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CONDITIONS AFFECTING THE DISCHARGE OF ELECTRODES IN PHENOMENA OF IONIZATION.¹

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IN the present paper is given a general outline of work that has been done at various intervals during the last two years. The original intention was to determine the influence of the temperature of the electrodes on ionization currents in flames, and to study the differences in phenomena when salts are ionized in flames and on hot metals. The results obtained in those fields led directly to some experiments in photo-electrical effects. Tables of readings are omitted because no new mathematical developments are investigated and the qualitative results are of chief importance. Only a few recent investigations are referred to, since full accounts of earlier researches are given in the standard works on ionization. Brief sketches of some of the writer's earlier results have previously been published.²

I. PHENOMENA OF FLAME CONDUCTIVITY.

Effects of Position and Temperature of Electrodes.

1. Many of the most striking phenomena of flame conductivity were known long before the ionic theory was advanced. Those most nearly related to the present work are (1) that the area and position of the anode are of small importance, (2) that the current increases with the area of the cathode and as it is brought into the

¹ Dissertation for the degree of Ph.D. in the University of California.

² J. G. Davidson, *Phys. Zeit.*, 7, 108, 1906 and 7, 815, 1906.

hotter parts of the flame and (3) that the introduction of salts of the more electropositive metals, especially under the cathode, greatly increases the conductivity. It is easy to understand how such facts as these, combined with the phenomenon of the copious emission of negative ions by incandescent metals, led to the idea that the ionization takes place at the cathode and is due to its temperature. The theory of a "volume dissociation" was introduced about 1904¹ and is now generally accepted. For example, H. A. Wilson² estimates the average number of molecules that are ionized in a flame at one time.

2. Some experiments carried out by the writer in the autumn of 1905 furnished the first direct evidence as to the influence of the temperature of the electrodes on the current through a flame. Thin

Fig. 1.

metal tubes were used as electrodes: these could be kept quite cold by passing water from an insulated reservoir through them. When the water was shut off, all the conditions but the temperature of the electrode remained unchanged. Tests were made with tubes of aluminum, copper, brass, iron and platinum. In no case was the temperature of the anode found to have the slightest influence.

One special exception was discovered later and is recorded below (I., 15).

3. In a colorless flame, a cold cathode was unexpectedly found to give, within one per cent. as great a current as was obtained when the water was shut off and the tube raised to brilliant incandescence. Galvanometer deflections of 20 divisions with white hot tubes were reduced in every case by a fraction of a division too small to read on cooling the tubes (one galvanometer division

¹ Marx, *Phys. Zeit.*, 5, 298, 1904.

² H. A. Wilson, *Proc. Phys. Soc. Lond.*, 20, 147, 1906.

$= 1.4 \times 10^{-6}$ amperes in all the experiments recorded). If a platinum cathode is being used, great care must be taken to have it entirely freed from all traces of absorbed salts. The importance of this will appear throughout the paper. The experiments proved quite conclusively that the electrons which any of the above given metals emit at white heat and the secondary ions which may be produced by them in the flame in fields as great as 1,000 volts cm. are not sufficient in number to be comparable with the volume dissociation of the flame gases, due to temperature alone.

4. Slightly different results are obtained when the flame is colored by alkaline salts. In such salt flames the current increases decidedly when the cathode is allowed to become incandescent. With copper, iron, brass and aluminum the increase is small, amounting to between two and three per cent. when the flame is densely colored, while with platinum the current may be doubled. Typical readings in densely colored flames are:

Copper tube, cold, 400 div.; white hot, 410 div.

Platinum tube, cold, 320 div.; hot, 600 div.

If a platinum tube as cathode is kept cold for a time in a densely colored flame and then allowed to become suddenly white hot, the current will increase for a few seconds to two or three times its steady value. Now it is known that currents amounting to several amperes per sq. cm. may be obtained from platinum cathodes thoroughly coated with alkaline salt and heated in a strong flame. A platinum wire held in a dense salt flame and then introduced into a clear flame will color it for a short time, and while this lasts a large current can be obtained, if the wire is the cathode. Thus in the salt flames there is a steady amount of salt absorbed or occluded in the platinum cathode. As this is ionized, the cathode can take advantage of every positive ion set free within itself. When it is shown below (I., 7-11) that a cathode can gather positive salt ions from only a short distance about itself, the effect of the temperatures of a platinum cathode is explained.

5. Although it is thus proved that the greater part of the conductivity of a flame, under the usual conditions, is due to a volume dissociation, still the ionization of the vapor absorbed in the cathode may be facilitated by its being in contact with the metal. J. J.

Thomson¹ says: "Ionization involves the separation of a positive from a negative charge of electricity; if these charges are placed close to a metallic plate, other charges will be induced which will almost annul the attraction between the original charges." Several cases of some such assistance as this are recorded in this paper, especially in II., 8 and IV., 3, but, as platinum and palladium alone show the effects to any noticeable degree, it may be due rather to the absorptive and catalytic action of the metals. One example may be given here. A calcium salt sprayed into a flame causes a very slight increase in conductivity compared with that due to an alkaline salt. This harmonizes with our theory of line spectra, since the calcium lines barely appear in a flame spectrum, although the band spectrum, supposed to be due to undissociated molecules, is strong. Evidently very little calcium salt is ionized by the flame alone. If, however, the cathode is coated with either salt, the conductivities are enormously increased and approximately equal. With an alkaline coating the large current ceases when the coloration of the flame ceases but with an alkaline-earth it persists long after. Coating the anode alone with a calcium salt gives no increase in conductivity even though the cathode is just above it in the ascending gases. Since, then, the calcium salt is ionized on the cathode but not on the anode nor in the flame itself, where the temperature is the same, the metal must assist in separating the ions and in setting free the negative but not the positive. Wehnelt² has studied this emission of negative ions from calcium salts and shown that they are electrons at low pressures.

Influence of Position of Cathode in Colorless Flame.

6. It has long been known that, as the cathode is brought into the hotter parts of the flame, the current gradually increases, but no one seems to have noticed the following phenomenon before it was recorded in the writer's first paper. If a strong enough air blast is used to give a sharply-defined green cone and the cathode introduced into this, the current will be from ten to twenty times as great as can be obtained with it a millimeter away but outside the cone:

¹J. J. Thomson, *Cond. through Gases*, p. 174.

²Wehnelt, *Ann. d. Phys.*, 14, 425, 1904.

this is altogether out of proportion to the difference in temperature. This large current is barely decreased by cooling the cathode with water as described above, nor does it show any approach to saturation with the greatest electric fields available. Again, if the cathode outside the cone is further heated electrically, the conductivity of the flame is increased considerably, but even with the platinum melting it is not nearly so great as in the cone. Examples of readings are: platinum cathode, just outside cone, 15 div.; in the cone, 200 div.; 5 cm. above cone, but in the flame and melted by a heating current, 90 div. Thus the cathode must be in the region of greatest ionization to give the greatest current, but the fact that in these positions its temperature is highest is an incidental and not the determining factor, unless it is coated with salt.

Velocity of Positive Ions in a Flame.

7. There has been a serious discordance of results in the researches on this point. The importance of the problem demands that some agreement should be reached. Wilson¹ placed the anode above the cathode, held a salt bead between them in such a manner that the colored vapor would not touch the cathode, and noticed the E.M.F. at which the current began to increase. Knowing the upward velocity of the flame gases, this gave at once, for the specific velocity of the positive ions, 62 cm./sec. With high E.M.F. he actually obtained greater currents with the anode above than with the cathode in the salt vapor. The writer has entirely failed to reproduce any such result, even a field of over 1,200 volts/cm. being insufficient to draw positive ions downward or outward from the colored vapor against the current of gas in any flame.

8. Moreau² placed the electrodes parallel and opposite each other, the cathode being in a colorless part of the flame. At the voltage at which the current begins to increase, it is assumed that the ions move from the salt vapor about the bottom of the anode to the top of the cathode diagonally. Now, the currents obtained in this way are of approximately the same magnitude if the salt is taken away entirely. I can see no reason whatever for assuming

¹ H. A. Wilson, Phil. Trans., A., 192, 499, 1899.

² Moreau, Ann. d. Chem. et d. Phys., 30, 33, 1903.

that the cathode gets its positive ions from the salt vapor rather than from the clear flame about itself.

9. Marx,¹ from a study of the potential gradient near the electrodes, deduced a value of 200 cm./sec. for the velocity of the positive ions. The validity of the method of measuring potentials in ionized gases by exploring electrodes is discussed below (I., 17).

10. Lenard² showed that the colored part of the flame is slightly deflected in a strong electric field in a direction indicating that it bears a positive charge. From his results he deduced a velocity of only .08 cm./sec. for the positive ions of lithium. This value was verified by the writer as to order of magnitude, but it varies, becoming smaller in more densely colored flames. Two confirmatory tests were also devised. An arc was started at various points in a colorless flame through which a current was passing between platinum electrodes. No increase was obtained until the arc was almost directly below the cathode, when the current became as large as in a small flame. Positive ions from metals which are not ionized in the flame were proved in this way to have very small velocities similar to those from alkaline salts. Again, a salt bead, which did not color the flame very densely, was held so that the colored vapor just surrounded the cathode, and no increase of current was obtained by using other beads to color the whole region between the electrodes.

11. It would seem proved that the positive ions which actually reach the cathode from the salt vapor in the flame come from a very thin layer surrounding it, and that most of the work on their velocities has been based on the misapprehension that they may be attracted to the cathode from salt vapor at a considerable distance.

12. No effort was made by the writer to find the velocity of the positive ions in a colorless flame, but it cannot be nearly so small as that of the salt ions, since in a moderately hot flame currents approaching saturation value can be obtained with fairly low voltages. On the other hand, it cannot be nearly so great as 200 cm./sec., since it takes such very great fields to enable a cathode to attract positive ions outward from the green combustion cone.

¹ Marx, *Ann. d. Phys.*, 2, 768, 1900.

² Lenard, *Ann. d. Phys.*, 9, 642, 1903.

13. Assuming, in accordance with the kinetic theory of gases, that viscosity may be neglected and that velocity vanishes at each collision, a simple calculation¹ gives about 10 cm./sec. as the specific velocity of an atom of sodium bearing ionic charge in a gas at atmospheric pressure and 2,000° C. Many recent investigations show that an ion outside the flame soon gathers many thousand molecules about itself. This tendency must be present in the flame, though the aggregates may be broken up almost as soon as formed. Hence the viscosity factor may be sufficient to reduce the velocities to the observed values which are of the same order of magnitude as those found by Professor Lewis² for the positive ions just above the flame.

Source of the Negative Ions that Reach the Anode.

14. Different convection methods have been used for finding the velocity of negative ions in a flame. In every case it is assumed that, at the "critical voltage," the field is just able to draw the ion from the cathode or from the colored part of the flame to the upper edge of the anode before it is carried away by the gas currents. The inaccuracy of this conception can be proved experimentally as follows: With apparatus arranged as in Fig. 2, almost exactly the same current-voltage curves and the same critical voltage were obtained when the anode was lowered or removed to a greater distance, while the cathode remained fixed, though the field, of necessity, changed. When several flames were arranged to touch only at tips and bases, the anode could be moved to any position with only a few per cent. change in current, and a large increase was noted only when the area of the electrodes was great compared with the distance between them. Again, it was interesting to use exploring electrodes, connected through a galvanometer with no voltage applied, in a colored flame through which a large current was passing between two other electrodes. With one exploring elec-

Fig. 2.

¹ J. J. Thomson, *Cond. through Gases*, p. 203.

² E. P. Lewis, *PHYS. REV.*, 21, 352, 1905.

trode in any relative position near each of the main ones, considerable currents could be tapped off. If the exploring electrodes were placed symmetrically above the main anode, the one with the greater area became the anode for the galvanometer circuit and conversely with the cathode.

15. Mention has been made of the great increase in current obtained by coating the cathode with salt instead of spraying it into the flame. Using small voltages, it was not found possible to increase the current by coating the anode also or by holding it in the colored flame above the cathode. However, as the voltage increased the advantage did appear and increase, until with several hundred volts it often amounted to ten per cent. Coating the anode with an alkaline-earth salt is never of any service, because no positive ions can be emitted from it. Again, a large current was obtained by coating the cathode with a salt; only a very slight decrease in current was noticed when the anode was removed to the base of an intense flame inclined to the first and touching it only at the tip. The current decreased rapidly as the second flame was made less intense, but coating the anode with an alkaline salt brought it back to its former value in every case. An exploring electrode took up positive potentials in the anode flame, negative in the cathode flame, and became neutral at the tip where the flames mingled, thus showing that above the anode there was a large excess of positive ions and an excess of negative above the cathode, the two neutralizing where the flames joined. This is like the case of an ordinary flame with the part between the electrodes cut out. Its absence makes little difference in the current, as we have seen. Now, with both electrodes in our flame and opposite each other, an exploring wire reveals a similar state above the electrodes, as in the case of two flames: there is always a part of the intervening space where a uniform fall of the potential shows equal densities of positive and negative ions.

16. It has already been shown (pars. 10 and 11) that the cathode gets its positive ions from only a very thin surrounding layer. Many experiments like the examples just given (pars. 15 and 16) have led me to believe that the anode gets enough negative ions from the clear flame about itself, even when the cathode is in salt

vapor and quite large currents are passing. This means that the remaining negative ions about the cathode and positive ions about the anode unite between the electrodes, and especially in the upper regions of the flame. If this conception of the action be correct, it invalidates any method as yet employed for finding directly the velocity of the negative ions, because a state of steady drift of negative ions from cathode to anode is assumed in each case.

Potential Gradient.

17. The method of finding potential gradient in regions of ionization by means of an exploring electrode has been attacked on the ground that when a wire takes up a potential it distorts the field. However, if the area of the wire is small as compared with that of the electrodes, the distortion can hardly be great enough to change the character of the results. But I would suggest more valid objections to the deductions that are ordinarily made from potential gradients found in this way. If the potential of the wire were any measure of the actual space potential, it would be proportional only to the relative numbers of positive and negative ions at that point. A little thought will convince us that it depends on their mass and velocity as well. Suppose the wire takes up a negative potential. A certain number of negative ions, depending on their density and momentum, will still strike it in spite of the repulsion, while its steady state will be maintained by an equal number of positive ions, depending, again, on density, mass and velocity, but assisted by attraction. In the published researches on the problem, the assumption is tacitly made that the potential gradient indicated by the wire and the ionic velocity are functions only of each other, thus ignoring the question of relative density and mass.

18. I have not as yet had the opportunity of gathering data for attacking the problem from this broader standpoint. However, during the course of the experiments, a number of series of measurements was made in which current, position of electrodes and so-called potential gradient were varied so widely as to give velocities varying from 500 to 10,000 cm./sec. if the usual assumptions were made in the calculation. There seemed no particular evidence that any one value was more nearly correct than another.

1,000 cm./sec. has hitherto been the most widely accepted value. Recently Gold¹ has obtained 12,900 cm./sec. by using the convection method and finding the potential gradient in the body of the flame. Calculation gives 13,000 cm./sec. for an electron, assuming no viscosity.

II. IONIZATION OF SALTS ON HOT METALS.

1. The experiments described in this section were undertaken in order to ascertain the variation of phenomena in ionization of salts when freed from possible effects of the chemical actions of the flame. Many of the results obtained have recently been published by others but some new facts are still to be recorded and some general relations to be pointed out.

2. J. J. Thomson² heated various salts to a red heat and measured the excess of electricity of either sign in the surrounding air by means of an electroscope. The sign depends on the salt, not on the metal. Oxides give excess of negative; phosphates a large and chlorides a small positive excess; nitrates give initial positive excess, but they soon turn to oxides. The salts remain with the opposite charge. He suggests in explanation that the salts have a double layer of electricity, the oxides having negative outside. Garret³ placed the salts in a platinum dish in a metal tube and heated them by insulated gas flames. The tube was one electrode and a wire along its axis the other. He used temperatures only as high as 360° and, naturally, got no general idea as to the action of different classes of salts. For example, he got neither positive nor negative ions from KBr, NaFl, NaHCO₃ and Ba(NO₃)₂. None that he tried gave negative ions only, while a few gave positive only.

3. I add the following observations: The other haloid and the sulphur salts, the hydroxides, and higher oxides, while changing to lower, also show initial excess of positive ions, as do the alkaline oxides alone among those tested. But none of these is permanent; ultimately an excess of negative ions always appears in the surrounding air unless the salt is all volatilized in the meantime. This change of sign is easily affected with the nitrates, chlorides and

¹ Gold, Proc. Roy. Soc., A, 79, 43, 1907.

² J. J. Thomson, Camb. Phil. Soc. Proc., 14, 105, 1907.

³ Garret, Phil. Mag., 13, 728, 1907.

bromides of calcium, strontium and barium but the sulphates are more permanent and require a higher temperature. In most other cases it takes long-continued heating of a very small quantity of the salt at a high temperature to affect it. It would seem that all salts ultimately break down into oxides and that chemical actions, which leave the metal behind and give off other products, give excess of positive electricity in the air. In those cases where negative ions alone are being given off, there is no reason to believe that any chemical action or volatilization is taking place. The same salt of different metals requires widely different temperatures to effect ionization. In general, the alkaline salts are most easily ionized. I detected ions from KNO_3 at 250° and from RbCl at still lower temperatures. Campbell has even found them at room temperatures.

4. To study the intense ionization of certain salts at high temperatures, they were placed on pieces of platinum wire 2 or 3 cm. long, heated electrically and earthed. The other electrode was a plate or wire whose distance from the hot wire could be adjusted. A battery of small accumulator cells gave adjustable E.M.F. to 550 volts. A d'Arsonval galvanometer of approximately 375 ohms resistance and giving a deflection of one scale division for 1.4×10^{-6} amp. indicated the currents. It was not sensitive enough to reveal the ionization of most salts.

5. Any salt of an alkaline-earth metal will give a current of four or five divisions with the hot wire as anode and slightly less with it as cathode, as long as volatilization is taking place. Then there is no sign of an anode current even with the cold cathode attached to an electrometer, while with the hot wire as cathode, the galvanometer deflection is as high as 500 divisions with 480 volts and 2 mm. between the electrodes. At white heat this current is about the same for all the salts of the same metal. This was attributed above (par. 3) to their all breaking down into oxides. Barium salts give the largest currents of the group, magnesium and zinc the least. Comparative readings under circumstances as nearly as possible similar, were, for instance: Barium, 600 divisions; strontium, 550; calcium, 500;

Fig. 3.

magnesium, 20; zinc, 30. An electrometer had to be used to detect the emission of the negative ions from beryllium salts.

6. With coatings of alkaline salts also, these large currents were obtained when the wire was hot enough to volatilize the salt. In most cases a dull red heat was sufficient. The currents were never persistent, disappearing as volatilization ceases. With these salts, deflections of not more than one division could be obtained with the hot wire as cathode, but with it as anode 400 or 500 divisions could easily be obtained. Every alkaline salt of the thirty or more that were used gave a similar result, though some were more persistent and needed a brighter red heat than others. Rubidium and caesium gave the largest currents of the group and lithium the least.

7. A great many salts of metals in every group of elements were examined to find if these large currents could be obtained. The wire was gradually raised to brilliant incandescence in each case; a much higher temperature than is necessary for the ordinary emission of negative ions. Brief and comparatively small anode currents of from one to four divisions were obtained from many salts, especially those of metals of large atomic weights, in all the groups. Some of them may be due to very slight traces of alkaline impurity as the currents died away while the salt was still volatilizing. Alone, of all the salts tried, except those of alkaline-earths, didymium nitrate gave a cathode current of one division and molybdenum oxide 3 divisions. These may also be due to impurities.

It is remarkable that this emission of positive ions from alkaline salts was not recorded earlier, as the property is so very marked.

Effect of the Metal of the Wire.

8. Wires of platinum and palladium, alone, were found by the writer to give these large ionization currents: the latter is the more effective. Wires of german silver coated with CaO were found to give a cathode current barely large enough to affect the galvanometer. With other metals an electrometer had to be used. Anyone studying the ionization of salts on platinum must be exceedingly careful in cleaning the metal. Washing in water or in acid is not sufficient. Long-continued heating in a flame or by an electric current will very gradually do it. But by far the most effective method

I have found is alternately to dip the wire in acid and place it as an electrode in a flame with large voltage applied, making it anode or cathode according as the absorbed material is alkali or alkaline-earth.

Action of New Wires.

9. It is known that a new platinum wire will give a large leak of positive ions at red heat, and that the current soon falls to a small steady value. Richardson has done a great deal of work on this subject and has practically concluded that the leak is due to occluded hydrogen. There is, apparently, no evidence for this other than that hydrogen diffusing outward through an anode increases the positive leak. To my mind there can be no doubt that it is due to alkaline salts. These placed on a clean wire will give the effects obtained from a new wire, and any new wire will give the sodium color to a flame. Some photo-electric phenomena described later in the paper (IV., pars. 5, 11 and 13) practically settle the question.

The Anomalous Action of Alkaline Salts.

10. It has been seen that coating an anode in a flame with an alkaline salt gives no increase in current if the cathode is clean and kept in the colorless part of the flame while, from alkali-coated cathodes currents, of several amperes per sq. mm. can easily be obtained. In air, on the other hand, an incandescent alkali-coated wire gives by far the largest currents when it is the anode; for example, in one case, with 250 volts between electrodes 2 mm. apart a platinum wire 3 cm. long, coated with NaHCO_3 , gave negative leaks of 4×10^{-7} amperes and positive leaks of 2×10^{-5} amperes when it was anode. The anomaly has been partially explained already (I., pars. 7 and 11). It has been seen that, in the flame the positive ions accompany, and probably constitute, the colored portion. Owing to their low velocity they are swept away in the flame gases so that the cathode must be placed in the salt vapor to obtain any greater current than that due to the colorless flame. Similarly it was found that a very slight blast of air will sweep away the positive ions and stop the large current from a hot alkali-coated anode in air.

The explanation of the very small negative leak from the hot alkali-coated cathode in air finally appeared in some modifications of Owens' experiment. He showed that a current of negative ions is stopped by blowing smoke between the electrodes: the ions appear to attach themselves to the smoke particles and be carried away. I noticed that the large negative leak due to a calcium salt on a hot cathode in air does not commence while any fumes are being given off. With alkaline salts there is volatilization as long as any current of either sign will pass. If the wire is cathode the small current is actually increased by a slight blast of air, if the temperature is kept constant, but it is entirely checked by smoke. On the other hand, dense smoke does not decrease the large positive leak in the slightest degree; either the positive ions have momentum enough, owing to their large mass, to carry the smoke particles to the cathode with them or they do not attach themselves to those particles nearly so rapidly as the negative ions. The volatile salt vapor acts the part of smoke sufficiently to make the negative leak from alkali-coated wires in air very small in comparison with the positive leak.

Relation between Current and Temperature.

12. Richardson's formula¹ is now generally accepted. Where i is the current, θ the absolute temperature and a and b constants, $i = a\theta^{\frac{1}{2}}e^{-b/\theta}$. The formula has been rigorously tested in a great many cases with currents of both positive and negative ions and gives fair agreement with experimental curves in all cases where the current is maintaining a steady value at any constant temperature; that is, where the rate of volatilization of the material ionized is comparatively small. I mention the matter in order to point out that the formula was first developed for negative leaks and that the theory from which it was derived is based on the assumption that electrons are circulating in the metal like molecules in a perfect gas. This, of course, does not apply to positive ions and a new basis for this formula or a new formula giving curves of similar shape, must be devised.

¹J. J. Thomson, *Cond. through Gases*, p. 166.

Relation between Current and Potential Difference.

13. The formula¹ $i = 9Rv^2/32\pi d^3$ is widely used for cases where the ionization is confined to a thin layer near one electrode. The writer has tested it for ionization of salts on hot wires and has found that the experimental curves depart widely from the calculated values. As an example, the diagram (Fig. 4) gives the current-voltage curve for an incandescent wire cathode, 3 cm. long, coated with CaO and about 2 mm. from the anode. When, however, the

Fig. 4.

voltage is kept constant and the distance between electrodes varied, the experimental curve is found to be considerably below the theoretical. One reason for this is that the velocity R varies with both the potential difference V and the distance between the electrodes d , since the ions increase in size with the time. The rate of variation of R with time and distance might be determined were it not for another difficulty. It is assumed in the development that, if the current is small, the potential gradient vanishes at the hot plate. An exploring electrode certainly indicates that this is true, but, as stated above, it can hardly be supposed to give the true potential of the space, and under any circumstances, one can hardly conceive of

¹ J. J. Thomson, *Cond. through Gases*, p. 175.

there being enough ions near the hot plate to prevent any fall of space-potential.

III. IONIC AGGREGATES AND APPARENT RECOMBINATION.

1. Ions formed in dry, dust-free gases at ordinary pressures by such ionizing agents as X-rays, radio-active substances or ultra-violet light, never seem to collect aggregates of molecules about themselves. Those escaping from flames or hot metals are much larger and they grow still larger and more sluggish the farther they are removed from the source and the lower the temperature becomes. The calculated values of their size have been steadily increasing until Langevin¹ in the latest paper on the subject gives an average of 64,000 molecules.

2. In many places in the work of Barus, it is shown that nucleation does not disappear with recombination of ions. In some preliminary tests on ionizations of salts the writer used the arrangements

Fig. 5.

of Fig. 5. If both wire and tube were kept hot for a time before the galvanometer circuit was closed, a considerable initial current and then a much smaller steady one was obtained. Both initial and steady currents were very much larger than when the heating

circuit was opened just before the galvanometer circuit was closed. This first suggested to the writer the following conception of the action. When two ions of opposite sign, consisting each of a charged particle surrounded with layers of molecules, come together, the combination will be neutral electrically, but molecules may still remain between the charges. In cases of such apparent recombination the field between the positive and the negative particles will be much weaker than in cases of genuine recombination. This neutral aggregate may attach itself to another large ion and so on until we may have thousands of molecules in which are fixed, at intervals, charged particles, the resultant charge of the whole being

¹ Langevin, *Ann. de Chim. et de Phys.*, 8, 201, 1906.

positive, negative or zero. If this view is correct, some of these aggregates should be capable of collection on a charged wire and then be more easily re-ionized than before. The experiments described in the remainder of this paper were all directly suggested by this conception. It can hardly be said to be proved, but at any rate, it has already been fruitful of results.

3. Flame gases were led through a metal tube in which was a central insulated electrode, consisting of about 3 cm. of platinum wire attached to larger supporting copper wires insulated from the tube. The central wire was kept charged in the gases to make the collections. The flame was then removed and the wire heated electrically, while cathode or anode, to obtain an ionization current, the tube being the other electrode. In all cases the currents were about equal, whether the wire had been charged positively or negatively during collection.

If an uncolored flame had been used, very slight and brief currents that could just be detected by the galvanometer were obtained. A dull red heat was sufficient to drive off all the collected material.

When the flame was colored by salt vapors currents were obtained like those described in the previous section and the large effects appeared at decidedly lower temperatures. In fact, it was in this way that the large positive leak from hot alkali-coated wires was first discovered. When the flame was colored by an alkaline-earth salt the wire had, of course, to be the cathode when heated to give a current. Small quantities of material will collect on an uncharged wire above a sodium flame, but practically none above a calcium flame. The currents obtained in this way are so large as to be of a different order of magnitude from the steady currents obtained between the tube and a cool central electrode while the flame gases are rising.

4. These collections furnish an extremely delicate test for the presence of minute quantities of such salts suspended in a gas that

Fig. 6.

has been exposed to any ionizing influence. Professor Rutherford, while at this university in the summer of 1906, kindly gave the writer some radium emanation for a test. A charged wire in a dry vessel containing the emanation collected no such deposit as those here discussed. When the vessel was dampened with distilled water I detected a very slight anode current when the wire was discharged, removed and heated. After tap water was poured into the vessel and shaken up, a wire charged to 500 volts would collect enough in two or three minutes to give a large but very brief anode current of 10 scale divisions with the wire at a dull red heat.

5. Anode currents, presumably due to minute traces of alkaline material, were obtained from wires that had remained charged in freshly-prepared gases, or in the air of the room, especially if it circulated past the wire. On days when the north wind was blowing enough would collect on a wire in a field of 500 volts/cm. in one minute to give 25 divisions of scale deflection, while on other days when a west wind was blowing not more than 1.5 divisions could be obtained under circumstances otherwise similar. Mr. F. A. Harvey, working in this laboratory, found abnormally large quantities of radio-activity in the air on the same days when a north wind was blowing, and there may yet prove to be some connection between the phenomena.

6. Something always collects, from the gases tested, on an uncharged wire. This could easily be extracted by passing the gas through long tubes of water or plugs of cotton wool, but some material which could be collected on a charged wire still remained in the gas in every case. Potentials approaching sparking values and very slow currents of gas must be used in order to collect as much as possible.

The Nature of the Collections.

7. For a long time it seemed that these collections might be due to purely electrostatic attraction of neutral particles and that there was no necessity for assuming any resultant charge on the aggregates. Evidence on the subject was given by an examination of the cold electrode when salts were heated on a neighboring one. When a salt that sublimates or volatilizes readily is used, the smoke is all

deflected to the cold electrode and forms a white deposit. With salts, like those of the alkali metals, that cause either a positive or a negative leak, the direction of the field causes comparatively little change in the rate of collection and the appearance of the deposit. Silver and thallium nitrates were found to give only a positive leak while volatilizing strongly, and with these the deposit formed much more rapidly with the hot wire as anode.

8. This theory of ionic aggregates suggests at once a simple explanation of the so-called "double layer" that occupies such a large place in the history of this subject. The aggregates may not allow the charged particle to reach the metal and, if so, a bound electrostatic charge will be induced on the surface. Thus it ought to be possible to obtain a kind of electrolytic polarization on a charged cold electrode, in a space where such ions are plentiful. In 1890 J. J. Thomson made the isolated observation that in certain cases an ionization current from a hot metal was increased when the other electrode was heated also. I investigated the question somewhat, as it seemed to bear on this point. When an alkaline-earth salt was heated on the cathode, heating the anode also did not increase the current if the wire was absolutely clean at the start. Very few aggregates appear in the air space in this case. When an alkaline salt was used there was a large increase when the second electrode was heated, but most of this was proved to be due to the salt being volatilized back and forth between the electrodes. When, however, a very small anode was used and the cathode removed while the anode was heated after the current had passed for a time there was a brief but decided increase in the current. Whether this was due to a non-conducting layer of salt or a genuine double layer as described above, could not, of course, be determined.

IV. PHOTO-ELECTRIC PHENOMENA.

1. In following out the ideas of the previous section, I undertook to find whether a wire held in regions of ionization will gather material upon its surface which can then be easily re-ionized by ultra-violet light. The investigation has led to a variety of important results, many of which are not connected with any theory of ionic aggregates except that they were suggested by experiments in that direction.

2. For measuring the negative leak under the influence of the ultra-violet light at room temperatures an encased electroscope was used in a part of the work. The wire to be tested was attached to the leaf support and projected beyond the case. This method gave the character of the results very expeditiously. For more accurate work and for high temperature effects a quadrant electrometer enclosed in a metal box was used. Covered wires connected one

Fig. 7.

pair of quadrants to a strip of corroded metal plate or gauze placed near the active wire or polished metal being tested. Shielding was practically unnecessary, as even with the electrometer electrode at a high negative potential there was practically no leak due to the light. Both pairs of quadrants were earthed at the beginning of each reading. The wire being tested could be

heated electrically and was kept at a high negative potential by connection with a storage battery giving a maximum of 100 volts. Hence, the rate of leak to the electrometer electrode measured the effect. An arc was used as source of light in most of the work. It is far more easily handled than a spark source and with a little practice can be made quite constant.

Wires Exposed to Flame Gases.

3. New platinum or palladium wires show very little activity; cleaned as indicated below, they show practically none. After being held in a colorless flame, however, they were found to be very active. Where, for example, such a wire gave 100 divisions of electrometer leak per minute when charged negatively and exposed to strong ultra-violet light, a strip of brightly polished zinc of approximately the same area gave no more than 40 divisions. Observations on wires held at various distances above a flame showed that the effect still exists but that it falls off rapidly. Passing a wire rapidly once or twice through the gases just above the flame, so that its temperature had no time to rise materially, made it more active than holding it for a minute at the top of a tube 2 meters

long through which all the gases from the flame were rising. Hence the gases, after leaving the flame, rapidly lose their power of making the wire sensitive. Charging the wire either positively or negatively while in the gas did not seem to hasten its gaining of sensitiveness. Ultra-violet light was admitted at various intervals through a quartz window into a tube through which flame gases were rising and into a large vessel filled with the gas, and only a very slight increase in ionization was observed. However, the wire will retain its activity most persistently; here again is an example of the effect of a metal in promoting ionization at its surface, spoken of above (I., par. 5). When wires were left in the open air their activity fell off gradually to half value in two or three days, but this seemed to be due to the formation of a layer of dust particles. After a wire had been kept covered in a bottle for a week the intensity of its activity was as great as at first but it would not maintain the discharge nearly so long. Wires that had been held in the flame maintained a constant discharge in a constant field for as much as two hours, and then the leak dropped to zero in two minutes. They did not recover their activity spontaneously. The activity gathered on wires held above the flame at various heights becomes rapidly less persistent as the distance increases; for example, a wire which had been held 10 cm. above a flame for 10 sec. maintained a steady leak of 40 divisions per minute for an hour before the rapid decrease in activity commenced, while, after being at the top of the tube 2 meters long for the same time, it gave 5 divisions per minute for 10 minutes; intermediate positions gave intermediate readings. In passing, I might remark that no one seems to have stated definitely that all the well-known cases of photo-electric "fatigue" are functions of the strength of the field.

4. Coloring the flame with an alkaline salt decreases the effect: in fact, when a charged wire was held for a minute above a dense salt flame it showed only a slight initial activity. The ionic aggregates from salt vapors, discussed in the previous section, are not, then, re-ionized by ultra-violet light. Oxidized or corroded pieces of metal were found to be slightly active after being held for an instant above a clear flame.

Electrodes from Electrolytic Cells.

5. With one exception, (given in par. 6) platinum wires that had been either cathode or anode in electrolytic cells of many kinds were found to be very active after being allowed to dry. A wire at which hydrogen had been liberated behaved like a wire from a colorless flame when tested at room temperatures. Various metals were deposited on wires and all showed the effect strongly, but for metals of the first two groups the current through the electrolyte must be very brief or the wire becomes saturated with the hydroxide which is not sensitive at low temperatures. The activity of all metals in these tests falls off with the time and is not recovered. Anodes in solutions of halogen salts also become active but the decay was not investigated. In all cases currents of several amperes through the electrolyte are advisable; it would seem that some ions have not time to become neutralized and that these are later set free by the light.

6. It was found that oxygen set free electrolytically at a wire would not make it active and would even destroy any activity which it may have possessed. However, really to clean the wire it is well alternately to dip it in acid and heat it in a flame to get rid of all metallic salts, before making it an anode in the cell, or the oxygen may leave it saturated with insoluble oxide. The discovery of this method of cleaning a wire made the whole investigation practicable. It was only after a great deal of experimenting that I realized what extreme care must be taken in cleaning the wires to get reliable results.

7. Such a clean wire, after being heated to a red heat by an electric current, is found to be active at room temperatures. This shows that the effect of the flame gases is not necessarily due to occluded hydrogen as one is likely at first to suspect. Heating to white heat by an electric current does not decrease the activity of a wire newly heated in a flame. When, however, such a wire had been kept for a week in dust-free air and then heated electrically to only 300° it lost its activity and did not regain it on cooling.

Measurement at Different Temperatures.

8. Zeleny¹ carried out what seems to be the only piece of work yet attempted that bears directly on the present paragraph. He

¹ Zeleny, PHYS. REV., 12, 321, 1901.

obtained temperature-activity curves for platinum and iron wires and attributed his results to the properties of the metals themselves. This conclusion, as will be seen, is not justified. Millikan and Winchester¹ have studied the photo-electric activity of metals at different temperatures in the highest vacua obtainable and have found no variation. Whether temperatures giving red heat were used is not stated in the published abstract of their work. My experiments and those of Zeleny were all carried out in air at atmospheric pressure when oxidation effects are important.

9. Only a single curve will be given (Fig. 8, one very similar to Zeleny's) that was obtained from a new platinum wire that had

Fig. 8.

been heated electrically once to a bright red heat and then was taken over the scale of temperatures again.

Curve I. is for increasing and Curve II. for decreasing temperature. It will answer every purpose to describe briefly a few of the curves actually obtained by references to the lettered points on the figure.

10. In many cases temperatures were reached at which negative ions due to the temperature alone began to cross in the dark from the wire being tested to the electrometer electrodes. The two influences were found to be practically additive; extending the curves due to light alone at lower temperatures and adding the ionizations in the dark gave the experimental curves.

¹ Millikan and Winchester, *PHYS. REV.*, 24, 116, 1907.

11. New wires showed no more than one or two divisions of leak per minute at 15° . This increased each time as the wire was raised to successively higher temperatures, and persisted for different periods with different wires, when the heating current was broken. Not until almost 400° had once been reached did the hysteresis effect with falling temperatures and the minimum from 100° to 300° with rising temperatures begin to appear. Then curves similar to those in the figure were obtained with each wire. The hysteresis is never an invariable phenomenon. If readings are taken slowly enough Curve II. retraces Curve I.; or we may stop at any point *D* on Curve II. and, by keeping temperature, field and light steady, gradually drop the activity to the corresponding point on Curve I., though it may take half an hour to do it. The point *E* never coincides with *A* unless the wire has been taken over the same or a higher scale of temperatures a short time previously.

12. A clean wire coated with any one of various alkaline salts that were tried gives a similar succession of results and, ultimately, curves of the same shape as the new wire, though the activities were quite different with different salts. This is considered a final proof that the occluded material in new wires is not hydrogen but alkaline salts.

13. A wire, cleaned as anode in an electrolytic cell, shows no activity until its temperature is raised to 400° , when it increases very rapidly. One wire gave 90 divisions of leak per minute at bright red heat and this included a slight ionization due to heat alone.

Dropped back to 15° , it gave 120 divisions. Then for rising temperatures, the drop in the curve appears at 80° as in the figure, but the minimum part *B*, reaching just to red heat was only 4-7 divisions. No hysteresis was observed unless the temperature is very rapidly lowered. This action of the clean wire must be due to occluded oxygen; it is certainly not a property of the platinum itself.

A clean wire that has been held in a flame gives results similar to those above, except that the point *C* is decidedly higher; in both cases it is lower than *A* until the wire is raised to white heat. A wire at which hydrogen has been liberated electrolytically gives curves almost identical with those from a flame.

14. I think that the curves obtained from new wires and wires

coated with salts are the resultant of the action of the salt and that of the clean wire, the minimum being due to the clean wire and the great activity at red heats with hysteresis effects being more especially the properties of the salt. McLennan¹ observed that some salts of calcium and sodium will give off negative ions when exposed to X-rays or ultra-violet light at temperatures between 200° and 300°. As research in these lines progresses we shall doubtless be able to obtain clear relations between these ionization phenomena and the chemical dissociation constants of the salts.

15. Several copper and iron wires were tested until it was found that polishing with emery paper leaves impurities on the surface that influence the result at high temperatures. Brightening the surface by scraping with a knife avoids this error. The leak remains constant from these two metals as temperature is raised quite rapidly to about 175°. Fatigue, however, is hastened by raising the temperature. At about 300° the leak from a polished surface can be seen to decrease rapidly. This must be due to oxidation. Again, at bright red heat, any oxidized piece of copper or iron which is quite inactive at ordinary temperatures becomes very active and brief hysteresis can be observed if the temperature is rapidly lowered. This is probably connected with reduction of some of the oxide to the metal by the heat.

Methods of Polishing.

16. It was accidentally observed that violently stretching a piece of copper wire that was not brightly polished greatly increased its sensitiveness, but not beyond that of a brightly polished surface. Squeezing in a vice and twisting were found to serve the same purpose. Violently scraping or rasping surfaces of iron, aluminum or german silver gives from 10 per cent. to 20 per cent. greater sensitiveness than thorough polishing in a lathe with smooth emery paper. On the other hand, the smooth polishing of copper gives about 15 per cent. the greater effect. A bright surface of any one of these metals has about the same sensitiveness after about half an hour of continuous leak, no matter what method of polishing was used. Allen² has shown that the fatigue of zinc can be rep-

¹ McLennan, Phil. Mag., 3, 195, 1902.

² Allen, Proc. Roy. Soc., A, 78, 483, 1907.

resented as the resultant of two exponential curves, one with a much greater time factor than the other. It would seem from the experiments of this paragraph, incomplete as they are, that the initial rapid decay is a function of the treatment to which the surface has recently been subjected.

17. In attempting to account for the fatigue of metals exposed to ultra-violet light, different investigators advocate different theories,—oxidation, formation of layers of neutral gases, double layers of electricity or a kind of chemical change in the metal itself. No one of these would seem to account for all the new phenomena recorded in this section and probably each will prove to be the true explanation of particular cases.

There are numerous cases of direct contradiction in the published researches on ionization phenomena. It is to be hoped that this paper has pointed out some of the real causes of these discrepancies. In particular, the difficulties arising from alkaline salts should be emphasized; they are found on all surfaces exposed to the atmosphere and it is extremely difficult to detach every trace of them; some of them, at least, are slowly ionized at room temperatures and all of them at 400° and above.

The main phenomena discovered during the research are:

1. The temperature of the electrode has only a slight influence on conductivity of flames: the apparent exception to this in the case of a platinum cathode in a colored flame is due to occluded salts.
2. The conductivity of the green cone in a colorless Bunsen flame is comparable with that of a colored flame.
3. Large currents due to the attraction of positive ions against the drift of the flame gases cannot be obtained.
4. Very rapid but brief leaks of positive ions can be obtained from hot platinum wires coated with alkaline salts.
5. The occluded material in new platinum wires is shown to be mainly alkaline salts.
6. A current carried by positive ions is not stopped by smoke.
7. Collections of molecular aggregation apparently bearing electric charges can be made on charged wires from many ionized gases and then easily re-ionized.
8. Platinum wires which have been held in flame gases or used

as electrodes in electrolytic cells (except where oxygen is set free) become very sensitive to ultra-violet light.

9. The minimum in photo-electric sensitiveness of platinum wires at temperatures between 100° and 200° is traced to the action of occluded gases.

10. The initial rapid photo-electric fatigue of metals is connected with the method of polishing.

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