Saha's theory holds approximately for gaseous explosions and therefore that the ionization is mainly thermal as in flames/

² Wied. Ann., 17,519, 1882.

³ Phil. Mag., 40,478, 1920.

⁴ Astroph. Jour., 57,20, 1923.

⁵ Physical Rev., February, 1924.

⁶ Phil. Mag., Vol. 3, January, 1927.

⁷ Trans. Far. Soc., October, 1926.

flames. The similarity between the origin of ionization in flames and explosions suggests that the present experiments may throw light or shadow on the views expressed by other writers on the relation between ionization and detonation, concerning which there is much diversity of opinion.

2. Measurement of Ionization.

Since the mobility of the electrons is so great compared with that of the positive ions, the current passing between two electrodes immersed in the excited flame medium is almost solely due to the electricity carried by the electrons. Accordingly, the electrical conductivity is proportional to the number of electrons present, and since the number of electrons is equal to the number of positive ions, the conductivity may be taken as a measure of the ionization. The specific conductivity at a point in the region between the electrodes depends upon the potential gradient at the point as well as the current per unit area of one of the electrodes, guarded to ensure that the lines of force between the electrodes go straight across. The present experiments were not intended to measure the absolute value of the ionization, and no measurement of the potential gradient at various points between the electrodes was made; it was therefore unnecessary to have one of the electrodes guarded. Precautions were taken to keep the electrodes at a constant distance apart, to keep their position constant in the flame and to keep the temperature of the flame constant; the area of the electrodes and the difference of potential between the latter remained unchanged. The current under these conditions is practically a measure of the degree of ionization.

3. Description of Apparatus.

Two platinum electrodes each $\frac{1}{2}$ centimetre square were placed just over the inner cone of an ordinary bunsen flame. They were made of thick foil and welded to wires $\frac{1}{2}$ millimetre in thickness. The wire connected to the cathode was made of platinum, but the anode was attached to the junction of two wires, one made of platinum, the other of platinum rhodium. The temperature of the anode could therefore easily be kept constant, the wires leading to the anode being connected to a millivoltmeter supplied by the Cambridge Scientific Instrument Company. The horizontal distance between the electrodes was a little over a centimetre, and the distance was kept constant by passing the wires through quartz tubes of small bore fused together lengthwise.

A battery of small cells supplied a constant potential difference of 30 volts between the electrodes and the current passing through the flame medium was measured by a Kelvin galvanometer, the sensitiveness of which could be adjusted by a control steel magnet. The deflection on the galvanometer scale indicated a fairly steady current when the flame was shielded by a chimney.

The effect of various substances on the conductivity of the flame was studied, the method of introducing each substance depending on its volatility. The more volatile substances were mixed with the air before entering the flame; the less volatile substances were burned at the end of a quartz tube introduced at the mouth of the burner. Care must be taken to have the connecting wires well insulated and the electrodes free from deposit.

4. The Flame Constituents.

Since the ionization depends on (a) the nature, and (b) the concentration/

concentration of the flame constituents, (c) the temperature of the flame, (d) the distance of the electrodes from one another, and (e) the amount of deposit on the electrodes, it was necessary to eliminate all these variables except (a) as far as possible, if the true effect of each substance was to be determined. By examination of the table of results it will be noticed that some substances decrease whilst others increase the conductivity of the flame. The action is not a catalytic one, but the variation of the conductivity of the flame is due to the variation of the concentration of electrons in the flame. The presence of substances of low ionization potential - which is the potential required to give an electron enough energy to ionize a neutral atom - increases the number of electrons present in the flame and therefore increases the current; substances of high ionization potential decrease the electron concentration and therefore decrease the current.

The following results with the Bunsen flame and the addition of various substances are typical of results obtained with other flames, as will be pointed out later.

5. Table of Results.

Substance.	Effect on Ionization.	Effect on Detonation ⁸
<u>Nitrogen Compounds.</u>		
Aniline	Slightly decreases.	Delays.
Methyl-aniline.	do.	do.
Di-methyl-aniline	do.	do. slightly.
Benzyl-ethyl-aniline	Slightly increases.	do. do.
Xylidine	Decreases	do. do.
Nitrogen-peroxide	do.	Markedly induces.
Ammonia	do.	Slightly delays.
Phenyl Hydrazine	Little effect	Slightly induces.
Amyl-nitrite ⁹	Markedly decreases	Greatly induces.
Picric acid.	Greatly increases	Induces.

Carbonyls/

⁸ Information obtained from the report on Dopes and Detonation by Callendar, King, and Sims¹ and from experiments made by the staff of the Air Ministry Laboratory.

⁹ Dark flame between electrodes only.

Substance.	Effect on Ionization.	Effect on Detonation.
<u>Carbonyls</u>		
Iron-carbonyl ¹⁰	Greatly increases	Greatly delays.
Nickel-carbonyl	do. do.	do. do.
<u>Organic oxides, etc.</u>		
Benzoyl-peroxide	do. do.	Greatly induces.
Hydrogen-peroxide	do. do.	Little effect.
Ether	Cooling effect	Induces.
<u>Halogens and Halogen Compounds.</u>		
Iodine	Greatly increases	Delays
Bromine	do. do.	Slightly induces.
Ethylene dibromine	do. do.	do. delays
Acetylene tetra-bromide.	Increases	do. do.
Chloroform	Greatly increases	Little effect.
Dichlorethylene	do. do.	Slightly induces.
<u>Aldehydes.</u>		
Valeraldehyde	Slightly decreases	Slightly delays.
Propylaldehyde	Decreases	Little effect.
Paraldehyde	Slightly decreases	Slightly delays.
Cenanthol	do. do.	Little effect.
Acetaldehyde	do. do.	Slightly delays.
<u>Miscellaneous.</u>		
Lead Xylol	Greatly increases	Markedly delays
Ethyl fluid ¹¹	do. do.	Greatly delays.
Carbon-disulphide	Decreases	Delays.
Tin oleate	Greatly increases	Little effect.
Sulphonal	do. decreases	Delays.
Water	Cooling effect	do.
Ethyl alcohol	do. do.	do.

6. Experiments with Different Flames.

Various experiments were made to confirm the results tabulated above by using flames other than the ordinary Bunsen. The influence of the various substances on the ionization in a hexane flame was examined and thereafter the ionization in flames of the substances themselves was determined.

The/

¹⁰ Reddish-brown deposit on cathode only.

¹¹ "Ethyl fluid" consists of a mixture of lead-tetra-ethyl and ethylene dibromide in the proportion of 3 grams of the former to 2 grams of the latter.

The method of producing the hexane flame consisted in burning a mixture of air and hexane vapour at the ends of four small quartz tubes which were sealed with sealing-wax to a rubber stopper. A long flame was thus produced and the electrodes were placed in the flame just over the inner cones. The rubber stopper was fitted to a vessel containing cotton wool soaked in hexane through which a stream of air was passed. The air which was supplied under slight pressure from a ten-gallon drum, was dried and freed from carbon dioxide by passing through a tower of granular calcium chloride, then through soda-lime and then by bubbling through concentrated sulphuric acid. The flow of air was adjusted by means of a screw clip.

The cathode became coated with deposit very easily and since the current varies very greatly with the amount of deposit on the cathode it was necessary to make each experiment as quickly as possible. The hexane was doped with each substance in turn and the results obtained were exactly similar to those given in the above table.

To complete the investigation, the hexane vessel was replaced by a weighing bottle containing the substance in liquid form to be examined. The weighing bottle was surrounded by a beaker of water placed on an iron plate which could be heated at will by a Bunsen flame. In this way the less volatile substances were vaporised. The air in some cases bubbled through the liquid and in others merely passed over the surface, the extent of the contact of the air with the liquid being varied to give the mixture strength desired. The amount of liquid used during each experiment was determined by weighing the bottle and contents before and after. In this way the mixture strength used in each case was kept constant. The temperature, of course, was kept constant as before by using the platinum-rhodium thermocouple. Those substances in the foregoing table which could be/

be used in this way gave results which showed that flames of substances which increase or decrease the ionization of a Bunsen flame possess electrical conductivity to a greater or less degree respectively.

In addition flames of "B.P." petrol, benzene, pentane, acetone, pseudocumol, turpentine, and various mixtures were used; a mixture of two substances was found to give a flame the conductivity of which lies between the separate conductivities of the two substances, e.g., "B.P." petrol and carbondisulphide. The current obtained with "B.P." petrol alone was 0.7 microamp., with CS₂ alone 0.03 microamp., with a mixture containing 25 per cent. CS₂, and 75 per cent. petrol 0.1 microamp.

7. Conclusion.

It is evident from these results that although in many cases knock-inducers increase and anti-knocks decrease the ionization of flames, this is by no means generally so. Consequently, Wendt and Grimms' theory¹² that the advance of free electrons before the flame front ionizes the unburnt gas, thus increasing the rate of flame propagation and causing detonation, does not seem at all possible in the light of the present results. If this theory were correct an increase in the ionization of the flame would increase the rate of flame propagation and induce detonation. But the carbonyls do not behave in this manner.

Neither does the view of Charch, Mack, and Boord,¹³ that there is a direct relationship between the intensity of detonation and ionization receive confirmation. Certainly for particular substances ionization will increase with increase of knocking since there is a rise in temperature, the degree of ionization is not generally a criterion from which to estimate the/

¹² J.Ind. Eng. Chem., 1924, 16,890,

¹³ J.Ind. Eng. Chem., April, 1926.

the intensity of detonation, for the carbonyls become exceedingly ionised in flames and the nitrites remain relatively in the neutral state whereas the former tend to delay, the latter to induce, detonation.

We must therefore conclude that, although ionization accompanies detonation as it does all flame phenomena, there is no simple relation between them. Ionization does not appear to be either a cause or effect of detonation, but mainly a temperature effect.

PART 2.THE ELECTRICAL CONDUCTIVITY OF VAPOURS AND LIQUID DROPS DURING INCIPIENT COMBUSTION.1. Introduction.

The problem of the slow beginning of combustion of liquid fuels has up till very recently remained relatively obscure. The chemistry of the subject has been dealt with by Callendar, King, Mardles, Stern and Fowler,¹ in their recent explanation of the cause of detonation in engines using liquid fuel. The object of the present experiments was to study the physical aspect of slow combustion, in the light of the ionic theory of the electrical properties of gases which has been developed and established by Sir J.J. Thomson and others.

By comparing the temperature variation of the rate of chemical action with that of thermionic emission at the surface of metals in the presence of various reacting gases, Brewer² has shown that chemical action is in that case intimately related to the physical processes occurring. Whilst the chemical action immediately preceding detonation in an engine cylinder has now been explained¹, it is possible that as in the above case the mechanism of the action may be explained on the ionic theory. The following experiments were prosecuted to lead the way to such an explanation. Callendar's nuclear theory of detonation³ led the writer to investigate the electrical conductivity of liquid drops.

2. Description of Apparatus.

The method of producing slow oxidation of gaseous mixtures was similar/

¹ Engineering, Feb.4th, 11th, 18th, 1927.
² Proc.Nat. Acad. Sc., September, 1926.
³ Aero. Res. Comm., R. & M., 1013, 1925.

similar to that used by Mardles,¹ a brief description of which will be given. Fig. 1 shows the general arrangement.

FIG. 1.

A, Air inlet. C, Calcium chloride. D, Ten gallon drum.
E, Platinum or gold electrodes and platinum-rhodium
thermocouple. F, Electric furnace with resistance
control. L, Soda lime. P, Filter pump. Q, Quartz tubes.
T, Combustion tubes. U, Sulphuric acid. V, Vaporiser.

Air supplied under slight pressure from a ten-gallon drum was dried and freed from carbon dioxide before entering the vaporiser, the rate of flow being adjusted by means of a screw clip. The air was bubbled through the liquid in the vaporiser if a rich mixture of vapour and air were desired, but to obtain a lean mixture the air was merely passed over the surface as in the figure. By raising or lowering the vaporiser relative to the tube which in the case of a rich mixture dips into the liquid, various mixture strengths could be obtained. The mixture of air and vapour was passed through a combustion tube, the temperature of which could be adjusted by means of a Gallenkamp electric furnace with resistance control.

The combustion tubes varied from 2 ft. 6 ins. in length, the diameter varied from 30 mm. to 15 mm. and both quartz and glass tubes were used. For comparative purposes tubes 15 ins. long and 15 mm. in diameter were used, and since the electrical conductivity of the gaseous mixtures was found not to depend on the material of the tube, the tubes were of glass, except for high temperatures, when quartz tubes were used. The pressure in the combustion tube was atmospheric approximately, since only a slight increase of pressure was necessary to maintain the flow of the mixtures.

Two electrodes, originally made of platinum and later replaced
by/

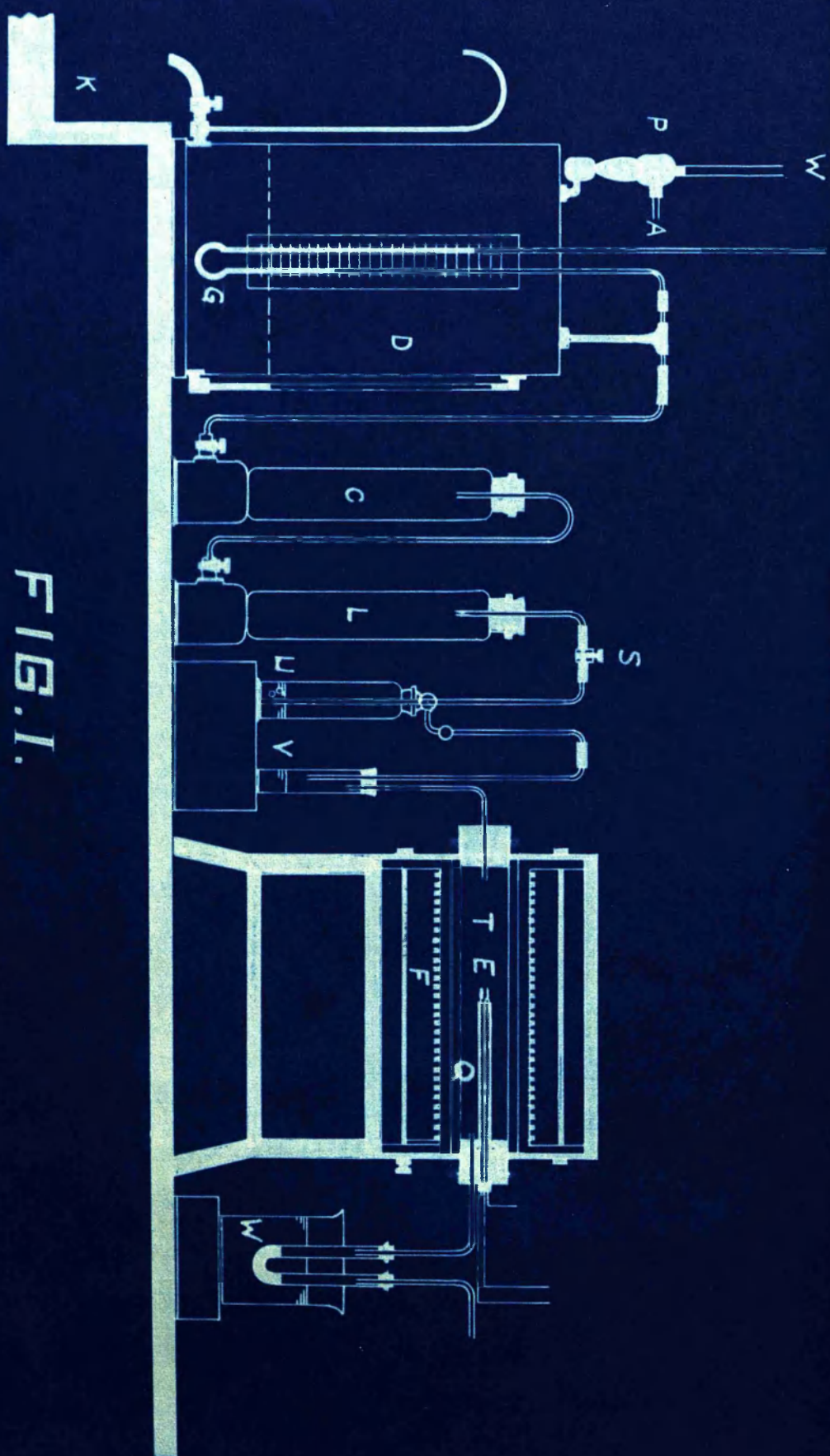


FIG. 1.

by gold were made of thick foil and were $\frac{1}{2}$ cm. square. They were fused and soldered in the case of platinum and gold respectively to wires $\frac{1}{2}$ mm. in diameter. Two wires, one made of platinum and the other of platinum-rhodium, had their junction at the anode; the wire connected to the cathode was of platinum. Surrounded by quartz tubes of small bore fused together lengthwise, these wires were kept insulated from the gaseous mixtures. The electrodes were thus rigidly placed nearly a centimetre apart.

The temperature was measured by connecting the wires from the anode to a millivoltmeter supplied by the Cambridge Scientific Instrument Company. The electrodes being kept at a constant potential difference of 30 volts by means of a battery of small cells, the current passing between the electrodes was measured by a galvanometer of the Lord Kelvin type.

In the experiments with liquid drops air supplied by a compressed air cylinder passed through a sprayer mechanically similar to that used by the writer in experiments with salt vapours in flames.⁴ The mixture of air and spray entered the combustion tube where the air and vapour mixture entered in the experiments with vapours.

3. Ionization in Gaseous Media.

The neutral atoms (M) are dissociated into ions (M⁺) and electrons (E⁻) according to the equation:-



where U is the quantity of energy absorbed in dissociation.

Since the mobility of the electrons is of a higher order than that of the ions the conductivity of the medium depends mainly on the number of free/

⁴ Phil. Mag., Vol. 111., p. 128, 1927.

free electrons present. Ionization in gases at normal temperatures is of a low order of magnitude and can only be measured by very delicate apparatus.

The apparatus described above was sufficiently sensitive to measure the electrical conductivity of an ordinary Bunsen flame with less than 1 per cent. of error. The degree of ionization in a salt-free Bunsen flame was taken as the standard relatively to which ionization in the media could be described as of a low or high order of magnitude. Thus, ionization in flames containing alkali salt vapours is of a high order of magnitude.⁵

6. The Electrical Conductivity of Vapours during Incipient Combustion.

Lean mixtures with air of pure ether, normal hexane, phenol, aniline, iodine, toluidine, and combinations of these were successively passed through the combustion tube and the temperature in each case slowly raised to the point of inflammation or explosion. At first no displacement of the galvanometer was observed, but after the mixture had passed through the tube for a short time a current was obtained. On dismantling the apparatus it was discovered that the measured conductivity was due to deposits on the electrodes. Consequently, the combustion tube and electrodes were carefully cleaned after each experiment and the temperature was raised as quickly as possible so that the electrical arrangements should not be fouled. In every case the ionization was found to be of a low order of magnitude, no deflection of the galvanometer being obtained.

The mixture strengths were then increased until it was found that with rich mixtures of the less volatile substances ionization was quite pronounced above 400° C. Before any displacement of the galvanometer was observed/

⁵ H.A.Wilson. Phil. Trans. A, p.63, 1915.

observed, however, a thick fog appeared in the combustion tube. Not until such a fog was formed was the medium measurably electrically conductive.

At this stage it seemed quite definite that ionization in vapours during slow combustion was of a low order of magnitude and the results were summed up by Callendar¹ thus: "No trace of ionization could be detected until the temperature was raised to the point of inflammation when the intense ionization which always accompanies flame was immediately apparent".

Subsequently, mixtures of hydrogen and acetylene with air appeared to be exceptions to this rule, but it was discovered that the conductivity obtained in these later experiments was due to leakage between the electrodes owing to the accumulation of various substances in the quartz tubes of small bore surrounding the wires leading to the electrodes. When the quartz tubes used in previous experiments had been removed and new ones substituted no conductivity was obtained in rich or lean mixtures of hydrogen-air and acetylene-air. These experiments show that unless total insulation of the electrodes is ensured misleading results may be obtained.

It is also important to make the time of each experiment as short as possible in order to prevent the electrodes from becoming fouled. As an example of the way a small deposit on the electrodes and supporting quartz tubes affects the results, an experiment with hexane-air will be cited. Whilst with a fairly rich mixture of hexane-air with tubes and electrodes completely free from foulness no current could be obtained up to 600° C., with tubes and electrodes which had become fouled through the time taken to make the experiment at 500° C., the displacement on the galvanometer/

galvanometer scale was 180, the indicator of the Ayrton shunt being at 300.

5. Surface Combustion with Platinum Electrodes.

That the presence of platinum had a marked effect on the combustion of the substances in the combustion tube was not at all obvious if the temperature of the tube were taken to be that measured by the platinum-rhodium thermocouple. It was the discovery of this so-called catalysis which led the writer to substitute gold electrodes for the platinum ones. With gold electrodes no surface action was apparent.

The temperature of the middle part of the furnace was measured by a Callendar platinum thermometer reading on a Whipple indicator. On heating the furnace, combustion of the hydrogen-air mixture was observed by the formation of water in the U-tube after the mixture had passed through the combustion tube. The hydrogen was supplied by a cylinder of compressed hydrogen and, after gently bubbling through concentrated sulphuric acid, joined the flow of air from the ten-gallon drum before entering the combustion tube.

The temperature of the furnace as measured by the Callendar platinum thermometer and the temperature of the electrodes as measured by the platinum-rhodium thermocouple were exactly the same until combustion commenced, when the temperature of the electrodes rose rapidly but that of the furnace continued increasing slowly at its former rate. Fig. 11 shows the variation of the temperature of the furnace with that of the electrodes for a 50 per cent. mixture of hydrogen-air. The chemical catalytic action of platinum seems therefore to be due to surface combustion.

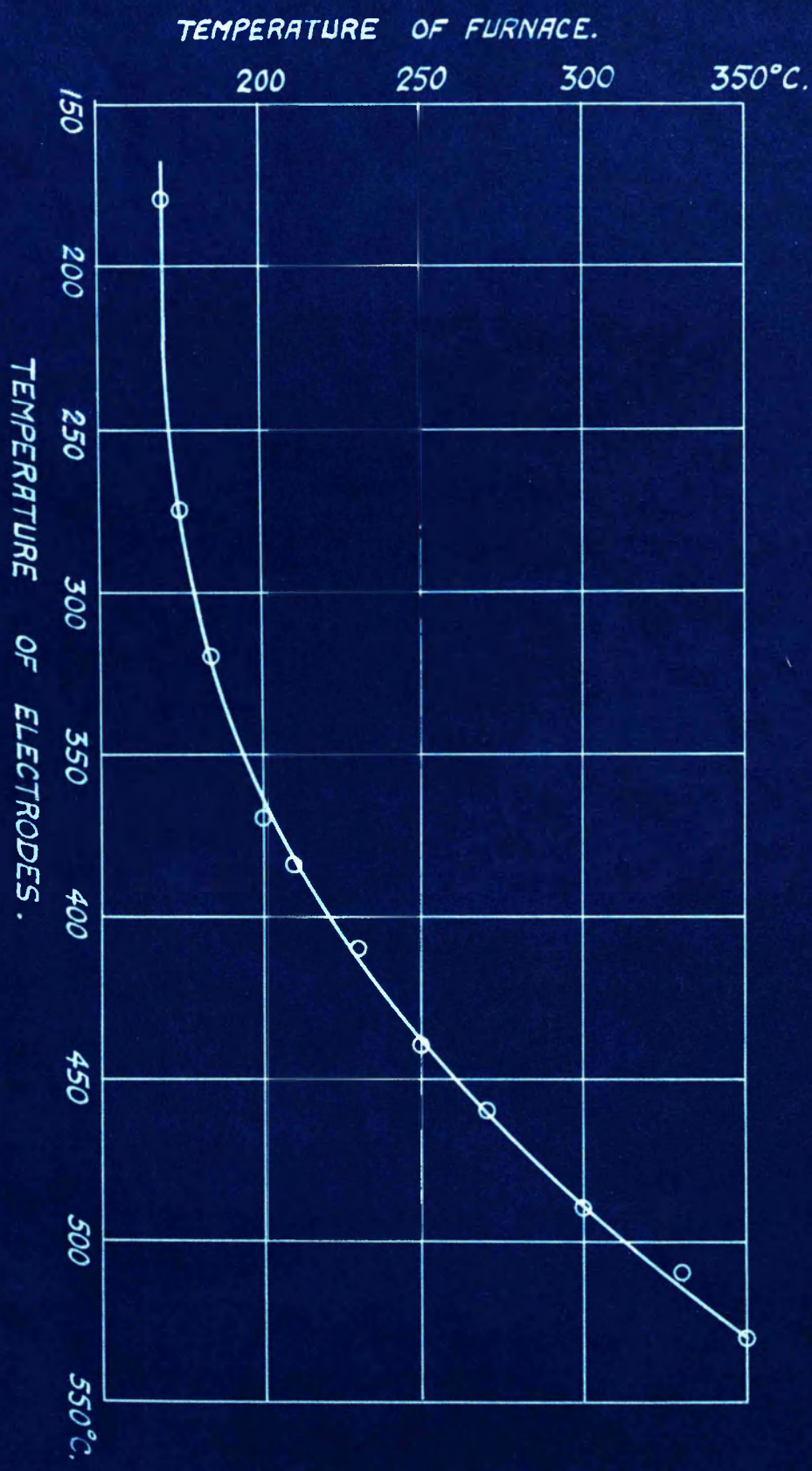


FIG. II.

6. The Electrical Conductivity of Liquid Drops-Air Systems During Incipient Combustion.

The only modification in the apparatus used in the preceding experiments in order to measure the electrical conductivity of liquid drops was that already mentioned. Since rich mixtures of vapour were previously found to be measurably conductive after fog formation it was expected the liquid drops should have the same order of conductivity. This was found to be so; about 300°C. there was a sufficient number of free electrons in the vapour surrounding the drops to cause a measurable current to flow between the electrodes. The temperature of each substance was raised gradually from 300°C. to 500°C. Throughout this range the conductivity increased exponentially with the temperature for each substance. With the tremendous increase of free electrons, the drops must become positively charged to a high degree, but, since they move very slowly relatively to the electrons, the current is due almost entirely to the movement of the free electrons.

Figures 111, 1V, V, and VI, give the experimental results for liquid drops of undecane (b.p. range 198-208°C) and undecane mixed with various organic substances. Experiments with different mixtures of undecane and toluidine were carried out, but no relationship could be obtained between mixture strength and conductivity, though for each mixture strength the conductivity increased exponentially with the temperature as in the above experiments.

7. Influence of Ultra-Violet Radiation.

The combustion tube, made of quartz, was surrounded by a coil of nichrome wire which was used instead of the furnace to heat the tube. Another quartz tube of similar dimensions was placed side by side with its axis at a distance of two centimetres from the axis of the combustion tube. This/

This second quartz tube formed part of a mercury arc lamp supplied by the Hewittic Electric Company Ltd., and was filled with luminous mercury vapour rich in ultra-violet light.

It was found that although the action of the light lowered the temperature of initial combustion, it did not supply enough energy to cause measurable ionization in the case of the combustion of vapours nor did it raise the conductivity of the liquid drops systems to an appreciable extent. At first it was thought to induce considerable ionization after exposure but further experiments showed that during the time of exposure deposits had been formed on the electrodes. The increase of ionization was due to the fouling of the electrodes only.

8. Discussion of Results.

The main conclusions from these experiments are that the slow combustion of a disperse system of liquid drops of various organic substances in air is accompanied by profuse liberation of electrons and that in mixtures of vapours and air comparatively few electrons are present. The importance of these conclusions with regard to internal combustion engines will now be indicated.

It is well known that liquid drops persist in an engine cylinder at temperatures far higher than are required for their evaporation. This effect is due to the increase of pressure necessarily accompanying increase of temperature. A review of this subject has been given by Callendar.¹

Consider one particular volume of the engine cylinder. Suppose the temperature of this volume to be suddenly increased relatively to that of the rest of the cylinder. The liquid drops which exist in this particular volume will evaporate and the substance of which the drops were composed will now exist in the molecular state. The electrons will recombine/

recombine with most of the positive ions into which the drops have been divided, and consequently the quantity U in page 15 liberated will be very large.

The fact that ignition occurs at a lower temperature in mixtures of gaseous fuels containing liquid drops than in a completely vaporised mixture may be accounted for by this supply of energy from the recombination of the electrons and ions. "Detonation", says Callendar¹ "requires the simultaneous ignition of a considerable proportion of the mixture by something uniformly distributed through the mixture itself". It is probable that such ignition may be started in detonation of the nuclear type by the source of self-ignition explained by the present experiments.

FIG. III.

Undecane and Miscellaneous Antiknockers -

- | | |
|---|---------------------------------------|
| A | Undecane plus trace of iron carbonyl. |
| B | do. do. saturated solution of iodine. |
| C | do. |
| D | do. do. 10% carbon-disulphide. |

FIG. IV.

Undecane and Nitrogen Compounds -

- | | |
|---|-------------------------------|
| E | Nitrobenzene. |
| F | Nitroxylol. |
| G | Undecane. |
| H | do. plus 10% phenylhydrazine. |
| J | do. do. nitroxylol. |
| K | do. do. nitrobenzene. |

FIG. V.

Undecane and aromatic bases and phenols -

- | | |
|---|---------------------------|
| L | Cresol. |
| M | Undecane plus 5% aniline. |
| N | do. do. phenol. |
| O | do. do. 10% xylidine. |
| P | do. do. 10% toluidine. |
| Q | do. |
| R | do. do. 10% cresol. |

FIG. VI.

Undecane and Alcohols -

S Benzyl alcohol.
T Undecane plus 10% ethyl alcohol.
U do. do. do. benzyl alcohol.
V do.
W do. do. do. amyl alcohol.
X Ethyl alcohol.
Z Amyl alcohol.

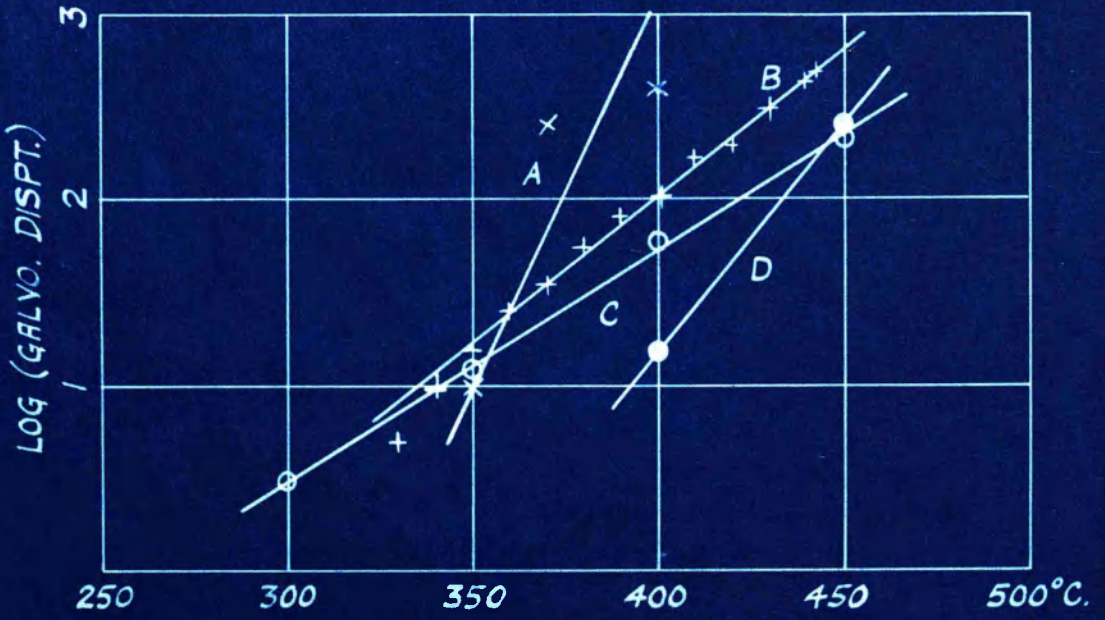


FIG. III.

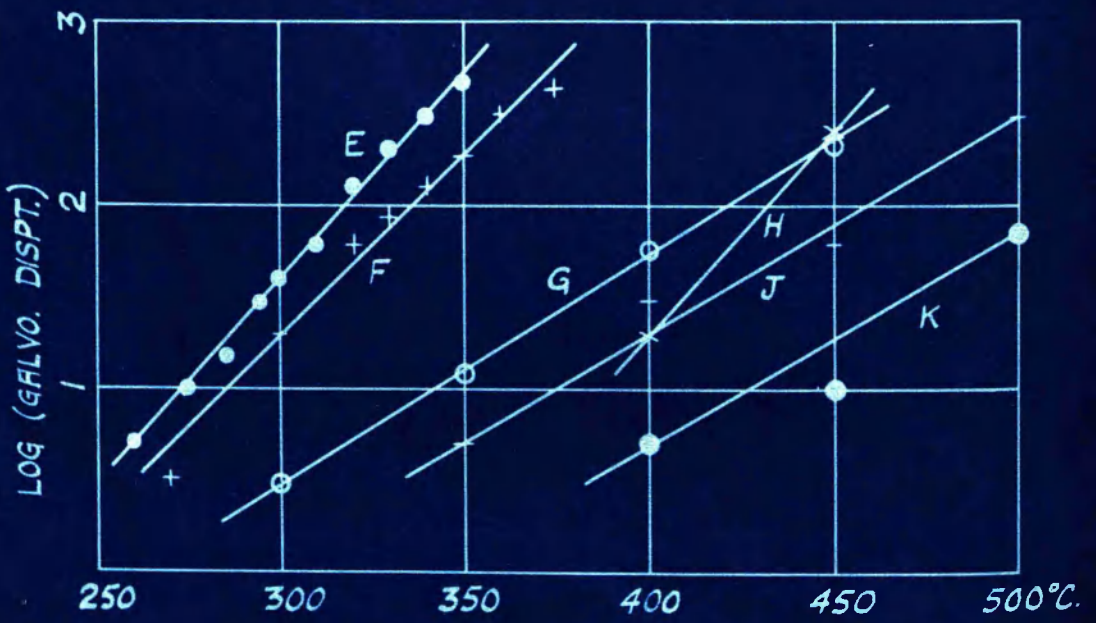


FIG. IV.

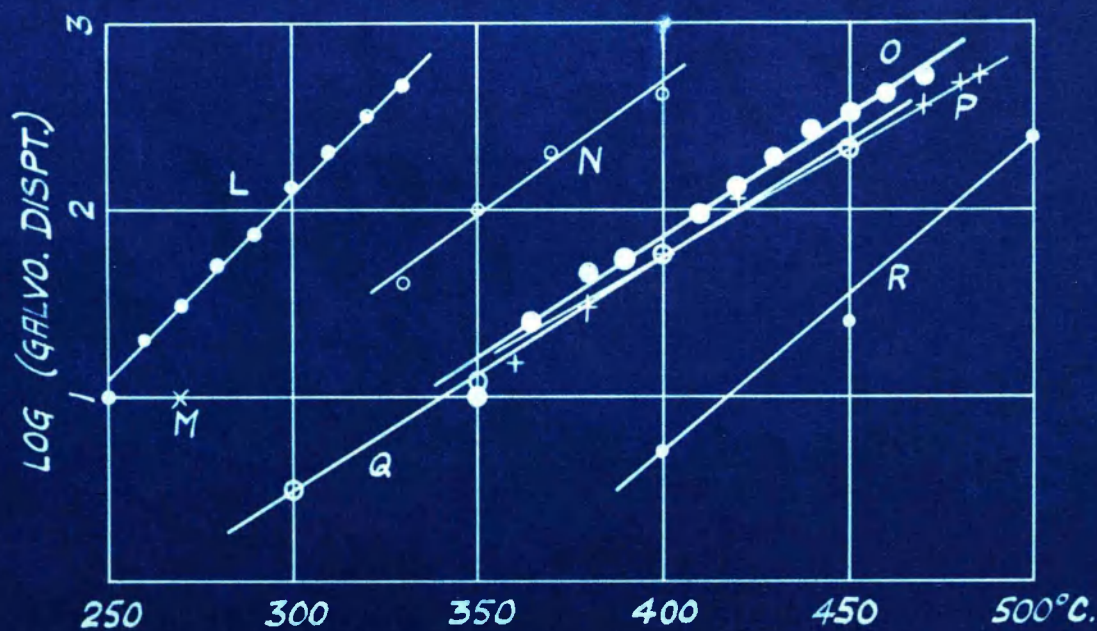


FIG. V.

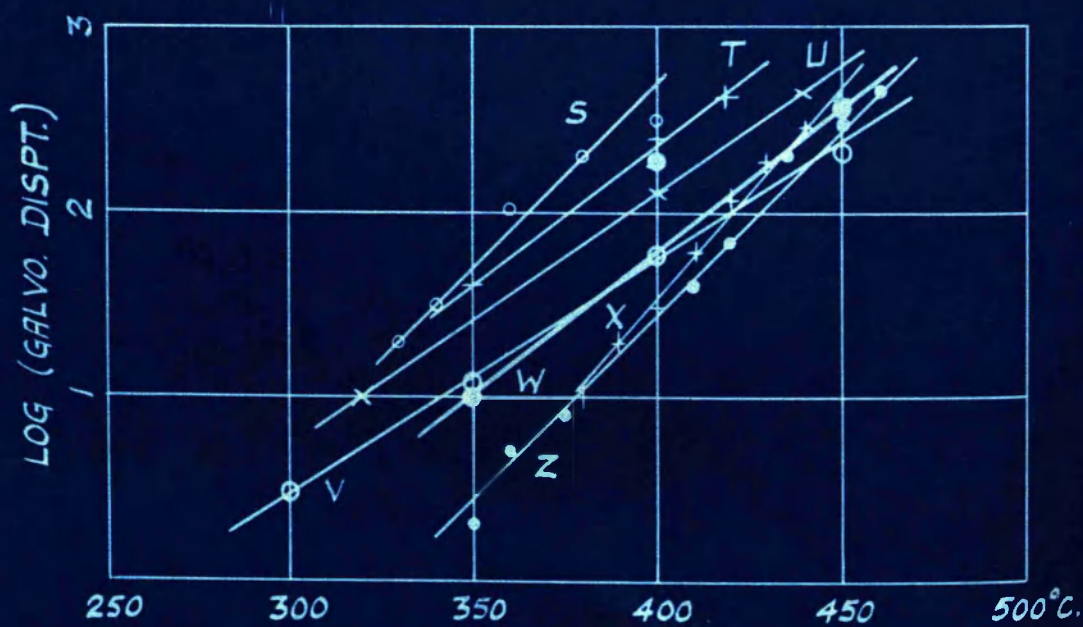


FIG. VI.

P A R T 3.

IONIZATION AND CHEMICAL CHANGE DURING SLOW COMBUSTION.

1. Ionization and Slow Combustion.

Although it is well known that flames are highly ionized it does not appear certain whether slow combustion is accompanied by any liberation of electrons since the high temperatures at which most gases become conducting are not attained.

During the period of incipient oxidation which precedes combustion important changes occur in the gas mixture rendering the mixture highly sensitive to inflammation. Thus, Bone, Fraser and Witt¹ have recently demonstrated that with mixtures of methane and oxygen when an electric spark is passed, there is a definite lag or induction period followed by the propagation of a "ghost-like flame" through the mixture before main combustion occurs; with a condenser discharge-spark, of 8 microfarads at 1000 volts, combustion immediately started with an intense luminosity in the region of the spark where strong ionization would occur.

Experiments conducted by passing gas mixtures through heated tubes to determine whether there was any difference in the spontaneous ignition temperature and degree of peroxidation of a system of liquid droplets and vapour respectively in air showed that not only with the drops did the mixture catch fire at a considerably lower temperature but inflammation occurred at still lower temperatures in tubes in which inflammation had just occurred, indicating that something remained in the tube from the burnt gases to sensitize the fresh mixture.

Subsequently/

¹ Proc. Roy. Soc., A. 114, 442, 1927.

Subsequently it was found that ionization occurred more extensively and at lower temperatures with the system of droplets during slow combustion than with the vapours, when ionization only became appreciable at the temperature of inflammation.

The possible importance of ionization on the propagation of the flame was suggested by Sir J.J.Thomson who pointed out that electron emission from the flame front into the adjacent unburnt gas layers would prepare the way for the flame, and recently considerable attention has been paid to ionization in the internal combustion engine where detonation in the familiar form of "knocking" or "pinking" occurs with certain classes of fuels with the accompaniment of intense ionization. The hypothesis that "anti-knockers" such as lead tetra ethyl or iron carbonyl absorb electrons has been tested,^(2,3,4,& 5) and it would appear that the large ionization value and radiant energy emission, although an accompaniment, is not the cause of detonation.

The important part in detonation that can be played by electrons follows from H.L.Callendar's nuclear drop theory which in brief accounts for the "knocking" in the petrol combustion engine by the spontaneous ignition of the system of droplets of fuel separated during compression.^{6,7} The electrons could act as nuclei for the condensate so that the gas mixture is dispersed with electrified droplets at the surface of which combustion begins. The electric charge would also tend to increase the specific surface and to lower the vapour pressure,⁸ whilst also sensitising the molecule to chemical change. Thus Lind & Bardwell have shown⁹ that complete/

² Wendt and Grimm, J.Ind. & Eng.Chem., 1924, 16, 890.

³ Clark, Brugmann & Thee, *ibid.*, 1925, 17, 1226.

⁴ Garner & Saunders, Trans. Far.Soc., October, 1926.

⁵ Bennett, *ibid.*, 1927.

⁶ Callendar, Aer.Res.Comm., R.& M. No.1013, 1925.

⁷ Callendar, King, Mardles, Stern and Fowler, "Engineering", Feb. 1927.

⁸ J.J.Thomson, "Conduction of electricity through gases", 1903, p.149 seq.

⁹ J.Amer.Chem.Soc., 1926, 48, 2335.

complete oxidation of methane occurs readily in the presence of gaseous ions produced by alpha particles.

When a mixture of hexane vapour or acetylene in air is passed through a heated glass tube at a temperature below its inflammation point but with occurrence of combustion a mist of pungent odour is formed and the mist persists after passing through absorption apparatus designed to collect the products of slow combustion. The mist becomes densely grey-white when ultra-violet radiation passes into the reacting gases and the mist formation and liberation of electrons appear to be simultaneous.

The following results (Table 1) were obtained with a fine spray in air of (a) cymene, b.p. 174° - 176°C ., (b) amyl ether, in presence of ultra violet light.

TABLE 1.

(a) <u>Temp.</u>	<u>Observation.</u>	(b) <u>Temp.</u>	<u>Observation.</u>
275°C	Incipient oxidation indicated by formation of aldehydes and peroxides.	120°C .	Incipient oxidation indicated by formation of aldehydes and peroxides.
300°	Ionization with the accompaniment of a white fog first observed.	300°	Ionization first observed; carbon dioxide in appreciable quantity also observed; pronounced fog.
450°	Very dense white fog and pronounced ionization; combustion occurring with formation of carbon dioxide, etc.	516°	Ignition.
571°	Ignition.		

Similar results have been obtained with undecane⁵ and it was concluded that the presence of liquid drops during slow combustion causes a tremendous number of free electrons to exist in the gaseous medium containing/

containing the drops. Only slight ionization was observed with most of the dilute mixtures when the mist formation was not so apparent and this raised the question as to whether ionization was due to the development of surface ¹⁰ the drop forming a home for the electrons or whether the mist resulted from the condensation of the products of slow combustion on electrons produced.

Numerous experiments have been carried out from time to time by various workers to investigate whether electrons are liberated during gaseous reactions. The results are not conclusive although it appears that with the use of very sensitive apparatus slight ionization has been detected but the order of magnitude is very much lower than in flames.

A. Pinkus ¹¹ found no ionization with nitric oxide and oxygen but observed some with nitric oxide and chlorine whilst more recently Trautz and Henglein ¹² in a paper entitled "The Constancy of electrical conductivity of gases during chemical reactions" concluded that the ionization observed by Pinkus was adventitious and that during gaseous reactions at moderate temperatures even when the heat of reaction is great no free electrons are produced.

A. K. Brewer ¹³ has observed ionization during the catalytic oxidation of a number of organic substances, e.g., xylene, acetone, alcohol etc.

The following experiments show that slow combustion is accompanied by ionization in some cases even when there is apparently absence of liquid drops as for example with carbon monoxide and air.

The main apparatus (Fig. 1) and methods employed have already been described⁵ Small square gold electrodes, 5 m.m. side; 5 m.m. apart were fixed in the stream of gas mixture which was passed through the heated glass tube 12 m.m. diameter.

With/

¹⁰ Cf., Simpson, 1909, Phil. Trans. A, 209, 379.

¹¹ Helv. Chim. Acta. 1910, 1, 141.

¹² Zeit. anorg. chem., 1920, 110, 237.

¹³ Proc. Nat. Acad. of Sciences, 1926, 12, No. 9, 560.

With a rising temperature the point at which combustion began was made evident by the formation of oxidation products such as water, carbon dioxide or peroxides. Not until combustion began, at least, was movement on the galvanometer scale observed and with some mixtures, especially the more dilute, ionization to any appreciable extent occurred only at high temperatures approaching those of the flame.

TABLE 11.

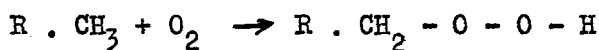
Mixture	Percentage of Vol.	Temp. of Incipient Combustion.	Temp. of initial appreciable ionization.
Hydrogen-air	50% H ₂	615°C	650°C
Acetylene-air	2.5% acet.	550°C	620°C
do.	20% acet.	405°C	450°C
do.	50% acet.	370	375
Ether-air	Rich in ether.	145	350
do.	10% ether.	173	400
Carbonmonoxide-air	48.5% CO.	465	500
do.	64% CO.	440	465
do.	30% CO.	450	480
do.	9% CO.	460	460
do.	1% CO.	500	500
Carbonmonoxide-hydrogen-air.	22% CO; 11% H ₂	430	430
do.	6% CO; 3% H ₂	445	445
Hexane-air.	30% hexane.	270	450
do.	5% do.	350	650

2. Mechanism of Chemical Reaction during Combustion.

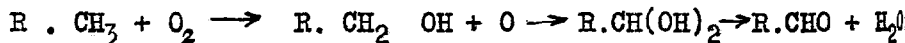
The delay in ionization during the slow combustion of lean mixtures of hexane, hydrogen, etc. until high temperatures were reached might appear to throw some light on the mechanism of chemical reaction during combustion. The scission of the oxygen molecule into atoms



would probably result in profuse liberation of electrons so that hypotheses of oxidation and combustion at moderate temperatures which involve this atomic separation are not so convincing as those in which the oxygen molecule is incorporated as a whole, e.g. as when $O = O$ becomes $- O - O -$ and the formation of alkyl hydrogen peroxide from a hydrocarbon



Bone's hydroxylation theory of the slow combustion of hydrocarbons assumes atomic separation, e.g. in the formation of the intermediate compound $\begin{array}{c} C - O H \\ || \\ C - O H \end{array}$ from acetylene¹⁴ and the intermediate formation of alcohols from hydrocarbons.



The modern conception of the atom consists of a number of electrons continually moving round a central charge of positive electricity. The number and arrangement of the electrons determine the chemical action of one atom on another, the number of electrons in the atom being roughly proportional to the atomic weight. Electrical conduction arises from the drifting of electrons in the direction of the applied electric potential gradient and the energy of heat motion of these "free" electrons increases with the temperature. Richardson¹⁵ has shown that at sufficiently high temperatures this energy is great enough to carry them out through the surface of hot bodies. The emission of electrons by many quite different substances at high temperatures proves that they are a common constituent of all forms of matter.

Electronic emission has been attributed by many writers to chemical action and by others to the purely thermal increase of electron kinetic/

¹⁴ Bone & Andrew, J.C.S., 1905, 87, 1232.

¹⁵ "The emission of electricity from hot bodies", 1921.

kinetic energy, but neither view has been established with certainty. Richardson has fully discussed this question¹⁵ (op.cit.) and the only experiments which can, without obvious objection, be quoted to support the former point of view are, in his opinion, those of Haber and Just.¹⁶ Haber and Just found that when drops of caesium or of liquid alloy of sodium and potassium are attacked, at low pressure, by several chemically active gases, the drops emit electrons. It seems in this case that the electrons are probably liberated by chemical action, the rate of emission being proportional to the chemical action occurring.

Recently Brewer¹⁷ found that ionization occurred during the oxidation of ethyl alcohol vapour at temperatures well below that of ignition where there appears to be no other accompanying phenomena which could give rise to the ionization observed. In his later paper¹³ (Nat.Acad.Sc., September, 1926) Brewer carried out experiments where chemical reaction and ionic emission took place at a hot electrode, the reacting gases being so attenuated that the heat of reaction did not materially affect the temperature of the electrode. These experiments suggest that the gas molecules are ionized at the surface by the combined image and contact forces. Starting at a distance of 10^{-8} c.m. from the surface the ions are thrown out by the processes of emission to a region of weak surface force where it is possible for them to combine with electrons to form neutral molecules, which are then able to escape from the surface region.

3. Correspondence between Ionization and Chemical Action.

The equation $i = AT^{\frac{1}{2}} e^{-a/T}$ (1)

and

$i = BT^2 e^{-b/T}$ (2),

where/

¹⁵ "Ann.der Physik", vol. XXXVI, p.308, 1911.

¹⁷ "Phys.Rev.," 26, p.633, 1925.

where i and T are the current and absolute temperature respectively and A, a, B, b , are constants, are given by Richardson (op.cit.) for the rate of thermionic emission for either positive ions or electrons. These formulae are approximations and although (2) rests on a more solid theoretical basis than (1) there is nothing to choose between them in practice.

A third formula of a similar type may be deduced from the thermodynamic equation used by Saha¹⁸ for calculating the thermal ionization of gaseous elements at high temperatures. Saha's equation has been found to satisfy temperature variation of ionization in flames of alkali salts¹⁹. From p. 140 of the latter paper we have

$$\log_{10} K = - \frac{5048 V}{T} + \frac{5}{2} \log_{10} T - \text{constant},$$

where $K \propto i^2$, V being the ionization potential.

$$\therefore i^2 T^{-5/2} = \alpha e^{-\beta/T}, \text{ where } \alpha, \beta \text{ are constants.}$$

$$\therefore i = CT^{5/4} e^{-c/T} \dots\dots\dots (3),$$

where C, c are constants.

It has been shown⁵ that the ionization during slow combustion in a disperse system of liquid drops - air increases exponentially with the temperature. Equations (1), (2), and (3) satisfy the results of experiments with different systems equally well. The results for under are taken as a typical case (see Fig.11). The formula

$$i = \theta T^\alpha e^{-\phi/T}, \quad \text{where } \alpha = \frac{5}{2}, 4, 2,$$

and θ, ϕ are constants,

therefore satisfies thermionic emission, ionization in flames and ionization in liquid drops-air systems during slow combustion, since in each case, within the limits of experimental error, all points plotted with/

¹⁸ "Phil.Mag.", 40, 478, 809, 1920; 41, 267, 1921.

¹⁹ Bennett, "Phil.Mag.", iii, January, 1927.

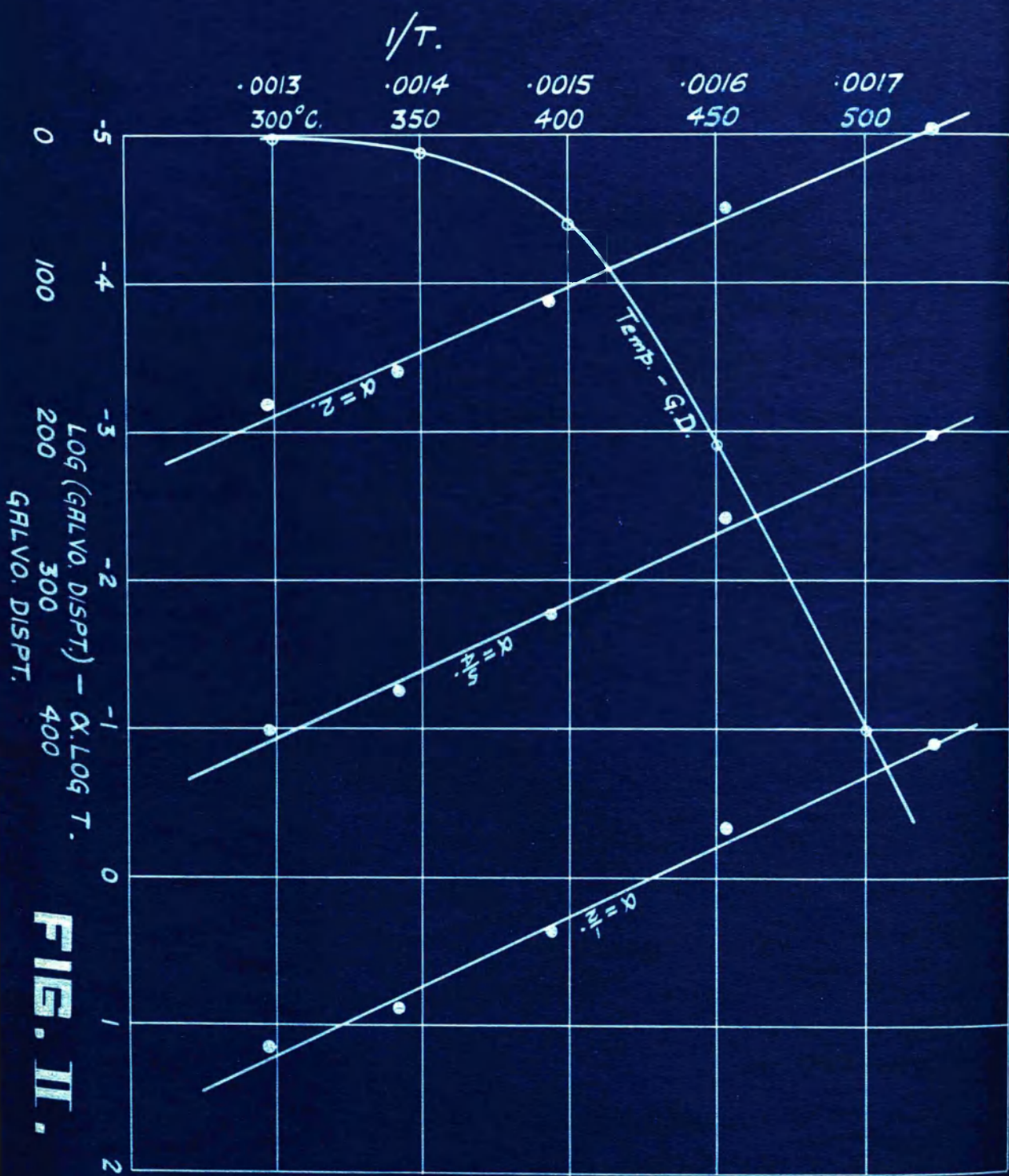


FIG. II.

with axes ($\log i - \alpha \log T$) and $1/T$ fall on straight lines.

The rate of chemical action is expressed by the equation

$$i = \theta T^\alpha e^{-\phi/T}, \quad \text{where } \alpha = \frac{1}{2}, i = \frac{\partial c}{\partial t}.$$

Richardson concluded that since ϕ in the case of chemical action differs from that in the case of thermionic emission the emission cannot be due to chemical action. Brewer¹³ (op.cit.) has now accounted for this difference.

The main features of correspondence between ionization and chemical action are (1) Ionization in gaseous media increases very slowly at first but when once begun it accelerates very rapidly; (2) appreciable ionization occurs whenever combustion becomes appreciable; (3) substances which promote combustion promote ionization; (4) the variation of the rate of thermionic emission, ionization in flames and ionization in liquid drops-air systems during slow combustion and of chemical action with temperature follow the same general law.

In the light of these results it seems very probable that the processes occurring at the beginning of and during combustion are (a) thermionic emission or thermal ionization; (b) as soon as ions are liberated they form centres for chemical activity.

4. Action of Iron Carbonyl, Lead Tetra Ethyl, etc., on slow Combustion and Ionization.

The presence of iron carbonyl, lead tetra ethyl, etc. even in traces, exert a great influence on slow combustion, delaying spontaneous inflammation and altering the temperature at which incipient combustion begins. The formation of higher oxygenated substances which induce autoxidation is inhibited by the presence of the "anti-knockers" the action appearing to depend on the thermal decomposition of these metallic/

metallic compounds yielding metal particles of colloidal dimensions in a highly active state⁷. The metal particles also appear to act a dual capacity of inhibiting peroxide formation and causing accelerated combustion at the metal surface at higher temperatures.

The results obtained in experiments with undecane and hexane with and without iron carbonyl (see Fig.111) show the initial inhibition of chemical change in slow combustion by the decrease in electron emission whilst increased ionization at higher temperatures indicates catalytic action.

Experiments with hydrogen, hydrogen-air mixtures, hexane-air mixtures, coal-gas-air mixtures and acetylene-air mixtures, with and without iron carbonyl, lead ethide and nickel carbonyl, were made at temperatures up to 600°C and in every case the addition of the organic metallic compound was found to increase ionization slightly. By a special device (see Fig.1) only a trace of iron carbonyl etc. was allowed to enter the stream of gases and then only for a few seconds whilst the reading was being taken. With CO-air mixtures there was a rapid movement on the galvanometer scale as the "doped" gas mixture passed across the electrodes followed by a return to the normal reading after the puff had passed. The fouling of the electrodes and tube caused much difficulty in measuring the ionization and they had frequently to be thoroughly cleaned during the experiments.

The mixture 67% CO + 33% H₂ + air gave very striking results. As a puff rich in iron carbonyl was passed through the combustion tube at 500°C . the current passing between the electrodes increased enormously. The actual readings were:-

Temperature/

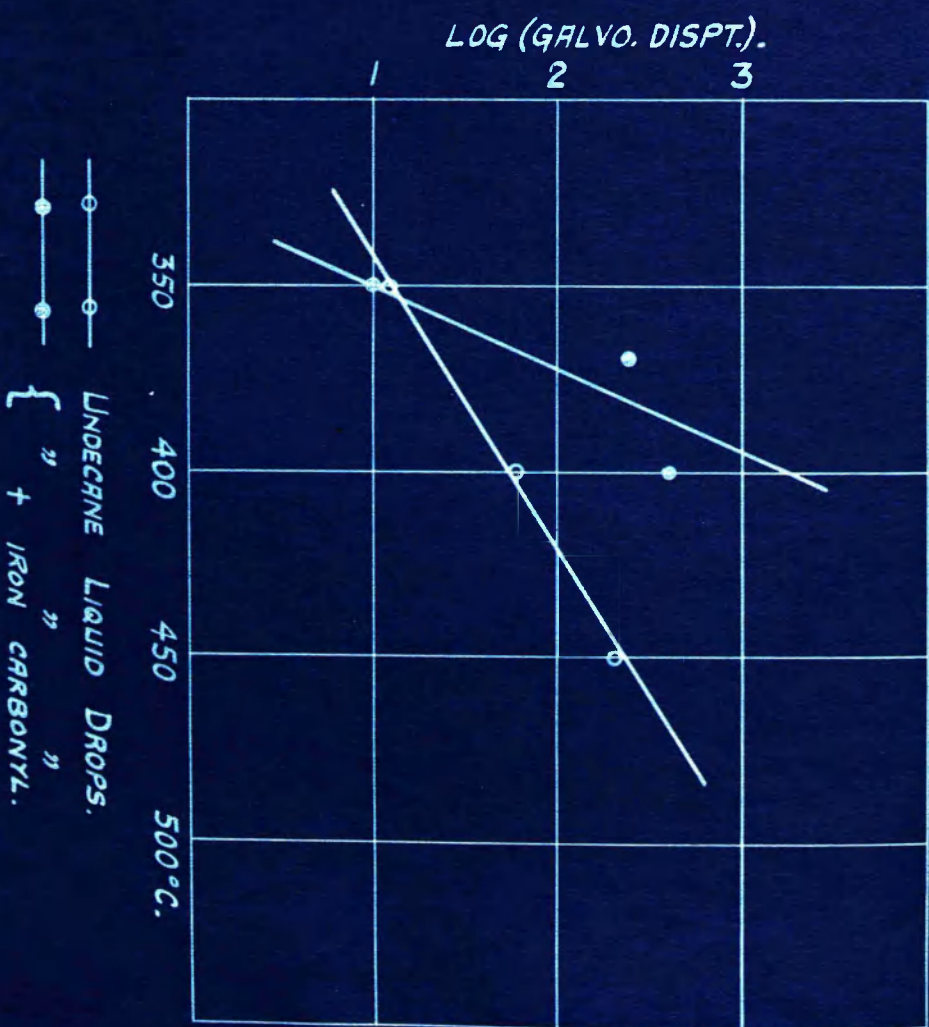
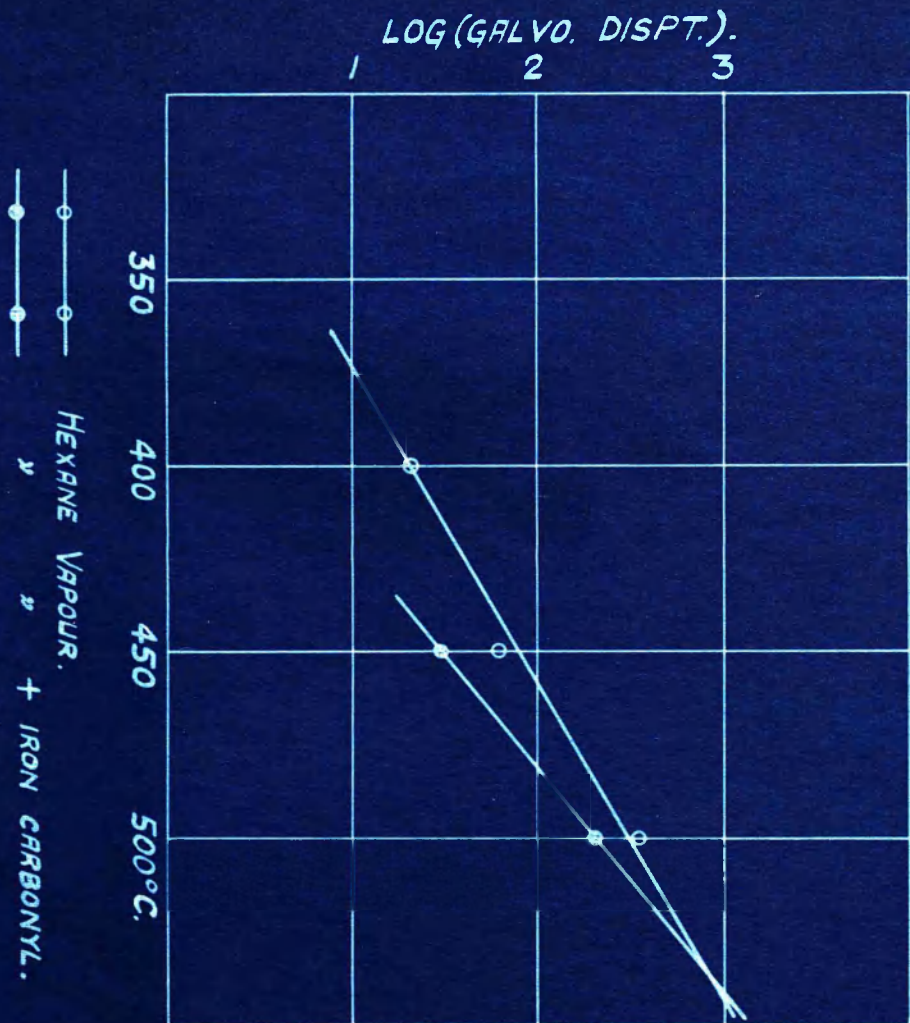


FIG. III.

Temperature.	Galvanometer Displacement.	Remarks.
430°C	3 m.m.	Without Fe (CO) ₅
500°C	25 m.m.	"
500°C	450 m.m. with shunt 100	With Fe (CO) ₅
500°C	35 m.m.	After passage of puff.

It was noticed that (1) the galvanometer reading did not increase suddenly but at first it moved gradually and then rapidly accelerated till when the spot had reached the end of the scale its velocity was very great, (2) after the puff had passed through the tube the conductivity decreased to its former order of magnitude, (3) there was a slight persistence of increased conductivity.

Less striking results were obtained when only a trace of iron carbonyl was present in the gas mixture.

The following are some typical results with the less effective mixtures.

TABLE 111.

Mixture	Strength of mixture.	Temp. °C.	Remarks	Galvanometer Displacement m.m.
Air	100%	up to 650	-	0
do.	do.	do.	with iron carbonyl.	0
Hydrogen	100%	up to 650	-	0
do.	do.	do.	with iron carbonyl.	0
Hydrogen-air	50%	up to 650	-	0
do.	do.	650	with lead ethide	2
do.	do.	do.	with iron carbonyl	5
do.	10%	570	with lead ethide	40
Carbon monoxide -air.	10%	520	-	0
do.	do.	600	-	2
do.	do.	550	with lead ethide	2
do.	do.	600	do.	7
Coal gas - air.	50%	610	-	10
do.	do.	do.	with iron carbonyl	20
Acetylene - air	Weak	up to 470	-	0
do.	do.	470	with nickel carbonyl	1
do.	do.	500	*	-

* On/

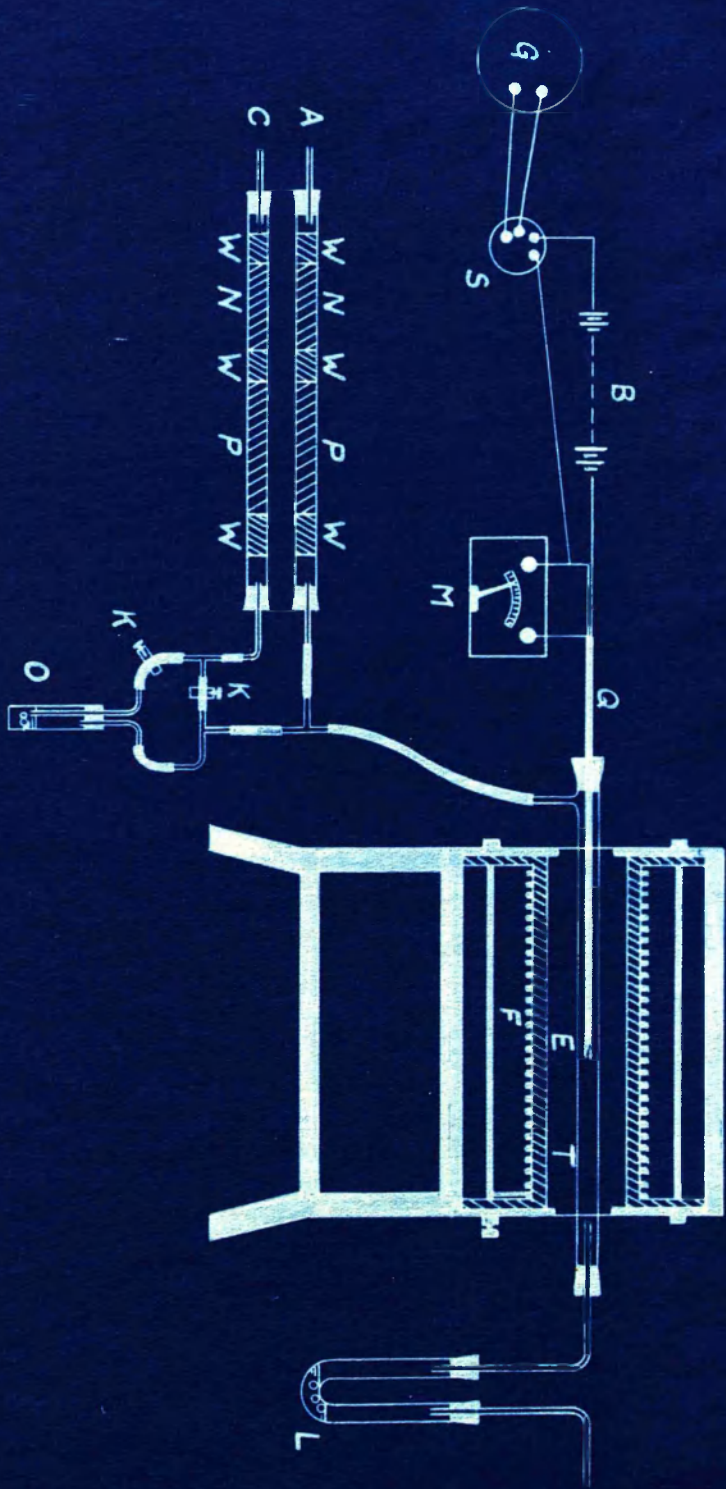


FIG. 1.

* On addition of iron carbonyl temperature rose suddenly to 800°C and mixture exploded.

A mixture of air and iron carbonyl was passed through the combustion tube and did not cause any movement of the galvanometer. The addition of a puff of the H₂ + CO mixture increased the conductivity to a high degree as described before. The temperature was not increased by the puff and it must therefore be concluded that the intense ionization and the chemical action occurring are intimately related.

FIGURE 1.

A Air inlet; B Battery; C Carbon-monoxide-hydrogen inlet; E Gold electrodes and platinum-rhodium thermocouple; F Electric furnace with resistance control; G Galvanometer; K Screw clips; L Lime Water; M Millivoltmeter; N Soda lime; O Organo-metallic compound; P Caustic potash; Q Quartz tubes; S Ayrton shunt; T Combustion tube; W Cotton wool.

5. Summary.

1. The presence of electrons and liquid droplets in the products of slow combustion appear to render the system sensitive to inflammation.
 2. Mist formation and liberation of electrons appear to be simultaneous.
 3. Ionization sometimes accompanies slow combustion especially at higher temperatures and with rich mixtures.
 4. There are several striking features of correspondence between ionization and chemical action.
 5. Substances which promote combustion appear to promote ionization.
-

The above work was prosecuted at the Air Ministry Laboratory, Imperial College of Science and Technology, London, under the supervision of Professor H.L.Callendar, C.B.E., LL.D., F.R.S., and with the help of Dr.E.W.J.Mardles, F.I.C., to both of whom the author is deeply indebted.

"Additional Paper."

"ELECTRICITY

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FLAMES."

BENNETT.

Electricity in Flames. By JAMES A. J. BENNETT, M.A.,
B.Sc., *WilliamHouldsworth Research Student and Carnegie
Research Scholar, University of Glasgow* †.

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PART I.

ELECTRICAL CONDUCTIVITY OF FLAMES CONTAINING
ALKALI SALT VAPOURS.

Introduction.

THE main object of the experiments described in this paper was to find how the electrical conductivity of a Bunsen flame containing alkali salt vapours varies with the temperature.

† Communicated by Prof. E. Taylor Jones, D.Sc., F.Inst.P.

The temperature of the flame was varied by altering the gas supply and by the addition of carbon dioxide. Many papers on the conductivity of salt vapours in flames have been published, but the effect of the temperature of the flame on the conductivity has not hitherto been investigated.

The variation of the electrical conductivity of flames containing salt vapours with the concentration of the salt vapours in the flames has been investigated by H. A. Wilson (Phil. Trans. A, p. 63 (1915)), who found that the variation of the conductivity (c) with the concentration (k) for alkali salts can be represented by the equation

$$\frac{kc}{c^2-1} = b + ac,$$

where a and b are constants for any particular salt at a given temperature.

Most of the previous investigations on the electrical conductivity of flames have been made in an ordinary Bunsen flame the temperature of which is about 2000° K. The methods used in the present experiments are similar to those used by B. T. Barnes (Phys. Rev., Feb. 1924) except that all his measurements were done on a flame at about 2000° K., while in the present experiments the temperature was varied from about 1500° K. to 2000° K.

Description of Apparatus.

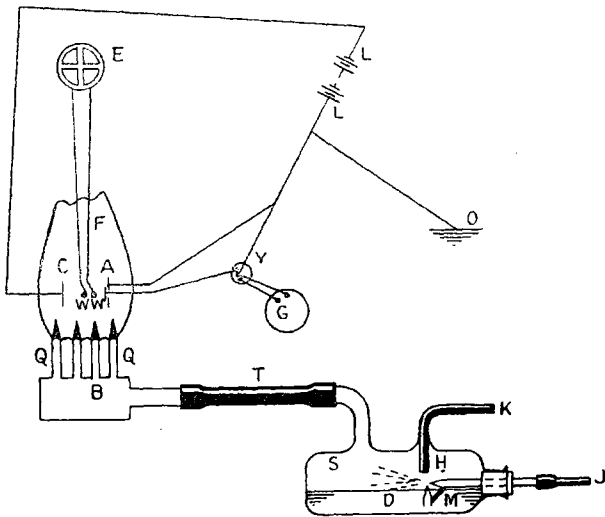
The Burner.—A special burner is used which gives a much steadier flame than other types of burners. It consists of four quartz tubes sealed with sealing-wax to a brass chamber. Fig. 1 shows the arrangement. A short piece of wide rubber tubing connects the burner to a specially constructed glass vessel, hereafter referred to as the sprayer.

The Sprayer.—It will be noticed from fig. 2 that this vessel, besides functioning as a sprayer, is the mixing chamber of air, coal-gas, and carbon dioxide, as well as the fine spray of the liquid being sprayed. Air supplied by an electric pump (P) enters the sprayer which contains a known volume of salt solution, distilled water, or some other liquid. The latter is sprayed in the manner shown in the diagrams. The reason that the rubber tube (H) is led well into the sprayer is to prevent improper mixing of the gas with the air and spray which would otherwise occur. The rubber tube (H) leads the coal-gas and CO₂ into the spray at its source.

The Coal-gas Regulator.—The gas before reaching the sprayer is passed through a regulator consisting of a

cylindrical jar (J) suspended from a balance with its open end downwards. This jar dips into a larger one (W₂) filled with water. An open vertical glass tube surrounded by one of larger diameter is clamped over a small vessel (V) of mercury which rests on the top of the jar (J). The gas enters through the outer tube, which dips well into the mercury, and escapes along the surface of the mercury into the inner tube. The gas is also led into the space within the jar (J). The arrangement is such that, when the gas

Fig. 1.



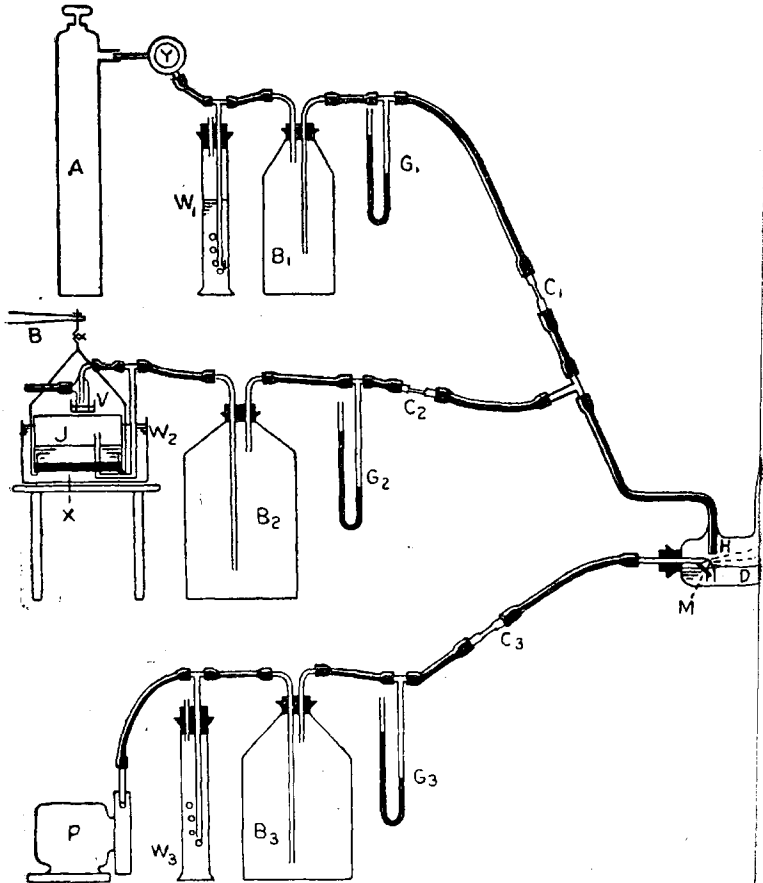
- | | |
|---------------------------|---------------------------|
| A. Anode. | K. Coal-gas inlet. |
| B. Burner. | LL. Battery. |
| C. Cathode. | M. Solid glass connexion. |
| D. Solution sprayed. | O. Earth. |
| E. Quadrant electrometer. | QQ. Quartz tubes. |
| F. Flame. | S. Sprayer. |
| G. Galvanometer. | T. Wide rubber tubing. |
| H. Rubber tubing. | WW. Exploring wires. |
| J. Air inlet. | Y. Ayrton shunt. |

pressure increases, the jar (J) moves upwards, pressing the mercury up against the inner tube and thus allowing less gas to flow. Conversely, when the gas pressure decreases the jar (J) moves downwards allowing more gas to flow.

After leaving the regulator the gas passes through a large bottle (B₂), which smooths out small oscillations in pressure, and in order to increase the sensitiveness of the water

manometer (G_2), which indicates the pressure, the gas passes through a constriction (C_2) before entering the sprayer.

Fig. 2.



A. Cylinder of compressed CO_2 .
 B. Arm of balance.
 B_1, B_2, B_3 . Large bottles.
 C_1, C_2, C_3 . Constrictions.
 D. Salt solution.
 G_1, G_2 . Water manometers.
 G_3 . Mercury manometer.
 H. Rubber tubing.
 J. Cylindrical jar.

M. Solid glass connexion.
 P. Air-supply pump.
 S. Sprayer.
 T. Wide rubber tubing.
 V. Vessel of mercury.
 W_1, W_2 . Jars of water.
 W_3 . Jar of mercury.
 X. Heavy brass ring.
 Y. Regulator.

The Air Supply.—Part of the air supplied by the pump (P) escapes by bubbling through mercury (W_3), thus securing constant pressure. The air supply is regulated by altering the current driving the pump. Any small variations in pressure are removed in the large bottle (B_3), and the pressure is measured by a mercury gauge (G_3) whose sensitiveness is increased by using a constriction (C_3).

The CO₂ Supply.—A cylinder (A) of compressed carbon dioxide is used to lower the temperature of the flame when required. After passing through a regulator (Y), the CO₂ partly escapes by bubbling through water (W_1) to secure constant pressure. Similarly to the coal-gas and the air, the CO₂ passes through a large bottle (B_1) and a constriction (C_1), the water-gauge (G_1) indicating the pressure.

The Flame.—The flame produced by burning the mixture of air, spray, coal-gas, and CO₂ from the quartz tubes (QQ) was very steady. On each quartz tube there was a well-defined inner cone. It is important that these cones should be free from any unsteadiness, and it was only after preliminary experiments with different burners and care in producing a perfect admixture of the gases that the cones refrained from jumping slightly.

The Electrodes.—Two platinum electrodes, made of thick foil, and welded to platinum wires about 1 mm. in thickness, are placed just above the cones in the flame (see fig. 1). The horizontal distance between the electrodes was $3\frac{1}{2}$ cm. The platinum wires are supported by covering them with quartz tubes having a small bore. In this way the platinum wires do not bend with the heat of the flame. Their ends are fused into glass tubes which are supported on stands, the platinum wires being sufficiently long to prevent the ends of the glass tubes getting very hot. The cathode (C) is 1 cm. square, and the anode (A) consists of a disk 4.5 mm. in diameter surrounded by a guard-ring 1 cm. square and inner diameter 5.5 mm. The disk is placed slightly in front of the guard-ring to keep the latter from shielding the disk from the heat of the flame.

Connections.—The electrical connexions are shown in fig. 1. The current from a battery of small cells (LL) is passed between the electrodes. The quartz tubes (QQ) insulate the flame (F). The guarded disk is connected to a galvanometer (G) through an Ayrton shunt (Y); previous preliminary experiments showed that the lines of electric force between the electrodes are practically straight across for a small area, like that of the disk, in the middle of the electrodes. In this way the current passing through a known area of the flame is measured.

The Exploring Wires.—Two fine platinum exploring wires are placed 1 cm. apart in the flame, perpendicular to the direction of the lines of force between the electrodes. These wires are covered with quartz which allows only their tips to be exposed to the flame, the wires being fused to glass tubes supported on a stand. The wires can be moved about between the electrodes, and they are called exploring wires because when they are connected to a quadrant electrometer the potential gradient can be measured at any part of the electric field between the electrodes. The cathode is coated with lime in order to reduce the electrode drop of potentials a discovery made by Tufts in 1904. There is a region between the electrodes where the potential gradient is uniform, and it is in this region that the exploring wires (WW) are placed while measuring the conductivity of the flame. The quadrant electrometer and the battery of 120 volts for charging the needle are supported on a table with ebonite legs.

Measurement of the Temperature of the Flame.

To measure the temperature of the flame by means of a thermocouple is not very satisfactory because the thermocouple is at a lower temperature than the flame itself. The method used in the present experiments is that used by Barnes (*op. cit.*).

A strong solution of a sodium salt was put in the sprayer so that an intensely coloured sodium flame was obtained. White light from a gas-filled tungsten-filament incandescent lamp was passed through the flame, and its spectrum observed in a direct-vision spectroscope which separated the D lines very clearly. The temperature of the filament was adjusted so that the D lines were not visible on the continuous spectrum of the filament. If the filament was too hot the D lines were seen reversed as dark lines, and if too cold they were seen as bright lines. The temperature of the filament when adjusted is that when the D lines were not seen and was measured with an optical pyrometer supplied by the Cambridge Scientific Instrument Company.

The flame is by no means at a uniform temperature, the hottest part being found to be just above the cones. It is here that the electrodes are placed, and it is here that the temperature is measured. Different temperatures are obtained by altering the pressures of gas and CO₂, the air pressure being kept constant, since an alteration in the pressure of air would alter the concentration of salt in

the flame when salt solutions are being sprayed. The following table gives the pressures of air, coal-gas, and CO₂ for the different temperatures measured :—

Temperature (° absolute).	Air pressure (mm. of Hg).	Coal-gas pressure (mm. of H ₂ O).	CO ₂ pressure (mm. of H ₂ O).
1920	90	17	0
1870	90	20	0
1720	90	20	20
1670	90	20	25
1570	90	17	33

These temperatures were measured when sodium-carbonate solution was being sprayed. It is of course assumed that the temperatures remain unaltered when other salt solutions are being sprayed so long as the conditions of spraying remain the same. The pressures of air, coal-gas, and CO₂ were very steady with the apparatus described above, and no difficulty at all was experienced in securing constant pressures.

Measurement of the Velocity of the Flame.

The special apparatus used for measuring the velocity of the flame is shown in fig. 3 and will now be described. A large wheel (W) having four openings (D D D D) round its circumference is mounted on the same shaft as that turning a stop-cock (S) which is open four times in each revolution of the shaft. An electric motor causes the shaft to rotate at about 2000 revolutions per minute; the stop-cock is therefore opened and closed very rapidly.

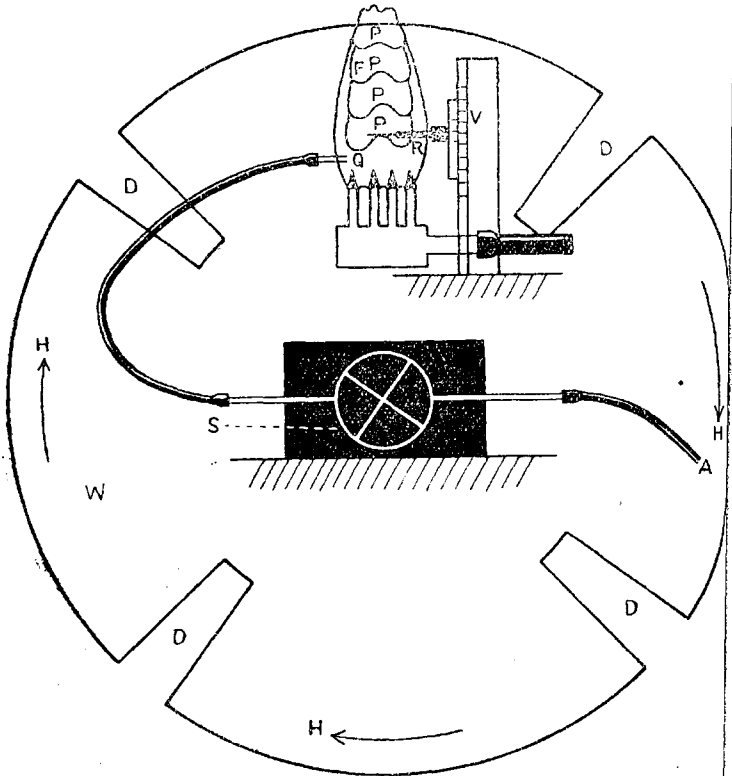
During this experiment distilled water is sprayed so that a non-luminous flame is obtained. A second sprayer containing a saturated solution of sodium chloride causes a mixture of air and vapourized salt (A) to pass through the stop-cock four times in each revolution of the shaft. Thereafter the mixture enters the flame through a narrow horizontal quartz tube (Q) placed at the bottom of the flame.

The wheel (W) rotates in the direction of the arrow-heads (H H H) with the same angular velocity as the stop-cock (S). The flame will therefore be seen as many times per second as the stop-cock is opened, when the flame is viewed through the stroboscopic wheel. By means of a pinch-cock the pressure of air and salt spray can be diminished till the puffs disappear, or increased until the puffs are very luminous.

The shape and position of the puffs can be seen from the diagram.

The flame is shielded from the draught of air caused by the rotation of the wheel by enclosing the latter in a wooden

Fig. 3.



A. Air and spray inlet.
 B. Burner.
 D, D, D, D. Openings on wheel.
 F. Flame.
 P, P, P, P. Puffs of sodium vapour.

Q. Narrow horizontal quartz tube
 R. Fine solid quartz tube.
 S. Stop-cock.
 V. Vernier and vertical scale.
 W. Stroboscopic wheel.

box with glass windows. The distance between the puffs is measured by inserting a fine solid quartz rod in the flame supported on a vertical slide. The slide is provided with a millimetre scale and a vernier.

If v is the upward velocity of the flame in cm. per second, n the number of puffs per revolution of the shaft, r the number of revolutions of the shaft per minute, x the distance between successive puffs in cm., as seen through the stroboscopic wheel, then

$$v = nrx/60.$$

About four puffs could be seen in the flame, the distance between successive puffs being nearly the same. The velocity of the flame was measured in this way for each temperature given in the preceding section. The values given in the following table are mean values obtained from a number of readings.

Temperature of Flame (° K.).	Velocity of Flame (cm. per sec.).
1920	422
1870	419
1720	394
1670	387
1570	392

Amount of Salt in the Flame.

The amount of salt per c.c. in the flame depends on (1) the amount of solution sprayed per second; (2) the upward velocity of the flame; (3) the cross-section of the flame. In the previous section we have determined (2) for each temperature. With regard to (3), since the flame is rectangular just above the cones the cross-section can easily be measured. The following table gives the results obtained:—

Temperature (° K.).	Cross-section of Flame (sq. cm.).
1920	$2.5 \times 5.3 = 13.2$
1870	$2.6 \times 5.4 = 14.0$
1720	$2.1 \times 5.2 = 10.9$
1670	$2.0 \times 5.2 = 10.4$
1570	$2.0 \times 5.1 = 10.2$

We have now to consider (1). Since the air pressure on the sprayer is kept constant throughout the experiment the volume of solution sprayed per second remains constant, no matter which solution is being sprayed. The method used for determining the volume of solution sprayed per second is the same as that of Barnes (*op. cit.*).

One hundred c.c. of sodium chloride solution, not necessarily of known strength, is put in the sprayer and sprayed for three hours under constant air pressure (viz. 90 mm. of Hg). The contents of the sprayer are then emptied into a beaker, and care is taken to see that no solution is left in the wide rubber tubing (T, fig. 1) and the burner. The latter are therefore washed out with distilled water, which is then emptied into the beaker.

One hundred c.c. of the sodium chloride solution is titrated with a solution of silver nitrate (not necessarily of known strength), and it is found that a volume V_1 of silver-nitrate solution is just sufficient to neutralize the sodium-chloride solution. If a volume V_2 of the same silver-nitrate solution is just sufficient to neutralize the contents of the sprayer, etc., in the beaker, after spraying, then the fraction of the salt sprayed = $1 - \frac{V_2}{V_1}$.

It is quite wrong to weigh the sprayer and burner before and after spraying to obtain the amount of solution sprayed, because when the solution is sprayed for a long time considerable evaporation takes place. In the experiments to be described later, when solutions of different salts are sprayed, the quantity of solution placed in the sprayer is always 100 c.c., in order that the conditions of spraying should be the same as when the present experiment was performed.

The number of litres (V) of solution entering the flame per second is given by the equation :

$$V = \left(1 - \frac{V_2}{V_1}\right) \frac{100}{3600 \times 3 \times 1000}$$

$\left(1 - \frac{V_2}{V_1}\right)$ was found to be .1026.

We have now considered (1), (2), and (3), and are in a position to determine the amount of salt per c.c. in the flame. Let m denote the number of gram-molecules of metal vapour per c.c. in the flame, k the concentration of solution sprayed into the flame in gram-molecules per litre, G a constant for any particular temperature ; then

$$m = Gk.$$

G is determined from the velocity (v) of the flame-gases in cm. per sec., the cross-section (a) of the flame in square cm., and the number of litres (V) of solution entering the flame per second. Thus

$$G = V/av.$$

The following table gives the values of G calculated from this equation from the values of V , a , v already given :—

Temperature.	$10^{10} G$.
1920	1.71
1870	1.62
1720	2.21
1670	2.36
1570	2.37

Since G has now been determined, m is known for any concentration (k) of solution sprayed.

Specific Conductivity of the Flame.

If i amperes is the current measured by the galvanometer, X volts per cm. the potential gradient measured by the electrometer, A square cm. the area of the guarded electrode, the specific conductivity (s) is given by the equation :

$$s = \frac{i}{AX} \text{ amperes per sq. cm./volts per cm.}$$

The method of making an experiment to measure the specific conductivity of the flame will now be described. The burner and sprayer are removed and washed out with distilled water. They are then replaced and thoroughly dried by air supplied by the electric pump (P). One hundred c.c. of distilled water, measured by a pipette, are inserted in the sprayer. The coal-gas is then turned on and lighted. Air is supplied until the mercury pressure gauge registers 90 mm., and as the air pressure gradually increases the cones in the flame begin to appear and then grow smaller and smaller. The flame when distilled water is sprayed is a non-luminous one, very different from the flame when ordinary undistilled water is sprayed which contains salt in small quantities, colouring the flame. The electrodes become intensely luminous, the guarded disk of the anode being less bright than the rest of that electrode unless the guarded disk is placed slightly in front of the latter, as shown in fig. 1. This shows that the guard-ring had a tendency to shield the disk from the heat of the flame. When the pressures of coal-gas and CO_2 are adjusted to the various temperatures, readings of the galvanometer and quadrant galvanometer are taken. The flame is then extinguished.

The burner and sprayer are removed as before, washed out with distilled water, and thoroughly dried by air. One hundred c.c. of the solution to be sprayed are inserted in the sprayer and, as in the case when distilled water was sprayed, galvanometer and electrometer readings are taken at each temperature.

The measurement of the conductivity of the flame when distilled water is sprayed before each measurement of the conductivity of the flame when salt solutions are sprayed serves a double purpose. Its first use is as a gauge of the constancy of the apparatus. Secondly, to obtain the conductivity of the vapourized salt in the flame it is necessary first to obtain the conductivity of the flame without salt, but without altering the flame in any other way. The spraying of distilled water gives the flame the same vapour content as when salt solutions are sprayed.

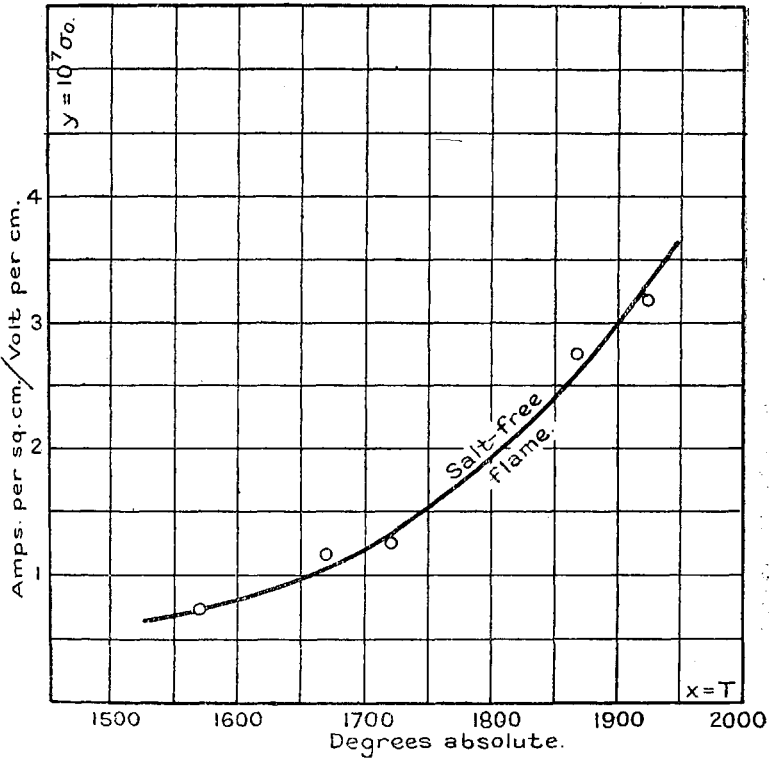
*Variation of the Conductivity of the Flame without Salt
with Temperature.*

Since the conductivity (σ_0) of the flame without salt was measured before each experiment on the conductivity (σ) of the salted flame, a considerable number of values of σ_0 were obtained. The curve shown in fig. 4 is therefore an average one, and the values indicated on the diagram by small circles are the average of the total number obtained during the course of the experiments. They are given in the following table:—

T.	$10^7 \sigma_0$.
1920	3.19
1870	2.74
1720	1.28
1670	1.13
1570	0.73

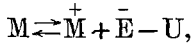
Throughout this paper the temperatures are expressed in degrees absolute and the conductivities in *amperes per square cm. per volts per cm.* It will be noticed that the conductivity of the flame increases with the temperature in accordance with the theory that the flame gases are ionized, electrons and positive ions being formed, and that there is equilibrium between these electrons and positive ions and those flame atoms which are not ionized.

Fig. 4.



Calculation of the Ionization Potential of Salt-free Flame from Temperature Variation.

Saha showed (Phil. Mag. vol. xl. p. 478 (1920)) that the thermal ionization of the neutral atoms (M) of gaseous elements into positive ions (M^+) and electrons (E^-) is a sort of chemical reaction satisfying the equation :



where U is the quantity of energy absorbed in the process. The electron is assumed to be a monatomic gas of atomic weight 1 836. The energy U can be expressed in terms of the ionization potential (V), which is the potential required to give an electron enough energy to ionize a neutral atom. If N is Avogadro's constant,

$$U = (VeN)/(J \cdot 300) = 2.302 \times 10^4 V \text{ calories.}$$

Since $2.302 \times 10^4 / 4.571 = 5048$, Saha's thermodynamic equation

$$\log_{10} K = -\frac{U}{4.571T} + 2.5 \log_{10} T - 6.56,$$

where K is the ionization equilibrium constant, becomes

$$\log_{10} K = -\frac{5048V}{T} + 2.5 \log_{10} T - 6.56. \quad (1)$$

If K_{01} and K_{02} are two values of the ionization constant for the flame gases at temperatures T_1 and T_2 respectively,

$$\log_{10} (K_{02}/K_{01}) = 5048V_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + 2.5 \log_{10} \frac{T_2}{T_1}, \quad (2)$$

V_0 being the ionization potential for the salt-free flame.

Let \bar{p}_0 denote the partial pressure due to the electrons in the flame without salt, $\overset{+}{p}_0$ that due to the positive ions, and p_0 that due to the neutral atoms. If K_0 is the ionization constant for the salt-free flame,

$$K_0 = \frac{\bar{p}_0 \overset{+}{p}_0}{p_0} = \frac{(\bar{p}_0)^2}{p_0}, \text{ since } \bar{p}_0 = \overset{+}{p}_0.$$

$\bar{p}_0 = \overset{+}{p}_0$ because the number of electrons in the flame is equal to the number of positive ions, and the partial pressures are proportional to the number of ions present. The conductivity (σ_0) is proportional to the number of electrons present, the conductivity due to the positive ions being negligible because their mobilities are so small compared with those of the electrons. Therefore

$$\bar{p}_0 = A\sigma_0,$$

where A is a constant inversely proportional to the velocity of the electrons,

for if the number of electrons is kept constant the conductivity would only increase by an increase in the velocity of the electrons. It is shown in Part III. that the velocity of the electrons is nearly independent of the temperature. A is therefore almost constant for different temperatures.

If \bar{p}_0 is small compared with p_0 , we have

$$K_0 \propto \sigma_0^2.$$

Equation (2) now becomes

$$2 \log_{10} \frac{\sigma_{02}}{\sigma_{01}} = 5048V_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + 2.5 \log_{10} \frac{T_2}{T_1}. \quad (3)$$

Putting

$T_1 = 1920$, $T_2 = 1570$, $\sigma_{01} = 3.19 \times 10^{-7}$, $\sigma_{02} = 0.73 \times 10^{-7}$, the value of V_0 obtained is found to be 1.8.

Amps. per sq. cm. / Volt per cm.

Using this value of V_0 , K_0 can be calculated for different temperatures from equation (1). The following table gives the results obtained :—

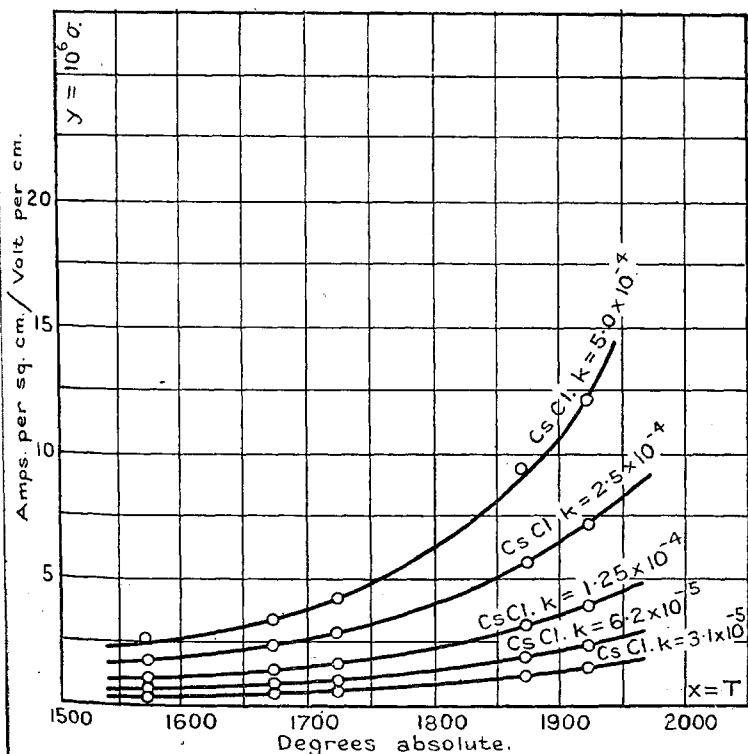
T.	$10^4 K_0$.	$10^{-4} K_0^{3/2} / \sigma_0 = \text{const.}$
1920	7.95	8.8
1870	5.50	8.5
1720	1.62	9.9
1670	1.05	9.1
1570	0.40	8.6

Since the last column in the table is nearly constant, the value 1.8 for the ionization potential of the salt-free flame holds good for a temperature variation of 350 degrees.

Variation of the Conductivity of Cæsium Chloride and Rubidium Chloride with Temperature and Concentration.

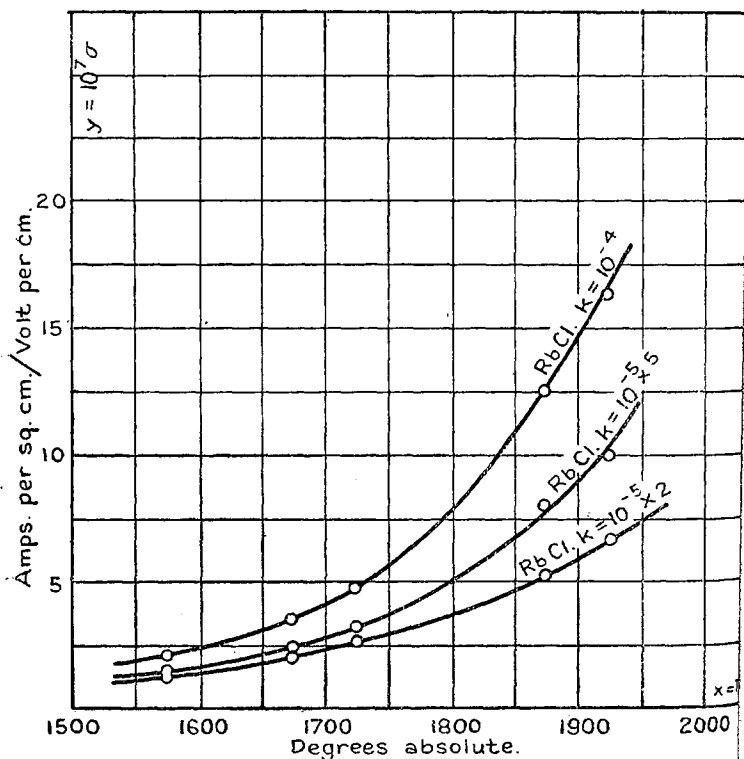
Figures 5 and 6 show the variation of the conductivity of the flame containing various salts in different concentrations

Fig. 5.



with the temperature. By comparing these curves with that for the salt-free flame (fig. 4) it will be noticed that the conductivity of the salt-free flame is several times less than the conductivity of a flame containing the spray of a very

Fig. 6.



dilute solution of salt. The following tables give the results obtained, k being the concentration of the solution sprayed in gram-molecules per litre :—

T.	CsCl.				
	$10^6 \sigma.$				
	$k = 31 \times 10^{-4}$.	$k = 62 \times 10^{-4}$.	$k = 1.25 \times 10^{-4}$.	$k = 2.5 \times 10^{-4}$.	$k = 5.0 \times 10^{-4}$.
1920 ...	1.45	2.37	3.81	7.13	12.1
1870 ...	1.35	1.83	3.13	5.61	9.3
1720 ...	0.69	1.11	1.69	2.91	4.22
1670 ...	0.58	0.87	1.32	2.39	3.40
1570 ...	0.46	0.76	1.03	1.75	2.55

RbCl.

$10^7 \sigma$.

T.	$k=2 \times 10^{-5}$.	$k=5 \times 10^{-5}$.	$k=10 \times 10^{-5}$.
1920	6.50	9.83	16.35
1870	5.28	8.10	12.60
1720	2.58	3.18	4.67
1670	2.00	2.45	3.40
1570	1.25	1.45	2.00

PART II.

THE THERMAL IONIZATION OF GASEOUS ELEMENTS AT HIGH TEMPERATURES—A CONFIRMATION OF THE SAHA THEORY.

H. A. Wilson's equation, viz.,

$$\frac{kc}{c^2 - 1} = b + ac,$$

is obtained in the following way, under the assumptions that both the salt and some constituent of the flame are ionized and that there is equilibrium between the electrons and positive ions formed and the neutral atoms (atoms not ionized). If K , K_0 are the ionization equilibrium constants for the salt and flame constituent respectively,

$$K = \frac{p^+ \bar{p}}{p}, \quad \dots \dots \dots (1)$$

$$K_0 = \frac{p_0^+ \bar{p}_0}{p_0}, \quad \dots \dots \dots (2)$$

p^+ , \bar{p} , p , p_0^+ , p_0 being the partial pressures respectively due to the positive salt ions, the electrons, the neutral salt atoms, the positive flame ions, and the neutral flame atoms. As pointed out in a preceding section, the conductivity is proportional to the number of electrons present, and therefore, if c is the ratio of σ to σ_0 , A a constant,

$$Ac = \bar{p} = p^+ + p_0^+, \quad \dots \dots \dots (3)$$

since the number of electrons is equal to the number of positive ions.

Assuming, as before, that \bar{p} is small compared with the total pressure, we have

$$p + p^+ = mRT, \quad \dots \dots \dots (4)$$

where R is the gas constant for one gram-molecule. From a preceding section we have

$$m = kG. \quad \dots \dots \dots (5)$$

From (1)
$$p = \frac{p_0 \bar{p}}{K};$$

therefore (4) becomes

$$\frac{p}{p_0} = \frac{kGRT}{\left(1 + \frac{\bar{p}}{K}\right)};$$

also, from (2),

$$\frac{p}{p_0} = p_0 K_0 / \bar{p};$$

substituting for $\frac{p}{p_0}$ and $\frac{p}{p_0}$ in (3), we get

$$Ac = kGRT / \left(1 + Ac/K\right) + p_0 K_0 / Ac. \quad (6)$$

When $k=0$, $c=1$; therefore $p_0 K_0 / A = A$.

Therefore (6) becomes

$$\frac{kGRT}{(Ac - A/c)} = 1 + Ac/K,$$

or
$$kc / (c^2 - 1) = A/GRT + cA^2 / GRTK.$$

Putting
$$b = A/GRT, \quad a = A^2 / GRTK,$$

$$kc / (c^2 - 1) = b + ac,$$

and

$$K = b^2 GRT / a. \quad (7)$$

Since a and b are constants for any one temperature $kc / (c^2 - 1)$ is a linear function of c . The curve represented by Wilson's equation will therefore be a straight line, the ordinates and abscissæ being respectively $kc / (c^2 - 1)$ and c .

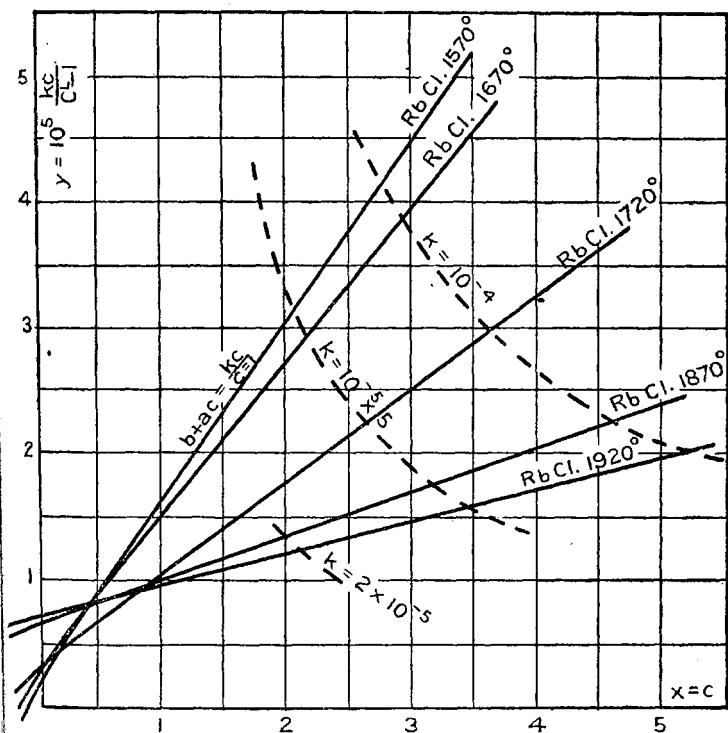
If the straight line be produced backwards to meet the $kc / (c^2 - 1)$ axis, b will be the ordinate at $c=0$. a will be the slope of the line. In order to obtain b accurately we must use small values of c , and therefore the solutions sprayed must be very dilute; but if c is so very small that $c^2 - 1$ is very small, the error in $kc / (c^2 - 1)$ will be very great. Hence those values of c which are very small are of little use to calculate b accurately.

The results which were obtained with rubidium chloride were considered the best for calculating b . H. A. Wilson showed in 1915 (*op. cit.*) that b is proportional to the molecular weight of the salt. For this reason the b 's of NaCl, KCl, and LiCl are too small to be calculated with any degree of accuracy.

Fig. 7 shows the straight lines represented by Wilson's equation obtained from the results of rubidium chloride at different temperatures. In order that the b 's should be obtained as accurately as possible small enough values of

must be used. The curves for caesium chloride (see fig. 5) do not give small enough values of c .

Fig. 7.



The following table gives details of the calculations, the last column being the values of $\log_{10} K$ calculated from Saha's theory on the assumption that the ionization potential of rubidium is 4.154; the second last column gives the values derived from the flame conductivities:—

T.	$10^{10}G.$	$10^7\sigma_0.$	$10^6b.$	$10^5a.$	$10^6 \frac{b^2}{a}.$	$\log_{10} \left(\frac{b^2}{a} \right).$	$\log_{10}(GRT).$	$\log_{10} K.$ Observed.	$\log_{10} K.$ Theoretical.
1570...	1.71	3.17	.71	.25	2.02	$\bar{5}.305$	$\bar{5}.436$	- 9.26	- 9.26
1670...	1.62	2.74	.65	.34	1.24	$\bar{5}.093$	$\bar{5}.401$	- 9.51	- 9.58
1720...	2.21	1.285	.32	.72	0.142	$\bar{6}.152$	$\bar{5}.500$	-10.35	-10.68
1870...	2.36	1.122	.26	1.24	0.054	$\bar{7}.736$	$\bar{5}.515$	-10.76	-11.05
1920...	2.37	0.73	.18	1.45	0.022	$\bar{7}.352$	$\bar{5}.491$	-11.16	-11.94

It will be noticed that the ionization constants derived from the flame conductivities are of the same general magnitude as those derived from Saha's thermodynamic equation at the highest temperatures, but there is considerable disparity at the lower temperatures. The results, therefore, show that Saha's theory holds good only at high temperatures.

PART III.

VELOCITY OF ELECTRONS IN A BUNSEN FLAME.

From the results of the experiments described in this paper, the velocity of the electrons in the flame can be calculated in the following way:—

If n is the number of electrons per c.c., u the velocity of an electron due to an electric field of one volt per cm., then

$$\sigma_0 = une.$$

If N is Avogadro's constant,

$$p = nRT/N.$$

Then, since $Ne = 96500$,

$$u = \sigma_0 / (bG \times 96500).$$

The following table gives the results calculated from the foregoing experiments:—

T.	$\sigma_0 \times 10^7$.	$b \times 10^5$.	$G \times 10^{10}$.	u (cm./sec.).
1920	3.17	.73	1.71	2700
1870	2.74	.65	1.62	2700
1720	1.285	.32	2.21	1900
1670	1.122	.26	2.36	1900
1570	0.73	.18	2.37	1800

In conclusion the writer wishes to say that the subject was suggested to him by Professor H. A. Wilson, F.R.S., under whose guidance the research was begun. The writer desires to thank Professor H. A. Wilson and Professor E. Taylor Jones for supervising his work, and the University of Glasgow for facilities for research in the Natural Philosophy Research Laboratory.