



## LXVI. The variation of thermionic currents with potentials

Horace Lester Ph.D.

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LXVI. *The Variation of Thermionic Currents with Potentials.*  
 By HORACE LESTER, Ph.D., Instructor in Physics, Princeton  
 University\*.

INITIAL thermionic currents from hot surfaces differ from the currents found after steady conditions have been obtained. The peculiarities of these currents have been studied by several investigators. Richardson† found that the positive emission was not permanent, that it did not “saturate” easily, and that the currents increased with the temperature according to an exponential law, at least for a limited range of temperature. He found the carriers to be of atomic magnitude, and considered them to be produced by thermal dissociation of impurities in the hot anode. A further investigation of the initial positive emission has been undertaken more recently by Richardson and Sheard. They were prevented from completing their experiments, but a preliminary account‡ of the results obtained has been published in a note in the ‘Physical Review.’ They found that the positive currents decayed with time, the rate of decay depending on the temperature, and that the current-potential relation at constant temperature followed a steep curve up to about 40 volts, at which point a bend occurred towards the potential axis, and beyond which there was a nearly linear increase up to 400 volts. According to Richardson’s theory referred to above one would expect saturation to occur at much lower potentials than those mentioned, since the number of negative ions or electrons present is negligible. Saturation for positive currents does not ordinarily occur, although Richardson and Sheard found that with time the slope of the curve above 40 volts decreased; so that approximate saturation was obtained eventually.

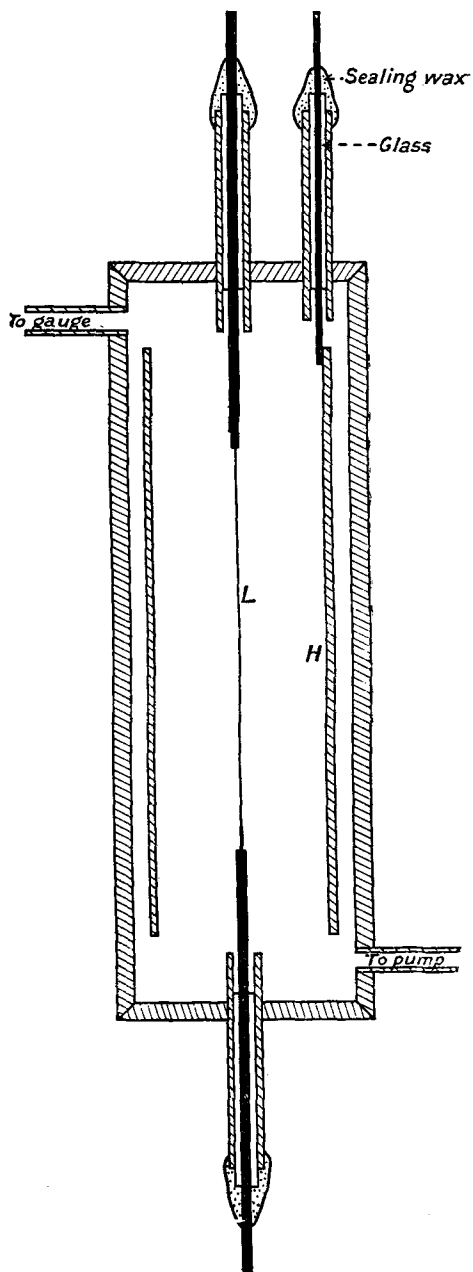
At the suggestion of Professor Richardson, the writer undertook the continuation of this investigation. As a result, the above-mentioned peculiarities of the current-voltage curves for the initial positive emissions have been confirmed, and similar phenomena have been found to occur with the initial negative currents. The further conclusion of Richardson and Sheard that the increase in the current beyond 40 volts is due to secondary ionization caused by the bombardment of a film at the opposite electrode has not been verified. It is possible that such an effect may occur, but it seems clear

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Phil. Mag. July 1903, Sept. 1904.

‡ Phys. Rev. vol. xxxiv. p. 392 (1912).

Fig. 1.

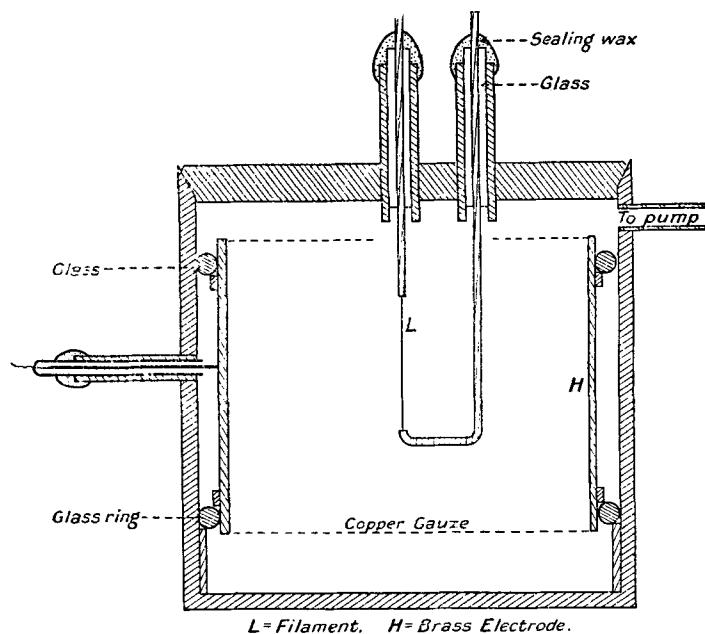


*L* = Filament. *H* = Brass Electrode.

from the experiments that it is not a necessary cause of the increase, and that it cannot have caused any considerable fraction of the increase observed in the present experiments. A number of other points connected with initial thermionic emissions have been examined in the course of the investigation.

The experimental investigation involved observations of thermionic currents in good vacua for various temperatures and potentials, and with various other conditions to be described below. The currents were obtained from platinum wires mounted axially in cylindrical vessels, which contained the receiving electrodes. Figs. 1 and 2 show two types of

Fig. 2.



vessel used. The currents were measured by an electrometer in the ordinary way. For large currents the electrometer was shunted across a resistance, and in some cases a microammeter was used. Generally speaking, the currents were chosen so as to be as large as possible subject to the decay being negligible during the course of the observations. The vacua were produced by a rotary mercury-pump, and were usually about  $3 \times 10^{-5}$  mm. of mercury on the McLeod gauge.

*Experimental Results.*

In the beginning it was found that lack of saturation characterized both positive and negative currents apparently without distinction. The potential-current curve showed a sharp bend towards the potential axis at about 40 volts. The increase at 400 volts over the value at 40 volts divided by the latter represents fairly the difficulty of attaining saturation. The lack of saturation will be represented by the expression

$\frac{\Delta i}{i}$ , where  $i$  is the current at 40 volts and  $\Delta i$  is the increase in  $i$  between 40 and 400 volts.

This extra current may be due to ionization at the surface of the cold electrode, to ionization of a gas or vapour layer near the hot surface, or to phenomena at the surface of the hot electrode. In order to test the first possibility, an apparatus was constructed whereby it was possible to rub the inner surface of the receiving electrode with emery-cloth. Readings could be obtained within 30 seconds after rubbing. This treatment showed no

appreciable change in the value of  $\frac{\Delta i}{i}$ . Another apparatus

was designed in which it was possible to heat the cold electrode to approximately 700° C. While the electrode was being heated the platinum wire was cold, and was drawn completely out of the experimental chamber. Repeated heatings, some of several hours' duration, showed no change in the lack of saturation. Another test was carried out as follows:—Experience has shown that after considerable

heating the value of  $\frac{\Delta i}{i}$  becomes very small, at least in many cases. If  $\frac{\Delta i}{i}$  is due to the ionization of the film at the surface

of the cold electrode, then the film having been destroyed by one wire,  $\frac{\Delta i}{i}$  should be permanently small for a second

wire not previously heated. Three or four tests of this sort showed that the value of  $\frac{\Delta i}{i}$  for the second wire was independent of the value of  $\frac{\Delta i}{i}$  for the first wire. The series of

experiments seemed to show conclusively that ionization at the cold electrode of a volatile film could not account for the observed lack of saturation.

To test the second possibility—viz., that lack of saturation was due to ionization in a dense vapour near the hot surface—a wire was mounted in a glass cylinder containing a cylindrical receiving electrode and a quantity of coconut-charcoal in a space below the open end of the cylindrical electrode. Liquid air could be applied to the charcoal and also to a trap in the pump-connexion just outside the glass cylinder. Observations were taken with liquid air off and on the charcoal, off and on the trap, and off and on both together. There was no detectable change in the value of  $\frac{\Delta i}{i}$ . The pressure on the McLeod gauge was  $1 \times 10^{-5}$

before applying liquid air, and no change occurred upon applying the liquid air. No change in the gauge-reading was expected, however, because the vapour, if it existed, would condense on the colder portions of the tube before it reached the gauge. The result of this experiment indicated that there could be no considerable amount of vapour around the hot surface. The fact that there was no appreciable cooling of the hot wire when liquid air was applied was a further indication that there was very little gas present.

Since the first two hypotheses concerning the location of the phenomena causing lack of saturation were apparently untenable, there remained only the hypothesis that the effect was due to phenomena at the hot surface. To get at the nature of these phenomena, a detailed study of the peculiarities connected with initial emissions was undertaken. In all twenty-three different wires were studied under various conditions of purity, surface-cleanness, pressure, &c. It was known that water vapour actively modifies thermionic currents, so water vapour was in all cases excluded from the apparatus. In parts of the experiments the wires were sprayed with salts, and in some cases they were heavily coated with CaO or BaO.

The results of the series of investigations may be summarized as follows:—In addition to the well-known time decay and variation with potentials, there were two features that characterized all of the emissions studied. The first of these was an initial growth in the value of  $\frac{\Delta i}{i}$ . This growth was rapid at first, and more gradual later. A stationary value often occurred followed by a period of slow decay. The initial growth was repeated for each succeeding higher temperature. The rate of subsequent decay was more rapid for high than for low temperatures.

The second general effect was a peculiar over-shooting in the current\*. For a field of 40 volts between the electrodes the currents became steady. Upon changing the potential to 400 volts there was a relatively large current that changed in a few moments to a smaller steady value. The magnitude of the initial current was often 150 per cent. of the steady value. The change occurred mostly in the first 20 seconds, and the total change took about ten minutes in most cases. Upon changing potentials from 400 to 40 volts there was an initially small current that *rose* to a steady value. In this case the greater part of the change occurred in the first five minutes, but the steady value was often not established after two hours.

In addition to the above general effects some special investigations established the following facts:—(1) Wires cleaned by boiling for a long time in  $\text{HNO}_3$ , wires not so treated, and wires purposely contaminated with dust from the floor of the room behaved essentially the same as regards the phenomenon of lack of saturation. Wires known to be very pure in most cases showed currents of smaller magnitude

and smaller values of  $\frac{\Delta i}{i}$ , and smaller over-shooting effects than wires known to be impure. However, there were some exceptions.

For instance, the largest value of  $\frac{\Delta i}{i}$  obtained was from a very pure wire. Its magnitude was 33 for negative and 27 for positive currents. The value of  $\frac{\Delta i}{i}$

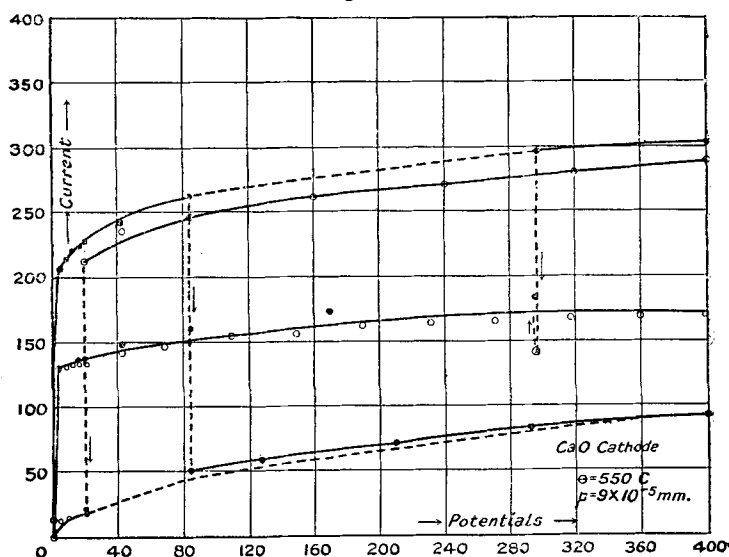
ranged from .1 to 25 for most wires, the most common values being between 10 and 15 for impure wires and between 2 and 7 for pure wires. For impure wires the over-shooting was generally large and the time decay small; for pure wires the over-shooting was generally small and the time decay fairly rapid. Wires sprayed with  $\text{NaOH}$  and  $\text{KOH}$  behaved essentially the same as unsprayed wires, except for the magnitude of the currents and the temperatures at which emission became noticeable. A wire coated with  $\text{CaCl}_2$  showed the remarkable property of perfect saturation when first heated, but after an hour the current had decayed

20 per cent., and there was a value of  $\frac{\Delta i}{i}$  of magnitude .3.  $\frac{\Delta i}{i}$  was still growing when observations were discontinued.

\* Effects similar to this have been recorded by Richardson, *Phil. Trans. A.* vol. c. vii. p. 29 (1906).

A wire coated with CaO and tested only for negative emissions showed an instability of currents with applied potentials. There were apparently three possible ranges for the current-potential curves. The current broke suddenly from one range to another. The behaviour may be understood best by reference to fig. 3. These double and triple range phenomena were obtained with two other CaO cathodes and with a BaO cathode.

Fig. 3.



It seems to the writer that the facts established in the above experiments fit very well into already proposed theories, if some further assumptions are made as to conditions at the surface. The lack of saturation, the initial growth, and the over-shooting effects are the most general facts to be adapted.

Richardson's theory of negative thermionic emission regards a discontinuity in the potential energy of an electron at the surface of the metal. Since this theory is well established, the probability of the existence of the discontinuity is great. The discovery and direct measurements of the cooling effect by Wehnelt\* and by Richardson and Cooke†, and of the heating

\* *Ann. der Physik*, [3] vol. xxviii. p. 537 (1909).

† *Phil. Mag.* April and Sept. 1913.



effect by Richardson and Cooke\*, have further established the fact of the potential discontinuity. It is probable that this drop of potential takes place in a film at the surface of the metal which has different properties in case of a new wire as compared with one which has been heated for some time. There is considerable evidence for the existence of surface-films. Langmuir†, for example, showed that films exist, and that it is extremely difficult to get rid of them. I have given evidence in another paper of the existence of ionized films, such that an escaping electron must do work against the field produced by the film‡. It seems to me that a consideration of the conditions in such a film will give an explanation of the peculiarities of initial thermionic currents.

There is evidence to support the idea that a double layer exists in the film even when the metal is cold and has not been heated§. However, during heating the escape of volatile impurities brings new material to the surface, and this material coming in contact with active gases forms chemical compounds, some of which are solid, and add to an old or actually form a new film.

If a positive potential is applied to the hot metal the more loosely held positive ions escape and form the initial large current which shows small values for  $\frac{\Delta i}{i}$  and negligible overshooting. This initial current decays rapidly to a smaller value that may be fairly constant for a long time.

The conditions under which the current shows slow decay may be very complicated. It is probable that an equilibrium condition results between the escaping ions and circumstances tending to prevent their escape. The simplest condition that occurs to me is a state in which the ions have to move through neutral material by thermal energy plus the force of the applied field before they are in a favourable position to evaporate. We should then have equilibrium conditions between the rate of formation of ions, the rate of drift to the film surface, and the rate of escape under the accelerating potential. The rate of formation represents an equilibrium condition between the rate at which dissociation occurs and the rate of removal of the ions. It might be

\* Phil. Mag. July 1910 and April 1911.

† Journ. Am. Chem. Soc. xxxv. p. 105.

‡ Phil. Mag. [6] xxxi. p. 197 (1916).

§ The fact that both the heating effect and the cooling effect are increased when active gases are present indicates that similar films exist at both surfaces.

considered that for a long time the ions are formed as fast as they are removed. The rate of removal depends on the rate of drift across the film due to thermal energy and to the applied field. Since the rate of escape is a function of the rate of drift to the surface, and since the rate of drift depends on the applied potentials, the emission clearly depends on the applied potentials. For potentials high enough for the drift under the applied field to be relatively more important than the drift due to the thermal energy there would be a nearly linear relationship between currents and potentials. This agrees with observation for potentials above 40 volts. For the current below 40 volts emission is a function principally of the escape due to thermal energy, and the current-potential curve is analogous to the unsaturated portion of an electronic current-potential curve. This, again, agrees with experiment. The initial condition where ions escape without having to cross a region of neutral material should give a small value of  $\frac{\Delta i}{i}$ . The later stage should give a large value whose magnitude depends upon the thickness of the film. Hence the observed initial growth in  $\frac{\Delta i}{i}$  is explicable also. It is known that wires may be "aged out." That is, after sufficient heating no more positive ionic currents are obtainable. This decay of the positive current corresponds to the using up of ionizable material. Presumably the film gradually evaporates. The last traces of film, no doubt, persist for a long time, but in many cases at least the film becomes very thin. Now observation showed that in all cases there was a value of  $\frac{\Delta i}{i}$  as long as the currents were obtainable. In most cases the final value was relatively small, something of the order .1. In some cases the value of  $\frac{\Delta i}{i}$  was large even to the end.

The over-shooting is also consistent with the theory of ionization within the surface-film. The escape of ions at, say, 40 volts is a function of the rate of drift to the surface of the film. Owing to the small velocity of drift with 40 volts there is a relatively large number of ions near the surface of the film. If now the rate of drift is accelerated by changing the potential to 400 volts, there occurs a relatively large current during the time in which a new equilibrium ion

density in the film is established consistent with the new velocity. Similarly, upon suddenly decreasing the potential from 400 to 40 volts, there is a decreased current during the time that the film "fills up" to an equilibrium density. The fact that equilibrium was established more quickly at high than at low potentials is consistent with the idea that the speed of the ion in the film depends largely upon the applied potential.

The above discussion has considered only positive currents. However, the same film-conditions would produce similar effects for both the positive and the negative emissions. In the case of the negative currents most of the carriers are electrons, since in only a few cases have negative ionic carriers been detected.

The double-range phenomena observed with CaO and BaO cathodes have been observed by Richardson and Cooke for an osmium cathode and by Langmuir for a tungsten cathode. The instability in current was no doubt caused by an instability in the surface-film. Probably the ionized material in the film becomes unstable, so that chemical combination occurs forming new compounds with characteristic emitting properties. The suddenness of the change from one compound to another was surprising. The large changes in current that occurred illustrate the great importance of surface-films in modifying thermionic emission.

### *Summary.*

It has been shown that there is an initial growth in the value of lack of saturation, and that there is a peculiar overshooting effect. These facts, together with more generally known behaviour of initial thermionic currents, indicate that the observed peculiarities of initial thermionic emission may be explained as due to the influence of ionized surface-films.

In conclusion, I would like to express my indebtedness to Professor O. W. Richardson, under whose direction the work was begun, and to Professor H. L. Cooke and Professor E. P. Adams, who have offered valuable criticism and advice.

*Note.*

A peculiar phenomenon was observed with a  $\text{CaO}$  cathode, that for purposes of better observation was mounted in a glass tube which contained a copper gauze anode. After the wire had been under constant temperature, constant pressure, and zero potential for five or six hours, a set of readings for a current-potential curve was taken. Upon changing the potential to 40 volts a blue glow appeared about the cathode, which was brighter at 400 volts, but which disappeared suddenly without affecting the magnitude of the thermionic current. The potential was switched to zero and then put again at 400. The tube lighted very brilliantly. The wire, which had been at about  $900^\circ$  and uniformly bright, became invisible except for a spot about 2 mm. long near the middle of the wire. This spot was dazzling white, and must have been near  $1800^\circ \text{C}$ . The thermionic current was too large for the instrument to record. The anode became heated opposite the glowing spot, and some red sparks passed. The walls of the glass tube glowed with a blue fluorescence except for a pattern corresponding to the shadow of the meshes of the gauze which did not show the fluorescent blue. A lateral tube connecting the experimental chamber with a vertical tube running to the pump happened to be just opposite the bright spot. There was a sharply defined fluorescent spot on the vertical tube opposite the open end of the lateral connexion, though this wall was 3 centimetres behind the gauze anode and 4 centimetres from the hot wire. The glow continued approximately two minutes and stopped abruptly. Subsequent investigation showed the  $\text{CaO}$  cathode to be covered with finely divided copper or copper oxide. Similar discharges were obtained later, but never a second time from the same spot on the wire. They were increasingly hard to stimulate, and after a time ceased altogether. It was found that a rest-period was necessary to get even a second discharge. Similar discharges occurred in another apparatus (the brass apparatus shown in fig. 2) and also with a  $\text{BaO}$  cathode.

Palmer Physical Laboratory,  
Princeton.  
July 1915.