ON TEMPERATURE AND SURFACE CONDITIONS WHICH AFFECT THE POSITIVE IONIZATION FROM HEATED PLATINUM.

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TWO general views as to the nature of the positive ions from heated metals and metallic salts have been advanced in recent years. Richardson and Hulbirt[1] came to the conclusion that the positive ions from heated metals have an average value of m/H of 25.7. Some later determinations with platinum made by Richardson[2] gave an average value of m/H of 32.5. Professor Richardson has advanced the theory that the positive thermions are in large part charged atoms of sodium or potassium which are present as impurities in the form of salts. J. J. Thomson,[3] Horton,[4] Garrett,[5] W. Wilson[6] and Klemensiewicz[7] hold in general to the view that the carriers of the positive electricity from hot metals are for the most part molecules of gas absorbed by the metal. Recently another paper on this subject has appeared in which the writer, Dr. Horton,[8] is of the opinion "that the ionization from platinum (and from metals generally) is largely due to the emission of absorbed gases on heating."[9] A considerable portion of the proof in support of his conclusions rests upon the observed increase in the ionization effects after heating the wire, or salted anode, in a Bunsen flame.

The writers of this article will present the results of some experiments showing (1) that there are at least two sources of ionization present as impurities in platinum and that one of these becomes more operative and the other less so with continued heating due to the greater ease with which one of the sources is driven off by heating, and (2) that a wire, which has been so treated as to have become non-efficient in its emissive

[1] Phil. Mag., p. 557, 1910.

[2] Phil. Mag., p. 989, 1910.

[3] Camb. Phil. Soc., Vol. XV., p. 64.

[4] Proc. Roy. Soc., Vol. 84, p. 433, 1910; Camb. Phil. Soc. Proc., Vol. XVI., pp. 89 and 318, 1911.

[5] Phil. Mag., Vol. 20, p. 582, 1910.

[6] Phil. Mag., Vol. 21, p. 634, 1911.

[7] Ann. der Phys., Vol. 36, p. 796, 1911.

[8] Proc. Roy. Soc., Vol. 88, p. 117, 1913.

[9] *L. c.*, p. 139.

power, may be revivified so as to give greatly increased thermionic currents when its surface is cleaned.

The experiments to be described were made in dry air at atmospheric pressure. There are several reasons to be advanced in favor of this procedure rather than to carry on such experiments in a good vacuum. (1) The reproducibility of conditions when the apparatus has been opened, the wire treated, re-inserted and its ionization currents again investigated. Richardson and Sheard[1] found that the linear current-E.M.F. relation which holds initially for the positive currents from platinum (heated at temperatures such that no negative ions were present) at low pressures ultimately disappeared, giving place to saturation current conditions. The large additional currents were restored by allowing the apparatus to stand with air at atmospheric pressure in it. In the light of these experiments some of the results which have been published relative to the restoration of emissive power when a wire has been heated in a gas may be questioned, for the increased currents obtained after repumping may be due in part to this cause. (2) The elimination of effects due to contamination of the wire with mercury or phosphorous vapor; the first mentioned effect has been discussed recently by Horton.[2] (3) The ionization phenomena are of the same general nature whether performed at atmospheric pressure or in a vacuum as shown by H. A. Wilson,[3] O. W. Richardson[4] and W. Wilson.[5] The bulk of experimentation in this field has been carried out at pressures ranging from a small fraction of a millimeter to twenty or thirty millimeters. It is reasonable to assume, if the presence of a gas about the heated wire is an important factor in ionization effects, that the pressure of the gas will not affect the phenomena *qualitatively* but rather *quantitatively*.

APPARATUS AND METHOD OF EXPERIMENTATION.

The main chamber used in these investigations is sketched in the accompanying diagram, Fig. 1. A cylinder of brass, A, 11.5 cm. long and 6 cm. diameter, was closed at the ends with quarter-inch brass plates. Through the lower plate, B, two well insulated, heavy brass leads were passed. The platinum wire, C, 0.01 cm. diameter and about 3 cm. in length, was fastened tautly across the ends of the brass leads. The receiving electrode, D, consisted of a hollow cylinder of brass, 4×1 cm., attached to a micrometer screw passing through a threaded bushing of

[1] PHYS. REV., Series I., Vol. XXXIV., p. 391, 1912.

[2] *L. c.*, pp. 121 and 133.

[3] Phil. Trans., A, Vol. 197, p. 415, 1901.

[4] Phil. Trans., A, Vol. 207, 1908.

[5] *L. c.*, under (6).

brass properly insulated from the remainder of the upper plate, E, by means of glass and sealing wax. The distance between the two electrodes could thus be changed at will; in the experiments to be described it was kept at 4 mm. The detecting electrode was kept cool by drawing air through a system of tubes, NN, passing inside the micrometer arrangement and attached at opposite sides of a brass partition within the electrode proper. With this form of apparatus it was possible to completely shield the insulation from the thermionic emission and also to avoid uncertainty as to the correct current values due to heating the receiving electrode. Such effects have been noted and investigated somewhat by Richardson.[1]

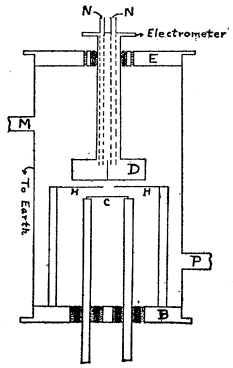

Fig. 1.

Some preliminary experiments showed that the length of wire made luminous increased considerably as the heating currents were augmented. The thermionic currents would in consequence be enhanced above true values as the temperatures increased. In order to avoid this source of error a plate, H, with a circular hole 1 cm. in diameter was placed 1.5 mm. from the platinum wire, the center of the opening in the plate being directly above the middle point of the wire. The plate H was fastened to metallic supports terminating in the plate B. This was earthed together with cylinder A and plate E.

Dry air or other gas was drawn into the main apparatus through calcium chloride towers connected at M, the needed suction being supplied by a water pump operating through P. Stopcocks were inserted in M and P; the plates B and E were sealed in with soft wax, the whole chamber being made air-tight. Ionization effects due to the presence of water vapor[2] were thus guarded against.

The platinum wire was heated electrically. The resistance of the wire was determined by the voltmeter-ammeter method. Two platinum leads (not shown in Fig. 1) were attached to the wire about 1 cm. from each end; the potential differences were read on an instrument graduated to 0.02 volt per division. It was possible to read the heating current to one one-thousandth of an ampere; constancy of current at any desired value was secured by a low-valued sliding resistance control. A linear relation existed between the calculated resistances and the currents; the projection of this line until it intercepted the resistance axis at the

[1] Phil. Trans., Vol. 207, p. 19.

[2] See W. Wilson, Phil. Mag., Vol. 21, 1911.

zero point gave a ready means of determining the absolute temperatures, the resistance at room temperature being that for which the value of the current was practically zero.

The thermionic currents were measured by a quadrant electrometer. Throughout this paper, unless specified to the contrary, one division per second represents 3.7×10^{-13} amperes. The wire was charged to any desired potential, while the receiving electrode was connected to one of the quadrants of the electrometer, the other being earthed. A subdivided microfarad condenser connected in parallel with the insulated quadrants was used for measuring currents beyond the range of the electrometer. Keys, electrometer, condenser and lead wires were properly screened in the usual manner.

The wire, before insertion in the apparatus, was cleaned in boiling dilute nitric acid and then washed in distilled water.

When the thermionic current had been reduced to the steady leak condition observations were made upon the relation between the current and the applied electromotive force. Saturation currents were obtained under an applied potential of 150–200 volts, the latter being used.

THE THERMIONIC EMISSION AS A FUNCTION OF THE TEMPERATURE.

Numerous experiments have shown the general applicability of Richardson's formula,

$$i = A\theta^{\frac{1}{2}}e^{-b/\theta},$$

to express the relation between the saturation thermionic currents and the absolute temperatures of the wire, provided the chemical nature of the source of ionization is unaffected by the temperature changes. This formula may be most conveniently used by testing the linearity of the relation obtained by plotting $\text{Log}_{10} I - \frac{1}{2} \text{Log}_{10} \theta$ against $1/\theta$. The curves given in Fig. 2 were plotted in this manner.[1] In Curve I the current readings were made in the following way: the heating current was adjusted to the desired value and, when constant, +200 volts was applied to the wire and the ionization current measured. The potential and the heating current were then cut off, the control resistance changed and the above procedure repeated. It was thus possible to obtain the maximum ionization current at any given temperature, previous experience having shown that there is no "fatigue" effect due to temperature alone. The values of the currents used in Curve I are given in Table I., column 2. A discontinuity is indicated at the points E, D_1. Repetition with a new wire gave a similar effect at about the same temperature (710–

[1] The current values used in the plot are the number of divisions per second multiplied by 100.

730° C.). The accuracy of EE_1, shifted as it is from the line D_1B, is to be questioned, especially in view of the fact that at still higher temperatures than those indicated the initial thermionic currents decayed so rapidly, even under the most rapid method of experimenting, as to fall

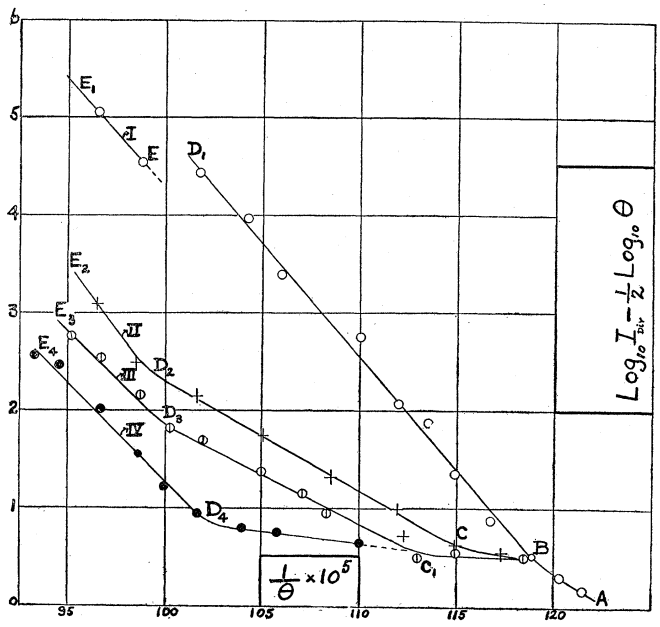

Fig. 2.

below the value of E_1 at 764° C. This is in part at least to be accounted for by the presence of the negative ionization which would make recombination a factor.[1]

The values in Curve *II*, Fig. 2, were obtained as follows. The wire was heated at a given temperature and the decay of the ionization with time determined. The "slow decay" values of the currents were made use of in determining the relations given in *II*. A sample set of readings at 740° C. is inserted below.

Time (minutes)	0	1	2	3	6	8
Current	200	168	154	140	123	116
Time (minutes)	10	13	19	24	26	31
Current	110	105	85	78.5	78.5	79

Hence 79 div./sec. was taken as the value of the slow decay-with-time

[1] Under a potential of − 200 volts a negative current of 1 division per second, remaining constant in value during an hour's testing, was obtained at 705° C. The negative values were, however, always very small in comparison with the positive currents. After the positive emission had reached the condition indicated in Curve IV. at 764° C., a negative current of 1.5 divisions per second was obtained at that temperature.

current. The order of heating, temperatures used, time of heating at each temperature and the slow decay current values are given in the appended table:

Column.	1	2	3	4	5	6	7	8
Temperature, ° Abs.....	845	869	893	923	953	983	1013	1040
Current, (div./sec.).....	1.05	1.2	2.6	6.7	16.6	42.5	78.5	495
Time heated (min.).....	30	35	35	28	28	28	30	18

Curve *III* was taken immediately after the highest temperature value of the current given in *II*. The readings were taken in the manner described in discussing Curve *I*, proceeding from lower to higher temperatures. Curve *IV* was obtained in an analogous manner after the wire had been left standing cold in the apparatus for eighty hours.

It appears, then, from an examination of these curves that there are two sources of ionization present as impurities in the wire. One of these becomes the predominant and permanent source of positive thermions at the higher temperatures as heating under potential is continued. The ionization from the second source is more easily driven off with heating and drops away with time more rapidly than that from the other substance capable of giving rise to positive ions and becomes in time practically inefficient as a producer of ions as shown in Curve *IV*, C_1D_4.

The tangent of the angles which the above lines (Fig. 2) make with the axis $1/\theta$ is a measure of the work done in setting free an ion. If it is legitimate to interpret all portions of these curves in this manner, then it is apparent, first of all, from the parallelism of EE_1, E_2D_2, E_3D_3 and E_4D_4 that the value of the work required to free a positive ion from one source of ionization remains constant under continued heating. The ratio of the tangents of the angles made by E_4D_4 and CD_2 with $1/\theta$ is equal to 0.57. The values of "b" calculated from the relation

$$b = \frac{\frac{1}{2}\log_e \theta - \log_e I}{1/\theta}$$

for the two portions C_1D_3 and D_3E_3 of Curve *III* are 2.4×10^4 and 4.5×10^4. Professor Richardson[1] has calculated the values of $\delta\phi$, the discontinuity of potential (in volts) between the metal and the surrounding space, as 2.45 for sodium and 4.1 for platinum. The ratio of these is 0.6. The writers of this paper venture the suggestion that the source of ionization operative at low temperatures is a sodium salt impurity and that the permanent source giving ionization from platinum at temperatures above 700° C. or thereabouts is a salt of another base, potassium, if we accept Richardson's recent work.

[1] Phil. Trans., Vol. 201, page 545.

The above experiments and the brief analysis made are in accord with Richardson's views. We quote the following from one of his recent papers:[1] "The gradual increase of m as the heating is continued is in agreement with the author's previous experiments on platinum.[2] It would seem to indicate that the source of positive ionization of lower atomic weight from platinum is more easily driven off by heating than that of higher atomic weight. The results are in agreement with the view that the ions of lower atomic weight are sodium atoms, but as the substance of higher atomic weight is less easily driven off by heat, it would appear that some impurity other than sodium or its salts has to be looked for."

CURRENT-TIME RELATIONS.

Additional support in favor of the above view is offered by the current-time relations plotted in Fig. 3. The wire was treated in a manner to be discussed later in this paper and its ability to produce ions under varying temperatures brought back approximately to the conditions indicated in Curve *II*, Fig. 2. Curve *1*, Fig. 3 (currents × 10), shows the steady

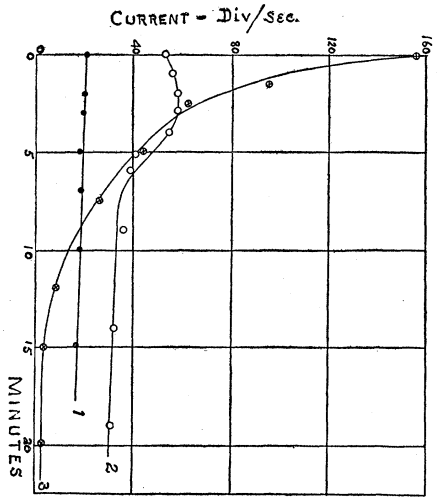

Fig. 3.

valued current condition at 642° C., the readings being made after the wire had been previously used at 800° C. and 725° C. In Curve *2*, obtained at 725° C., there is an initial increase of the current to a maximum after two to three minutes before the decay sets in. Before taking the readings the heating current was adjusted until constant, the poten-

[1] Phil. Mag., Dec., 1910, p. 993.

[2] Phil. Mag., Vol. 21, p. 759.

tial was then applied and the observations made. This method of operation it seems to us ensures the legitimacy of the results, for it eliminates errors due to slight resistance—and hence temperature-changes which often occur in the early stage of heating. Results similar in nature to those in Curve *2* were obtained when the current-time effects were investigated at temperatures considerably below those at which a wire had been previously treated until its steady current stage was reached. Horton has also noted the occasional occurrence of the initial increase of emission from reheated platinum.[1] The ionization currents, however, fell away from an initial maximum value when the wire was heated at 800° C. as shown in Curve *3* (currents × 100).

Current-time relations showing an initial increase were also found when obtaining the data used in Curve *II*, Fig. 2, at 596°, 620° and 643° C.

This initial rise of current during the first few minutes heating would be overshadowed completely if the second source of ionization, decaying with time in the manner shown in Curve *3*, were operative to any considerable extent. It is probable then that these two distinctive types of decay curves, indicating two sources of ionization, have not been definitely differentiated previously because (1) the current-time effects have not been investigated within the proper temperature regions after the wire

TABLE I.

Column 1. Temperatures in degrees absolute.
Column 2. Initial currents in divisions per second. See Curve *I*, Fig. 2.
Column 3. Currents after 30 hours' heating under potential at different temperatures.
Column 4. Currents after wire heated for 10 minutes in gas flame.
Column 5. Currents after heating electrically in hydrogen.
Column 6. Currents after wire brought back to "steady current condition."
Column 7. Currents after cleaning wires in nitric acid.

1	2	3	4	5	6	7
838	0.93	0.83	0.62	0.92	0.83	0.75
857	2.27	.....	.....	.....	.....	.....
868	6.65	2.00	6.75	3.6	0.80	0.74
881	23.4	.....	.....	.....	.....	.....
892	46.8	2.18	32.4	15.4	.....	.....
910	183.0	1.88	61.5	64.7	1.16	13.3
934	835.0	1.82	78.0	110.0	1.18	46.2
958	2,900.0	2.00	92.5	423.5	1.18	819.5
982	8,850.0	2.94	.....	4,785.5	.....	.....
996	.....	5.9	92.5	10,000.	4.15	2,035.5
1,012	10,400.	12.5	157.	12,210.	.....	.....
1,036	38,400.	34.3	110.(?)	11,000.	5.5	3,666.
1,057	.....	91.6	209.	16,940.	10.0	5,200.
1,072	.....	110.0	363.	22,000.	17.0	10,000.(?)

[1] Proc. Roy. Soc., Feb., 1913, p. 136.

has been treated for some time, and (2) the products of decomposition of one of the sources, the active and inactive, giving an ionization-time relation expressible by $e^{-\lambda_1 t} - e^{-\lambda_2 t}$, have rates of decay, λ_1 and λ_2, not widely different from each other; hence the initial increase of currents might be missed.

THE EFFECT OF A CHANGE IN THE SURFACE CONDITIONS OF THE WIRE UPON THE POSITIVE EMISSION.

Table I. contains a summary of the increased thermionic emission obtained when a wire, which has lost in a marked degree its power of producing ionization, was heated in the flame of a Bunsen burner (column 4), heated electrically in an atmosphere of hydrogen (column 5) or cleaned in hot dilute nitric acid (column 7). For the purpose of comparison the initial thermionic currents, as plotted in the ionization-temperature Curve *I*, Fig. 1, are given in column 2; the emission after thirty hours' treatment under potential and under various conditions of temperature in column 3. The lower plate *B* carrying the wire was removed from the apparatus after the readings recorded in column 3 had been made; the wire was heated intermittently for about ten minutes in the outer edge of the Bunsen burner flame, care being taken that the wire was not heated at a higher temperature than any previously used in these experiments. This was done by a visual observation of the luminous condition of the wire.[1] On re-inserting the wire and testing its emission it was found that the currents were considerably increased, especially at the lower temperatures. The effects were somewhat erratic, however, as an inspection of column 4 shows; the ratio of the values given in columns 4 and 3 showing a falling off from 40 to 1 at 934° Abs. to 3 to 1 at 1072° Abs. This general condition of increased currents disappeared very rapidly with continued heating and in thirty minutes time the currents had approximately the values given in column 3.

The wire was then heated electrically at 760° C. for five minutes in an atmosphere of dry hydrogen.[2] The current readings at various tempera-

[1] The heating of the wire at temperatures in excess of any previously used in testing the ionization from a hot wire or salt must be carefully guarded against, for such a treatment of the wire will give greatly increased thermionic currents when again heated at any lower temperature which may be chosen. These last mentioned effects are being investigated further. It is possible that the increased emission observed by Horton after introducing a platinum wire or salted anode into a flame and heating it may be attributed to this cause and not wholly to the absorption of gas.

[2] Air became mixed with the hydrogen at this point causing an explosion. The wire was not disturbed from its supports and was used in further tests. In view of latter results it is probable that part of the increase of current obtained was due to the mechanical cleaning of the wire produced by the explosion.

tures are recorded in column 5; the values of the currents being roughly one third to one half of the initial effects. The increased emission obtained after heating electrically in hydrogen did not decay to the low-valued emission condition, such as indicated in column 3, as quickly as when the wire was heated in the Bunsen flame.

Following the current readings given in column 6, the wire was washed for a minute or two in boiling dilute nitric acid, then cleansed in distilled water and when dry was replaced in the apparatus.[1] The thermionic currents following this treatment of the wire are contained in column 7. The relative magnitude of the currents before and after the cleaning in acid is as large and at several temperatures greater than the effects obtained by heating the wire in hydrogen.

The ionization from heated platinum is apparently a surface effect, and any change in the surface conditions of the wire, whether by heating in a gas or chemically cleaning, affects the subsequent ionization. That the use of a chemical reagent, which in itself has no effect upon platinum, should cause such changes in the ionization effects indicates the formation of a layer of practically non-ionizable material built up at or carried to the surface of the wire when heated for some time under potential. The residue of materials thus formed and not capable of producing ions would increase and become more operative with time and act as a blanket toward the "evaporation" of ions from the surface. It seems impossible to explain results such as those just presented on the theory that the chief source of the carriers of positive electricity from heated metals consists of absorbed gases. The function of a gas in restoring the power a wire has of producing ionization may be due to one or to all of several causes: first, a chemical change of such a nature as to render an inactive surface layer an efficient source of ionization; second, the removal of surface material by volatilization of new chemical compounds or combinations formed at high temperatures; third, in accord with some experiments by Reboul and de Bollemont,[2] the violent evaporation of absorbed gas may mechanically cleanse the surface. Some time ago Richardson[3] advanced the theory that "the effect of hydrogen is due to some changes it produces in the platinum surface"; he discusses this hypothesis at some length in the concluding paragraphs of the article referred to.

In the face of these experiments the writers are of the opinion that the weight of evidence is in favor of Richardson's view that the positive

[1] The wire was not removed from its supports in any of these operations; otherwise criticism might justly be offered on the grounds of contamination in replacing the wire, etc.

[2] Comptes Rendus, 153, 1911, pp. 628–630.

[3] Phil. Trans., Vol. 207, 1908.

emission from heated platinum consists chiefly of charged atoms of sodium and potassium present as impurities.

SUMMARY.

1. Two sources capable of producing thermions are present as impurities in platinum.

2. One source of ionization is more easily driven out by heating than the other.

3. After continued heating and when investigated within the proper temperature region, two distinct types of current-time curves are obtained; one showing a decay with time from an initial maximum, the other giving rise to a maximum after two or three minutes heating followed by the usual decay effects.

4. The thermionic emission from a wire which has lost its power of producing ions may be enhanced and made comparable with the initial effects by (*a*) heating in a Bunsen flame, (*b*) heating electrically in hydrogen, (*c*) cleaning the wire with acid.

5. The proposition is advanced that any change in the surface conditions of a wire or a salt will affect the subsequent ionization effects.

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