Thermionic emission properties of a lanthanum hexaboride/rhenium cathode†

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Abstract. This paper describes an experimental investigation of the thermionic emission properties of a rhenium tape coated with lanthanum hexaboride, and considers its usefulness as a low temperature emitter for demountable vacuum ionization gauges and mass spectrometers. Methods of preparation and processing are described and measurements of the Richardson emission constants are given. The poisoning of the emission by those gases generally found in vacuum systems has been studied and the extent to which the activity can subsequently be restored is described. Measurements have also been made of the rate of evaporation of active material from the cathode surface.

1. Introduction

The need for more accurate and reliable measurement of pressure, both total and partial, in high vacuum systems has encouraged a much closer examination of the extent and the manner of the interaction between the atmosphere being measured and the component parts of the gauges used for the measurement. In this respect the behaviour of the electron emitter is of major importance.

Ideally a cathode for such an application should possess, in addition to an adequate life, the following properties. It should operate at a low temperature and be chemically inert. It should be able to function satisfactorily to the maximum operating pressure of the gauge and, if its emission should become poisoned, then easy and full reactivation should be possible. The rate of evaporation of active material should be low and, probably most important, it must be able to withstand frequent exposure to the ambient atmosphere.

Of all the emitters presently available the conventional barium and strontium oxide cathode most nearly meets the above requirements, but is, in general, unusable for this type of application since, on exposure to the atmosphere, hydration occurs with consequent damage to the coating which may even be lost completely due to flaking.

Tungsten is the material most commonly used but whilst it is adequate for many applications it is well known that, when its behaviour is assessed in relation to the above specification, serious shortcomings appear due to the several ways in which it can react with and modify the atmosphere being measured. Various alternative materials have been investigated and one of the more promising appears to be lanthanum hexaboride.

The thermionic emission properties of the borides of some of the rare earth metals, including that of lanthanum, were studied by Lafferty (1951). However, the majority of his results were based on the properties of the bulk material and when, as is more generally required, a directly heated cathode is prepared by coating a refractory metal with a boride powder, certain physical problems arise which severely limit the life and usefulness of the cathode. It is perhaps this limitation which accounts for the apparent lack of interest in boride cathodes since the appearance of Lafferty's paper, little having been published since then except in the U.S.S.R., where Samsonov and his co-workers have written a number of papers. However, it has been found that the problems associated with the use of a coated filament can be at least partially overcome by adopting rhenium as the

† Some aspects of this paper were presented at the Conference on Fundamental Problems of Low Pressure Measurement, held at the National Physical Laboratory in September 1964.

substrate material and this paper describes the results obtained from an experimental investigation of the properties of a rhenium/lanthanum hexaboride cathode.

2. Hexaboride properties

Lafferty has shown that a cathode of lanthanum hexaboride will generate a given level of emission at a lower temperature than will any of the other commonly used materials, except barium oxide but, as previously mentioned, barium oxide is generally unsuitable for use in demountable pressure measuring gauges.   In addition he states that lanthanum boride cathodes are easy to activate and are atmospherically stable, and that they exhibit considerable chemical inertness together with a low rate of evaporation.   Indeed, on comparing the rate at which active material was evaporated when each type of cathode was heated to a temperature necessary to give the same density of emission, he found that the rate was lowest for LaB_6.   This relationship between emission and evaporation rate, as shown for instance by Wright (1953), constitutes the most important parameter to be considered when assessing the usefulness of an emitter, particularly for an application of this kind and on such a basis a lanthanum hexaboride cathode would appear to be the most promising emitter presently available for vacuum gauge applications.
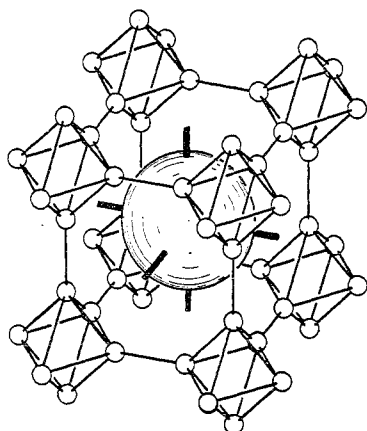

Figure 1.   The lattice of LaB_6.

These attractive characteristics result from the rather unusual properties of the series of interstitial compounds which can be formed between boron and the rare earth metals. The crystal structure of lanthanum hexaboride, which has been extensively studied by Johnson and Daane (1961), is shown in figure 1.   It is typical of all the hexaborides, which have the general formula MB_6.   The small boron atoms form a three-dimensional framework surrounding and enclosing the relatively large metal atom, but there are apparently no valence bonds between the metal atom and the surrounding boron atoms so that the valence electrons of the metal atom are free.   The experimental evidence indicates that the boron framework requires two electrons from each metal atom present, i.e. two from each B_6 group, so that when extra electrons are present, as in the case of lanthanum hexaboride, these behave as free electrons and impart a metallic character to the material.   Paderno *et al.* (1960) have shown that it behaves as a typical metallic conductor having a resistivity of 50 $\mu\Omega$ cm at 20°c with a positive thermal coefficient of resistance of $0 \cdot 060$ $\mu\Omega$ cm degc^{-1} and measurement of the Hall coefficient (Lafferty 1951) indicates the presence of one negative carrier per lanthanum atom.   The stability of the compound on the other hand is determined by the boron framework rather than by the metal atom and, as long as the electronic requirements of this framework are maintained, it appears that the stability is unaffected by other changes such as, for instance, the creation of vacant sites by the diffusion of lanthanum during the emission process.   This stability accounts for the high melting point (approximately 2200°c) and the chemical inertness, properties more akin to those of pure boron.

However, as previously mentioned, physical difficulties arise when a directly heated emitter is prepared by coating a refractory metal wire or tape with a suspension of lanthanum hexaboride powder. These result from a tendency of the boron to diffuse into the underlying metal lattice with the formation of an interstitial metal–boron alloy and, as this diffusion proceeds, the boron framework holding the lanthanum atoms collapses. This collapse allows the lanthanum atoms to escape and evaporate and, in addition, the diffusion produces considerable embrittlement and ultimate failure of the base metal. It continues until either all the interstitial spaces have been filled or the whole of the lanthanum has evaporated. The rate at which it proceeds varies with the base metal. Experiments with a coated tungsten filament have given a maximum life of approximately 50 hours, but with platinum and iridium filaments boron diffusion was so rapid that the whole structure had physically collapsed before normal activating temperatures had been reached. The diffusion into rhenium, a material which was apparently not examined by Lafferty at that time, is by comparison much slower. A lanthanum boride coated rhenium tape emitter has been used, apparently quite satisfactorily, in an Omegatron (Steckelmacher and Buckingham 1963), several of which have achieved lives of some thousand or so hours. In support of this application a detailed investigation, including measurement of the rate of evaporation of active material from the cathode together with an evaluation of the emission properties and the poisoning and reactivation of the cathode when exposed to certain known atmospheres, has been undertaken.

3. Experimental techniques

3.1. *Filament preparation and processing*

The filament material was of rhenium, either as wire of 0·010 in. diameter or tape 0·025 in. × 0·002 in. The tape, produced by rolling and slitting, was somewhat superior in quality to the wire, which was drawn. The rhenium was processed by cleaning and slightly roughening the surface by a vapour-blasting technique which was then followed by vacuum furnacing at 950°c for 30 min.

Whilst the lanthanum boride powder can be applied to the substrate in a number of ways, the correct choice of coating method is rather important; because, whereas cathodes of boride powder sinter to themselves at temperatures as low as 1400°c, their adherence to the base metal is poor, especially at the beginning of life. Of the various coating methods tried, cataphoresis appeared to be the most satisfactory. This should perhaps have been expected since it is a property of cataphoresis that only those particles within a rather limited range of sizes are deposited, giving rise, therefore, to a continuous coating of quite uniform density which provides the greatest chance of self-adhesion by sintering. Fine grain powder, 5 to 8 μm particle size, was suspended in methanol and, to aid the cataphoresis process, a little magnesium nitrate was added as an activator. The time of coating and the current density required varied appreciably, being markedly dependent upon the precise dimensions of the substrate, but the correct conditions were not difficult to assess in practice, since a well-coated filament had a typical appearance which was readily apparent under microscopic or pyrometric examination. When a newly coated cathode, or an activated one which had not been used for some hours, was first heated quite large quantities of gas were sometimes evolved and if this was driven off too rapidly damage to the fine structure of the coating occurred; at worst it was found that the whole coating could be explosively blown away from the base metal. This difficulty was overcome by controlling the rate of increase of the cathode temperature such that the pressure above it did not rise beyond 10^{-6} torr.

Filament temperature was measured by optical pyrometry, brightness temperatures being converted to absolute values using a figure of 0·70 for the spectral emissivity (Samsonov *et al.* 1963). It was the original intention to measure temperatures with a thermocouple but this had to be abandoned owing both to the problems involved in spot-welding the thermocouple to the substrate, since rhenium exhibits the property of 'hot shortness', and to the rapid diffusion of boron from the coating into the thermocouple wires, causing the filament to fracture at the thermocouple junction.

3.2. *Vacuum systems*

The experimental pumping system, constructed mainly from stainless steel, is shown diagrammatically in figure 2. It consisted of two vacuum systems mounted side-by-side and connected by a small bore conductance tube, this tube being chosen to give a pressure difference of about three orders of magnitude across its ends. The left-hand system had an ultimate pressure of approximately 10^{-8} torr but the right-hand side, which was bakeable to 450°c within the dotted line shown, approached a limit of 10^{-10} torr. A 6 in. diameter stainless steel test chamber on the ultra-high vacuum side carried a modulated Bayard–Alpert gauge to monitor total pressure, various designs of diode for the measurement of emission and for poisoning experiments, and a more complex tube for the measurement of the rate of evaporation of active material from the cathode. In several of the experiments the test diode was mounted, as shown in the diagram, from the side of an Omegatron so that the composition of the atmosphere in the diode could be monitored as required.
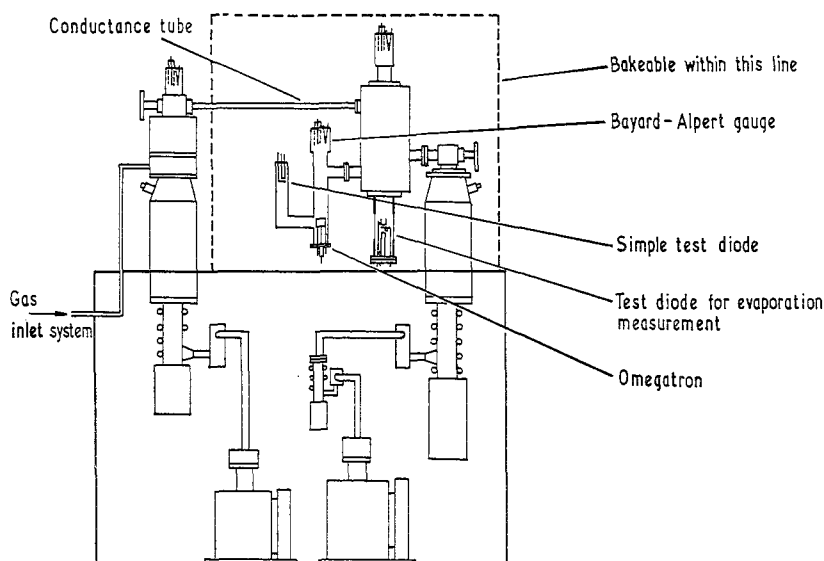

Figure 2. Experimental pump system.

For the poisoning experiments, the test gas, suitably dried and monitored, was introduced into the upper part of the left-hand system and, by regulating the pressure there, any desired pressure level within the range 10^{-9}–10^{-5} torr could be established in the test chamber and maintained sensibly constant under dynamic flow conditions for periods, if required, of several hours. For the poisoning experiments with water vapour, a second vacuum system, similar to that used by Jenkins and Trodden (1959) but with the vapour being introduced into the test diode through an 8 μm orifice in a glass disk, was used.

To maintain reasonably stable operating conditions in the vacuum system throughout the experimental period, which often occupied several weeks, it was general practice at the beginning of each week to bake the ultra-high vacuum section of the equipment at 450°c for three hours, this being followed by a thorough outgassing of the Bayard–Alpert gauge by electron bombardment and of the Omegatron by eddy current heating.

4. Experimental results

4.1. *Emission measurements*

A coaxial triple-anode guard ring structure with a close spacing between cathode and anodes was used for these measurements. The cathode was operated from a transistor-stabilized power supply fed from a 12 v car battery which was maintained fully charged

throughout operational periods by a trickle charger. Such precautions ensured that the long-term stability of the cathode temperature was always within the experimental error inherent in optical pyrometry.

Before each series of measurements, the anodes were outgassed by eddy current heating and the filament outgassed by slowly raising its temperature to approximately 1300°c, filament outgassing being continued until the system pressure was better than 10^{-9} torr. After this degree of processing the cathode was found to be fully active and the drawing of electron current from the cathode produced no significant increase in the level of activity.
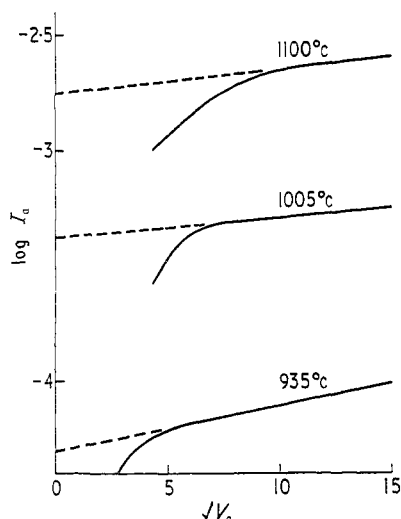

Figure 3. Example of a Schottky plot of the d.c. emission from a typical diode.

(I_a, V_a) plots for various values of filament temperature showed that, whereas saturation of the emission occurred at the lower temperatures, this was not the case at higher temperatures where the current was still rising quite steeply at voltages several times the 'knee' value. An estimate of the saturated current could not, therefore, be deduced from such curves; but it has been shown (Compton and Langmuir 1930) that the true value of anode current to be used in determining the emission constants is that corresponding to zero anode voltage. By replotting the data in the form of $\log I_a$ against $\sqrt{V_a}$, as shown in figure 3, a Schottky plot is obtained and the required value of emission current is given by extrapolating the linear portion of the characteristic down to zero voltage (the broken lines of figure 3). The emission constants (ϕ and A) of the Richardson equation

$$I = AT^2 e^{-e\phi/kT}$$

can then be found from a Richardson plot using ordinates appropriate to the equation

$$\log \frac{I}{T^2} = \log A - \frac{11\,600}{2\cdot303} \phi \frac{1}{T}$$

where I is the current density in amp cm^{-2} and T is the absolute temperature. The slope of such a line gave a figure for the work function of $2\cdot70$ ev, this being, of course, the average for the emitting surface considered as a whole. This value is in close agreement with the results, varying from $2\cdot68$ to $2\cdot74$ ev, reported by Samsonov (1957), and the earlier value of $2\cdot66$ ev found by Lafferty. The value obtained from the graph for A, the second Richardson constant, was 30. In the course of many such measurements it was found that, provided the cathode had been fully outgassed and the partial pressures of any poisoning gases were less than 10^{-10} torr, the work function was essentially constant at $2\cdot70$ ev, but there was some variation in the value for the constant A. However, since the A value is known to be a function of the detailed structure of the surface, some variation between

samples is to be expected due to slight differences in the preparation and processing of the cathode. Indeed, in an early measurement with a simple diode as used in poisoning experiments, an A value of 300 was obtained. Whilst the effective area of this cathode may perhaps have been a little larger than that estimated due to migration of active lanthanum along the uncoated parts of the filament, the general appearance and behaviour of the cathode was so good that the assumption of an A value several times the average might well have been justified.

4.2. *Poisoning experiments*

A more simple plane parallel test diode consisting of a tape filament coated over a length of $\frac{1}{4}$ in. which was mounted parallel to, and distant 3 mm from, a 1 in. diameter dish anode was used for these experiments. The anode and cathode were rigorously outgassed before each experiment.

To investigate poisoning the cathode temperature was set at a particular level and saturated emission was drawn by applying to the anode a set d.c. voltage at least twice the knee voltage, this having been obtained from a preliminary (I_a, V_a) plot of the diode characteristics. The test gas was admitted to the left-hand vacuum system of figure 2, its flow rate there being controlled to give the required pressure in the test diode. The level of emission was monitored continuously and, in the first experiments, poisoning was allowed to continue until the anode current had reached a new equilibrium level whereupon the test gas was rapidly pumped away and the recovery of the emission recorded. This was then repeated, the pressure of the test gas being increased by suitable increments to cover a range of, say, 10^{-9} to 10^{-5} torr. At high filament temperature this method was satisfactory but at lower temperatures, more akin to those found in practice in ionization gauges and mass spectrometers, it was observed that poisoning, once having started, generally tended to continue indefinitely, no true equilibrium level of diode current being obtained. The procedure was, therefore, modified slightly; the change in diode current being recorded whilst the cathode was exposed to the test gas for a fixed period of 10 minutes.

An initial series of measurements showed that the gases which poisoned the emission were oxygen, water vapour, carbon dioxide and hydrogen; those which did not poison were nitrogen, carbon monoxide and the inert gases. Except for hydrogen, these groupings are the same as those found by Jenkins and Trodden (1959, 1961, 1962, 1964) who have made similar studies of various types of oxide-coated cathode. Hydrogen, which is an electropositive gas, would not normally be expected to produce poisoning and it is likely, therefore, that the mechanism by which it occurs will be different from that responsible for the production of poisoning by the other gases mentioned, all of which are electronegative. In consequence, these initial investigations were followed by two sets of experiments, one with oxygen which had been shown to be the most effective of the electronegative gases in producing poisoning, and the other with hydrogen.

4.2.1. *Oxygen poisoning.* Figure 4 shows the changes in diode current that occurred when a freshly prepared cathode, held at a temperature of 1275°C, was first subjected to a series of poisoning experiments as described above. It is seen that poisoning first occurred when the oxygen pressure was between 10^{-7} and 10^{-8} torr and, although the decrease in anode current was more rapid and more extensive as the pressure increased, complete recovery of emission could be achieved without having to increase the filament temperature. However, when this cathode was subjected to a series of poisonings, each for a duration of 10 minutes at a constant oxygen pressure of 10^{-7} torr, then, as shown in figure 5, the speed and extent of the decrease in anode current increased with successive poisonings and, after the first two, full reactivation could only be obtained by temporarily increasing the filament temperature. The dependence of the time for reactivation on the temperature of the filament is shown in figure 6, but since the behaviour of a cathode, with regard both to poisoning and reactivation, has been found to be markedly dependent upon its previous treatment, the data of figure 6 are typical rather than absolute.
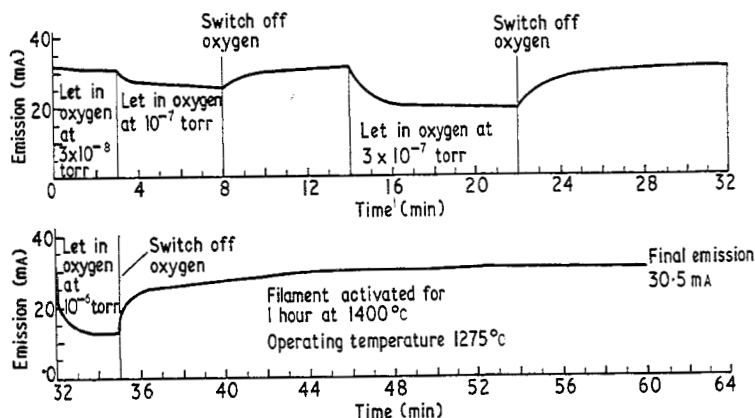
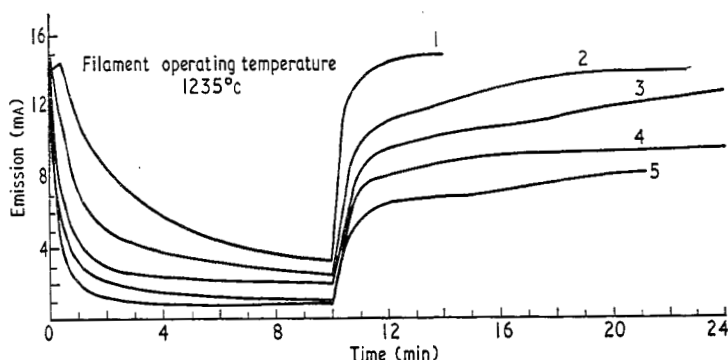Figure 4. Variation of poisoning and recovery of LaB$_6$ with pressure of oxygen.

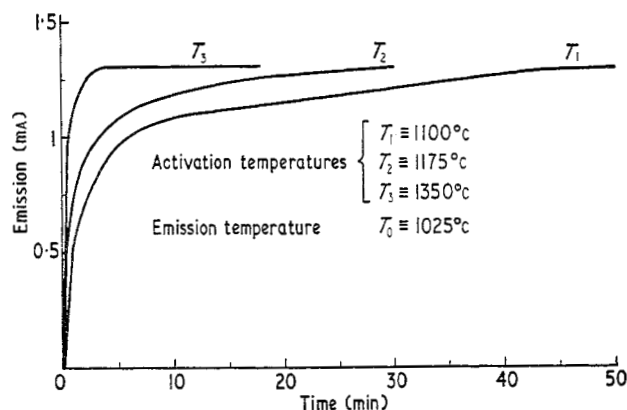Figure 5. Poisoning and recovery of LaB$_6$ for oxygen at 10^{-7} torr.

Figure 6. Variation of reactivation time with temperature.

Further series of poisonings similar to those depicted in figure 5, but at oxygen pressures of 10^{-6} and 10^{-5} torr, produced the same pattern of behaviour but with the anode current now falling very rapidly to less than 1% of its original value. However, the significant and encouraging feature of such experiments was that the filament was able to withstand quite a large number of such poisonings before any permanent impairment of its emissive capability occurred, full reactivation being obtained merely by raising its temperature temporarily to 1350°C. The time required to reactivate increased as the number and the severity of the poisonings increased, varying from a few seconds for a new cathode to several minutes towards the end of life.

In similar experiments at various levels of filament temperature the resistance to poisoning decreased as the temperature was reduced. The critical pressure at which poisoning first occurred decreased with temperature, and for any particular pressure of oxygen above this critical value the fall of anode current was both more rapid and more extensive as the filament temperature was reduced.

A relationship between poisoning and the physical processes taking place at the cathode surface is desirable, and the following, somewhat tentative, ideas may account for the behaviour observed. It seems likely that the activity of the cathode results from a monolayer of lanthanum atoms on the surface of the coating since the absence of any improvement in activity by the application of d.c. ageing processes, full activity being obtained merely by complete outgassing, coupled with the observation that the d.c. emission is substantially equal to the pulse emission, indicates a simple metallic film emitter with an absence of ionic charge carriers. Poisoning of the emission by adsorption of an electronegative gas, for instance oxygen, on to the cathode surface would then occur due to conversion of some or all of this mono-layer of lanthanum to the oxide, which, it is known (Samsonov 1959), has a work function of $3 \cdot 30$ ev. Prolonged exposure to oxygen at high pressures would allow penetration of gas into the interstitial spaces of the surface layers of the boron framework, giving rise to more severe poisoning and, also, by limiting the rate at which fresh lanthanum atoms are able to diffuse to the surface to replenish the monolayer, increasing the time required to reactivate the cathode. The mean dynamic work function of the surface, operating under some given conditions of total pressure, would then be a function of the fractional coverage of the emitting surface with poisoning gas. This equilibrium level would be determined by the balance achieved between the rate of arrival of oxidizing atoms (proportional to the total pressure), and the complex function governing the supply and distribution of lanthanum atoms over the surface.

4.2.2. *Hydrogen poisoning.* In common with previous observations on other types of cathode, the exposure of a poorly activated lanthanum boride cathode to an atmosphere of hydrogen, at a pressure of 10^{-6} torr, say, often produced some slight improvement in activity.
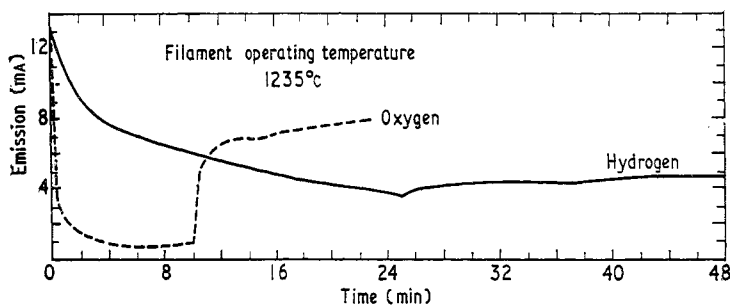

Figure 7.   Poisoning and recovery of LaB$_6$ for hydrogen at 10^{-6} torr.

However, when a well-activated cathode, operating in an ultra-high vacuum system where the partial pressures of any poisoning gases were less than 10^{-10} torr, was exposed to hydrogen, a substantial reduction in emission occurred. A typical plot of the fall in anode current, and the subsequent slow recovery of emission that resulted when the hydrogen test gas was removed, is shown by the full line of figure 7. The broken line shows the way in which the current changed when the same cathode was then immediately subjected to poisoning by oxygen at the same pressure. The marked difference in the rate, both of poisoning and of recovery of emission, as shown by the two curves suggests that the mechanism by which hydrogen causes loss of activity is fundamentally different from that responsible for poisoning by oxygen.

A clue to the process occurring at the surface was obtained by using the Omegatron to analyse the atmosphere in the test diode. A spectrogram, taken before the introduction

of hydrogen, confirmed the absence of any peak with a magnitude corresponding to a partial pressure greater than 10^{-10} torr, but when poisoning was in progress with a hydrogen pressure of 10^{-6} torr, a number of peaks, in addition to those for hydrogen, appeared. Their positions and amplitudes indicated the presence of some or all of the boranes, the most likely member having the formula B_2H_6. It is known that this would be gaseous under the conditions of the experiment so that the mechanism causing the loss of activity would appear to be a chemical reaction between the hydrogen and the surface layers of boron. The consequent loss of boron would produce some disruption of the boron lattice in the vicinity of the surface and many of the trapping sites for free lanthanum diffusing to the surface from within would not then be available. Any excess lanthanum left behind on the surface by such a reaction would be rapidly removed since the vapour pressure of lanthanum at $1500°K$ is 10^{-6} torr, so that a mono-layer would be removed in less than 1 sec. The relatively long reactivation time observed might also be expected since re-establishment of a mono-layer of lanthanum on the surface would be dependent on the recreation of the boron framework in the surface layers. This would require the diffusion of boron over the surface to fill any vacant sites and the evaporation of any excess boron, and the high thermal stability of the boron lattice, suggests that both of these processes would be slow ones.

4.3. *Evaporation measurements*

Measurements of the rate of evaporation of active material from a boride cathode has been carried out by the conventional Becker (1929) method using an electrode arrangement as shown in figure 8. A shutter, which could be opened and closed magnetically and
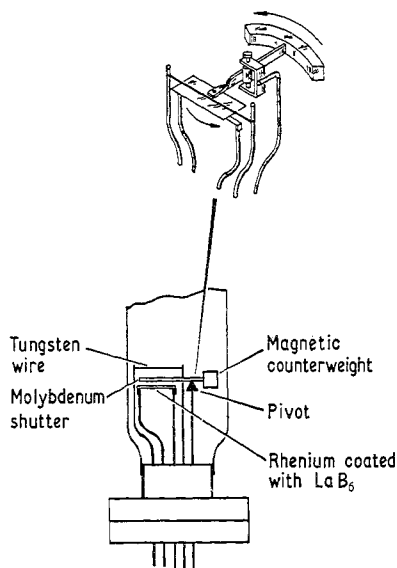

Figure 8.   Test diode for evaporation measurements.

which also served as an anode, was placed between two filaments. One of these was of rhenium tape coated over a known length with lanthanum hexaboride, the other being a tungsten wire of $0·008$ in. diameter; the separation between filaments was $2·5$ mm.

When the shutter was open lanthanum, evaporated from the coated filament, was able to fall on to the tungsten filament, which was gently heated. The emission from the tungsten filament then increased, passing through a maximum value when monolayer coverage occurred. The precise value of the temperature of the tungsten filament had to

be chosen with some care and was decided upon only after certain preliminary tests, since, whilst the filament had to be sufficiently hot to produce a measurable change in the emission from it, it also had to be cold enough to prevent any re-evaporation of lanthanum or migration of lanthanum along the tungsten surface thereby enlarging the area of increased activity. A temperature of 820°C was chosen and both filaments were operated from stabilized power supplies, as previously described, so that the long-term drift of filament temperature was always less than the experimental error associated with the optical pyrometer measurements. Prior to each experiment the tungsten filament was cleaned by flashing it to 2200°C for several minutes and, to avoid poisoning of the filament, it was essential that the partial pressure of any poisoning gas was less than 10^{-10} torr and that the elements of the evaporation diode, especially the shutter, were rigorously outgassed.
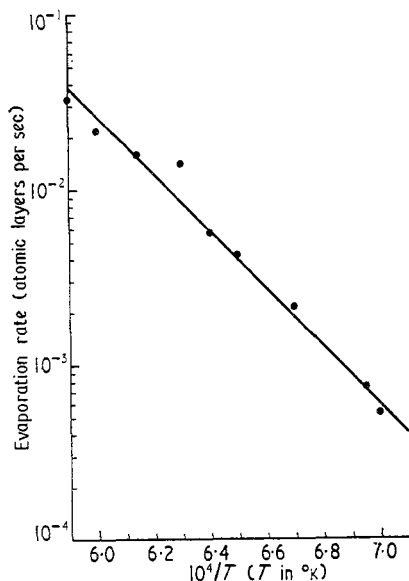

Figure 9. Variation of evaporation rate with temperature.

Figure 9 shows the rate of evaporation of lanthanum in monolayers per second plotted against $10^4/T$, where T is the absolute temperature of the lanthanum hexaboride filament. Since a straight line results from such a plot, an estimate of the effective activation energy for the evaporation of lanthanum can be obtained, using the relationship

$$\log R = \log A - 5040 \, \phi \, \frac{1}{T}$$

where R is the evaporation rate, A is a constant and ϕ is the activation energy in volts. The slope of the line gives a value for the mean activation energy of $3 \cdot 25$ ev.

The results plotted in figure 9 are typical for the rate of evaporation of active material from a freshly prepared and activated cathode and, as such, represent the most severe conditions to be contended with in practice, since it has been observed that the rate of evaporation slowly decreases with increasing life of the filament. It is seen from the figure that the time required to form a monolayer varies from 30 sec at 1425°C to 3000 sec at 1125°C and, by extrapolation, the time has increased to 10^6 seconds at 900°C. These figures compare rather unfavourably with those quoted by Lafferty for the rate of evaporation from pure lanthanum hexaboride. After having made allowance for the considerable difference in geometry between the two experimental arrangements used, it appears that the rate of evaporation from the solid boride held in a carbon crucible is at least 3 orders of

magnitude lower than that when the boride is supported on a rhenium substrate. The difference must presumably lie in the different rates of penetration of boron into these two materials; whereas it is known to be negligible for carbon, the diffusion into rhenium must be sufficient to cause considerable collapse of the boron framework, releasing excess lanthanum atoms which are then free to diffuse to the surface of the coating and evaporate. However, in the Omegatron mass spectrometer, for which the rhenium coated cathode was originally developed, the maximum current requirement is only about 100 μA and, since this can be provided at a filament temperature of approximately 850°C, the time to coat surfaces within a few millimetres of the filament with a monolayer of lanthanum should be about 1000 hours. In practice, several Omegatron tubes have given lives considerably in excess of this figure, due partly to the decrease in the rate of evaporation with life, and also to careful screening of any nearby surfaces where the maintenance of a high leakage resistance or a clean electrode surface of known and stable work function is necessary. In this instance, therefore, an adequate life can be achieved under normal operating conditions, but in experiments with Bayard–Alpert and Magnetron ultra-high vacuum gauges, loss of performance can occur quite quickly due to deposition of lanthanum unless care is taken in the method of operation of the filament. Reasonable lives can however be achieved if emission currents of less than 1 mA, say, are drawn and if particular care is taken to perform the initial activation of the filament, and any subsequent reactivation after poisoning, at the lowest temperature that is convenient as indicated in figure 7.

5. Conclusions

The experiments described here have shown that a filamentary cathode consisting of a rhenium wire or tape coated with lanthanum hexaboride is suitable for use in some demountable pressure measuring gauges and mass spectrometers. The limitation to its use is determined by the extent to which the evaporation of active material from the surface of the coating can be tolerated; this process is very dependent upon temperature, and therefore emission.

The substrate is best coated by cataphoresis, and full activation, or reactivation after poisoning, can be achieved merely by outgassing, although this must be carried out with some care to avoid damage to the coating, since this may be somewhat poorly adherent to the substrate, particularly at the beginning of life.

Measurements have confirmed the favourable low-temperature emitting properties and have shown that these are not altered by repeated exposure to wet or dry air. All the electronegative gases, and also hydrogen, produce some loss of emission by poisoning, but it has been found that the cathode can withstand many such poisonings before any permanent impairment of its activity occurs.

Since this paper was written, Dr. R. E. Honig, R.C.A., Princeton, has kindly sent a copy of an internal report he had written in 1960, aptly entitled 'Lanthanum Hexaboride— the strange case of the neglected emitter'. This describes some preliminary tests he had made which had confirmed the findings of Lafferty and many of those made here, and also concluded that rhenium was the most useful material to use as the substrate of cathodes for vacuum gauge application. He had also recommended that a technique for depositing the coating cataphoretically should be developed.

Appendix

An analysis of the lanthanum boride powder gave the following composition

	La	B	C	Fe	O	N
%	68·0	31·5	0·1	0·05	0·08	0·02

Although it is technically difficult to estimate the amounts of LaB_4 and of free lanthanum in the presence of LaB_6 the suppliers consider that such amounts would in practice be negligible.

References

BECKER, J. A., 1929, *Trans. Amer. Electrochem. Soc.*, **55**, 153–75.

COMPTON, K. T., and LANGMUIR, I., 1930, *Rev. Mod. Phys.*, **2**, 147–242.

JENKINS, R. O., and TRODDEN, W. G., 1959, *J. Electron. Control*, **7**, 393–415.

—— 1961, *J. Electron. Control*, **10**, 81–96.

—— 1962, *J. Electron. Control*, **12**, 1–12.

—— 1964, *J. Electron. Control*, **16**, 407–23.

JOHNSON, R. W., and DAANE, A. H., 1961, *J. Phys. Chem.*, **65**, 909–15.

LAFFERTY, J. M., 1951, *J. Appl. Phys.*, **22**, 299–309.

PADERNO, Y. B., SAMSONOV, G. V., and FOMENKO, V. S., 1960, *Fizika Metallov i Metallovedevie*, **10**, 633–4.

SAMSONOV, G. V., 1959, *Usp. Khim.*, **28**, 189–217.

SAMSONOV, G. V., PADERNO, Y. B., and FOMENKO, V. S., 1963, *Poroshkovaya Metallurguja*, **3**, 24–31.

STECKELMACHER, W., and BUCKINGHAM, J. D., 1964, *Nuovo Cim.*, Suppl. No. 2, Series 1, **1**, 418–34.

WRIGHT, D. A., 1953, *Proc. Instn. Elect. Engrs.*, **100**, 125–40.