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A STUDY OF THE 'M'-CATHODE

Thesis presented for the degree of Ph.D.

at the University of Birmingham

by

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Synopsis

The thermionic emission from cathodes made by milling together barium carbonate and nickel powder, pressing the mixture to a desired shape and sintering, has been studied as a function of cathode temperature in the range from 300 - 1300°K. The effect of oxygen and sulphur upon the emission in this temperature range has been investigated. A simple diode structure was used for this work.

The radioactive isotope, ^{140}Ba , was used in order to determine the activation energy of evaporation of barium from the cathodes. This was compared with the value obtained by use of the Becker method. The effect of an electric field upon the evaporant was studied. The isotope was used to help determine the diffusion rate of barium in the cathodes in both vacuum and argon and also the surface diffusion rate of barium over nickel.

The apparent work function of a typical cathode is 1.7 - 1.8 eV. The best practical cathodes had the composition by weight of 70 - 75% nickel and 30 - 25% barium carbonate with a small quantity of silicon added as a reducing agent. Oxygen and sulphur poisoning of the emission from such cathodes is reversible. Recovery of emission from oxygen poisoning is faster than from sulphur poisoning. By reversing the polarity of the anode voltage during recovery from oxygen poisoning the emission is re-poisoned. This effect has not been noticed during recovery from sulphur poisoning.

The activation energy of evaporation is 2.2 - 2.5 eV, the results from the two methods being in reasonable agreement. The evaporant from the cathode is not ionised. The diffusion measurements revealed

that two diffusion processes operate. One, probably the diffusion of material along the pore walls, predominates below 1,150 °K and has an activation energy of 0.5eV. The other, Knudsen flow of material through the pores, predominates above this temperature and has an activation energy of 2.5 eV. The activation energy of surface diffusion is 0.89 eV.

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Appendix I

Appendix II

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SYMBOLS

A	constant in the thermionic emission equation
A_0	theoretical constant in the thermionic emission equation = $120 \text{ amps.cm}^{-2} \cdot ^\circ\text{K}^{-2}$.
C	concentration of diffusing material
C_p	molal heat capacity
D	diffusion coefficient
D_1	disintegration rate
E	applied field
E_c	efficiency of counter
F	rate of transfer by diffusion per unit area
G	Gibbs free energy
H	heat content
I	current per unit area
I_r	retarding field emission current per unit area
L	pore length
M	molecular weight
M'	dipole moment
M_d	total substance diffusing
N	counting rate
P	equilibrium pressure
Q	charge
R	gas constant
ΔS	entropy of reaction
T	temperature in $^\circ\text{K}$
V	applied potential

d	distance between electrodes
e	electronic charge
f_B	correction factor for backscattering
f_S	correction factor for self-absorption
f_T	correction factor for dead time of counter
f_W	correction factor for absorption in air and in counter window
h	Planck's constant
k	Boltzmann's constant
m	mass of material evaporating
n	number of dipoles per square centimetre
p	vapour pressure in dynes cm^{-2} .
r	reflection coefficient
r_e	effective pore radius
α	accommodation coefficient
α'	polarisability of atom or ion
ν	total number of electrons striking unit area in unit time
σ	charge density
ϕ	true work function
$\bar{\phi}$	emissive mean of work function
ϕ_A	anode work function
ϕ_C	cathode work function
ϕ_D	activation energy of diffusion
ϕ_E	activation energy of evaporation
ϕ_{eff}	effective work function
ϕ_S	activation energy of surface diffusion

Introduction

This thesis is concerned with studies on thermionic emission which is part of a wider programme of work in the field of solid state physics currently in progress at the University College of North Staffordshire under the direction of Professor F.A. Vick, O.B.E. The particular investigation is a study of dispenser cathodes; the rest of the programme is concerned with the oxide-coated cathode and so the parallel work on the dispenser cathode enables a comparison of the two types to be made, in addition to the major object of the present investigation which is to establish the mechanism of operation of the dispenser cathode.

The type of cathode studied is termed the matrix or 'M'-cathode which is constructed by milling together nickel powder, barium carbonate and a small proportion of reducing agent; this mixture is pressed to the desired shape and sintered in vacuum or hydrogen at about 1300°K . The percentage composition by weight of the cathodes is 70 - 75% nickel, 30 - 25% barium carbonate and 1% or less of reducing agent.

The experimental work carried out consists of the development of techniques to be used and then an investigation into the variation of thermionic emission with temperature of these cathodes. A simple diode structure is used. The temperatures covered in the experiments range from room temperature to 1300°K . All temperatures are measured by means of a nickel-tungsten thermocouple.

The effect of oxygen and sulphur on the cathode is investigated

over the same temperature range as emission. The recovery of the emission from poisoning by oxygen or sulphur provides information which enables deductions to be made concerning the operation of the cathode. Following this the activation energies of evaporation and diffusion in the 'M'-cathode are measured concurrently by use of the radioactive isotope ^{140}Ba . The evaporation rate measurements are compared with those made by use of the Becker method. A study of the effect of an electric field upon the evaporation rate is also made.

The isotope is employed to measure the diffusion rates when the cathode is in an argon atmosphere and also to measure the surface diffusion rate of barium over nickel. A qualitative picture of the cathode surface is obtained from several autoradiographs.

An introductory survey of dispenser cathodes and their general properties is given before an account of previous work on the 'M'-cathode and the effect of oxygen and sulphur poisoning. The initial experimental work is then described in Part II. Part III consists of a survey of previous work on evaporation and diffusion measurements with dispenser cathodes, a description of the techniques employed with the isotope and then the results from this work. The thesis is concluded with the results and a discussion of their possible interpretation.

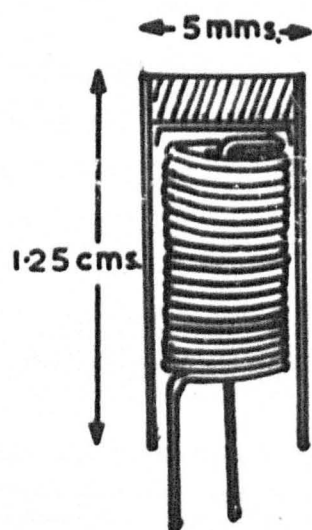


DIAGRAM OF CATHODE-HEATER ASSEMBLY

fig. 1. 1. 1.

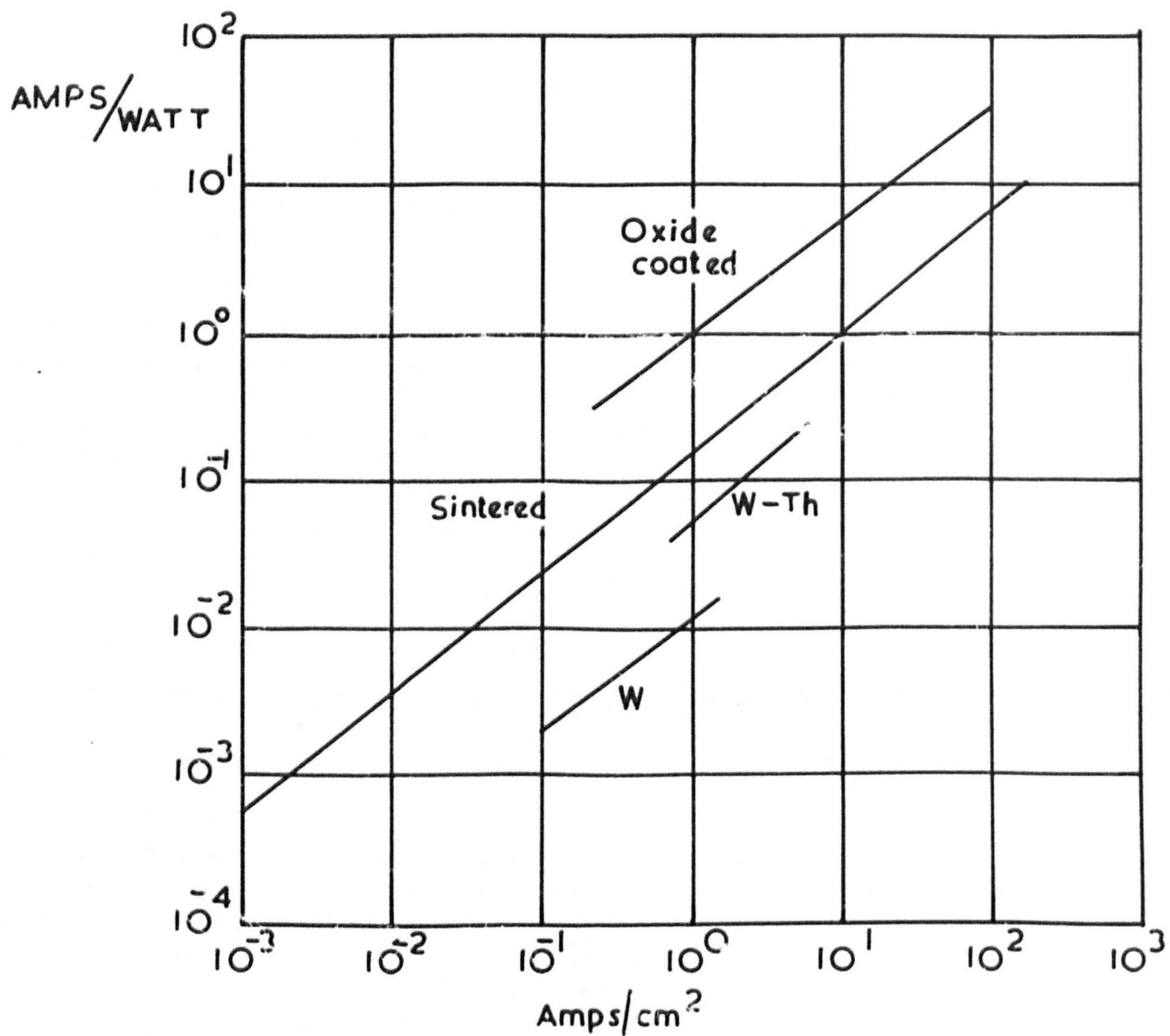
in the base metal or below it. The emissive material is one or more of the alkaline earth oxides. The cathode is usually raised to operating temperature by an insulated heater inserted in a tube, one end of which contains the cathode (see fig. (1.1.1.))

The base metal of the dispenser cathode is tungsten, nickel or a mixture containing one or other of these metals. Tungsten has the advantage of a higher melting point and a lower rate of evaporation, which is an important consideration at the high operating temperature of the dispenser cathode, but it has the disadvantage that it forms compounds with barium oxide⁽³⁾ which may lower the efficiency of the cathode.

Small quantities of other elements or compounds may be introduced into the base metal to aid activation by reduction of barium oxide to barium. Tungsten itself will reduce barium oxide at temperatures above 1300°K .⁽³⁾ If nickel is used as the base metal small quantities of silicon or magnesium or Zirconium may be added to act as reducing agents.

Enhanced emission is obtained from dispenser cathodes if mixed alkaline earth oxides are used^(4,5,6,7) As with the oxide-coated cathode a mixed barium-strontium oxide gives a higher emission than a cathode containing only barium oxide, as does a cathode containing barium-calcium oxide.

The dispenser cathode was introduced to overcome deficiencies in the oxide-coated cathode which became more evident at higher powers, higher frequencies and higher electrostatic fields. Al-



Thermal efficiency as function of saturation emission

Fig. (1.2.1)

though it is a more efficient emitter than the tungsten or thoriated-tungsten cathodes, the dispenser cathode is not so efficient, in terms of thermal efficiency, as the oxide-coated cathode, as shown in fig. (1.2.1.) Advantages of the 'M' - cathode include its mechanical stability and its resistance to electrostatic effects at high voltages; the ease with which it can be formed and machined accurately to desired dimensions; the large reserve of oxide; its resistance to ion bombardment and 'poisoning' by gases such as oxygen, etc; the ease with which it reactivates and finally, its suitability for use in pulse work. Thus the dispenser cathode, to a certain degree, provides a practical answer to the demand for robust cathodes with a comparatively large emission per unit surface area.

1.3. Form of the Reservoir.

The main variation in the preparation of dispenser cathodes is the manner in which the reservoir of emissive material is introduced into the cathode. The forerunner of the dispenser cathode, the multicellular cathode,⁽³⁾ had the emissive material deposited on radial vanes which were surrounded by concentric cylinders and a perforated lid. The vanes were indirectly heated and the electrons were emitted through the holes in the lid. This allowed a reduction in heater power but the cathode life was limited by evaporation and sputtering.

The first cathode to employ a reservoir was Hull's improved form of the multicellular cathode, which he called 'the dispenser

cathode'.⁽⁹⁾ The cathode used was initially uncoated and a coating material was dispensed to the cathode surface from a closely woven mesh stocking of fine molybdenum wires filled with granules of fused barium oxide - aluminium oxide eutectic. The proportions by weight of the eutectic were 70% barium oxide and 30% aluminium oxide. The temperature of the dispenser ~~was~~ was maintained at 1150°C by a current of 20 amps at a p.d. of 5 volts passing through it. The dispenser also served as a radiation heater for the cathode. The electron emitting members were clean molybdenum of 200cm² surface area. The measured work function of the cathode was 1.215 ev and the constant of the emitting surface from Richardson's equation, $A = 0.85 \text{ amps. cm}^{-2} \text{ } ^\circ\text{K}^{-2}$.

In 1950 the Philips' Laboratories at Eindhoven announced a new dispenser cathode which they called the 'L'- cathode⁽¹⁰⁾ and this is now widely used. The base metal of this cathode is a disc of porous tungsten which is made by compressing tungsten powder and then sintering it. High pressures and sintering temperatures are used but are not specified in the report. Underneath the tungsten disc a tablet of barium and strontium carbonates mixed in equal proportions by weight is enclosed by the tungsten above and a molybdenum sheet below. The heater is situated under this molybdenum sheet.

The method of activation used is to heat the cathode in a vacuum to 1100°C, when the oxides are formed from the carbonates,

and then by raising the cathode to an unspecified temperature it is activated by reduction of the oxide by one of the reducing agents present. The active metal, in the form of vapour, together with some of the oxide, passes out through the pores of the tungsten to form a monatomic layer on the surface which lowers the work function and gives a good cathode. Work on the performance of the 'L' - cathode has been reported by Babakian,⁽¹¹⁾ Brodie,⁽¹²⁾ and Venema.⁽¹³⁾ The structure and mechanism have been studied by Schaefer and White,⁽¹⁴⁾ Du Pre and Rittner,⁽¹⁵⁾ Haperson,⁽¹⁶⁾ and more recently, in great detail by Rittner, Rutledge and Ahlert.^(17,18) The response to gas contamination has been reported on by Fugawa and Adachi.⁽¹⁹⁾

In a paper by Hughes and Coppola⁽²⁰⁾ on bariated tungsten emitters, after discussing the chemical reactions which occur between barium oxide and tungsten, means are suggested by which the barium oxide may be introduced into the tungsten without simultaneous oxidation of the tungsten. These processes are:-

- a. the formation of barium oxide and mixing with tungsten rapidly to avoid reversion to hydroxide and carbonate.
- b. use of two or more barium compounds which react together to form barium oxide and by-products which are not capable of oxidising tungsten; for example, by forming the oxide from barium nitride and barium formate, the other products being nitrogen, carbon monoxide and hydrogen.
- c. the addition of an element or compound which reduces the

barium compound used to the oxide; for example, the use of carbon with barium carbonate to give the oxide and carbon monoxide.

d. the stabilising of barium oxide by fixing with other oxides, the product giving a decreased reaction rate and consequent lower rate of barium evolution.

All of these methods have been attempted with some measure of success and all of the tungsten cathodes with the alkaline earth oxides fall into one or other of these production categories. Becker and Moore⁽²¹⁾ have studied thermionic emission from barium on tungsten, and Brodie and Jenkins⁽²²⁾ that from a mixed monolayer of barium and calcium on tungsten.

Levi⁽⁷⁾⁽²³⁾ has described what is termed the 'impregnated' cathode. In this cathode the alkaline earth material consists of a mixture of normal and basic barium aluminates, which are dispensed through the pores of a tungsten matrix. The matrix is produced by pressing tungsten powder and then sintering. The resultant disc has a density of 80 - 85% of the normal value. In order to machine such a disc to fine tolerances it is impregnated with copper which acts as a filler and as a lubricant. The disc is machined and the copper is removed by volatilisation. The impregnation of the tungsten matrix is carried out in vacuum, the impregnant consisting of a melt of 5 moles of barium oxide to 2 moles of aluminium oxide. More recently, Levi⁽²⁴⁾⁽²⁵⁾ has published an account of an improved 'impregnated' cathode. This

is essentially the same as the earlier form, the only difference being that the impregnation is performed in an atmosphere of hydrogen and that the impregnant consists of 5 moles of barium oxide, 2 moles of aluminum oxide and 3 moles of calcium oxide. Venema, at a colloquium on thermionic cathodes in 1954,⁽²⁶⁾ described the Philips' impregnated cathode which is formed by heating a porous tungsten plug in contact with barium aluminate at $1,750^{\circ}\text{C}$ in vacuum. The aluminate penetrates the pores and in operation is reduced by the tungsten.

Brodie and Jenkins⁽⁴⁾ have made an impregnated cathode consisting of a porous tungsten disc which was impregnated by barium silicate to which 0.5 mole of calcium oxide was added to each mole of silicate. The calcium oxide lowered the melting point of the impregnant and gave enhanced emission. Further work was then carried out on the addition of calcium and strontium oxides to barium silicate and aluminate impregnants. All impregnations were carried out in hydrogen.

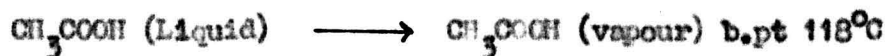
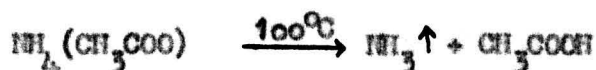
Dispenser cathodes with a nickel base have been prepared by impregnation. Thien-Chi and Lussignassy⁽²⁷⁾ report that they have prepared cathodes from a porous nickel plug, formed by pressing the powder and sintering in hydrogen. The cathode is then impregnated with barium carbonate by immersion in an appropriate solution, the composition of which is not revealed. Belas, Dempsey and Texer⁽⁶⁾ have prepared a cathode by pressing and sintering nickel powder in hydrogen. The nickel matrix

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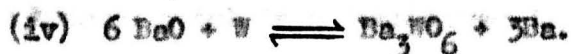
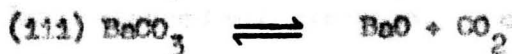
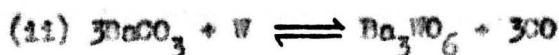
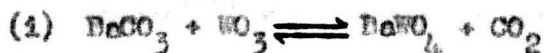
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formed is impregnated with a water-soluble barium-strontium salt and the double carbonate is precipitated within the interstices by a second impregnation with a water-soluble carbonate. For efficiency and rapidity a salt solution of high concentration is used. The initial impregnation is with the acetate, since it has a high solubility. Ammonium carbonate is used as the precipitating agent since its by-products are water-soluble and decompose at low temperatures. The reactions involved are:-



The introduction of the alkaline earth into the cathode matrix has so far been considered from a reservoir external to the matrix and by impregnation into an already formed matrix, both of which are very similar. Another means of achieving the same end is to mix together the base metal powder and the alkaline earth compound before pressing and sintering. It is not possible to form a good cathode by mixing the alkaline earth carbonates with tungsten as there occurs a reaction which prevents subsequent reduction of the oxide to free metal. Hughes, Coppola and Evans⁽³⁾ made a study of the reactions between barium carbonate and tungsten and showed that the following reactions take place progressively as the temperature is increased:-



Only one reaction gives rise to the free metal and if the first two are predominant poor cathodes will result. Cathodes formed by mixing tungsten powder and the alkaline earth carbonates have been reported by Usan⁽²⁸⁾ and by Neenard and Usan⁽²⁹⁾. These cathodes are improved by the addition of carbon or nickel to the tungsten.

Since there is difficulty in producing a tungsten-alkaline earth cathode by mixing before sintering, work has been carried out on the use of barium compounds other than the carbonate. Huber⁽³⁰⁾ and Huber and Freytag⁽³¹⁾ have made a study of the chemical reactions which can be utilised to supply barium to a tungsten surface and find that the aluminate, silicate, titanate, thorate and tungstate of barium could be used. Eisenstein, John and Affleck⁽³²⁾ have shown which reducing agents are appropriate for each compound. Huber⁽³⁰⁾ describes a cathode formed by mixing the powdered oxide, tungsten and a suitable reducing agent, which is pressed and sintered. The preferred cathode consists of 5 molecular parts of barium tungstate, 15 of aluminium powder and 80 of tungsten powder, although similar results are obtained if tungsten carbide replaces the aluminium and molybdenum can replace the tungsten powder.

Venona⁽²⁶⁾ reports that a cathode was being developed in which tungsten powder and barium aluminate are mixed in powder form, pressed and sintered. Coppola and Hughes⁽⁵⁾⁽³³⁾ describe a cathode which is a development from Levi's impregnated cathode. The cathode consists of 10% by weight of barium aluminate to which a small proportion of calcium oxide is added, and 90% of molybdenum-tungsten alloy. The alloy consists of 25% by weight of tungsten. The alloy in powdered form and the aluminate are mixed, pressed and sintered. Mesnard and Uzan⁽³⁴⁾ have made cathodes by mixing tungsten and zirconium powders in an 8:1 atomic ratio with barium-strontium carbonate, pressing and then the usual sintering.

Since nickel is a more inert metal than tungsten it is found that a good cathode can be prepared by mixing directly the alkaline earth carbonates with nickel powder, pressing and sintering. A reducing agent is added to assist in the formation of the free metal from the oxide. Dodds⁽³⁵⁾ describes such a cathode formed by mixing 30-40 parts by weight of carbonate with 70-60 parts of nickel powder, then pressing and sintering. 0.1% silicon is added as the reducing agent. Beck⁽²⁾⁽³⁶⁾ uses the same percentage composition with 1% zirconium hydride as the reducing agent in his 'B-N'-cathode. The original cathode of this type is due to MacNair, Lynch and Henny⁽¹⁾ whose 'M'-cathode consisted only of nickel and alkaline earth carbonate powder. Uzan,⁽²⁸⁾ and Mesnard and Uzan⁽³⁷⁾ have worked on 'M'-cathodes with no added reducing agent and also with a reducing agent. Finally, (3) by stabilizing the various oxides with zirconium added.⁽³⁴⁾ The announcement by La Rocque⁽³⁸⁾ of a cathode by firing with other oxides such as aluminum oxide. The details of

cathode which is called the 'P'-cathode must also be included in this category. The cathode consists of carbonyl nickel and columbium metal powders mixed with triple carbonates, then pressed and sintered in dissociated ammonia.

Fane⁽³⁹⁾ has recently reported work carried out on a cathode made from carbonyl nickel powder of 3-5 micron particle diameter (68% by weight), co-precipitated triple carbonates (30.6%) baron (0.4%) and barium stearate to serve as binder and lubricant (1%). The barium:strontium:calcium ratio in the carbonate is 45.5:45.5:9. The powders are ball-milled, pressed and sintered.

There are many other variations of sintered cathodes. Work has been carried out in Germany on what are called capillary cathodes. Katz⁽⁴⁰⁾⁽⁴¹⁾ has described this work which includes the use of thorium and thorium with tungsten and carbon and also a barium-beryllium alloy with tungsten and with molybdenum. The evaporation of barium depends on the metal capillary size. Three other cathodes which have been developed include a sintered thorium and tungsten mixture described by Fan,⁽⁴²⁾ and hollow cathode due to Poole,⁽⁴³⁾ the lanthanum boride cathode of Rafferty⁽⁴⁴⁾ and the 'E'-cathode of Ekkera.⁽⁴⁵⁾

Summarising briefly, cathodes have been prepared (a) by producing the barium oxide in contact with a metal matrix into which it can diffuse, (b) by use of two compounds which react to form barium oxide in the metal interstices plus gaseous by-products, (c) by mixing the carbonates and metal before pressing with the addition of a reducing agent, and finally, (d) by stabilising the barium oxide by firing with other oxides such as aluminium oxide. The details of

Chapter II

Mechanism of the Diode Cathode.

Thermionic emission is the phenomenon in which an electronic current evaporates from a heated solid in the absence of an external electric field. In the presence of an accelerating applied field the work function of the metal is lowered, giving an increased emission. The correction which is made to the zero-field thermionic emission to account for the increase is the Schottky effect. Both types of emission are strongly temperature dependent. An additional temperature independent emission occurs when the accelerating field becomes very large. This is field emission and can be explained in terms of the quantum mechanical picture of penetration of electrons through a potential barrier. ⁽⁴⁶⁾⁽⁴⁷⁾

2.1. The Theory of Emission from Metals

In deriving a theory of emission from metals the simplest assumption made is that the metal atoms of the crystal lattice lose their valency electrons, which are free to move in the crystal. If the field of the positive ions is smoothed out and its local violent fluctuations are disregarded, the electrons can be regarded as completely free and can be considered as an electron gas. The total field on one electron is that due to the positive ions and the other electrons, which number one less than the positive ions, so the smoothing out gives a good first approximation.

The states of motion in which an electron can exist correspond to discrete energy levels in an atom, but the levels are very close

together. The energy distribution is determined by application of quantum theory and the exclusion principle and is described mathematically by the Fermi-Dirac statistics which are based on the indistinguishability of electrons.

One of the earlier equations derived theoretically for the emission from a metal is the Richardson-Dushman equation (48) which was first derived on the basis of thermodynamics. The equation is

$$\mathcal{D} = \frac{4\pi m (kT)^2}{h^3} \exp \left[-\frac{\phi_{Ef}}{kT} \right] \dots \textcircled{1}$$

where \mathcal{D} is the total number of electrons that strike unit area in unit time, m is the electronic mass, T is the absolute temperature, k is Boltzmann's constant and h is Planck's constant, and ϕ_{Ef} is the effective work function when there is a field present. The latter is given by

$$\phi_{Ef} = \phi - \sqrt{E} \cdot e^{3/2} \dots \textcircled{2}$$

where ϕ is the real work function, i.e. the lowest energy which is necessary to eject electrons from the metal at $T = 0$, E is the applied field and e is the electronic charge.

If r designates the probability that the electrons which have sufficient energy to cross the barrier are reflected back, the current per unit area is

$$I = A_0 T^2 (1 - r) \exp \left[-\frac{\phi}{kT} \right] \exp \left[-\sqrt{E} \cdot \frac{e^{3/2}}{kT} \right] \dots \textcircled{3}$$

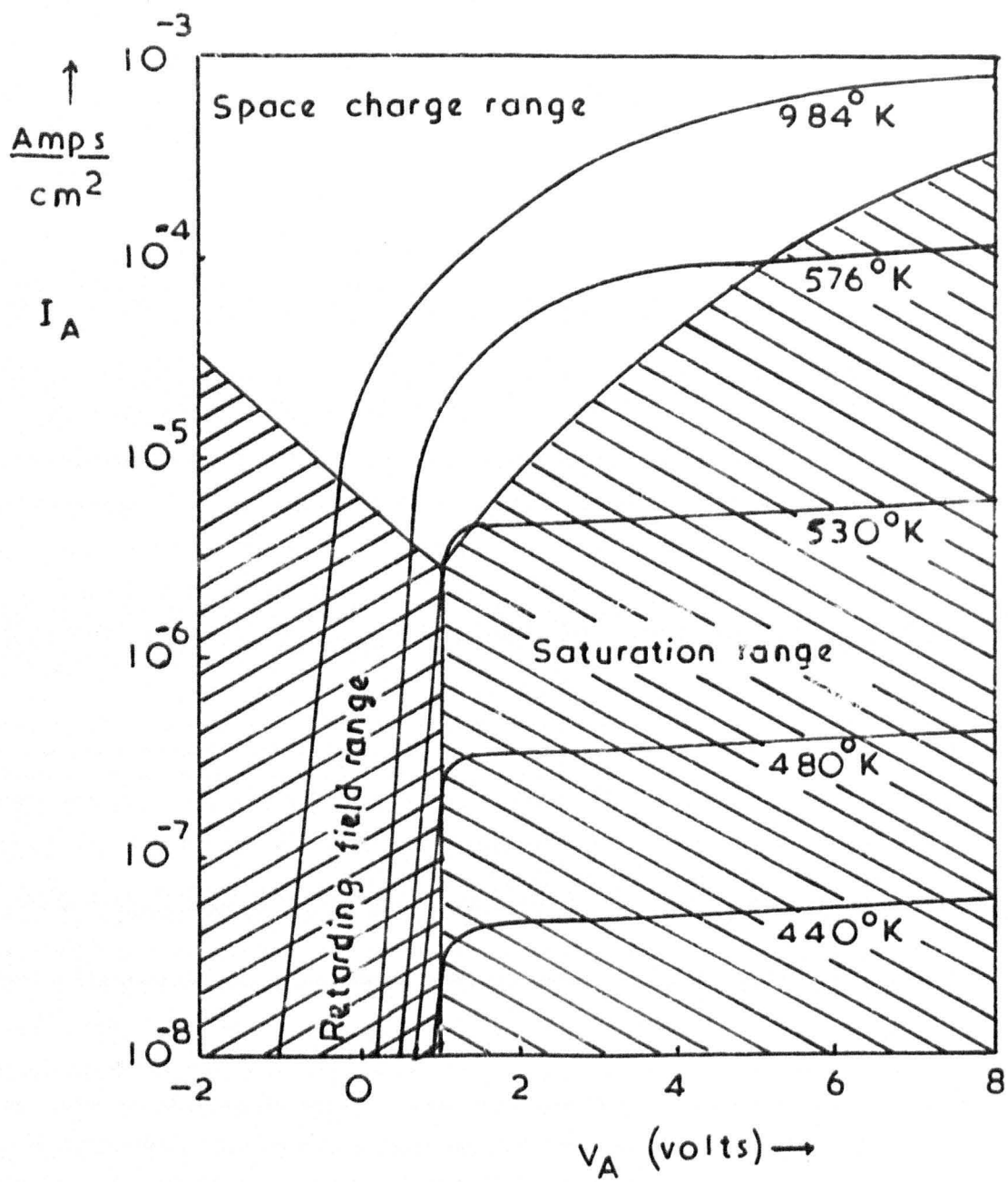


FIG (2.1.1)

curves similar to those in fig (2.1.1) are obtained. The saturated emission can then be obtained for any temperature and a graph of $\log \frac{I}{T^2}$ plotted against $\frac{1}{T}$ will have a slope which gives ϕ and an intercept of $\log A$ on the $\log \frac{I}{T^2}$ axis. This is the usual Richardson plot for obtaining the experimental work function of a surface. It applies to a metal but not to a semiconductor or a dielectric.

In the shape of the current-voltage curve, when an emission current is being drawn under normal conditions, three well-defined regions may be distinguished (fig (2.1.1)). They are

- a. emission in retarding fields
 - b. space charge limited emission
 - c. emission in accelerating fields.
- a. Retarding Field Emission

In the first region of the characteristic only those electrons will reach the anode which have energies greater than the potential barrier imposed between the electrodes by the retarding voltage. This barrier includes any contact potential difference between anode and cathode.

For a diode with plane parallel electrodes the current density at an applied potential V is given by

$$I_x = A_0 (1 - r) T^2 \exp \left[- \frac{(V + \phi_A)}{kT} \right] \dots (7)$$

where ϕ_A is the work function of the anode. This equation is

valid for values of V giving a barrier height greater than the work function ϕ of the cathode. For more positive values of V , I_0 is given by equation (6).

A graph of I_r/I_0 against V should have a slope of $-e/kT$ which joins a horizontal line when $V + \phi_A = \phi$. Thus ϕ may be found if ϕ_A is known. In practice ϕ_A is unknown and is changing continually due to contamination by materials evaporated from the cathode. The current voltage characteristics when plotted in the form $\log I$ against V are most convenient, since the retarding region may then be represented by a straight line with the gradient related to $1/T$, which becomes horizontal when the applied field changes from a retarding to an accelerating one.

b. Space-charge Limited Emission

The space charge limited emission is a function of the geometry of the electrode system of the valve and not a function of the cathode. When small emission currents are drawn at sufficiently low temperatures the space-charge effect does not occur appreciably and the change from retarding field to accelerating field emission is very abrupt.

c. Emission in an accelerating field

The emission in an accelerating field is given by the Schottky equation, which has been discussed previously, very briefly, and in a little more detail below.

If the field strength at the surface is not negligible then equation (5) must be used

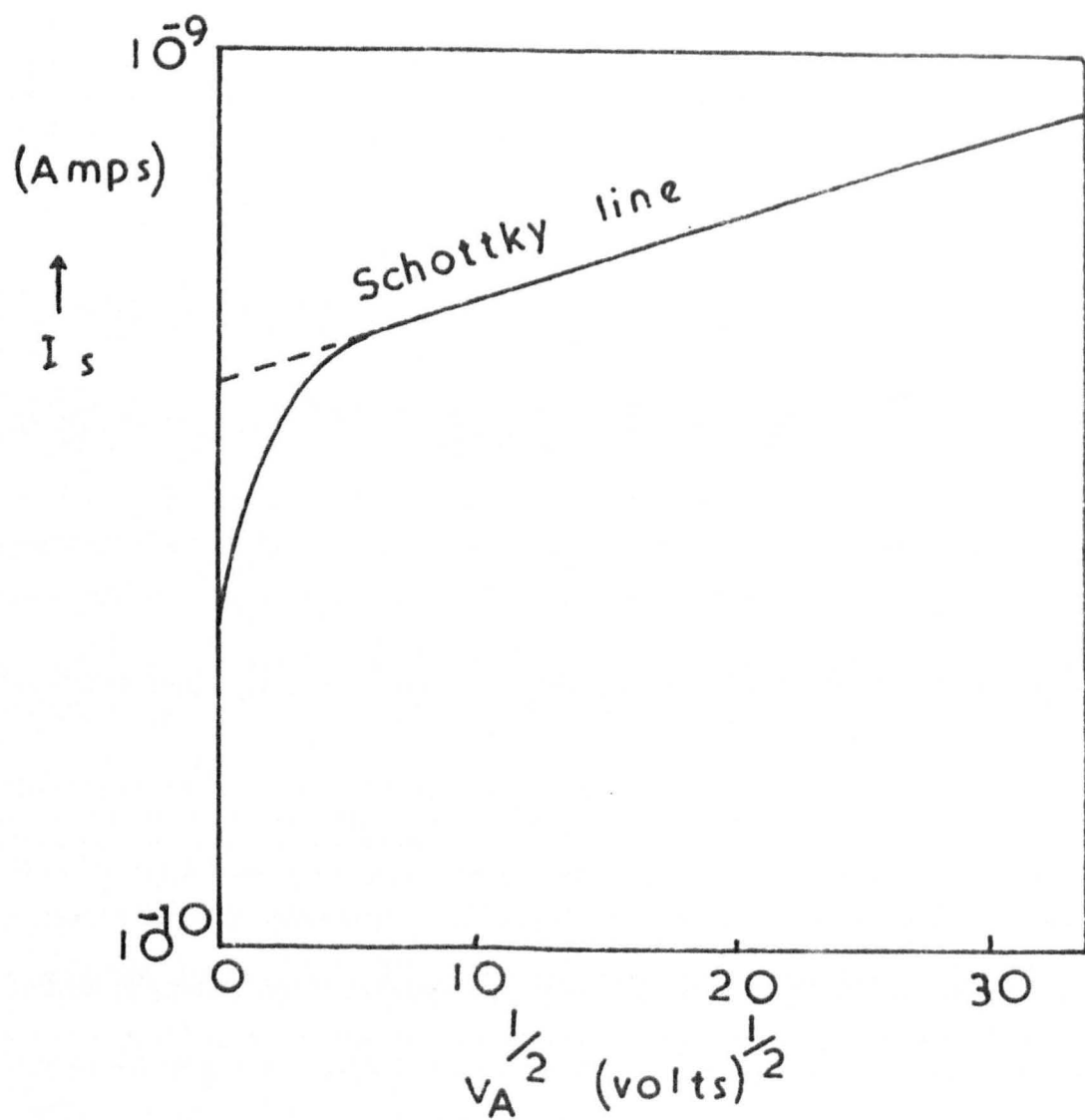


fig. 2. 1. 2.

$$I = A_0 T^2 \exp \left[-\frac{\phi}{kT} \right] \exp \left[-\sqrt{E_0} \frac{a^{3/2}}{kT} \right]$$

$$= A_0 T^2 \exp \left[\frac{-\phi - \sqrt{E_0} a^{3/2}}{kT} \right]$$

If a plot of $\log I$ against $E^{1/2}$ is made, the result should be a straight line. This is known as a Schottky plot. Since $E = V/d$, where V is the applied voltage and d is the distance between the electrodes, the Schottky plot in practice consists of $\log I$ against $V^{1/2}$. A typical example is shown in fig (2.1.2). An exact experimental check of the equation is difficult as the ideal conditions of perfectly plane surfaces assumed for the derivation do not exist in practice. As the surface is rough the field strength varies over the surface. The work function, too, varies over the surface, and so produces variations from Schottky's Law. Nottingham⁽⁵⁰⁾ obtained a correspondence to within 20% between measured and calculated saturation current. Deviations from the law at low field strengths are due to the variation in work function mentioned above. With higher field strengths the linear dependence in accordance with equation (5) is obtained. At very high field strengths an entirely new effect, the tunnel effect, occurs. This effect is explained by wave mechanics. In this case the potential barrier in front of the cathode becomes so narrow that the electrons can pass through unimpeded. Consequently with very high field strengths there is electron emission even at room temperatures, termed field or cold emission.

The apparent work function of an emitting surface is obtained by measuring the emission at various temperatures, extrapolating the emission at zero field at each temperature from a Schottky plot, and plotting the resultant $\log I/T^2$ against $1/T$. The slope of this Richardson plot is a measure of the apparent work function. If the emitting surface is uniform the extrapolated zero-field emission will obey the Richardson equation and the value of the apparent work function will be

$$\phi_{Ap} = \phi - T \cdot \frac{d\phi}{dT} \quad \text{--- (8)}$$

since the work function may depend on temperature⁽⁵¹⁾ and assuming a linear dependence as a first approximation. If this is introduced into the emission equation

$$\begin{aligned} I &= A_0 T^2 \exp \left[- \frac{(\phi - \frac{d\phi}{dT} T)}{kT} \right] \\ &= A_0 \exp \left[\frac{d\phi}{dT} \cdot \frac{1}{k} \right] T^2 \exp \left[- \frac{\phi}{kT} \right] \quad \text{--- (9)} \end{aligned}$$

If this is plotted as a Richardson line the slope gives the work function at zero temperature and the intersection on the ordinate has the value

$$A = A_0 \exp \left[- \frac{d\phi}{dT} \cdot \frac{1}{k} \right] \quad \text{--- (10)}$$

This will be different from the theoretical value $A_0 = 120 \text{ amps. cm}^{-2} \text{ } ^\circ\text{K}^{-2}$ if the temperature dependence of the work function is

large. Thus when using the Richardson line only the value of the work function at $T = 0^\circ$ is obtained.

Since the work function differs over a surface the Richardson plot gives a curve instead of a straight line, the curvature being very small over a measured range of temperature. Application of the Richardson line then gives the emissive mean, $\bar{\phi}$, of the work function. The curvature of the line also influences the value of A which is reduced by this effect.

2.2. The Influence of Adsorbed Materials on the Work Function.

An electric dipole is characterised by its dipole moment, M' , which is given by

$$M' = Qx$$

where Q is the charge moved and x is the distance through which it is moved. If the field is not too great, M' is proportional to the applied field, E , or

$$M' = \alpha' E$$

where α' is the polarisability of the atom or ion.

The effect of a dipole layer on the surface of a solid is to produce a change in potential energy of an electron passing through it. The force on an electron of charge e near to a plane sheet of charge density σ is $2\pi\sigma e$. The force between two planes of equal and opposite charge density is $4\pi\sigma e$. There is zero force outside two such sheets. Suppose the sheets are distance d apart, then the potential difference between them is $4\pi\sigma d$. If the sheets correspond to a dipole layer of n dipoles cm^{-2} each formed by pos-

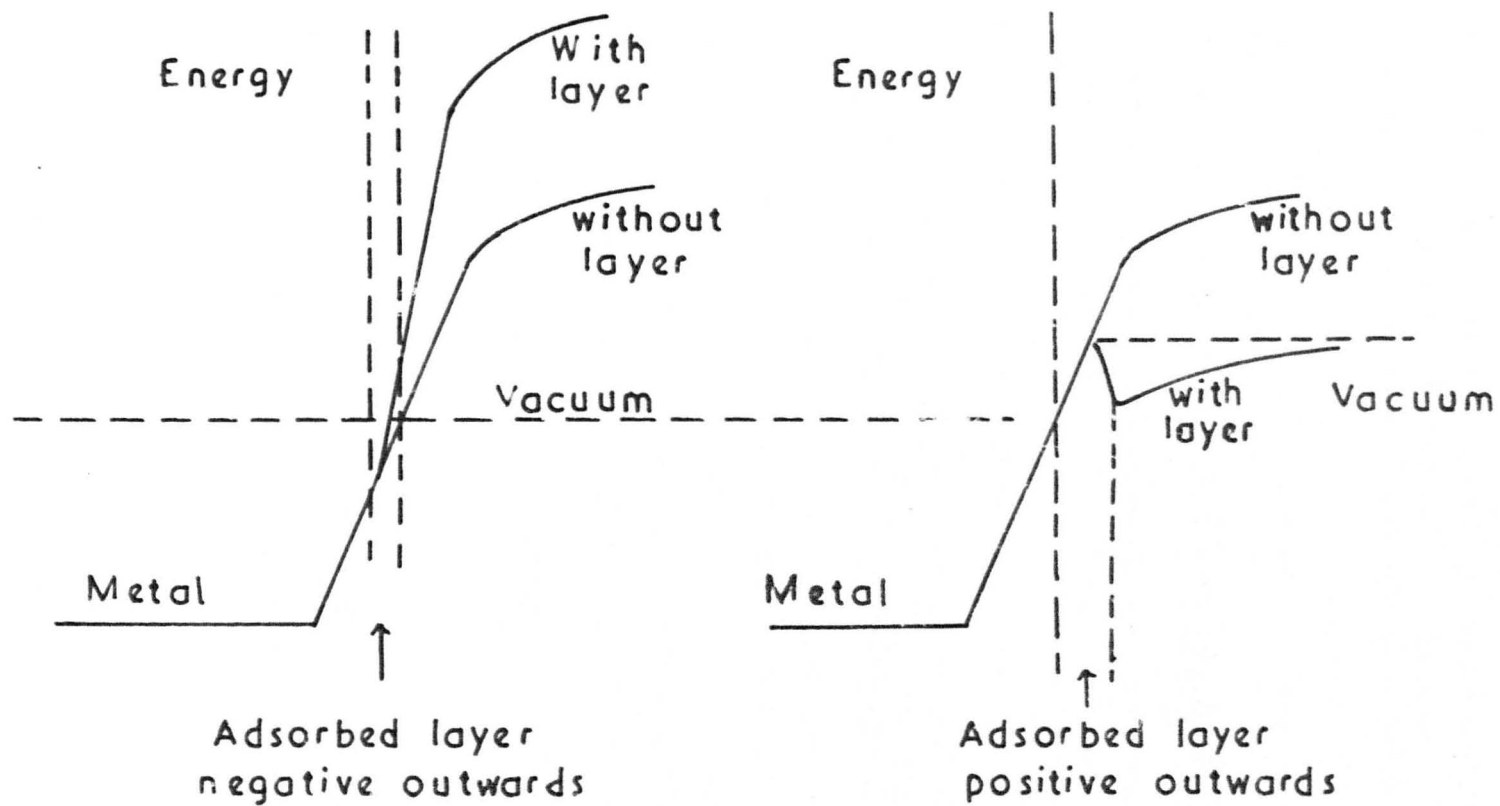


FIG. (2.2.1)

itive and negative charges e with separation d , the moment of each is

$$M' = ed.$$

and since $\sigma = ne$, the potential difference is $4\pi nM'$. There is, therefore, with adsorbed dipoles a change in work function of $4\pi nM'$, the work function being decreased if the positive charges are outwards and increased if the negative charges are outwards as shown in fig (2.2.1). With adsorbed ions the change is $2\pi nM'$ where M is the moment of the dipole formed by the ion and its image.

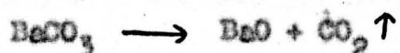
Several types of cathode are metals with a single adsorbed layer of atoms which reduce the work function. For partially covered surfaces the work function varies with the fraction of the surface covered. If more than a monolayer is present the work function of the surface approaches that of adsorbed substance. A larger difference between the values of ϕ and A and their true values may be obtained from a Richardson plot with such surfaces than with a metal surface, since the work function may be changing during attempts to measure it by plotting $\log I/T^2$ against $1/T$. This may still give a linear plot, however, over a small temperature range.

2.3. Theories of the Mechanism of Operation of Dispenser Cathodes

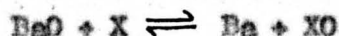
Since the dispenser cathode and the oxide cathode both employ the carbonates of the alkaline earths from which carbon dioxide is driven out leaving the oxides, it might be thought that the former cathode is merely a variation of the latter. This, however, is

not the case as far as the mechanism of operation goes.

Barrens, Jansen and Locajen⁽¹⁰⁾ in the initial report on the 'L'-cathode suggest that the operation of the cathode is due to the carbonate dissociating to give the oxide



The oxide is then reduced to a certain extent by one of the surrounding metals,



At 900°C the vapour pressure of barium is very high and so the metal will escape and the reaction will move to the right, although the very large heat of formation of barium oxide tends to force the reaction to the left. Thus barium vapour will be formed in the closed chamber of the cathode under a low pressure determined by the speed of the reduction of the oxide. At 900°C the oxide has a considerable vapour pressure so there will also be a noticeable amount of oxide vapour present.

The mixture of the two vapours passes out through the tungsten pores and in the pores forms a monatomic layer on the tungsten. A multi-atomic layer would evaporate again owing to the high vapour pressure, whilst the monolayer is held by adsorption forces. The monolayer of barium then moves about over the surface eventually covering the whole tungsten surface, both internal and external, with a monatomic layer of barium mixed with some oxygen. Thus the work function of the barium is reduced

considerably. The adsorbed oxygen atoms obstruct the escape of electrons from the metal but also promote a stronger binding of the barium atoms on the surface, the latter predominating as long as there is not too much oxygen present.⁽⁵²⁾ It has been shown that barium and barium oxide evaporate from the 'L'-cathode and in the pores of an activated cathode a quantity of barium was found corresponding to that required for the formation of a continuous monatomic layer.

Further work on the mechanism of the 'L'-cathode has been carried out by Du Pré and Rittner⁽¹⁵⁾ and by Schaefer and White⁽¹⁴⁾ and their conclusions do not agree. Du Pré and Rittner consider the emission to come from the tungsten, the work function of which is lowered by a surface double layer of barium on oxygen. The unactivated cathode is believed to have a chemisorbed layer of oxygen on the tungsten and the activation process supplies the required barium to the outer surface by the following sequence. The barium oxide is reduced by the tungsten to give barium vapour of low partial pressure at the base of the porous tungsten plug. This barium is then transported through the plug by means of Knudsen flow through the pores and by means of surface diffusion over the pore walls. When it reaches the external emitting surface the barium diffuses over it. Barium is slowly lost by evaporation from the surface and by pore flow. The termination of cathode life is associated with the exhaustion of the barium supply.

Schaefer and White studied the degree of surface coverage of the cathode by emission microscopy and found that the coverage of barium increased as the operating temperature decreased. The work function of an operating cathode was 1.67 volts which could correspond to a partially covered surface since the work function of a monolayer of barium on tungsten is 1.56 volts.⁽⁵³⁾ Since the work function of barium in bulk is over 2 volts, the barium could not be present in more than a monolayer. Evaporation studies were made by collecting evaporant from the cathode on a tungsten wire at constant temperature and maximum emission from the wire collecting the evaporant occurred for a monolayer coverage and gave a work function of 1.58 volts which agrees well with the accepted value within experimental error. This also indicated that the evaporant was barium, since barium oxide would have given a lower work function. Schaefer and White found that the rate of barium evaporation was controlled by the rate of diffusion of the barium over the tungsten surface, and a separate experiment indicated that on or near the emitting surface barium transfer occurs by diffusion over clean tungsten rather than over a sorbed layer of oxygen, as supposed by Du Pre and Rittner.

Venema⁽¹³⁾ suggests that after reduction of the oxide the barium moves towards the cathode surface through the porous tungsten, meaning, presumably, by Knudsen flow, since the reasoning continues that having collided with a pore wall the barium atoms remain attached to the tungsten surface for some time.

They are able to move about a certain distance on this surface for some time. This distance is greater than the pore separation and thus the whole surface must be covered by barium. Venema then suggests that oxygen may play some part in the linkage of barium.

Espersen⁽¹⁶⁾ only goes as far as to suggest that barium in the 'L'-cathode plays the same role as thorium in the thoriated-tungsten cathode, without discussing the mechanism. After studying emission and evaporation from the 'L'-cathode Brodie and Jenkins⁽⁵⁴⁾ conclude that the emitting surface must be a monolayer of barium and oxygen on tungsten, in agreement with Rittner. At operating temperatures the oxygen remains permanently in the emitting layer and the barium evaporating from the surface is replaced at a higher rate than necessary by the dispensing mechanism.

More recently, Rittner, Ahlert and Rutledge have published a paper in two parts on the mechanism of operation of the 'L'-cathode. Their studies were based on the ideas of Rittner published previously⁽¹⁵⁾. In the first part of the paper⁽¹⁷⁾ measurements of emission, evaporation rate and evaporant composition are described. The barium migration length and the 'lifetime' of an adsorbed barium atom were measured. It was found that on depositing barium onto a clean tungsten wire and onto a tungsten wire having an adsorbed oxygen monolayer, the emission from the latter was an order of magnitude higher than

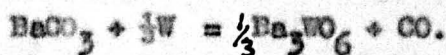
that from the former and agrees well with 'L'-cathode emission. Further evidence for the presence of oxygen was obtained by depositing monolayers of barium and barium oxide in known ratio on a clean tungsten wire. The 'L'-cathode value of emission was not approached until the barium oxide content neared 100%. For a complete barium on oxygen monolayer, the emission exceeded that from the 'L'-cathode by about 50% at 675°C and by lesser amounts at higher temperatures.

Evidence for the degree of surface coverage by barium was obtained from a comparison of the work functions of a monolayer of barium on oxidized tungsten and of the 'L'-cathode. Confirming evidence was obtained from measurements of emission from a tungsten wire maintained in the range of cathode operating temperatures, as a function of the arrival rate upon it of barium.

The conclusions drawn from these measurements are that the Richardson parameters are $A_R = 2.5 \text{ amp.cm}^{-2} \cdot \text{deg}^{-2}$, $\phi_R = 1.67 \text{ eV}$. After initial activation, the emission remains constant throughout life and then terminates suddenly. Life increases with the barium oxide content of the reservoir and decreases with tungsten porosity, reflecting an increased evaporation rate. The evaporant contains barium and barium oxide in nearly equal amounts, the oxide content decreasing with plug porosity. The migration length of barium and barium oxide over tungsten is large compared with the average pore separation so all the surface contributes to emission. The lifetime of barium oxide on tungsten is of the order of hours.

and tens of hours at operating temperatures. The corresponding energy is about 2.1 eV and the diffusion activation energy is 0.7 eV. The dipole layer, which comprises of oxygen, present monatomically, covered in turn by a complete monolayer of barium, reduces the tungsten work function. The presence of oxygen leads to improved emission and an increased lifetime. Oxygen losses during life are replenished by the barium oxide component of the activating stream.

In the second section of the paper⁽¹⁸⁾ a thermochemical study of the 'L'-cathode is made in conjunction with an experimental study which includes the chemistry of the carbonate decomposition and barium generation, the origin of barium oxide in the evaporant, the barium transport mechanism through the tungsten matrix and the factors determining cathode life. It is found that carbonate decomposition is accompanied in low porosity cathodes by the deleterious reaction

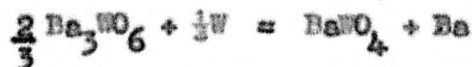


Barium is generated in the cavity at an equilibrium pressure by the reaction



and is transported through the tungsten predominantly by Knudsen flow. In transportation the barium acquires oxygen from the tungsten, producing in the evaporant a large barium oxide content which helps to activate the surface. The life of the cathode ends

with completion of the barium oxide-tungsten reaction and onset of the subsequent reaction



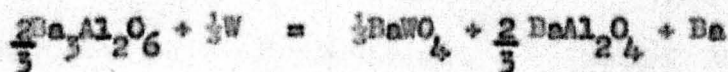
which is accompanied by release of a poisoning agent, the identity and origin of which is still unsolved. Material decrease in evaporation rate and a corresponding increase in cathode life was gained by addition of strontium carbonate.

Much work has been carried out recently in an effort to elucidate the mechanism of operation of the impregnated cathode. Levi⁽²³⁾ suggests that it is as follows:- the basic barium aluminate component of the impregnant reacts with the tungsten to produce a vapour pressure of barium sufficient to maintain a high degree of surface coverage of adsorbed barium on the tungsten. The predominant seat of emission in this cathode is the same as that in the 'L'-cathode, namely tungsten, the work function of which is lowered by a dipole layer comprising barium and some oxygen. Brodie and Jenkins⁽⁵⁴⁾ find that the patches of barium compounds at the pore ends contribute to the emission if the impregnant contains calcium oxide, the suggested reason being that during ageing a thin film of calcium oxide is left at the end of the pores and is activated by the free barium. If the impregnant does not contain calcium oxide the pore ends form poorly emitting patches.

Rittner, Rutledge and Ahlert⁽⁵⁵⁾ followed up their work on

the 'L'-cathode by a study of the mechanism of operation of the impregnated cathode. The impregnant used had the empirical composition $5\text{BaO} \cdot 2\text{Al}_2\text{O}_3$. It was found that Child's law is obeyed by the emission density-voltage characteristics in the space charge region and the Schottky equation in the accelerating region with an anomalously steep slope. The Richardson parameters are $\phi = 1.53 \text{ eV}$ and $A = 0.14 \text{ amp.cm}^{-2} \text{ } ^\circ\text{K}^{-2}$. After initial activation the emission density remains constant throughout life at a value about one-fifth that of the 'L'-cathode and then terminates suddenly. The emission density is several amps.cm^{-2} , and the lifetime is 5000 hours.

Barium necessary for activation is generated by the reaction



at an equilibrium pressure computed as

$$\log P_{\text{Ba}} (\text{mm}) = -20360/T + 8.56$$

The BaAl_2O_4 component of the impregnant is inert chemically but lowers the melting point. (35) Transport through the tungsten matrix is mainly by Knudsen flow of barium vapour through partially blocked pores, the length of which increases with time as the seat of the reaction moves progressively deeper inside the pores. Emission is substantially lower than the 'L'-cathode, presumably because of the release of a poisoning agent which counteracts the effect of much of the activator.

It is suggested that the role of calcium oxide in the improved cathode may be to neutralise the influence of the poisoning agent, the identity of which is not given.

Beck⁽²⁾ after work with an electron microscope on the 'E-N' cathode found that diffusion of emitting material over the surface of the cathode is included in the activation mechanism. The work function was measured in three different ways:-

- a. by the retarding field method, which gives the arithmetic mean work function,
- b. by a Richardson plot which gives the minimum work function,
- c. by comparison with the charts of Loosjes and Jansen⁽⁵⁶⁾ which give a work function which depends on temperature.

By plotting this latter work function as a function of temperature the value of the minimum work function was obtained, in agreement with the Richardson plot value. Assuming the work function of nickel to be 5.0eV and inserting the values obtained in

$$\phi_0 = A \phi_{\min} + (1 - A) \phi_{Ni}$$

where A is the proportion of surface covered by emissive material and ϕ_0 is the mean work function, the results gave a surface coverage of 70%. The workers conclude that the 'E-N' cathode is a barium on nickel diffusion emitter in which the surface covered by barium is about 70%.

In the nickel-boron cathode, Fene⁽³⁹⁾ finds that after

activation the cathode surface consists of 20-25% nickel, the remainder being mixed alkaline earth oxides. From a consideration of the work function obtained it is suggested that the cathode consists of emitting oxide grains within a nickel matrix, the work function of the nickel being reduced by at least a partial barium coverage.

As is apparent, there is no general agreement on the mechanism of operation of the dispenser cathode. That the alkaline earth metal itself diffuses to the surface there does not seem much doubt, but the role played by oxygen is not agreed upon, although the majority of opinion now holds that oxygen does play some part in the mechanism of operation of the cathode. When this problem is solved there is still the question of how the transport mechanism operates. The suggestions are that it is by Knudsen flow through the pores or by migration of the alkaline earth along the pore walls, or by a combination of the two. It is towards finding some information which may help in clarifying the unsatisfactory position of the theory that the present work is directed.

Chapter III

The Preparation of the 'M'-cathode.

This chapter is concerned with a survey of the various methods used to produce 'M'-cathodes in more detail than the mention in Chapter I, which was concerned with dispenser cathodes in general. In the production of an 'M'-cathode several variables must be considered. These are the percentage composition of the cathode mixture, the forming pressure used, the atmosphere and temperature for sintering and the method of activation employed. An outline of the possible ranges of these variables is sketched.

3.1. Cathode composition

In Chapter I a brief account has been given of the various materials which have or are being used in the production of dispenser cathodes. The 'M'-cathode consists of nickel powder mixed with one or more of the alkaline earth carbonates and in some cases a small proportion of a reducing agent, which is pressed and sintered to form a robust, metallic cathode of the shape desired.

The first consideration must be given to the state and purity of the cathode ingredients. It is not essential that the nickel be 100% pure so long as the impurities are elements which will act as reducing agents to aid in the reduction of barium oxide to barium and that the amount of each present is known. The usual nickel powder used⁽²⁾ is obtained commercially as carbonyl powder which is prepared by decomposition of nickel carbonyl. This nickel has a high degree of purity and can be obtained as spherical particles over a range of diameters from a lower limit of one micron. The porosity

of the final nickel matrix is governed by the choice of powder size, pressure used and sintering temperature of the cathode. Any variation in one of these towards greater porosity can be counterbalanced by a variation to give a result in the opposite sense in one, or both, of the others. Thus any particular choice is not so important as the combination of selected values for the variables.

Beck and his co-workers⁽²⁾ use carbonyl nickel of 1-5 microns in diameter. Thien-Chi and Dusseaussey⁽²⁷⁾ use nickel powder obtained from the oxide instead of the carbonyl. Balas, Dempsey and Rexer⁽⁶⁾ for their impregnated cathode use nickel powder of 37-44 microns diameter and specify the impurity content. Carbonyl nickel of grain diameter less than 10 microns is used by Wessard and Ugan.⁽³⁷⁾ Kane uses 3-5 microns diameter carbonyl nickel. The properties of the powder chosen is important since the properties of the sintered compact depend on those of the powder. The usual grain size employed is less than 10 microns, although the impregnated cathode base⁽⁶⁾ is constructed from much larger particles, giving a more porous compact for a given pressure and sintering temperature.

The alkaline earth carbonates are obtained in a high state of purity commercially for the manufacture of oxide-coated cathodes and these carbonates are used in the 'M'-cathodes. Some workers⁽³⁷⁾ eliminate carbonate particles larger than a desired size by passing the powder through a sieve of appropriate mesh.

The next step in the production of a cathode is the preparation of the cathode material. The porosity of the resulting nickel matrix is dependent upon the amount of carbonate in the mixture before sin-

tering. The density of barium carbonate is 4.43 gms.cm^{-3} and that of nickel is 8.9 gms.cm^{-3} , and in order to obtain a fairly rigid cathode the percentages by weight of the two components must be less than 50% of the carbonate and more than 50% of nickel. The cathode has amongst its advantages the ability to be machined and its metallic aspect; in order to preserve these the percentage of nickel must be as high as possible. The life of the cathode is determined primarily by the amount of barium carbonate initially present, so for longer life more carbonate is necessary. The position thus resolves itself into one in which a compromise has to be made at the optimum composition. This composition must be found experimentally and varies according to the exact requirements of the cathode. An important point which has to be remembered when making a cathode is that it shrinks during sintering; the more carbonate there is present, the greater is the shrinkage.

The percentage composition used by the workers in this field for their cathodes does not vary very much, all having reached similar conclusions about the optimum composition as seen from table I.

Table I.

WORKER	Reference	% Ni	% Carbonate
Beck, Brisbane, Cutting and King	2	70	30
Dodds	35	70	30
Mognard and Uzan	37	54.75	42.25
" " " (a better cathode)	"	65	35
Thien-Chi and Dusseaussey	27	75	25
Fane	39	68	30.6

The other possible component of the cathode mixture is a reducing agent. The mechanism of the cathode is dependent upon the production of the free alkaline earth metal in the cathode. The free metal is produced from the oxide. Since barium oxide has a melting point of 1923°C and does not dissociate at the temperatures at which the cathode is operated, a reducing agent is necessary to promote the production of free barium. The nickel powder used is not pure and contains some silicon, manganese, magnesium, etc. which act as reducing agents, resulting in the formation of complex salts in the cathode itself. Cathodes prepared from very pure nickel are difficult to activate. The salts when formed in the cathode serve no beneficial purpose. In the oxide-cathode such salts form an interface layer between the nickel core and the oxide coating, and Rooksbey and Finemann and Eisenstein⁽⁵⁸⁾ (using X-ray diffraction analysis) have found Ba_2SiO_4 and Ba_2TiO_4 . It is reasonable to suppose that such salts are formed in the 'M'-cathode where nickel and oxide are in contact. It is still necessary to use the purest available nickel as any reducing agent may then be added in controllable quantities. In practice this is generally the procedure followed, although the reducing agent used varies from worker to worker.

Dodds⁽³⁵⁾ uses 0.1% silicon as a reducing agent and manganese has also been used. The difficulty with silicon is the formation of the silicate which is not beneficial to the cathode and may impede diffusion through the matrix. Beck⁽³⁶⁾ uses 1% Zirconium hydride as his reducing agent which is the commercial name for a solution of hydrogen in Zirconium. Beck found that tungsten, tantalum and

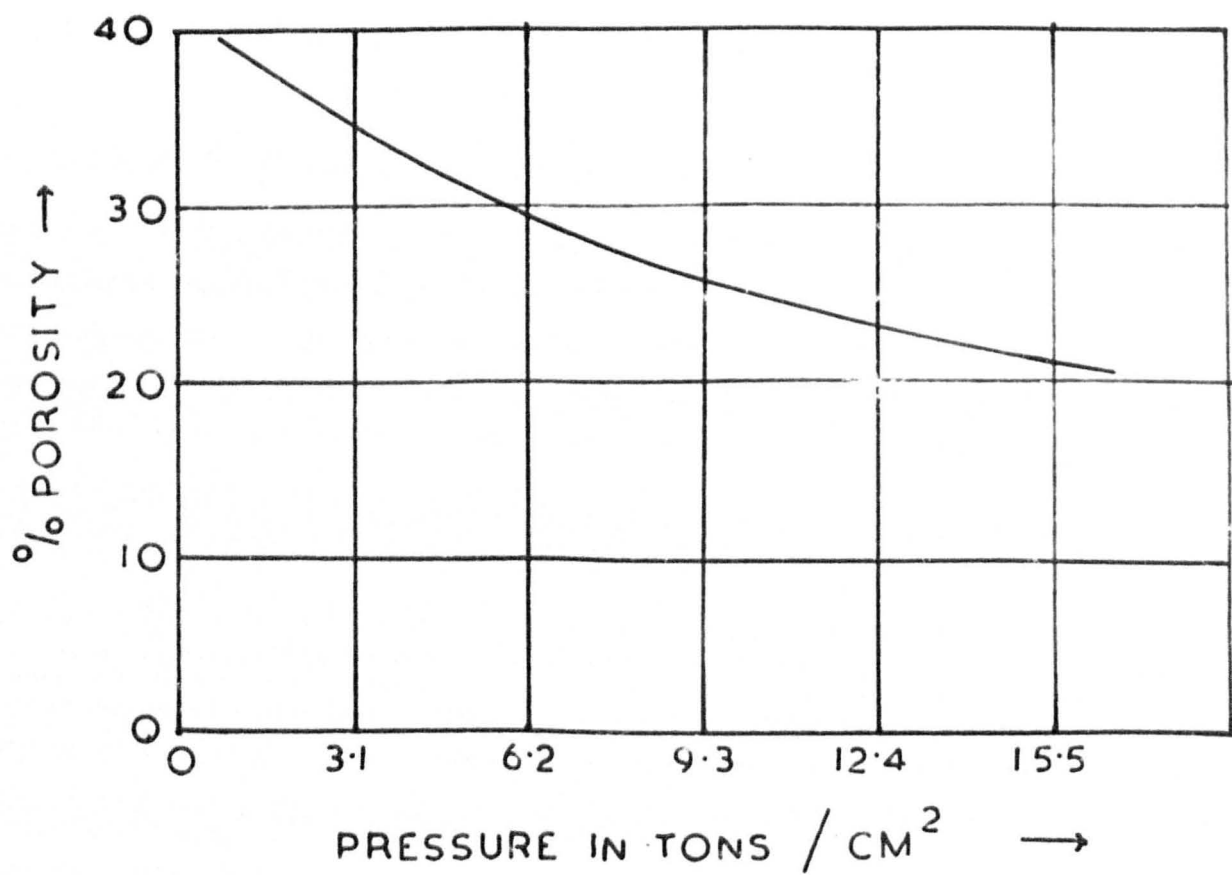


FIG (3.2.1)

titanium tend to produce excess barium evaporation, whereas carbon reacts very slowly with prolonged evolution of gas. Tungsten present as 3% by weight or as 1% by weight has been used by Thien-Chi and Dussaussey,⁽²⁷⁾ Mesnard and Uzan⁽³⁴⁾ have used zirconium as a reducing agent and have even attempted to make a cathode from zirconium and the carbonates alone, which was unsuccessful. Fane⁽³⁹⁾ uses boron as reducing agent although Hughes and Coppola⁽³³⁾ prefer aluminium to boron in their pressed cathode.

3.2. Pressing the cathodes

The pressure used to form the cathodes varies over three orders of magnitude, from 0.1 tons.in⁻² to 100 tons.in⁻². The porosity of the resultant cathode depends upon several factors, as already mentioned, but of these the pressing and sintering are the two most important and to a certain extent are complementary. Beck⁽²⁾ has published a curve (fig (3.2.1.)) of pressure in tons.cm⁻² against % porosity of the resultant cathode. For pressures greater than 50 tons.in⁻² the change of porosity is very small. The pressures used by various workers are shown in table II.

Table II.

WORKER	Reference	Pressure
Beck, Brisbane, Cutting and King	2	50-100 tons.in ⁻²
Dodds	35	10 "
Thien-Chi and Dussaussey	27	0.1 "
Mesnard and Uzan	34	47.6 "
Coppola and Hughes	5	70 "
Fane	39	50 "

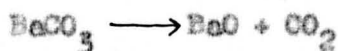
La Rooque⁽³⁸⁾ has found that emission over a range of temperature plotted as a function of the applied field is inversely proportional to the forming pressure.

3.3. Sintering

The sintering of the 'M'-cathode is made more complex by the presence of the carbonate in the metal powder during the sintering process. The atmosphere and the temperature of sintering are the two most important variables in the process. Much work has been done on sintering atmospheres employed in the practice of powder metallurgy.⁽⁵⁹⁾ In the production of 'M'-cathodes sintering is usually carried out in vacuum or in hydrogen. Mesnard and Usan⁽³⁷⁾ have compared the two methods and conclude that sintering in vacuum gives a cathode with better emission. Thien-Chi and Dussaussey⁽²⁷⁾ and Fane⁽³⁹⁾ use a hydrogen atmosphere and Beck⁽²⁾ sinters under vacuum. La Rooque⁽³⁸⁾ sinters his nickel-columbium matrix cathodes in dissociated ammonia.

The first essential when sintering is to prevent the formation of oxide films which cannot be broken down later. It seems that any nickel oxide formed can be broken down by heating to over 600°C. The prevention of the formation of the oxide can be brought about by sintering in hydrogen or, to a less extent, in vacuum, hence the choice of the sintering atmosphere. If there is a difference in the cathodes sintered in hydrogen from those sintered in vacuum it is more likely that the effect is due to interaction with the alkaline earth compound and not concerned with the nickel.

to the oxide and carbon dioxide.



If the sintering is carried out in vacuum the carbon dioxide is pumped away as it is liberated; if a hydrogen atmosphere is used the carbon dioxide is swept out by the hydrogen. The breakdown of barium carbonate is complete at about 950°C when the pressure is about 10^{-6} m.m.Hg. Since the temperature of sintering is considerably higher, the breakdown of the carbonate is completed during sintering. Barium oxide is thus left in the nickel matrix. Barium oxide quickly absorbs water vapour to give the hydroxide, but does not lose it again unless heated above 850°C in hydrogen. This, then, is another advantage of using hydrogen as the sintering atmosphere if any hydroxide is likely to be present due to residual water vapour in the system. The chemical system of the oxide is very sensitive to chemical influences produced by impurities or residual gases. This is due to the fact that barium oxide and especially barium are very active chemically.

If the sintering temperature is about 1200°C , the barium oxide will, to some extent have broken down to give the metal and oxygen. The vapour pressure of the oxide at such a temperature is of the order of 10^{-5} m.m.Hg. so some of it will evaporate from the cathode. The vapour pressure of barium at this temperature is 10 m.m.Hg. so this will evaporate more rapidly⁽⁶⁰⁾ than the oxide. Since barium is so reactive it combines with hydrogen to give the hydride⁽⁶⁰⁾



but this decomposes well below the temperatures attained in sintering.

Many though the possible reactions are during sintering no unwanted compounds are likely to be stable at the sintering temperature. The great difficulty is in removing all unwanted substances during and after sintering. This illustrates the necessity for the chemical purity of the materials used in the cathode manufacture.

The sintering temperature is important in determining the porosity. When sintering at no time does the whole mass become molten. In the case of pure metals the temperature at which a reasonable sintering rate can be achieved is of the order of 90-95% of that of the melting point.⁽⁶¹⁾ In this case the mechanism of sintering is one of diffusion in the solid state between surfaces of adjoining particles. This atomic diffusion is sufficient to close up the spaces between the particles resulting in a general shrinkage. During this process recrystallisation occurs, and an increase in sintering temperature will increase the rate of grain growth and the final grain size of the finished material.

The sintering of an 'M'-cathode is made more complex by the presence of the alkaline earth compound. The melting point of nickel is 1455°C ⁽⁶²⁾ so that 1310°C should be roughly the sintering temperature of nickel. However, the cathode porosity needs to be quite high, so providing the required mechanical properties are maintained to a high degree, a lower sintering temperature could be used. The presence of the alkaline earth material, too, tends

to increase the porosity of the nickel. The time of sintering also plays a part in determining the final state of the matrix, the longer the time, the more dense the resultant matrix.

The sintering times, temperatures and atmospheres used are given in table III. Generally the temperatures are 900 - 1000°C in hydrogen

Table III

Worker	Ref.	Time	Temp. °C	Atmosphere
Beck et al	2	10 mins	1100	vacuum
Thien-Chi and Dussausay	27	1 hr.	900	H ₂
Mesnard and Uzan	37	1 hr.	950	H ₂
" " "	"	1 hr.	1100	vacuum
Balas et al	6	10 mins	1000	H ₂
Fano	39	30 mins	1100	H ₂

and 1100°C in vacuum. The processes described determine the pore size in the cathode and since it appears likely that the cathode functions by a diffusion process, then the porosity of the cathode is of primary importance. Matrix porosity is usually defined as the volume of pores per total volume, or as Balas⁽⁶⁾ expresses it

$$1 - \frac{(\text{density of matrix})}{(\text{density of nickel})}$$

Assuming for the moment that the process controlling the operation of the cathode is a diffusion one, either by flow through the pores or by diffusion along the pore walls, then the types of pores formed are important. If the cathode is fully activated when the rate of

diffusion through the matrix is at least equal to the rate of evaporation from the cathode surface then there will be an optimum value of the number of pores and of their size. The life of a cathode depends on these conditions and will be longest when the optimum conditions are found.

3.4. Activation

After breakdown the cathode must be activated before it becomes an efficient electron emitter. It is generally assumed that the activating process produces free alkaline earth metal in the cathode. This may be done in several ways. The temperature of the cathode may be raised to about 1200°C for a few minutes. This is termed thermal activation. With the cathode at about 900°C a potential may be applied to the anode and an emission current drawn which increases to a steady value over a period of several hours; this is current activation. A combination of thermal and current activation has wide appeal as the most rapid method of activating a cathode. A third method of activation is to admit a reducing gas into the valve while the cathode is at 900°C . This has been employed mostly in the oxide cathode work by several authors; Prescott and Morrison,⁽⁶³⁾ Eisenstein⁽⁶⁴⁾ who used methane, and more recently by Forman⁽⁶⁵⁾ who used ethane. Wagener⁽⁶⁶⁾ made a study of the process and showed that hydrogen, water vapour and methane are all activating gases below 10^{-5} mm.Hg. pressure. The reducing gas technique has not been used, as far as is known, with 'N'-cathodes as the added reducing agents perform the same function during thermal activation.

All the authors ⁽²⁾⁽²⁷⁾⁽³⁷⁾⁽³⁹⁾ dealing with moulded cathodes use a combination of thermal and current activation, which offers the most rapid means of activating the cathode in the presence of reducing agents. Beck ⁽²⁾ heats his cathodes to 1100°C to complete breakdown and perform the sintering; at this temperature a voltage is applied to give an emission of 1 amp.cm^{-2} . The cathode is 'aged' i.e. emission is stabilised, by drawing this current for 24 hours. The cathode temperature is reduced from 1100°C to 950°C during the first two hours of ageing and maintained at 950°C for the rest of the ageing time. Similar methods are employed by the other workers.

After activation and ageing the valve is usually gettered and sealed off under a vacuum better than 10^{-6} mm.Hg . The valve is then ready for use. In some cases measurements are taken after activation with the valve still on the vacuum system. Depending upon the use to which the valve is to be put, the cathode can be constructed to give best results by due consideration of the composition, porosity and robustness required. Such cathodes provide engineers with a degree of control over the behaviour of a valve than has been previously known.

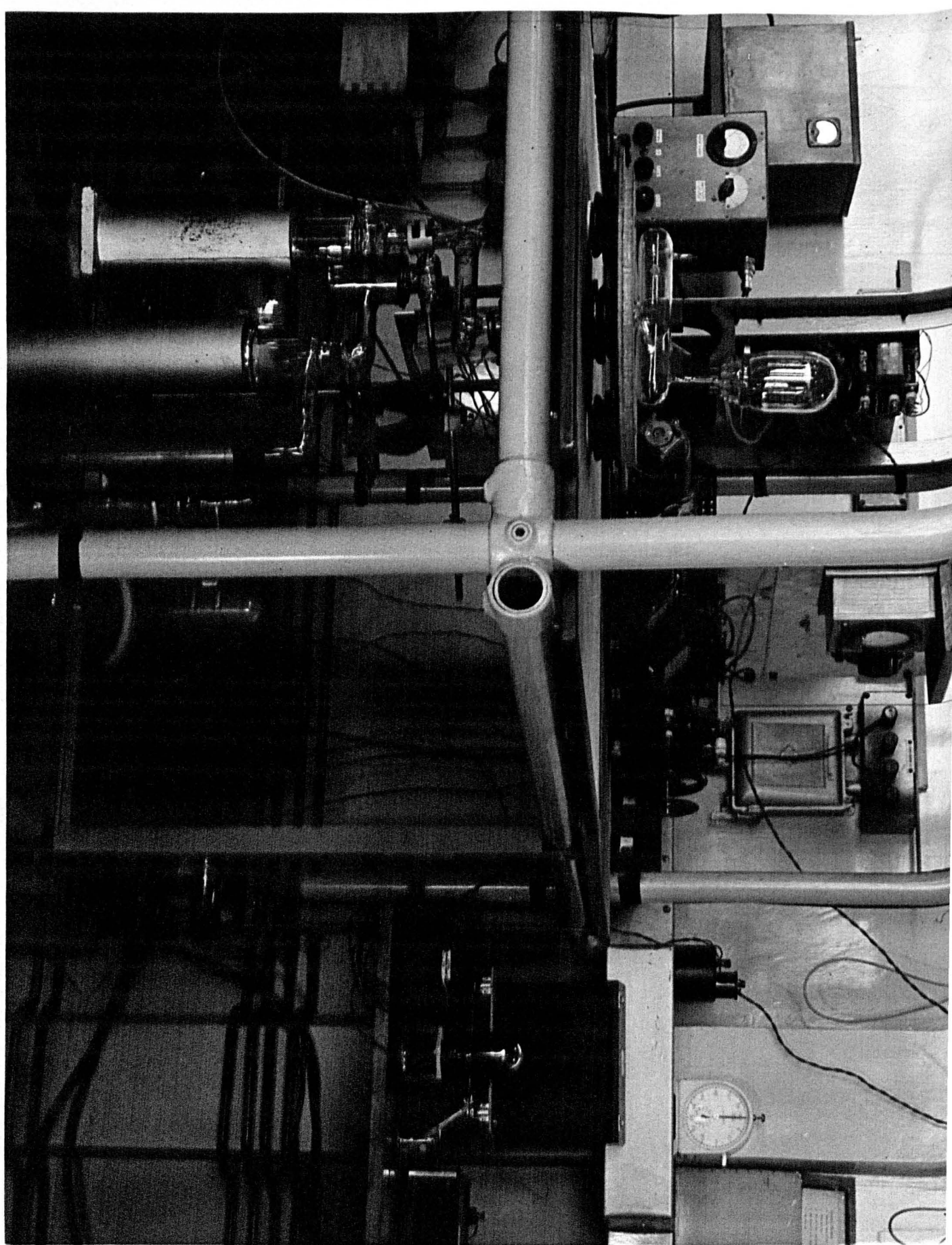


fig. 4.1.1.

Chapter IV

Apparatus and Experimental Techniques.

The chapter concerned with a description of the apparatus is included in Part I of this work since most of the apparatus is common to the work described in Parts II and III. The later work on evaporation and diffusion necessitated the use of almost all of the apparatus used for the work function measurements and for the study of the effects of oxygen and sulphur on the thermionic emission. In addition counting apparatus was required for the later work and is described in this chapter.

4.1. General arrangement

The apparatus consists of a vacuum system for the preparation of the sealed-off diodes used in this work, together with an oven and various necessary power supplies for valve heaters, etc., mounted on a framework of $1\frac{7}{8}$ " diameter steel 'Kee-Klam' tubing. Measurements on the sealed-off tubes are made on an adjoining bench using laboratory power supplies, except that for the valve heaters, which are independent of the frame. A general view of the apparatus is shown in fig (4.1.1.)

4.2. The vacuum system

A high vacuum is essential in any work on cathodes in order that a stable and reproducible emission is obtained. Conflicting evidence can so easily arise from failure to produce a good enough vacuum. The vacuum system was designed with a view to its being used to produce either sealed-off or continuously pumped tubes. The final pressure required is less than 10^{-6} mm.Hg. and in addition

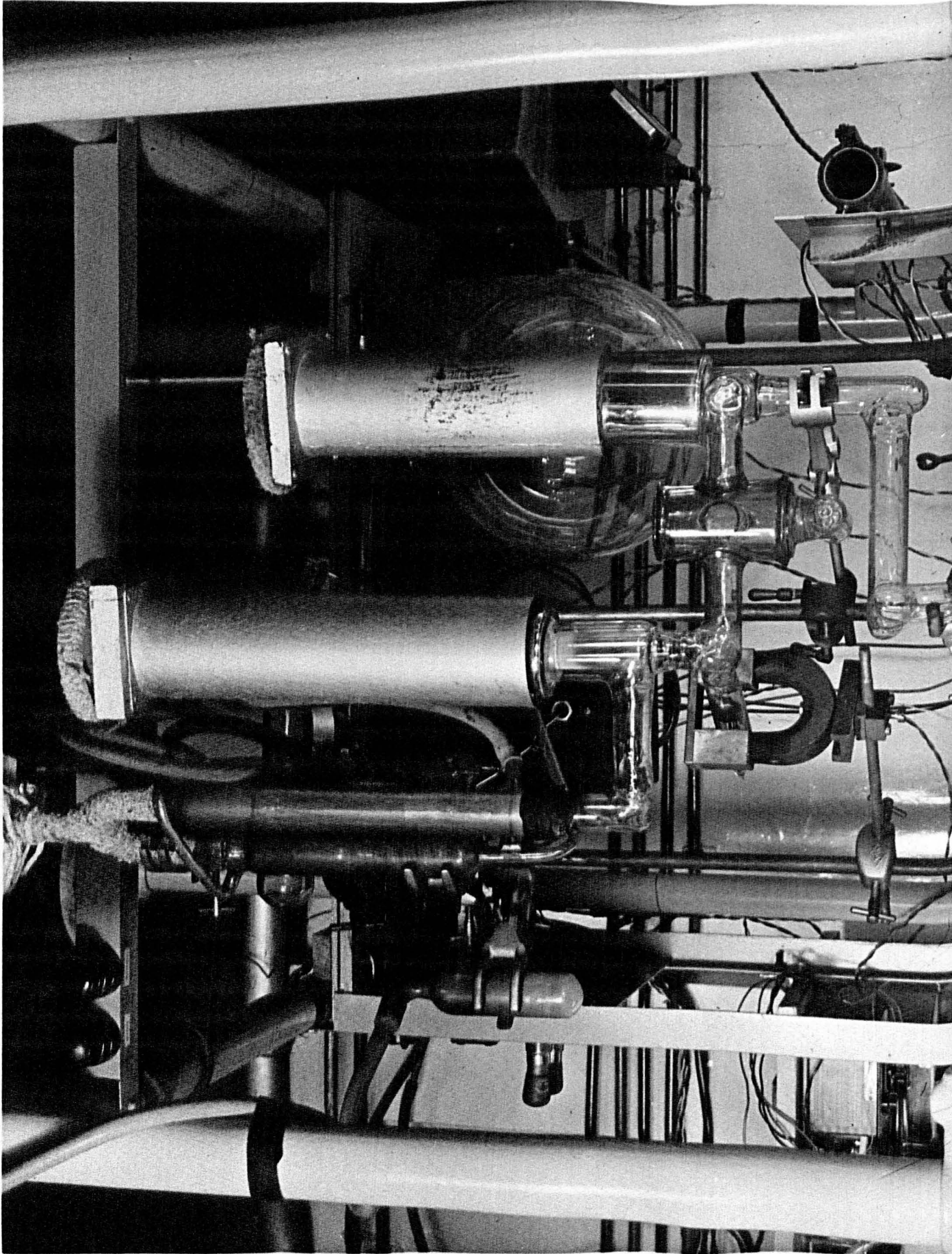


fig. 4. 2. 1.

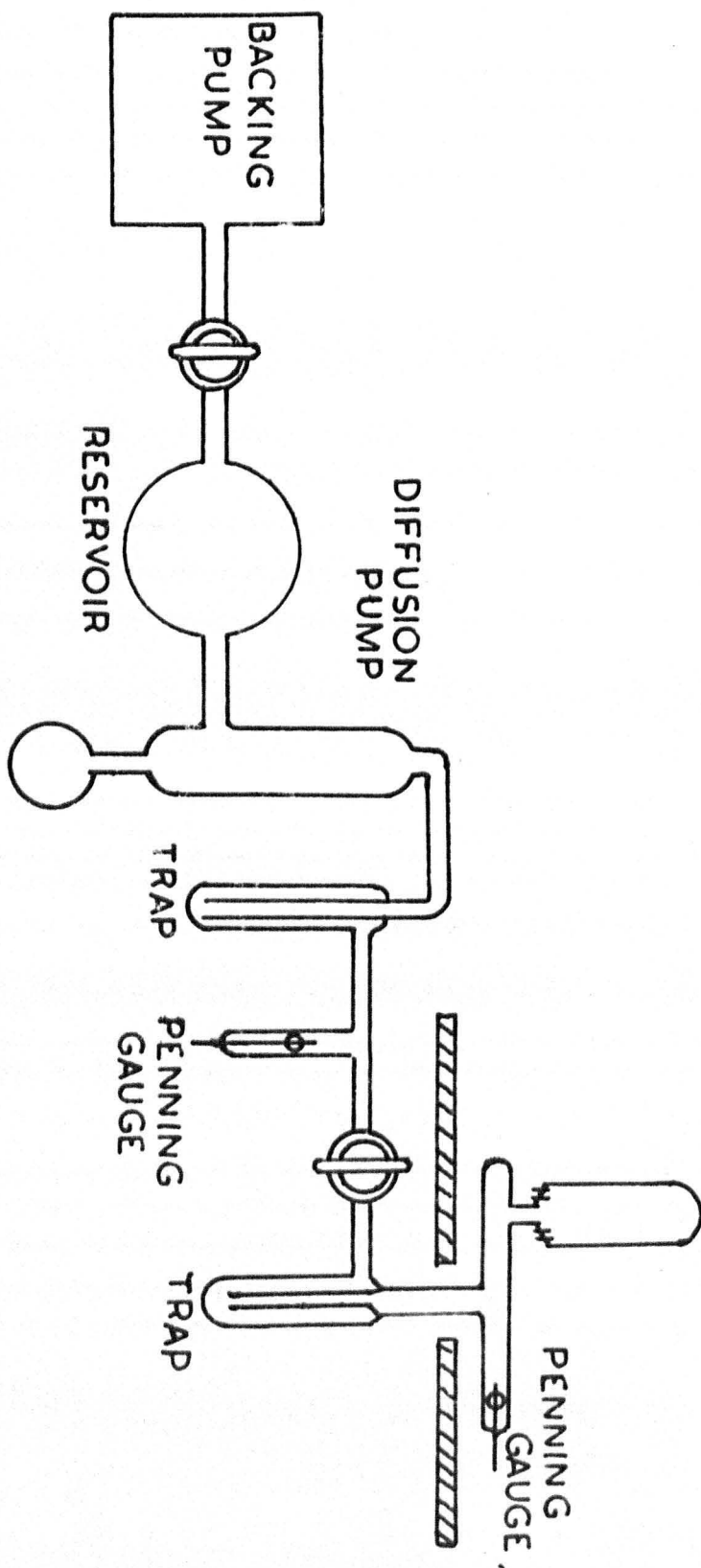


fig. 4. 2. 2.

to obtaining such a vacuum the system has to remove the large quantity of gas liberated during the activation of the cathode as quickly as possible. The system, shown in fig (4.2.1.) is constructed of C9 glass throughout. A diagram of the system is given in fig (4.2.2.) It consists of a two-stage mercury diffusion pump backed by a single stage Edwards' Speedivac rotary pump. The experimental tube is pumped through two liquid air traps, one being between the experimental tube and a wide bore tap and the second between the tap and the diffusion pump. The tap permits a pressure of 10^{-6} mm.Hg to be maintained overnight in the experimental tube. All tubing on the high vacuum side of the diffusion pump is as short and wide as possible in order to maintain a reasonable pumping speed which is then limited by the cold traps. A reservoir is incorporated on the backing side of the diffusion pump to permit pumping to be continued for some time, if required, after the backing pump has been switched off.

To enable a high vacuum to be maintained an oven is incorporated which can be lowered over the experimental tubes to bake them at a temperature of 420°C . Great care is taken to ensure that all materials used in the vacuum system are scrupulously clean. All the glass used is treated with concentrated nitric acid and carbon tetrachloride to remove any traces of grease. It is then thoroughly washed with distilled water and oven-dried. The metal components are thoroughly outgassed by eddy-current heating when the tube is being pumped. Apiezon N-grease is used on all taps except the main tap cutting off the experimental tube, on which T-grease is used.

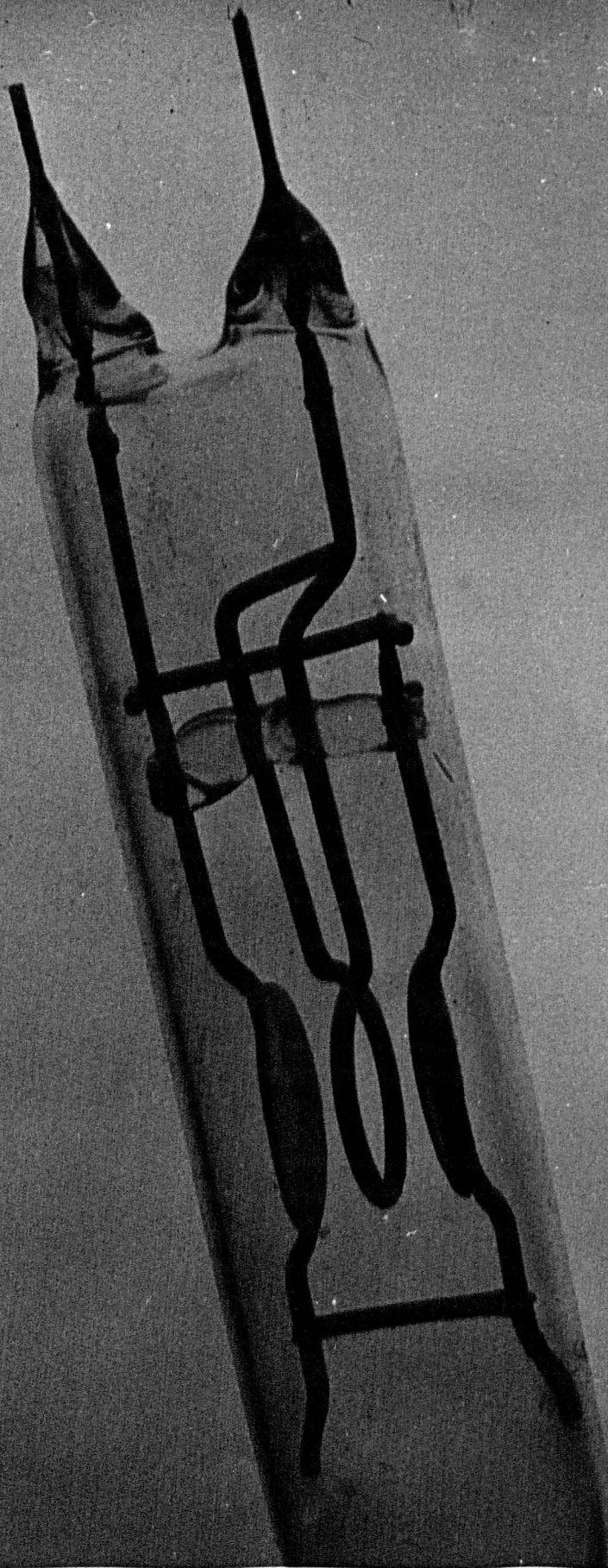


fig. 4. 3. 1.

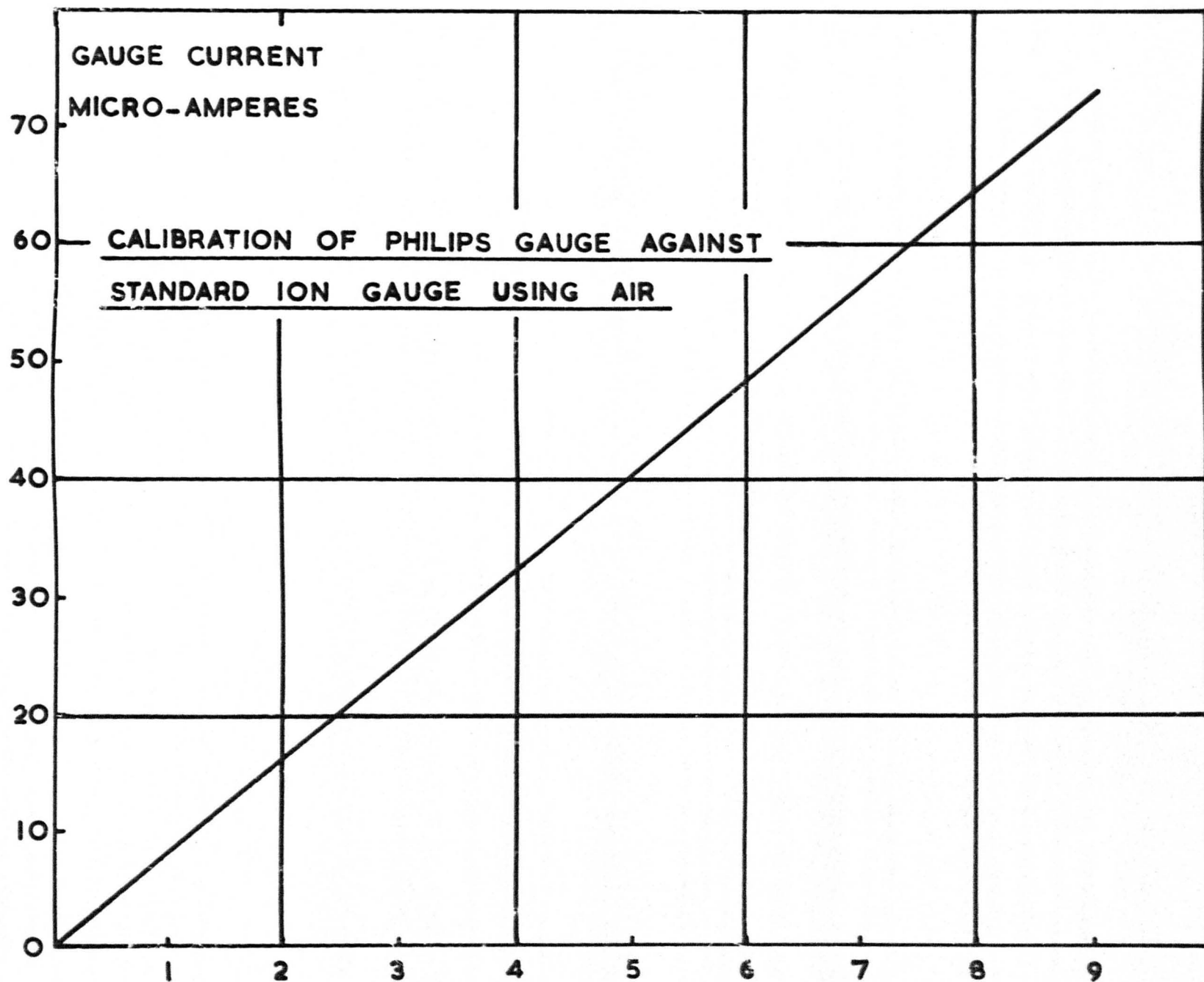


fig. 4. 3: 2.

4.3. Measurement of pressure

The vacuum obtained in the system is measured by means of a modified form of a Penning or Philips' vacuum gauge⁽⁶⁷⁾ designed in this laboratory. This type of gauge is employed so that the vacuum can be continuously monitored by placing one gauge immediately below the experimental tube, and, since this gauge can not be operated during the baking of the apparatus, by having a second gauge situated below the oven table but above the main tap.

The gauge consists of two flat, circular nickel discs, 2.0 cms in diameter, as cathodes (see fig (4.3.1)). These discs are 1 cm. apart and a nickel wire loop (18 S.W.G.) of the same external diameter as the discs is placed midway between the latter. This loop is made the anode. A constant voltage of 2000V is applied across the gauge and a magnetic field of 600 gauss is maintained at right angles to the plates by a small, external, permanent magnet. When the voltage is applied a discharge in the gauge results in which the gas ions are accelerated towards the anode, pursuing helical trajectories of considerable length due to the magnetic field. A Tinsley triple-range micro-ammeter is employed to measure the ionisation current. This current gives an indication of the vacuum in the system and the calibration curve used is shown in fig (4.3.2). The aim is to always attain pressures of less than 1 micro-asp (i.e. 10^{-6} mm.Hg. or less) before any measurements or work is attempted.

4.4. Experimental tubes

The experimental tubes used for thermionic emission measurements only and those used in the poisoning studies are exactly the same

except for a filament coated with 'poisoning' material which is used in the latter. The tubes used for the evaporation and diffusion rate measurements are similar to those used for the emission measurements except that instead of an anode a movable collector is included. Constructional details of these tubes is given in the section concerned with that work.

The tubes are simple diodes. The anode consists of an 'A'-nickel cylinder 1 cm. in diameter and 4 mm. in thickness. The nickel is supplied by Henry Wiggin and Co. Ltd., and the figures given for the limiting composition are given in table I.

Table I

Composition of 'A' Nickel	
Element	%
Carbon	0.10 max
Silicon	0.07 "
Copper	0.20 "
Iron	0.25 "
Manganese	0.25 "
Magnesium	0.15 "
Sulphur	0.01 "
Nickel & Cobalt	99.0 min

In the evaporation measurement tubes the collector is an 'O'-nickel disc, 2 cms. in diameter. The composition of 'O' nickel is given in table 2. The anode or collector is hydrogen furnace at red heat for 15 minutes before insertion in a valve and when in the valve on the pump it is eddy current heated for some time to complete the

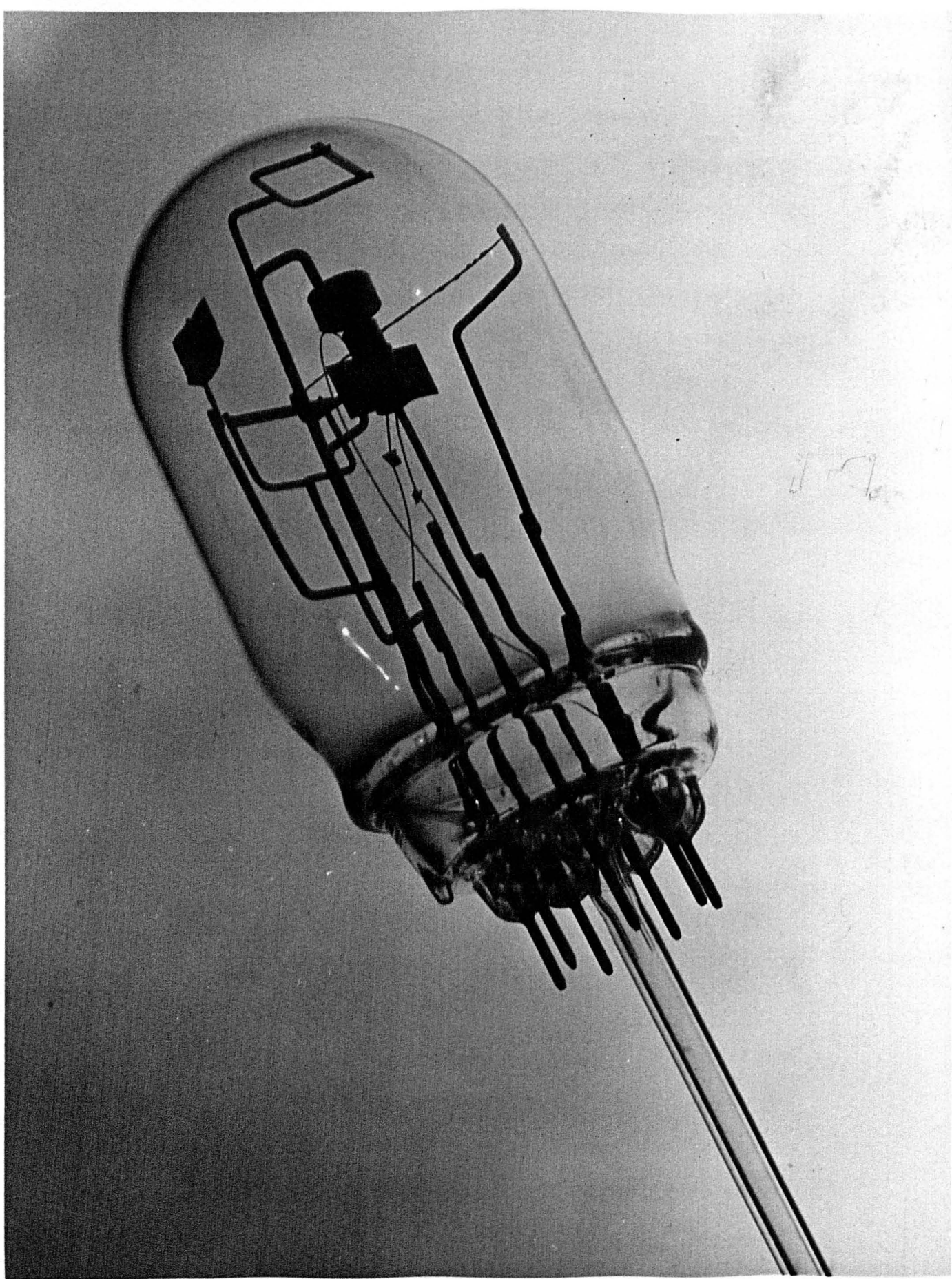


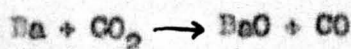
fig. 4. 4. 1.

cleaning. After activation the anode or collector is again eddy current heated to remove any material evaporated from the cathode during the activation process, at the same time maintaining the cathode at a fairly high temperature to prevent the material evaporating back to it. An alternative method suggested by Stoll⁽⁶⁸⁾ is to maintain the anode at 600°C during breakdown of the carbonate.

Table II

Composition of 'O' Nickel	
Element	%
Nickel	99.5
Cobalt	0.5
Magnesium	0.07 - 0.15
Manganese	0.15
Iron	0.2
Silicon	0.1
Copper	0.1
Sulphur	0.005
Carbon	0.01

He has shown that most of the gas on the anode is carbon monoxide arising from the action of carbon dioxide on free barium evaporated around the tube



The anode is supported by 18 S.W.G. nickel wire as shown in the view of the valve structure in fig (4.4.1).

The cathode is constructed from an 'O' nickel tube, 1.25 cms.

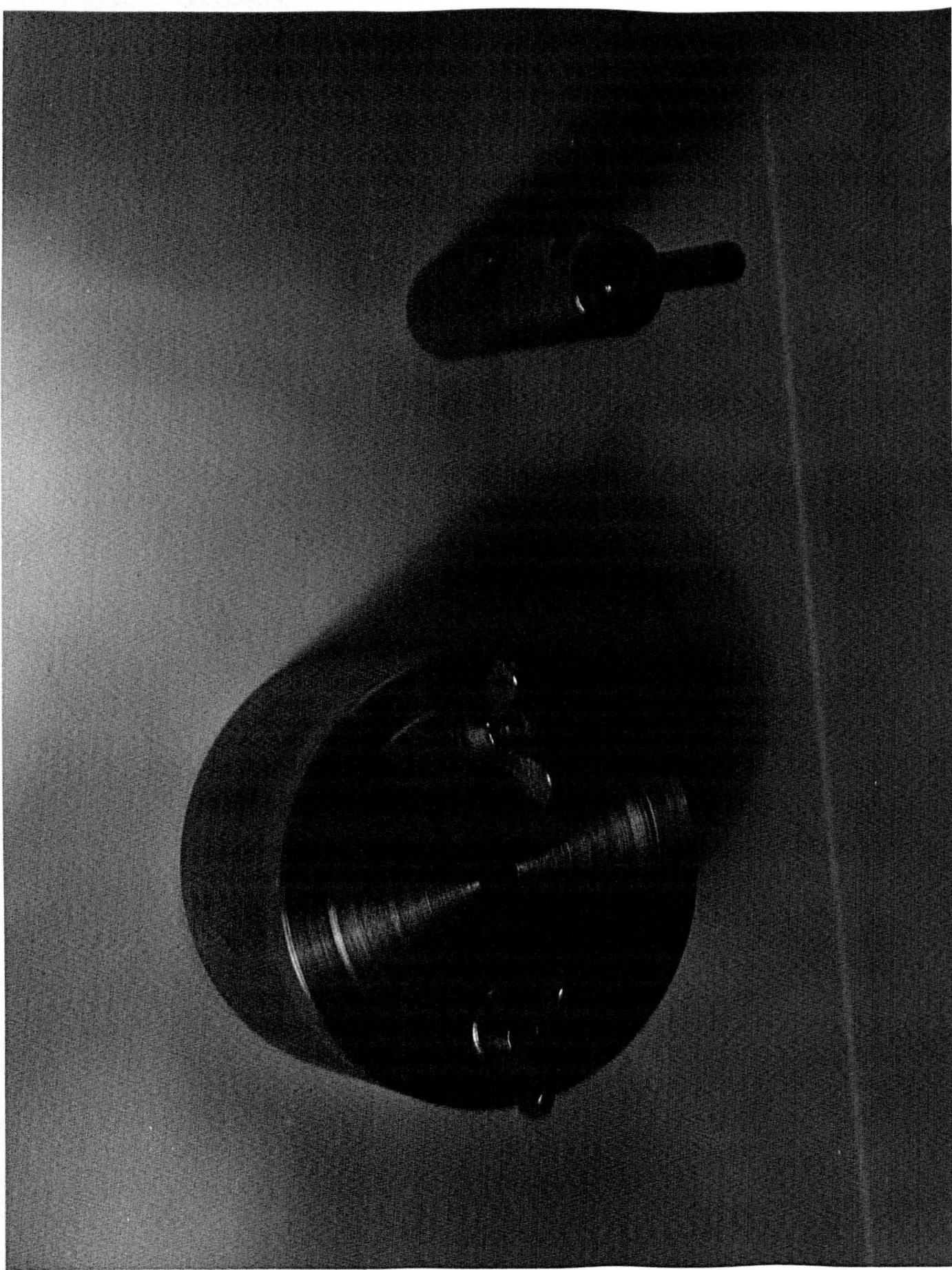


fig. 4. 4. 2.

SCALE 1cm. \pm 0.5cm.

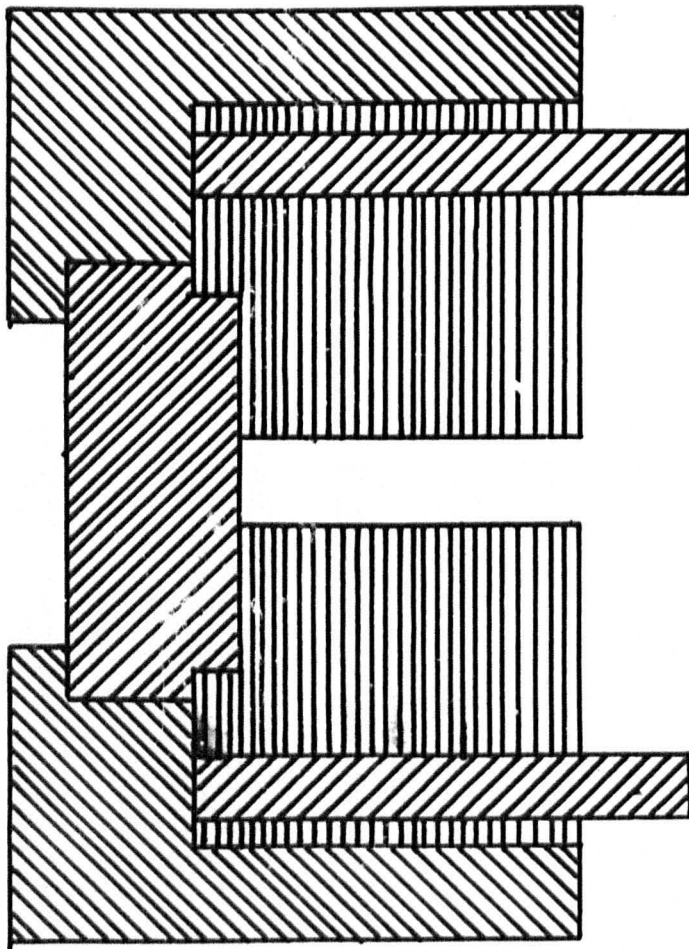


fig. 4. 4. 3.

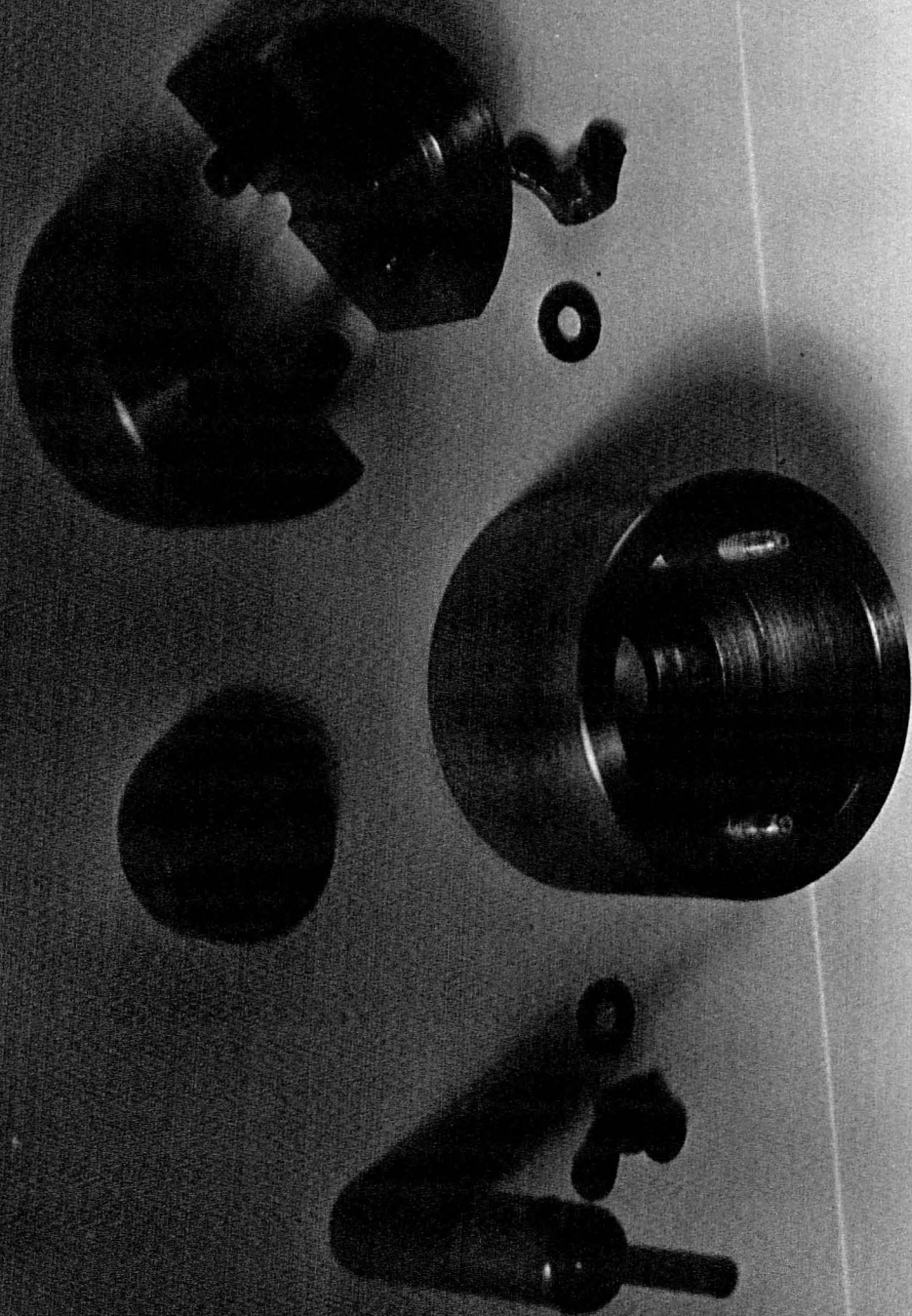


fig. 4. 4. 4.

long and 0.5 cms. internal diameter into one^{end} of which the emissive material is pressed, the remaining cavity housing the cathode heater. The nickel tube is hydrogen furnaceed before use. Then the cathode mixture is pressed into a small disc closing one end of the tube by use of the punch and die shown in fig (4.4.2.) These are constructed of carbon crucible ('silver') steel. The die comprises a cylinder hollowed out from one end, the dimensions of which are height 3.7 cms, diameter 6.1 cms, wall thickness 0.6 cms and hollowed out to a depth of 2.5 cms, as shown in fig (4.4.3). Into a further recess at the bottom is inserted a block of diameter 2.9 cms and depth 0.8 cms on which is a raised platform which protrudes above the bottom of the containing cylinder. The dimensions of this platform are diameter 2.5 cms and depth 0.3 cms. Below this block is an aperture in the containing cylinder of 2.1 cms diameter which enables any force to be applied to the inserted block to remove it.

Into the remaining cavity a cylinder 4.9 cms in diameter is fitted. This cylinder is 2.5 cms high with a recess in its base into which the platform on the block below it fits. The centre of this cylinder is bored out to hold the cathode tube, the lower edge of which then rests upon the platform of the block underneath. In order to press the cathodes a plunger 0.5 cms in diameter and 4 cms long, fitted in the press, passes down the nickel tube and presses the material at the lower end of the tube with the cathode face forming against the face of the lower block. To remove the cathode tube easily after pressing the block containing the tube consists of two symmetrical halves which are held together by two

Allen screws and can be parted by removal of these screws. This block is held in the containing cylinder by two threaded columns, 0.4 cms in diameter, which pass through the block and protrude through the top so that washers and butterfly nuts can be fitted.

The cathode material is varied slightly in composition but essentially it consists of 70-75% by weight of nickel powder, 30-25% of barium carbonate and a very small percentage of reducing agent. Three reducing agents have been used at different times in this work; they are zirconium, zirconium hydride and silicon.

The nickel powder is of grain size 4-5 microns supplied by Johnson, Matthey Ltd. The major impurities it contains are 0.1% carbon, 0.001% sulphur and 0.02% iron. The barium carbonate used is the Analar compound of British Drug Houses Ltd. The powders are weighed out accurately and with the reducing agent added are ball-milled in drylacetate for 48 hours. The mixture is stored in an airtight tube until required for use. When the powder is pressed it is always aimed to produce a cathode of 1 mm. thickness. When the mixture has been pressed a thin layer of nickel powder is pressed onto the back of it. This is done as a preventative measure against a phenomenon which occurred in the first few cathodes made, namely that the heaters burnt out after a few hours operation at the point where the tungsten wire leaves the top of the spiral and passes down the centre of it. It was found that a layer of nickel pressed on to the back of the cathode material prevented this. The effect may have been due to back diffusion of barium on to the heater.

The pressing is done using a fly press. No control is exerted

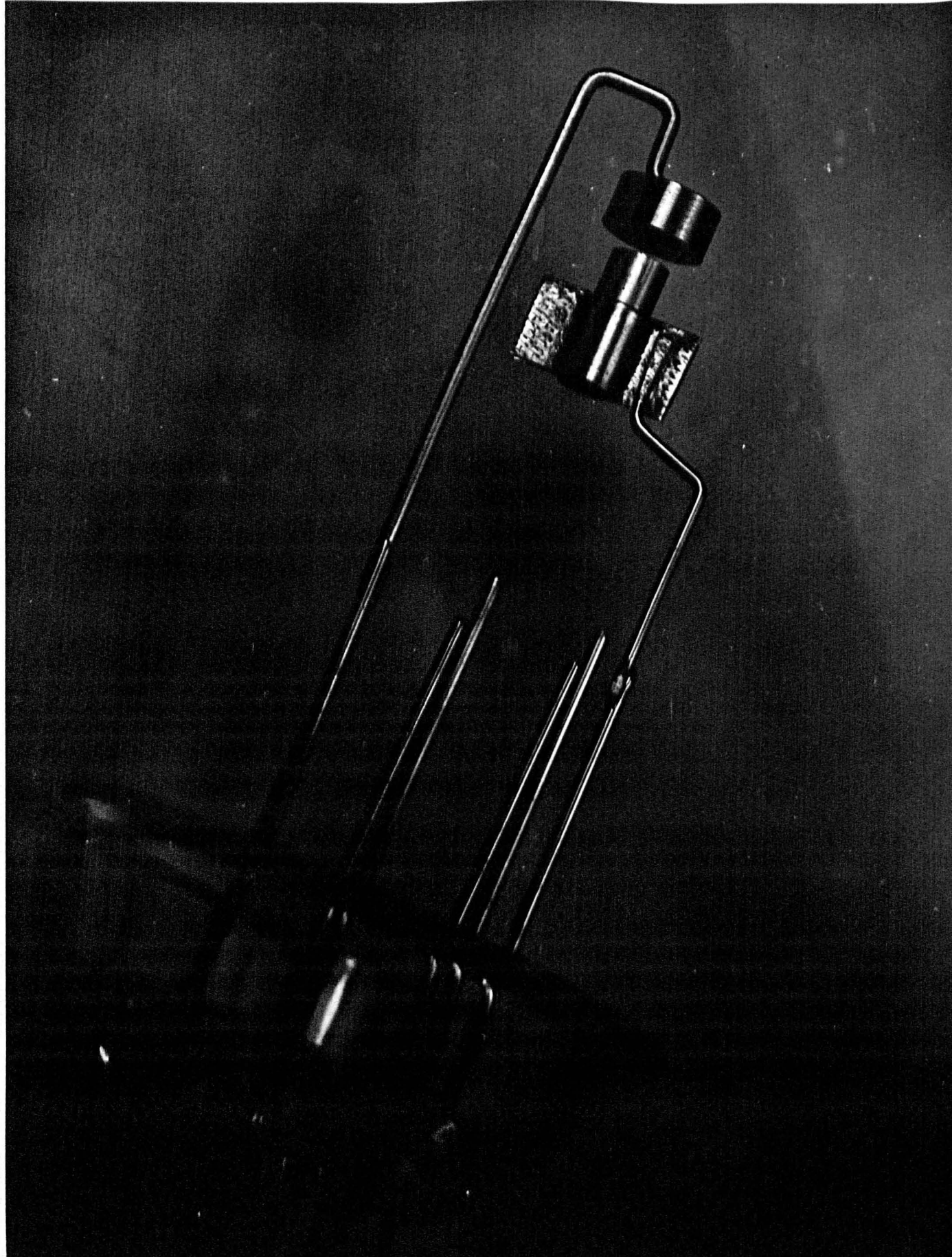


fig. 4. 4. 5.

on the pressure used other than that it is attempted in pressing always to use the same pressure. A calculated estimate of the pressure used is about 50 tons per square inch.

After forming, the cathode is held in two pieces of '0'-nickel sheet which are shaped to fit round the cathode cylinder and are spot welded together on each side of the tube as shown in fig (4.4.5). The cathode is supported on the pinch used by a piece of 18 S.W.G. '0'-nickel wire welded to one of the protruding fins. All the nickel used is hydrogen furnaceed before use.

The cathode temperature is measured by means of a tungsten-nickel thermocouple as described by Fan⁽⁶⁹⁾. A tungsten wire of diameter 0.095 mm. is spot welded onto the upper edge of the cathode cylinder as close to the emitting face as possible. This is taken to one of the tungsten pins in the pinch.

The heaters used in the cathodes are supplied by the General Electric Company Ltd. It consists of an alumina-coated tungsten wire coil with the return lead brought back down the centre of the coil. The heater rating specified by the makers is 2.4 amps at 12 volts and when running at this rating the cathode temperature is about 1,250°C. The diameter of the heater is 4 mm. and its coil length is about 1 cm.

The poisoning filament, i.e. the oxygen or sulphur producing filament, when used is 4 cm. long and consists of an alumina-coated tungsten wire onto which is painted a suspension of barium per oxide for oxygen, or molybdenum disulphide for sulphur, in amylacetate and 5% collodion, the latter acting as a binder. This filament is sup-

ported on two 20 S.W.G. '0'-nickel wires and is horizontally aligned with the electrode gap about 1 cm. away.

4.5. Assembly of valve

When the component parts of the valve have been completed they are mounted on an FK10 Edison Swan 7-pin pinch made of C9 glass with tungsten leads. The cathode is first mounted, with the thermocouple lead attached, centrally on the pinch. The tungsten thermocouple wire is spot welded to one of the tungsten leads through the pinch. The nickel cathode cylinder is used as the nickel section of the hot junction of the thermocouple.

The heater is next inserted in the cathode cylinder and connected to two pins of the pinch by tungsten extensions spot welded onto its ends. 0.5 mm. diameter wire is used for the extensions. The anode is then mounted with its face parallel to the cathode surface and symmetrical with it. The separation of the two electrodes is 1 mm, which is obtained by using a nickel spacer which is afterwards removed. In the valves, on which poisoning experiments are carried out, the 'poison'-producing filament is mounted in alignment with the electrode gap on the two remaining pinch pins. The valve assembly is completed by the inclusion of two barium stirrup getters.

The whole assembly on the pinch is then inserted in a C9 glass envelope, Edison Swan type T64, which has been cleaned thoroughly with nitric acid and distilled water and then oven-dried, after which the envelope is drop-sealed onto the pinch.

4.6. Sintering

The valve, when completed, is mounted on the manifold of the

vacuum system. The pumping procedure employed is as follows. The whole system is backed out and tested for leaks with a Tesvac coil. The main tap in the system is closed and the diffusion pump is switched on and left for 20 minutes. Liquid air is then added to the trap on the pump side of the main tap, time is allowed for cooling whilst adding the coolant. The main tap is opened and the pressure in the valve falls to about 10^{-6} mm.Hg. The oven is lowered over the valve and the latter is baked at 420°C for at least 4 hours after which the oven is switched off and allowed to cool to 100°C before raising. The metal parts of the valve are then eddy current heated in order to thoroughly outgas them.

The breaking down of the carbonates is commenced by gradually raising the temperature of the cathode, ensuring that the pressure in the system never increases beyond 10^{-4} mm.Hg. At about 650°C the breakdown starts and is complete at 950°C . In two cases the carbonate was broken down rapidly in a period of an hour, no heed being given to the pressure produced in the valve. No differences in performance are detectable between these cathodes and those produced by slower breakdown. However, the slower breakdown is employed in the majority of cases as it does give some form of control over the process. If the pressure in the valve is maintained below 10^{-4} mm.Hg, the breakdown takes about 24 hours. This is carried out automatically by supplying the heater current from a transformer in the primary of which is a variac. The variac is driven by an electric motor and high ratio reduction gearing to the optimum speed to raise the cathode temperature to the required value in the de-

sired period of time.

After the completion of the evolution of gas the cathode temperature is increased to $1,050^{\circ}\text{C}$ to sinter the cathode, at which temperature it is held for 20 minutes.

4.7. Activation

A voltage of 250 volts is applied across the valve after the sintering period, at the same cathode temperature. Gradually the temperature is reduced to about 850°C keeping the emission constant at about 5 milliamps i.e. $0.25 \text{ amps.cm}^{-2}$. The valve is then aged under these conditions for 24 hours.

In some cases measurements are made on the valve prior to seal off. The procedure adopted in such a case is to bake the valve at 420°C for 4 hours and eddy-current heat the metal components. The required measurements are made and the usual procedure for sealing off a valve is then followed. This consists of rebaking the valve for 4 hours and eddy-current heating the metal parts. Both getters are carefully outgassed and then fired and the valve is sealed off. The main tap on the vacuum system is closed, the diffusion pump is switched off and the trap is allowed to warm up to room temperature. When the diffusion pump is cold the backing tap is closed, the backing pump switched off and air is admitted into it.

4.8. Measurements

The emission measurements are made with reversible D.C. voltage supplies, upto 100 volts being obtained from the standard laboratory supply and from 100-250 volts obtained from an Edison Swan stabilised power unit (Type R1095). Anode currents are measured by means of a

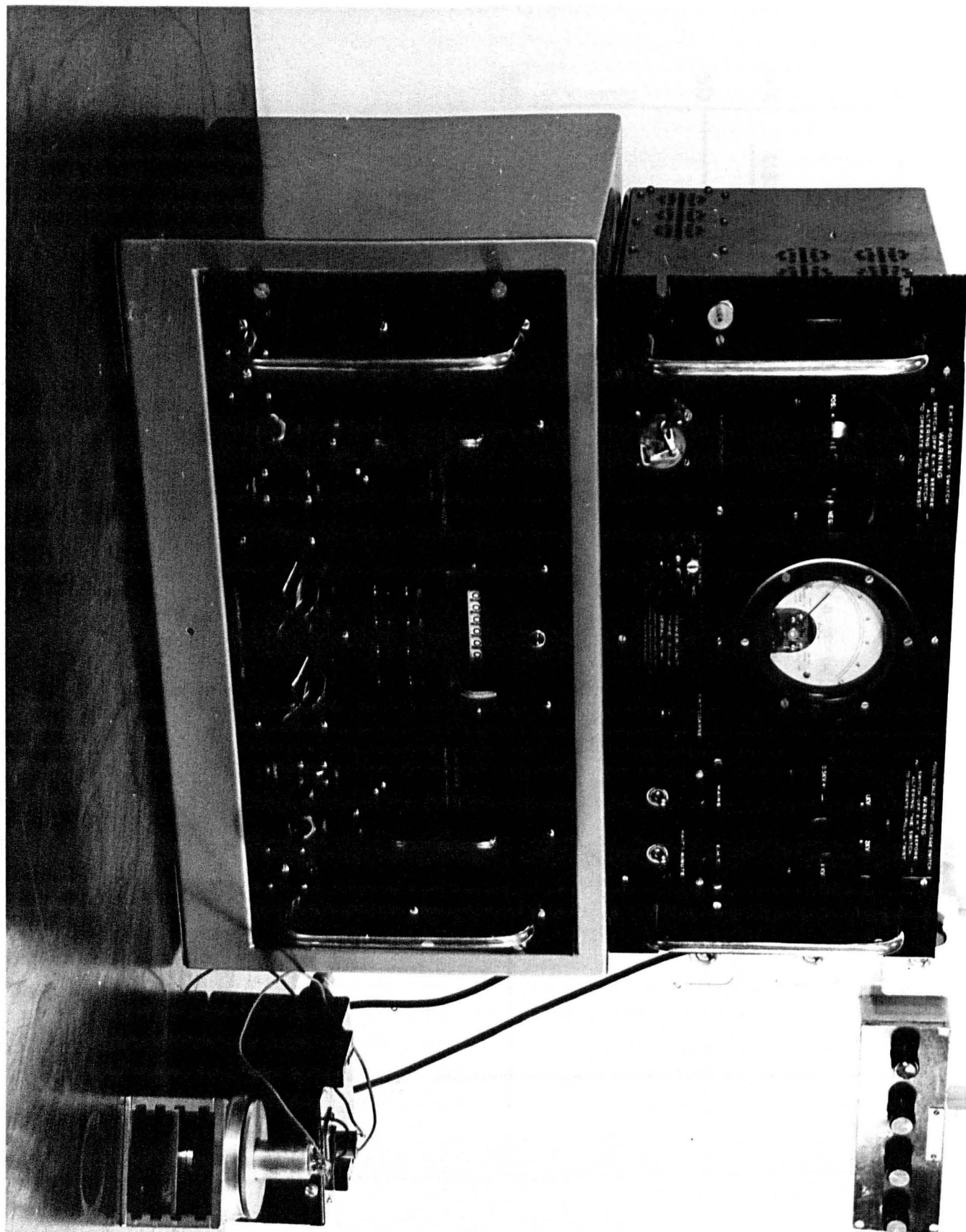


fig. 4. 8. 2.

Cambridge galvanometer of sensitivity 5.6×10^{-8} amps. cm^{-1} deflection at one metre, provided with a Universal shunt.

The cathode temperature is estimated by measuring the e.m.f. developed in the thermocouple by means of a thermocouple potentiometer (Croydon Precision Instrument Co., Type P4). This instrument will measure voltages from 0-105mV in two ranges. The first range is from 0-21mV with a limit of error of 0.01mV and the second range is from 0-105mV with a limit of error of 0.05mV. A calibration curve for the nickel-tungsten thermocouple is given in fig (4.8.1). Fan claims that with a particular junction the temperature of a cathode may be measured to within 0.2°C . Experiments in this laboratory, however, indicate that an accuracy of better than $\pm 2^{\circ}\text{C}$ is not possible with such an arrangement, for the measured e.m.f. is found to depend not only on the junction temperature, but also, though to a lesser degree, on the tension in the wire, the size of the wire used and the degree of hydrogen furnacing to which the junction has been subjected. This type of thermocouple should only be used above 400°C since nickel undergoes a molecular transformation between 250° and 390°C (70).

For the work described in Part III in which radioactive material is used, the cathodes were sectioned on a lathe. The counting is done by means of a G.E.C. Geiger-Müller counter, type GM4, used with a probe unit, type 1044A, a Dynatron power unit, type P200A, and an Ekco scaler unit, type N526. This apparatus is shown in fig (4.8.2). The Geiger-Müller tube is fixed in a holder which also carries the sample of material at a variable fixed distance from the counter face.

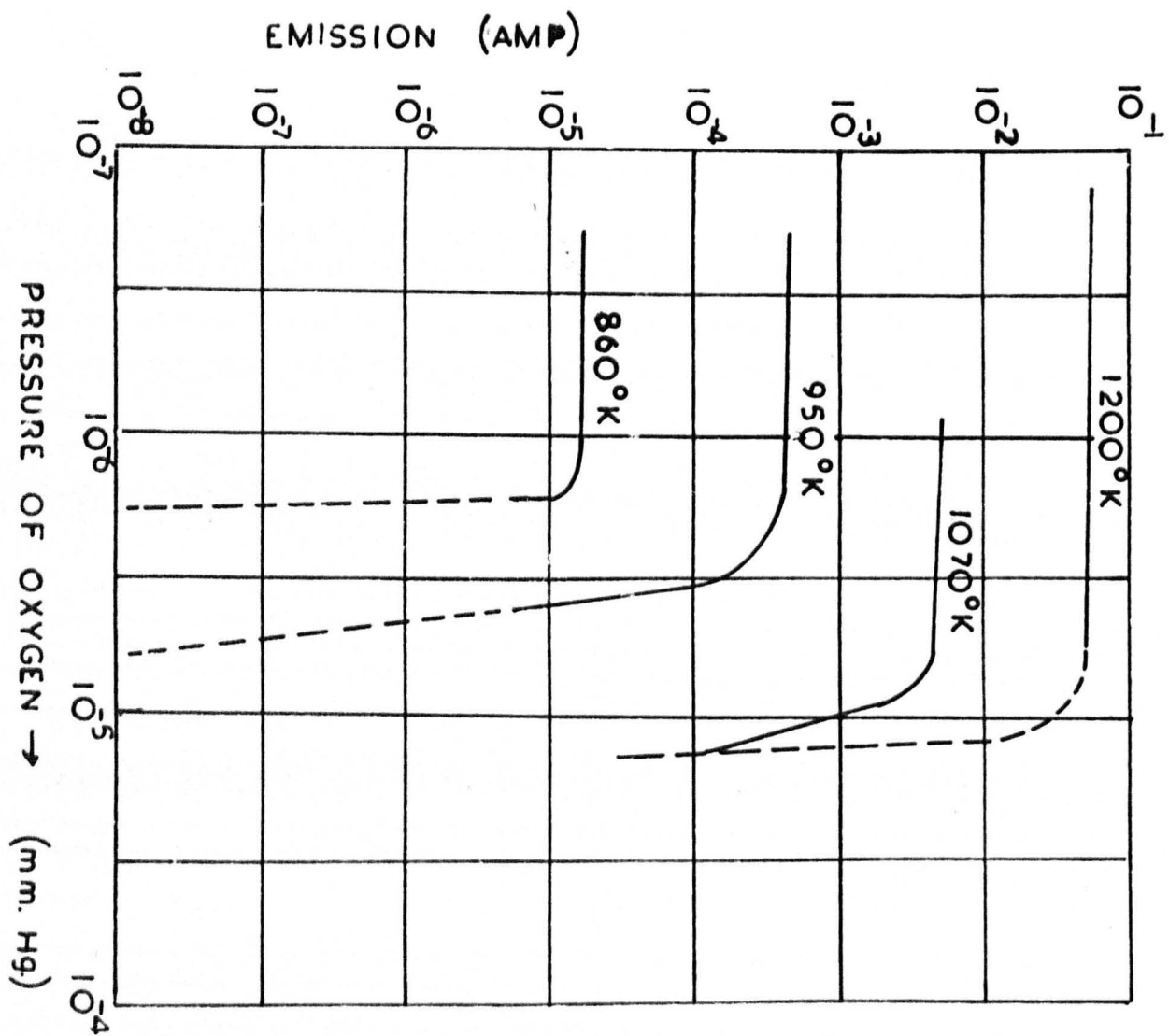


fig. 5. 1. 1.

PART II

Thermionic Emission from the 'M'-cathode and its Poisoning
by Oxygen and Sulphur

Chapter V

The Effect of Oxygen and Sulphur on the 'M'-cathode

One of the advantages of the 'M'-cathode is its resistance to contamination by the majority of common gases. It is possible to expose such a cathode to the atmosphere for several days, replace it in a valve and the cathode will reactivate. This ability has frequently been remarked upon, but no systematic work has been carried out upon the effect of individual gases upon the cathode. The effect of oxygen and sulphur upon the emission from the 'M'-cathode has been studied by the author⁽⁷¹⁾ and this brief chapter will include an account of allied work that has been done previously, to link up with the discussion of results in Chapter VII.

5.1. The effect of oxygen on electron emission

The deleterious effect of oxygen on the emission from a fully activated 'M'-cathode has been studied only by MacNair and co-workers⁽¹⁾ who admitted oxygen to a cathode for up to 30 minutes at a pressure of oxygen of 4×10^{-5} mm.Hg. and found that the emission fell to 10% of its original value. No work on the study of recovery from poisoning by oxygen, other than that reported herein, has been published. The emission decay of the 'L'-cathode when contaminated with oxygen at known pressures has been studied by Fugawa and Adachi⁽¹⁹⁾ who show their results as the curves in fig (5.1.1). These indicate that the oxygen contaminated emission remains fairly constant until a certain pressure of oxygen is present, when the emission falls

rapidly. The critical pressure at which the fall in emission commences is dependent upon the temperature of the cathode. The authors suggest that the steady emission ends due to an equilibrium state being set up between the absorption of oxygen atoms on barium atoms and the supply of barium atoms from the reservoir.

Much work has been carried out on the effect of oxygen on the oxide-coated cathode and it seems relevant to consider the main points arising from this work. Fig (5.1.2) shows the change in Richardson line obtained by Koller⁽⁷²⁾ for an oxide-coated cathode after admitting oxygen at 10^{-3} mm.Hg. If the cathode was operated at usual temperatures (about 750°C) it could be reactivated by pumping away the gas evolved.

From the results of oxygen poisoning Kawamura⁽⁷³⁾ deduced the following empirical relationship between the partial pressure of oxygen, p , and the saturation current, i ,

$$i = Kp^{-\frac{1}{n}}$$

where both K and n are constants.

This was verified by Arizumi and Harita⁽⁷⁴⁾ who also studied recovery of emission from oxygen poisoning. The conclusion was reached that only the surface of the coating was poisoned and that during the recovery excess barium diffused from the body of the coating to the surface layers.

An extensive study of the reversibility of oxygen poisoning was made by Metson⁽⁷⁵⁾. A tungsten heater wire coated with barium peroxide was used as an oxygen source placed close to the cathode

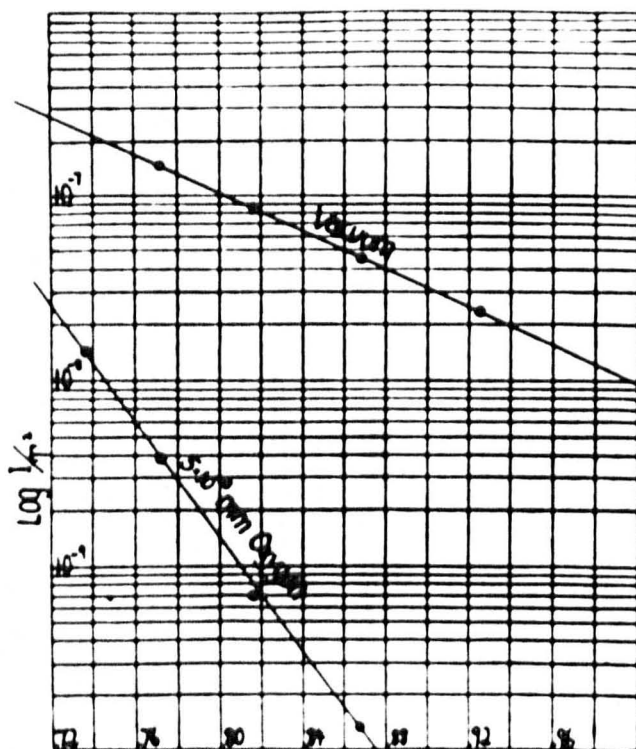


fig. 5. 1. 2.

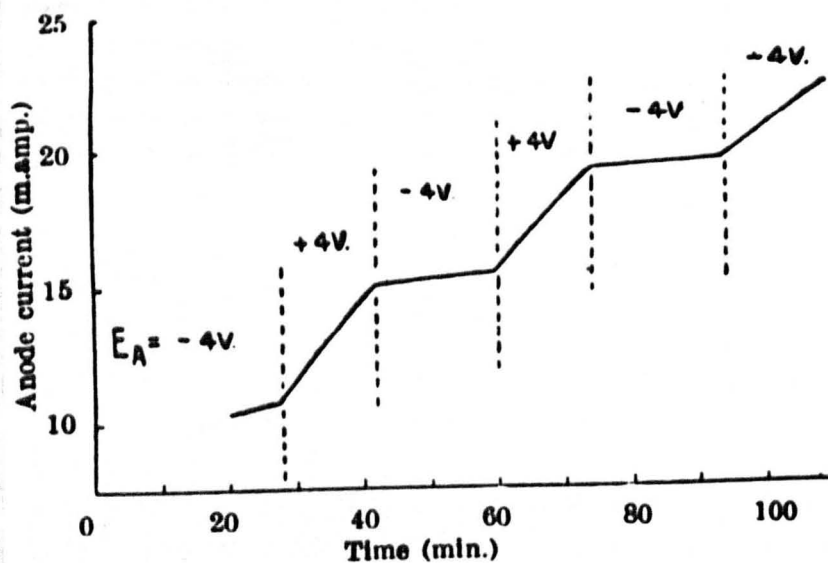


fig. 5. 1. 3.

in an experimental tube. The procedure was to poison a cathode to 10% of its initial emission with oxygen and then record continuously the recovery of the cathode. Complete recovery of the cathode was obtained even after several repetitions. Another experiment performed by Metson was to reverse the anode voltage during the recovery period. Fig. (5.1.3) shows the observed recovery characteristic. Recovery was rapid while a current was drawn, but became much slower during the period when negative anode voltage was applied. The explanation of this assumed that after the oxygen atoms or molecules have entered the coating they become negatively ionised and thus the presence of an emission current leads to a potential gradient across the cathode which tends to assist the ejection of these ions. Metson pointed out that such assistance is not essential, for a cathode will recover by heat treatment alone.

The complete reversibility of oxygen poisoning of oxide cathodes as observed by previous authors was confirmed in this laboratory by Shepherd⁽⁷⁶⁾ who showed that oxygen ions, O_{16}^{-} , are evolved during recovery, which was suggested by Metson's results. The energy distribution of the emitted ions was measured by use of a mass spectrometer. This showed that oxygen poisoning was not only a surface phenomenon since some of the ions possessed energies which indicated that they were evolved from the interior of the coating.

5.2. The effect of sulphur on electron emission

The only previous studies of the effect of sulphur on thermionic emission have been concerned with the oxide-coated cathode. Stahl⁽¹⁰⁹⁾

reported that cathodes subjected to atmospheric pollution by sulphur before insertion in a vacuum tube give reduced emission after breakdown of the carbonate and activation. Work⁽⁷⁷⁾ has been carried out in these laboratories of the 'poisoning' of oxide-cathodes by sulphur. A tungsten filament coated with molybdenum disulphide was found to be a suitable source of sulphur. The oxide-cathode recovers from sulphur poisoning but more slowly than from a similar poisoning by oxygen. Recovery was assisted by raising the cathode temperature to 1200°K and applying 50V to the anode. Twenty or more poisoning-recovery cycles could be performed on each cathode without any permanent effect. From the observation that applying a positive potential to the anode increased the recovery rate, it was concluded that the sulphur emitted during recovery is negatively charged.

In the next chapter similar experiments are described using 'H'-cathodes poisoned by oxygen and by sulphur. This was done so that a knowledge of the recovery process could be gained, which, in turn, may help to determine the mechanism of the emission process.

Chapter VI

Preliminary Results.

The experimental work in Part II is divided into two sections. The preliminary work included the development of techniques, measurement of the work function of the 'M'-cathode by the Richardson plot method, a study of the effect of varying the composition and of using different reducing agents. The second section is devoted to a study of the effect of oxygen and of sulphur upon the emission from the 'M'-cathode. This work is described in Chapter VII. In all, 22 cathodes have been made and studied in various ways in this first part of the work. Results typifying each type of cathode have been selected.

The ultimate aim of the project was to determine the mechanism of operation of the matrix cathode. The first goal was the production of cathodes which compared favourably with previously reported cathodes of this type, upon which measurements could then be made.

6.1 Cathode composition.

Cathodes were made up of three different compositions and two cathodes were machined from a larger cathode kindly provided by Metropolitan Vickers Ltd. The first two mixtures from which the cathodes were made contained zirconium as the reducing agent, the third contained zirconium hydride and the M-V cathodes contained silicon. In the work on emission poisoning cathodes were made up containing silicon. The compositions of the four mixtures used are shown below and in the following pages the cathode composition is referred to by its mixture number.

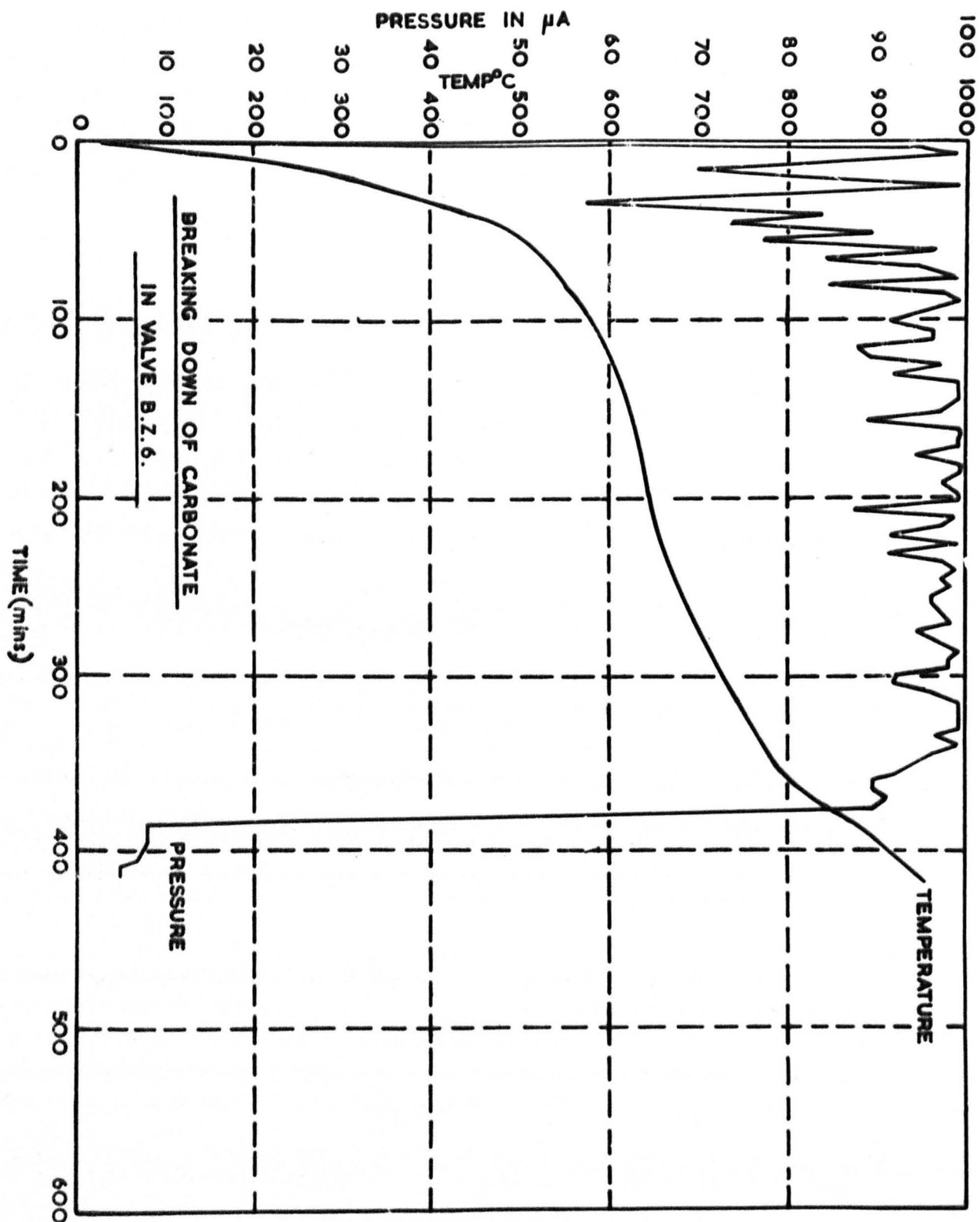


fig. 6. 1.

Table I

Mixture No	Reducing Agent	% Nickel	% Barium Carbonate	% Reducing Agent
I	Zr	70	25	5
II	Zr	70	28	2
III	ZrH ₂	74	25	1
IV	Si	69.9	30	0.1

The results are presented in subsections, the divisions being based on the cathode composition. All currents on the graphs are shown in units of centimetres. With the galvanometer used $1\text{cm} = 3.7 \times 10^{-8}$ amperes.

1. Measurements on cathodes containing 5% Zr.

Four cathodes were made from mixture I and cathode BE3 is described as typical of this group.

The cathode was prepared from 0.1 gas of mixture I which gave a cathode thickness of about 1 mm and so a porosity of 45%. It was heated by two helical 6.3V., 0.5 amp G.E.C. heaters in parallel. The carbonate was broken down slowly; similar pressure and temperature against time curves were obtained to that shown in fig (6.1). After breakdown the heater burnt out. Before the new heater was inserted an 'O'-nickel disc was placed between the heater and the cathode and subsequent operation showed that this prevented the heater from burning out.

The cathode was again assembled in a diode, mounted on the vacuum system and baked out at 420°C for five hours. The metal parts of the valve were eddy-current heated and then the temperature of the

VALVE BZ.3.

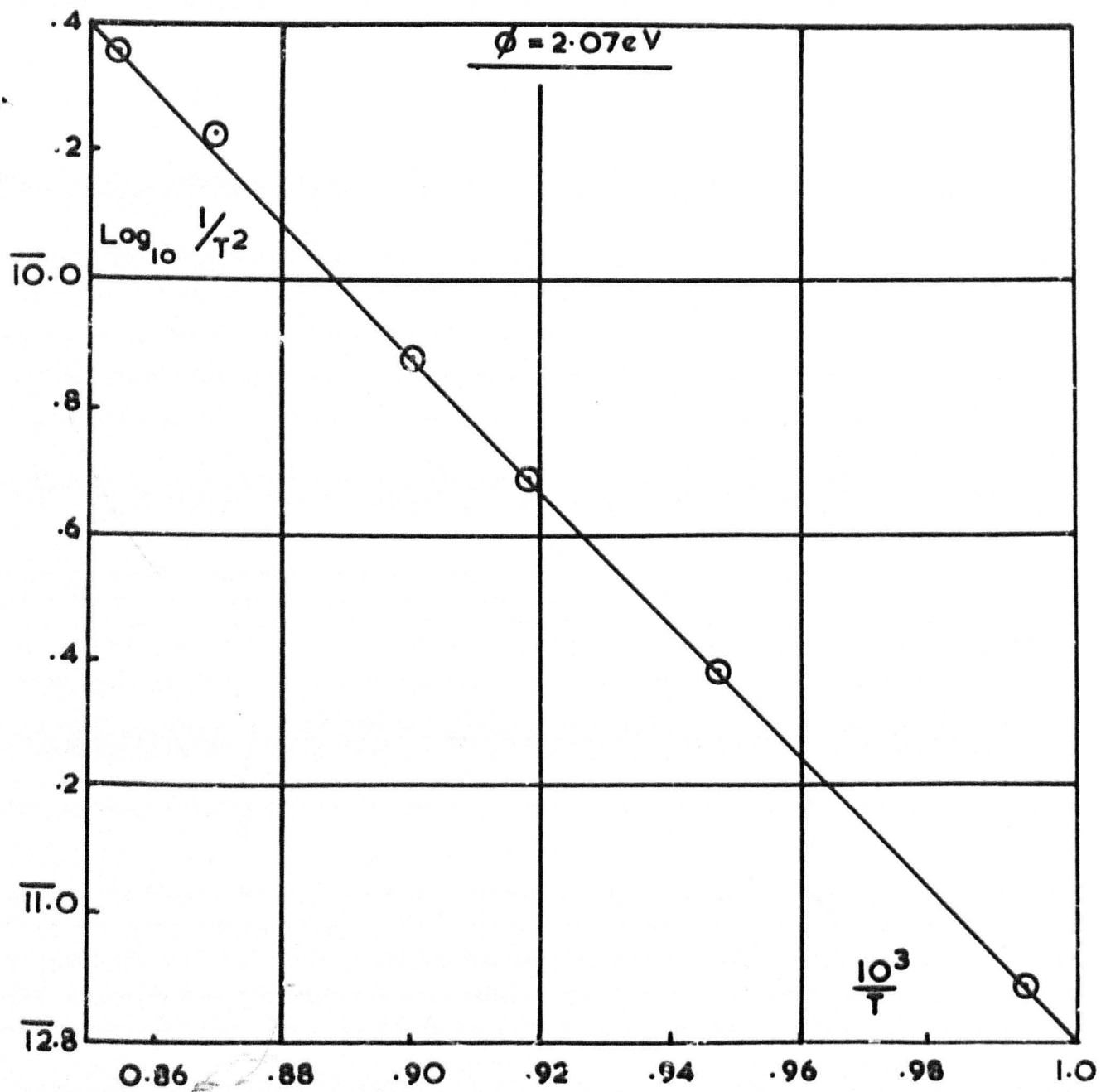


fig. 6. 2.

cathode was increased gradually to 950°C , keeping the pressure in the valve below 10^{-4} mm.Hg. The cathode temperature was increased to 1050°C for 20 mins. to sinter the cathode. A potential of 100V was then applied to the anode and the emission increased rapidly to about 1mA. The cathode temperature was decreased gradually over the next two hours to about 850°C , the emission remaining approximately constant. The valve was left in this condition to age for the next 40 hours, after which the supplies were disconnected and the valve was baked for 4 hours at 420°C . The metal parts of the valve were eddy-current heated with the cathode at about 600°C to prevent any released gas from being adsorbed by the cathode. The valve was allowed to cool, the getters were fired and the valve was sealed off from the system.

After seal off the cathode was run at 850°C with $V_a = 100\text{V}$ for 7 hours in which time the emission increased slightly. At this stage an indication of the work function of the cathode was obtained by means of a Richardson plot (fig (6.2)). The method employed was to measure the emission from the cathode for various anode voltages (0 to 15 V) at certain temperatures. After plotting the I_a - V_a characteristics, the point of intersection of the two linear portions of the graph was taken as giving the value of the saturated current for zero field, the voltage reading of this intersection giving the contact potential difference between the electrodes. Using this value of the saturated current I_s , a Richardson plot was made of $\log_{10} \frac{I_s}{T^2}$ against $10^3/T$, the slope of which was given by -5.040ϕ , where ϕ is the work function of the cathode existing at $T = 0$, i.e.

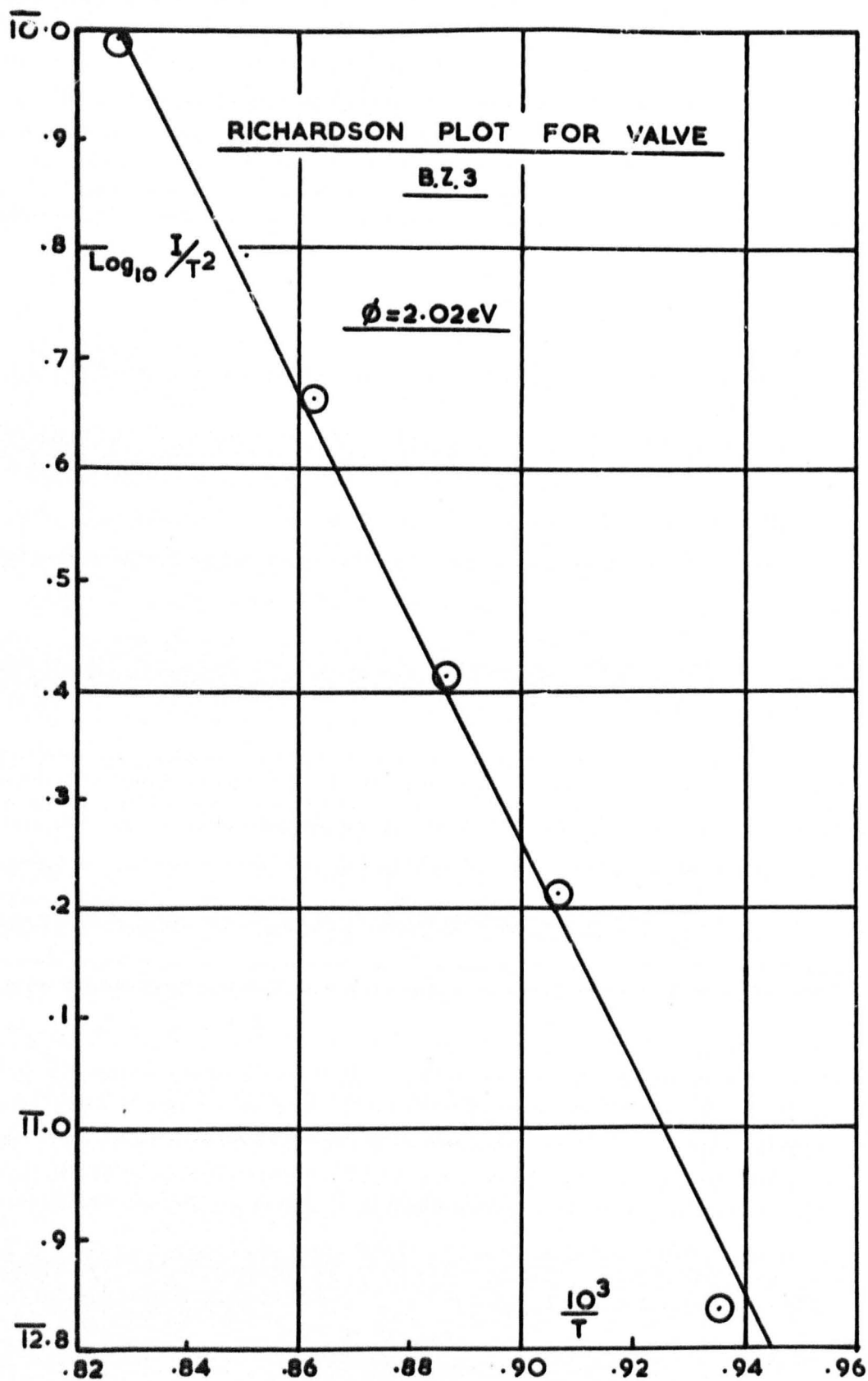


fig. 6. 3.

it is the emissive mean work function of the patchy surface at zero temperature. The intersection on the ordinate gave $\log_{10} AS$, where A is the emissive constant and S is the surface area of the cathode.

The value of ϕ obtained for BE3 at this stage was 2.07eV with $A = 1 \text{ amp.cm}^{-2} \cdot \text{K}^{-2}$. After a further 10 hours with the cathode at 850°C and $V_a = 100\text{V}$ a second Richardson plot gave $\phi = 2.02\text{eV}$ (fig (6.3)) and $A = 2 \text{ amp.cm}^{-2} \cdot \text{K}^{-2}$. The two values of ϕ were in good agreement. The value of A , in practice, very rarely approached the theoretical value of $120 \text{ amps.cm}^{-2} \cdot \text{K}^{-2}$, due to it being subject to so many experimental errors and is difficult to interpret. If the cathode temperature was 1000°K, say, and the temperature can be measured to the nearest 5°, then if a work function of 2eV is assumed, from

$$\frac{\partial A}{A} = \frac{e\phi}{kT} \frac{\partial T}{T}$$

in this case
$$\frac{\partial A}{A} = \pm 12\%$$

For A to be found, S must be known, and since the surface area is considerably larger than the geometric surface, due to roughness, A cannot be found accurately. The temperature dependence of the work function also enters into the value of A , and since the theoretical value is obtained from simplifying assumptions, it is obvious that the value of A obtained from a Richardson line has little significance in this work, although, as will be seen in later results, the change in A does follow a regular pattern.

Two of the most important points arising from the work on BE3

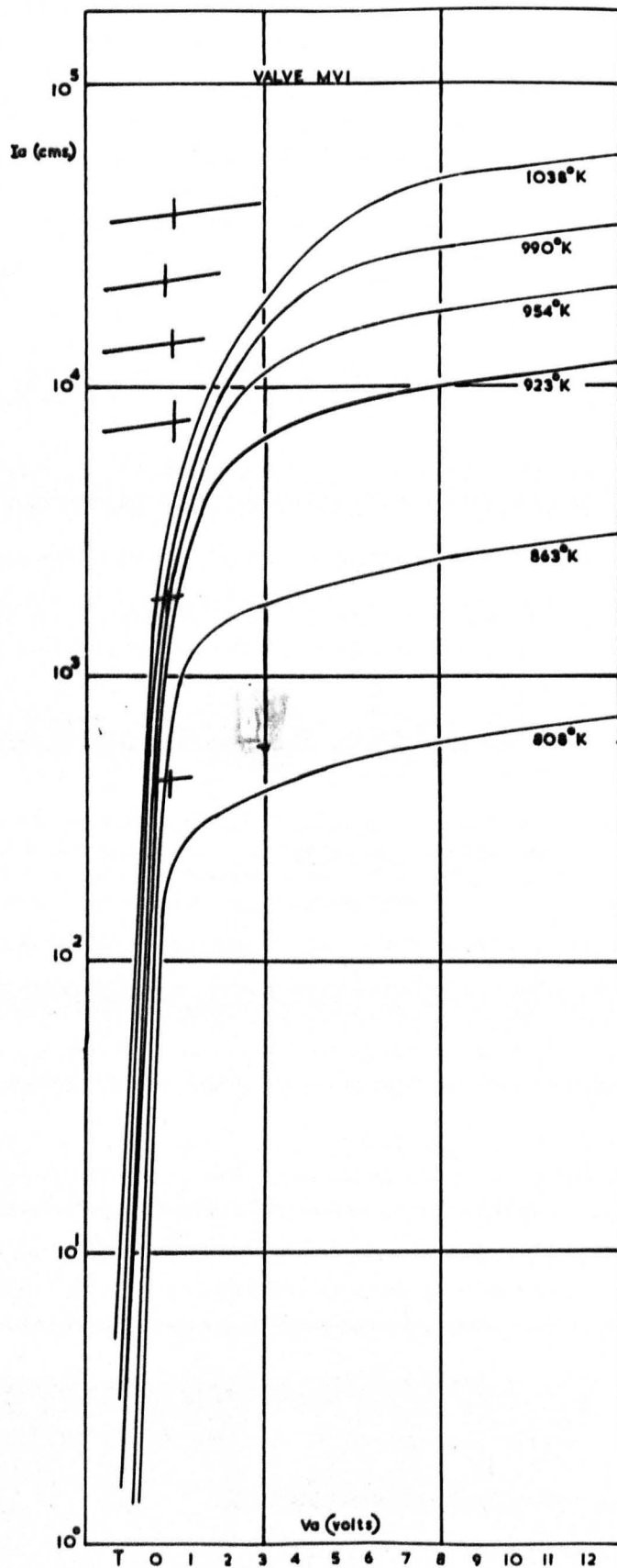


fig. 6. 4.

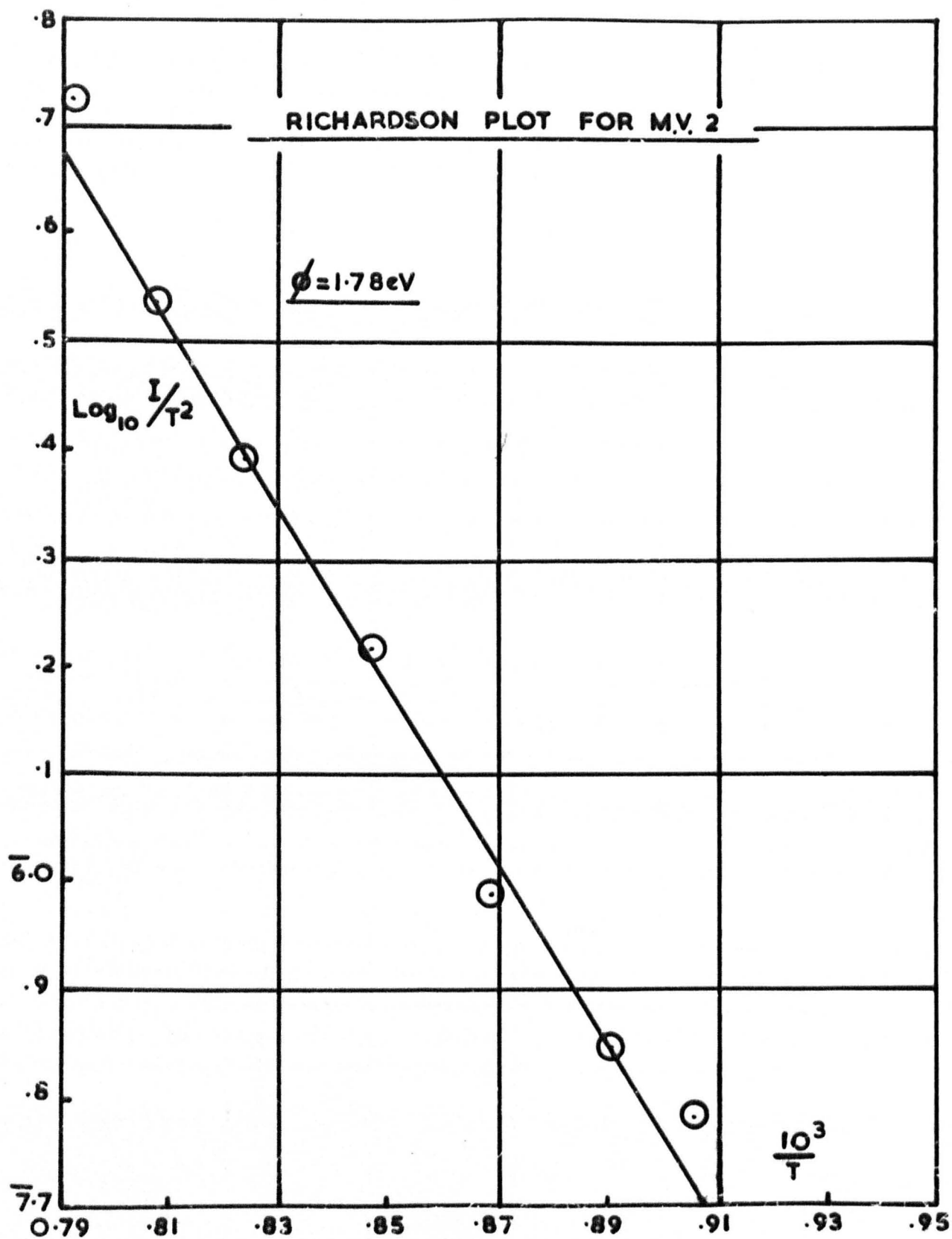


fig. 6. 5.

were the necessity for a nickel backing on the cathode and that the cathode could be exposed to the atmosphere after breakdown and still be activated. The maximum emission drawn from this cathode was 50 mA. cm^{-2} at 787°C and $V_a = 100\text{V}$. The emission from BEL, a similar cathode was $0.7 \text{ amps. cm}^{-2}$ at 1230°C and $V_a = 100\text{V}$.

2. Measurements on cathodes containing Si

Two cathodes were machined out of a larger cathode made by Metropolitan-Vickers, Ltd. The cathodes were designated MVI and MV2 and since the behaviour of both was very similar, the former only will be described in detail. Before cutting up the original large cathode the conductivity of it at room temperature was measured, the $\log I$ against $\log V$ plot yielding a slope of 1.1, indicating that the material was a normal ohmic conductor.

Cathode MVI was machined from the large cathode, having a coating 1 mm thick with 0.5 mm of nickel backing. This was placed in one end of a 5 mm diameter 'O'-nickel tube, as employed to hold the other cathodes, and spot welded in position. The cathode was built into a diode assembly as described in section 4.5., mounted on the vacuum system and processed as previous valves had been. After activation the emission at 850°C and $V_a = 100\text{V}$ was about 6mA.

After ageing for 24 hours at 850°C a series of characteristics were taken, a typical example of which is shown in fig (6.4), and the corresponding Richardson plots were made. The value of the work function from these Richardson lines was consistent at 1.4 eV. With cathode MV2 the work function obtained was 1.7 to 1.8 eV (see fig (6.5)). No reason was apparent why MVI gave such a value and,

as will become obvious later, it seems that it was MVI which was behaving uncharacteristically.

The results from this cathode clearly indicated that the initial cathodes prepared could be improved upon in performance since their work functions were high and hence the emission correspondingly less.

3. Measurements on cathodes containing 2% Zr.

Four cathodes were prepared from mixture II. Two of these were sintered in hydrogen at 1000°C for 1 hour and the other two were sintered in vacuum as previously. One cathode of each pair had its carbonate broken down rapidly and the other two were broken down as usual, the pressure remaining below 10^{-4} mm.Hg. No difference was detectable in the performance of the resultant cathodes and from this it appears that fairly identical cathodes result from sintering in hydrogen and vacuum. The rate of breakdown of the carbonate, too, appears to have no pronounced effect upon the cathode's properties. One of the cathodes of this group, B28, will be taken as a typical example.

Cathode B28 was formed from 0.1 gms of mixture II with a 0.5 mm layer of nickel pressed onto it as a backing. The cathode was sintered in hydrogen before mounting in a valve. A tubular furnace was used and the cathode was sintered at 1000°C for 1 hr. The cathode was mounted in a valve, sealed on the vacuum system, pumped out and baked for 4 hours at 450°C . Breakdown of the carbonate was carried out by raising the cathode temperature to 950°C in 2 mins. Very little gas was evolved, confirming that the carbonate had been broken down during sintering in hydrogen. The valve was then baked

VALVE B.Z.6

RE-ACTIVATION AFTER EXPOSURE TO AIR

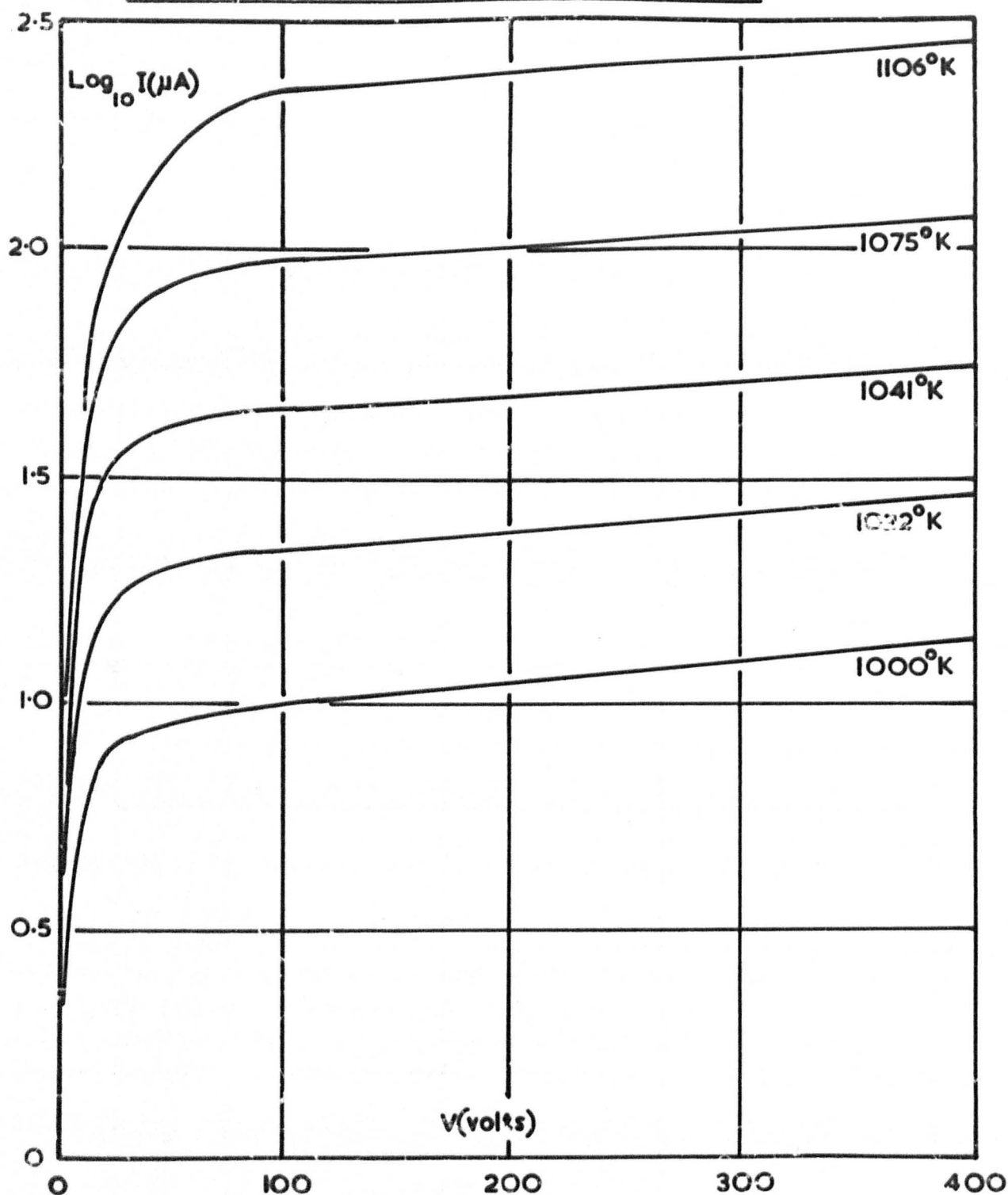


fig. 6. 7.

for $3\frac{1}{2}$ hours at 450°C and the metal parts were eddy-current heated. The cathode was heated to 1050°C and 250V were applied to the anode. The emission drawn was 10mA. During the subsequent two hours the temperature was gradually reduced to 850°C and the cathode was aged at this temperature for 24 hours.

After ageing a set of characteristics were taken. These showed poor saturation (see fig (6.6)) and the corresponding Richardson plot gave $\phi = 2.16\text{eV}$. The valve was again baked and eddy-current heated, the getters were fired and the valve was sealed off from the vacuum system. The cathode was left at 600°C for 2 hours with emission being drawn. Another set of characteristics were taken. The work function from the Richardson plot was 1.70eV . The valve was then operated at 800°C for 6 hours, the work function being determined every 2 hours. The results all lay between 1.65 and 1.75 eV.

The work functions of the other three cathodes in this group came out between 1.7 and 1.8 eV. R26 was exposed to the atmosphere twice after activation and each time was reactivated to its original condition (fig (6.7)). It appeared from the results obtained that if the processing of the cathode, i.e. the breakdown of the carbonate, the sintering and the activation, was repeated for each cathode of similar composition, then reproducible results could be obtained. This meant that cathodes were reproducible. As a final confirmation two more cathodes were prepared from a different mixture and measurements were made on these.

4. Measurements on cathodes containing 1% Zirconium hydride

Two cathodes were prepared originally from mixture III, R211

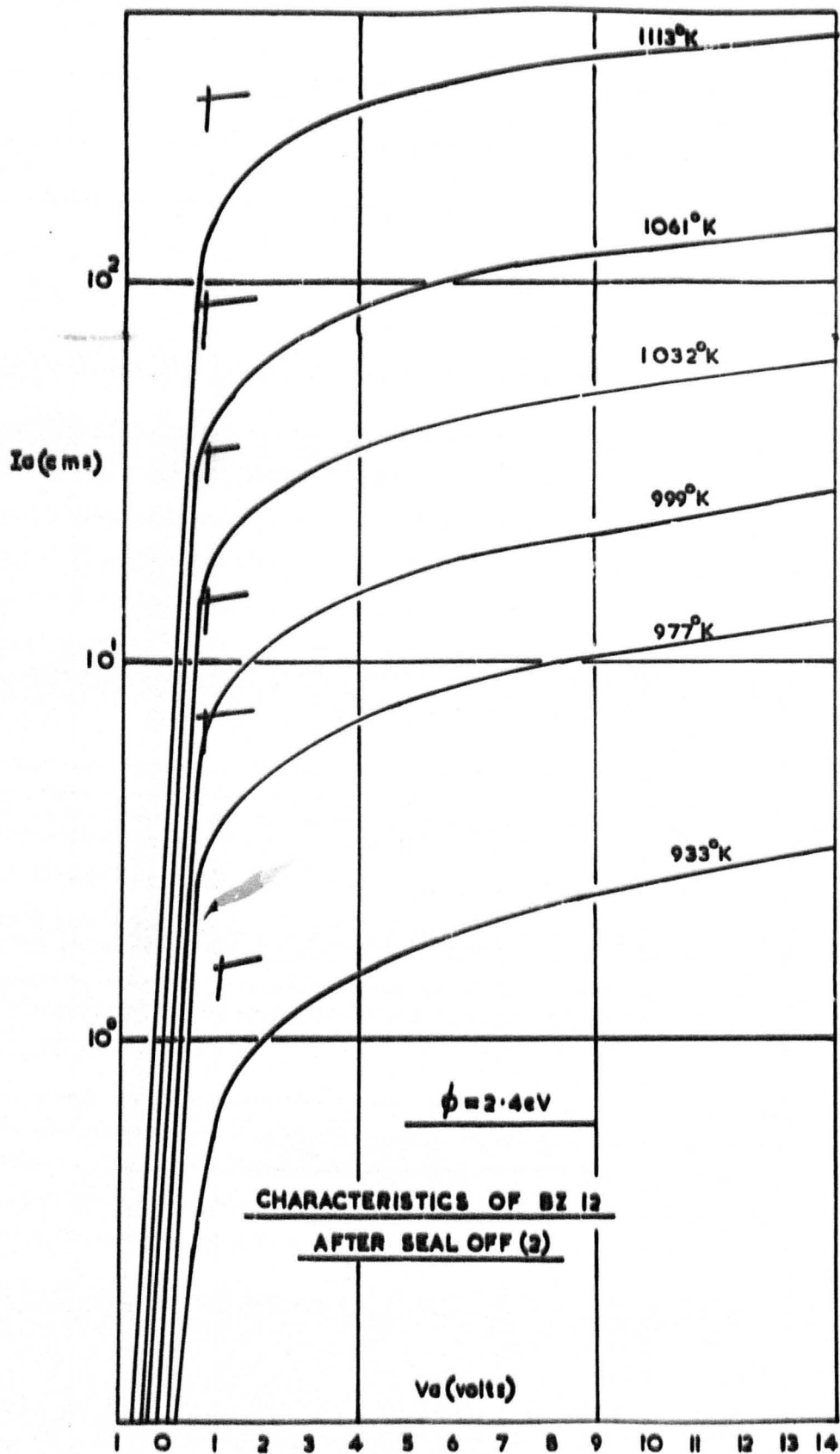


fig. 6. 9.

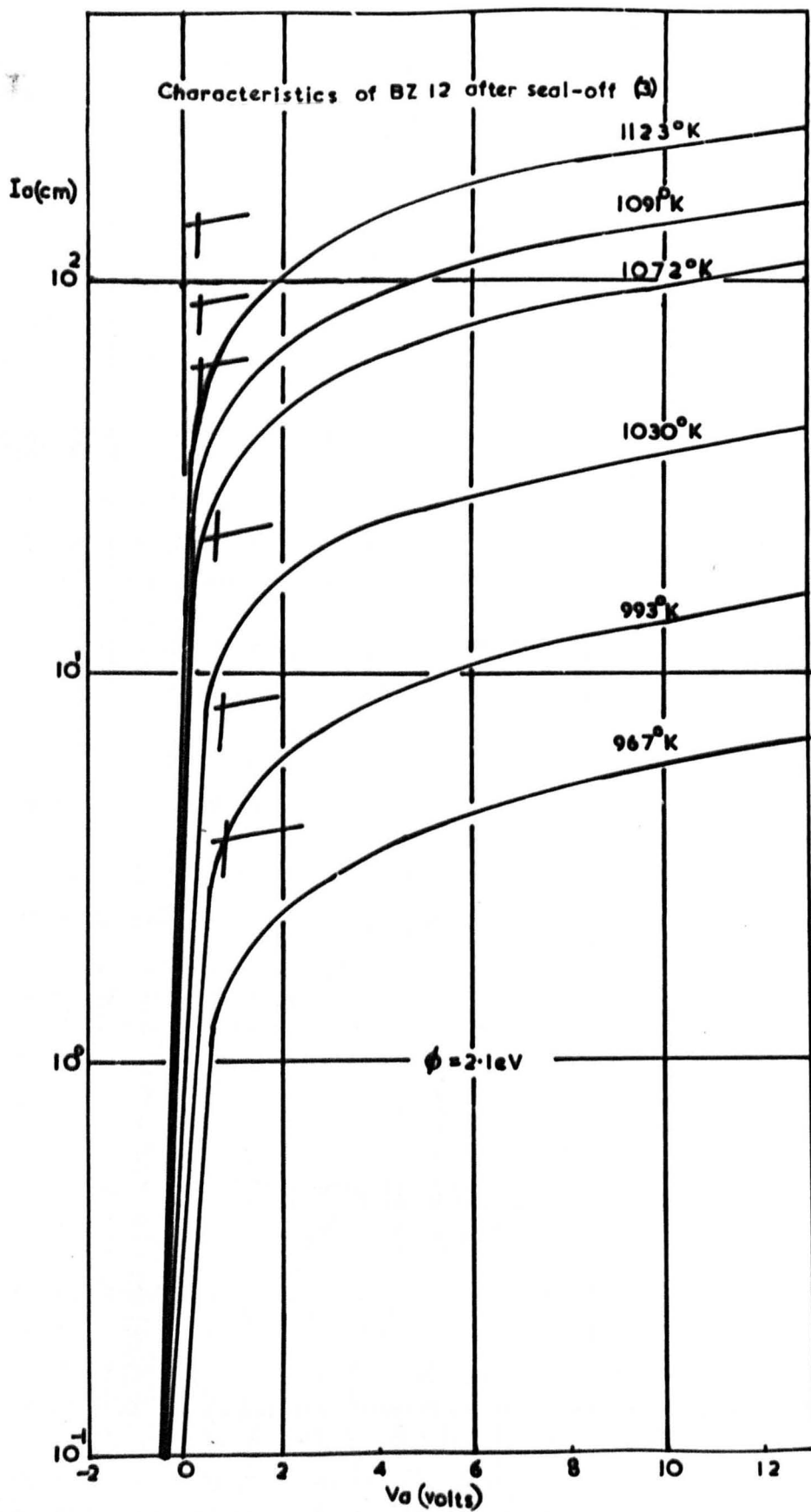


fig. 6. 10.

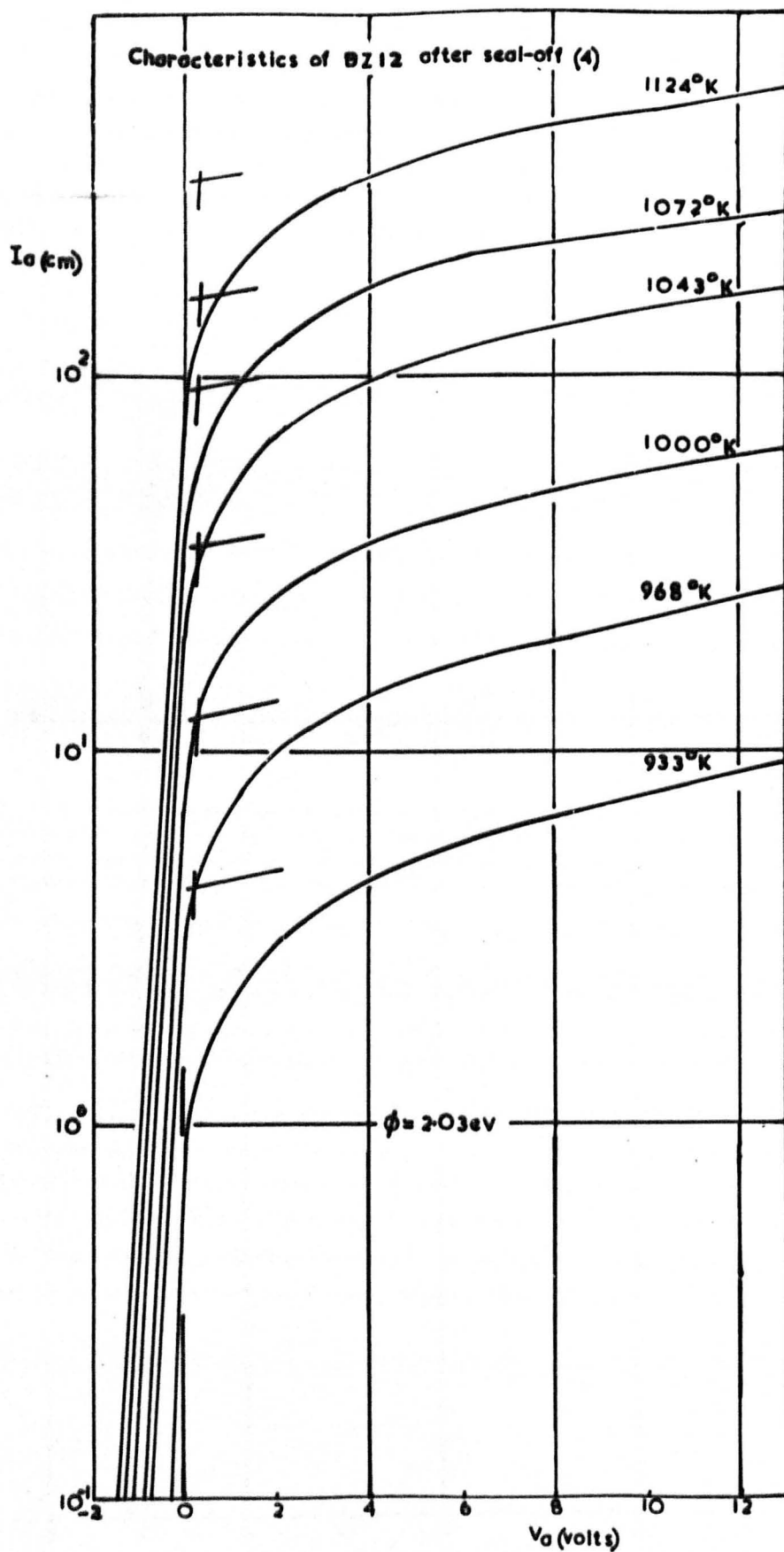


fig. 6. 11.

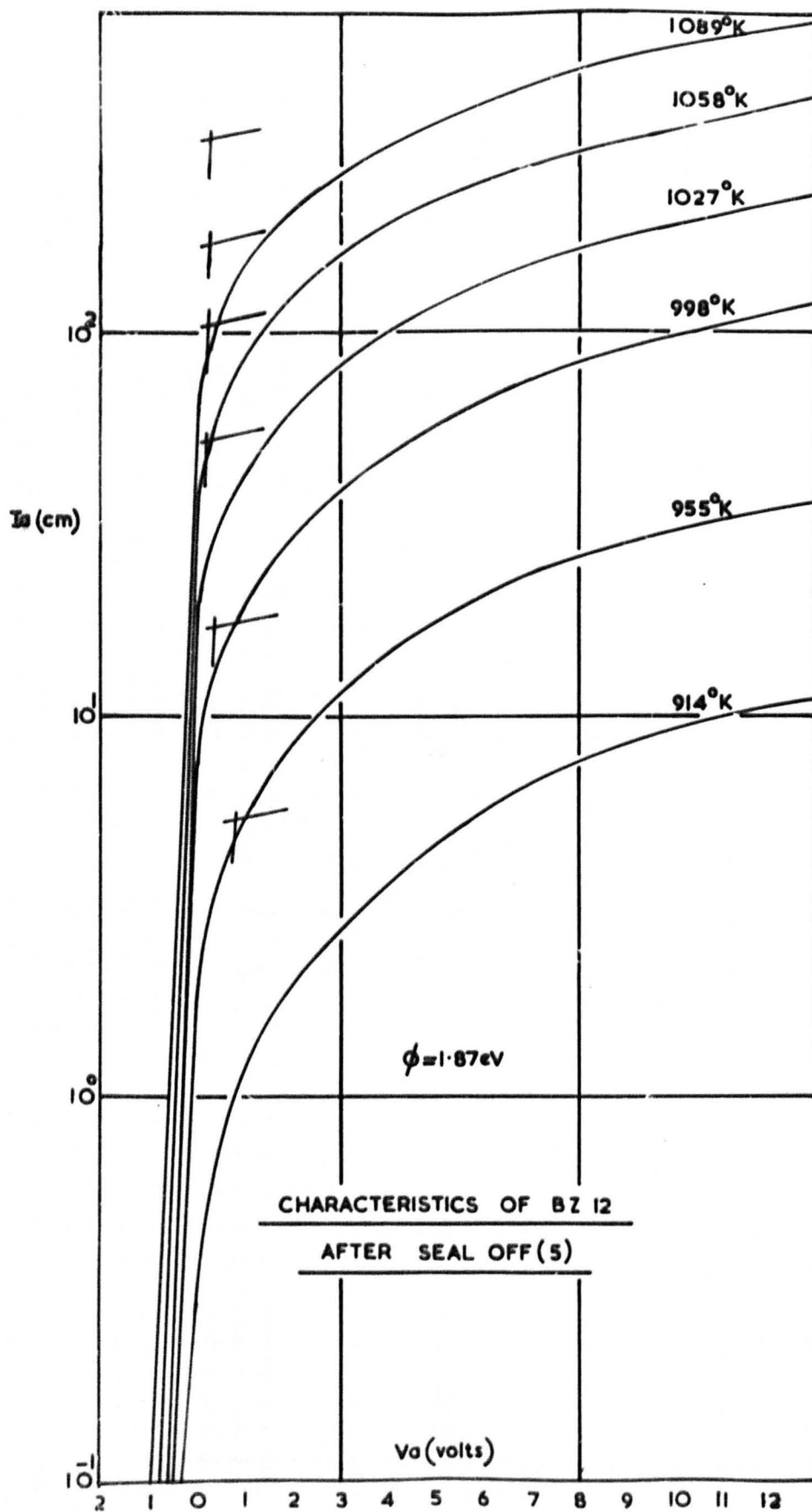


fig. 6. 12.

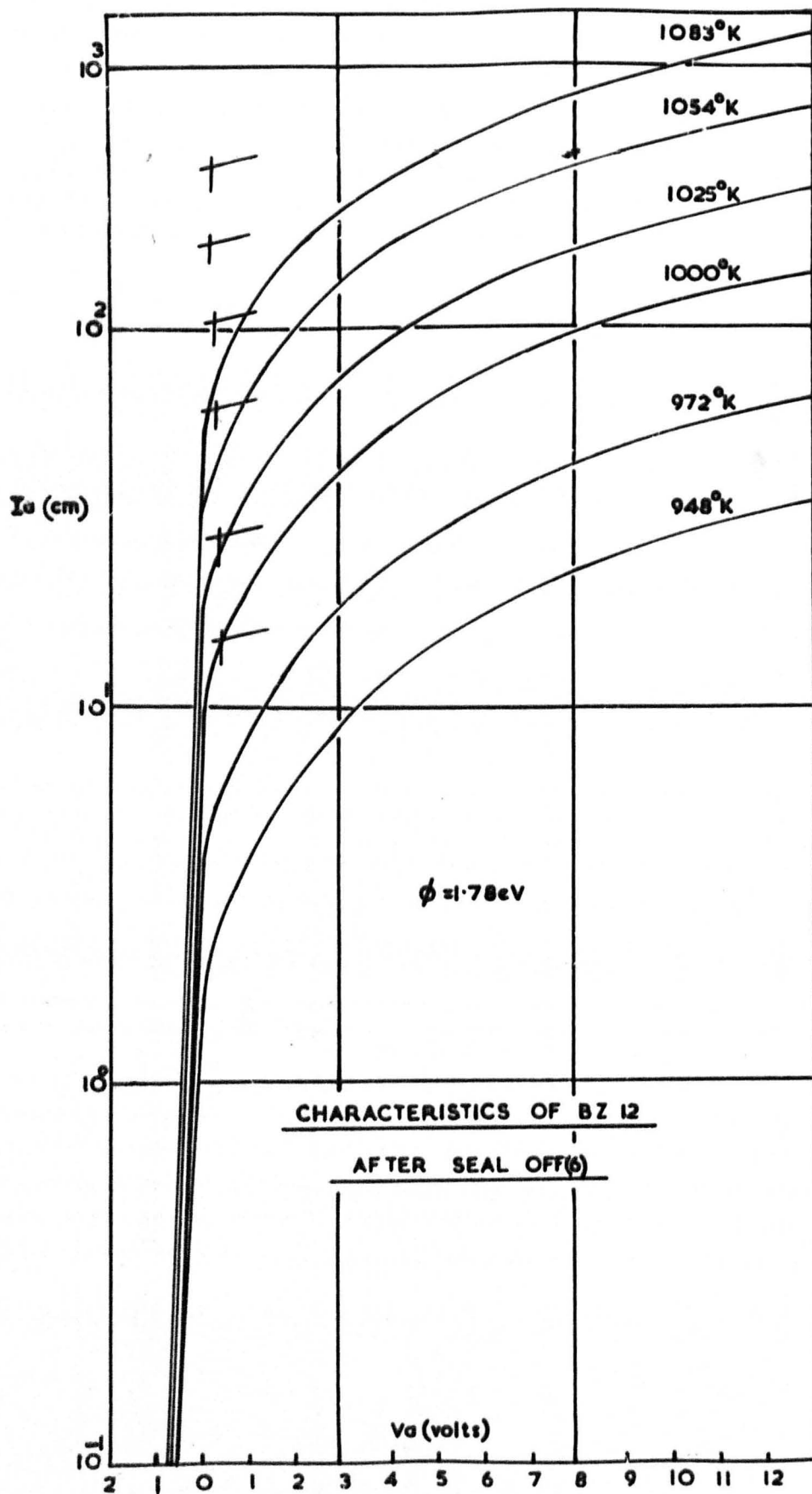


fig. 6. 13.

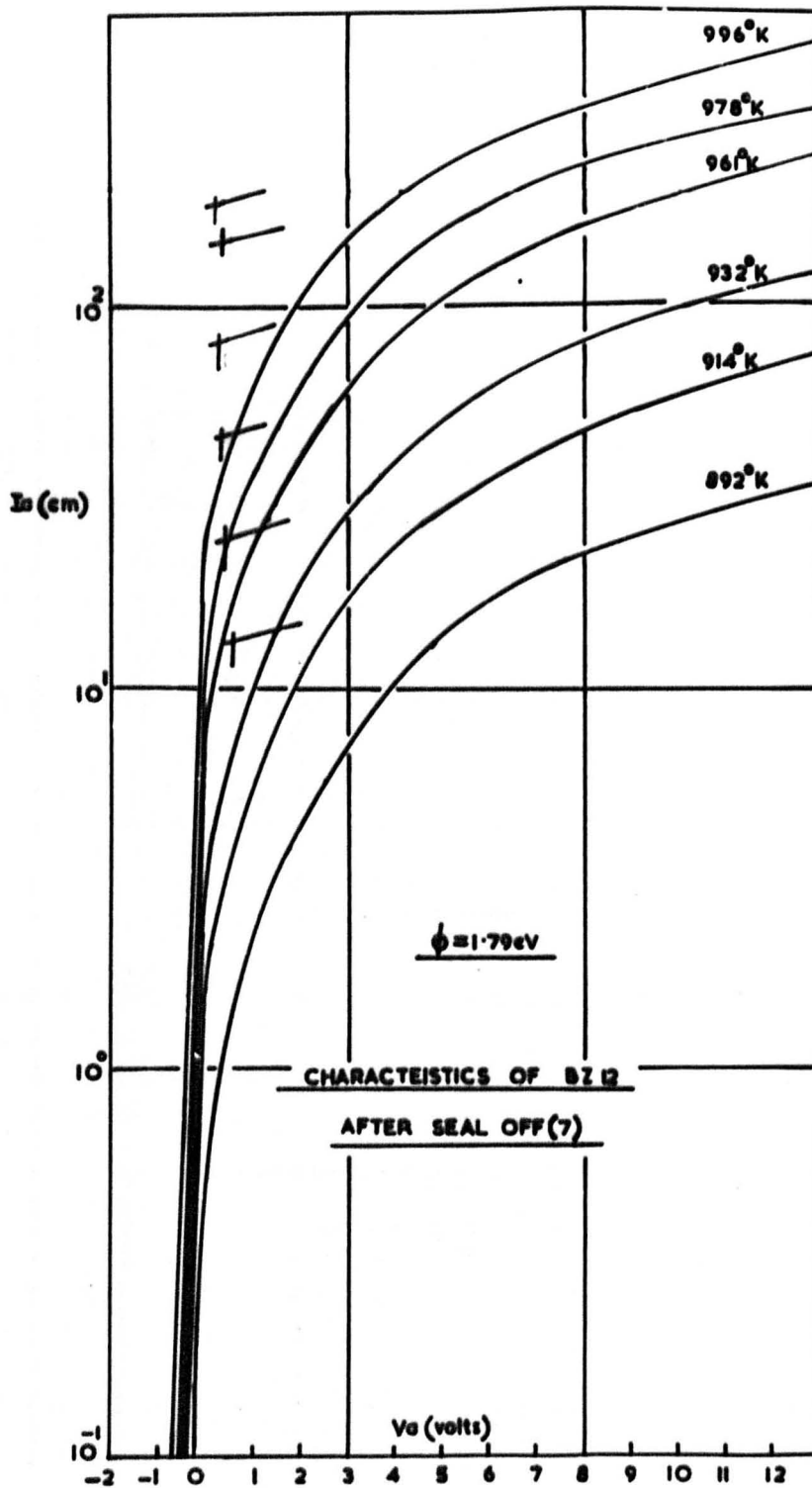


fig. 6. 14.

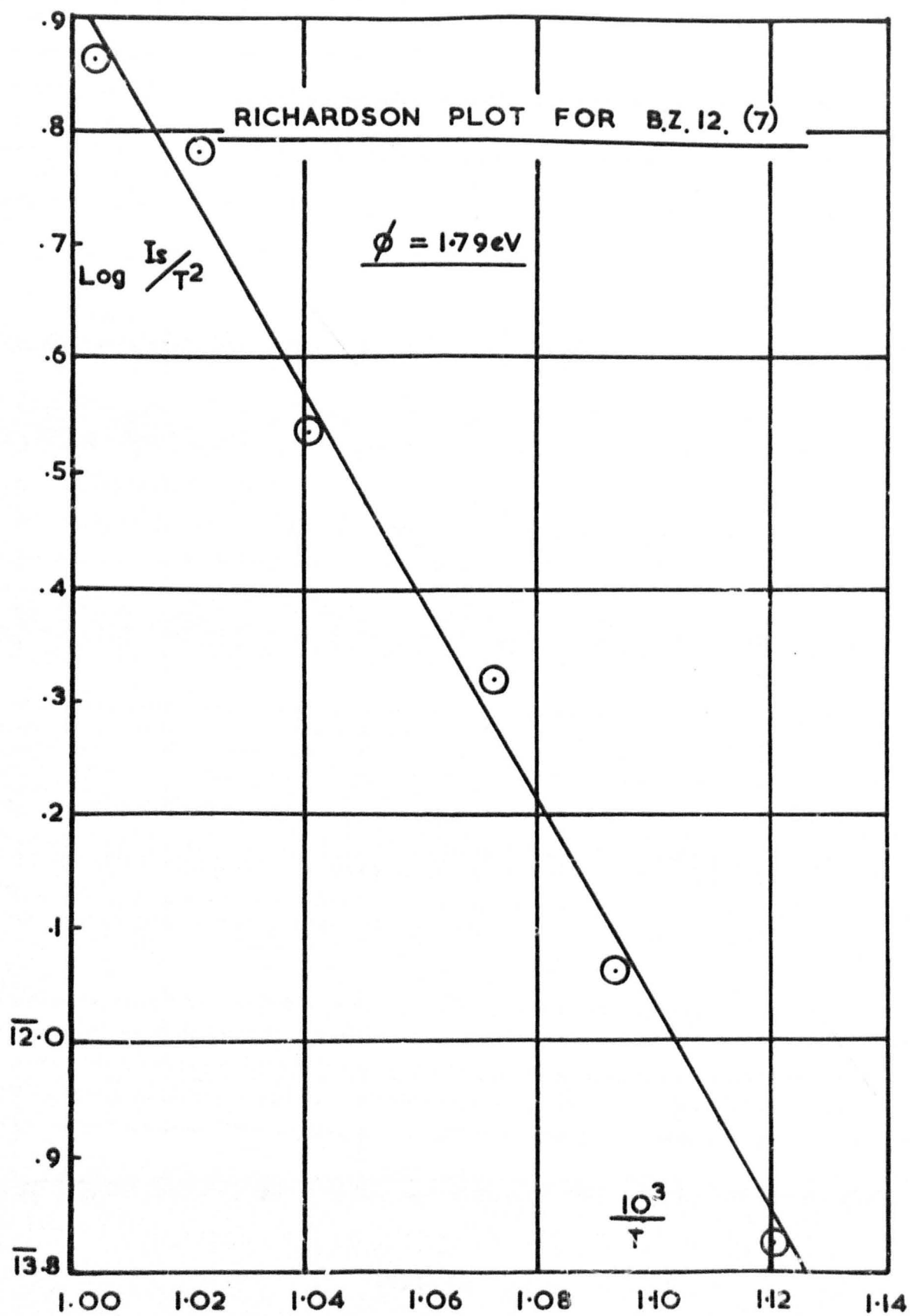


fig. 6. 16.

and BZ12, and both gave similar performances. More work was carried out on BZ12 so the results from this cathode are described.

BZ12 was made from 0.1 gas of mixture III. The nickel backing for this cathode was pressed from 10μ grain diameter carbonyl nickel instead of the $4-5\mu$ nickel as used previously. The breakdown, sintering and activation were carried out with the cathode made up in the valve, exactly the same procedure being followed as with BZ3. Shrinkage during sintering had been noticed with some of the previous cathodes and it was noticed again with this one. The valve was baked at 450°C for 4 hours and eddy-current heated. The emission was 6.5mA at 850°C with $V_a = 100\text{V}$ which was slightly higher than the emission from MVI. A set of characteristics was taken with the valve on the pump; the value of the work function so obtained was 2.43eV . After ageing for a further 4 hours another Richardson plot gave $\phi = 2.39\text{eV}$. The valve was again baked, eddy-current heated, the getters were fired and the valve was sealed off.

A series of Richardson plots was made at various stages of ageing of the cathode. One measurement made immediately after the valve was sealed off (fig (6.7)) yielded $\phi = 2.52\text{ eV}$. This value was higher than those obtained before seal-off, which could be due to material being deposited on the cathode during baking or eddy-current heating prior to seal off. BZ12 was aged by running at 700°C with $V_a = 100\text{V}$. A set of characteristics was taken every two hours (see figs (6.8) to (6.14)) and the corresponding Richardson plots were made. Two typical Richardson plots from this series are shown in figs (6.15) and (6.16). The summarised results are shown in table 6.2.

VALVE BZ 12			
Measurement	ϕ (eV)	$A(\text{amps. cm}^{-2} \text{ } ^\circ\text{K}^{-2})$	C.P.D. (volts)
1	2.52	2.	1.15
2	2.40	3.6	0.8
3	2.14	0.1	0.4
4	2.03	0.1	0.25
5	1.87	0.025	0.25
6	1.78	0.01	0.25
7	1.79	0.04	0.3

The work function as given by the Richardson line decreased until it reached 1.78 eV when it remained constant. The value of the emission constant A also showed a decrease as ϕ decreased. As the cathode became more activated, i.e. as ϕ decreased, the emission was less saturated, as can be seen by a comparison of the characteristics. If it is assumed that the work function decreases as more surface coverage by a barium monolayer is obtained, then a greater departure from the typical metallic behaviour is to be expected. Since an atomic film cathode must have a larger surface field than a pure metal cathode the work function and the saturated current will depend more on the external field, and so an increased Schottky effect will be observed as the amount of barium on the surface increases in the case of the 'M'-cathode. The surface fields are due to additional electric fields in front of the surface of the cathode which are due to potential differences set up between the various patches on the cathode surface.

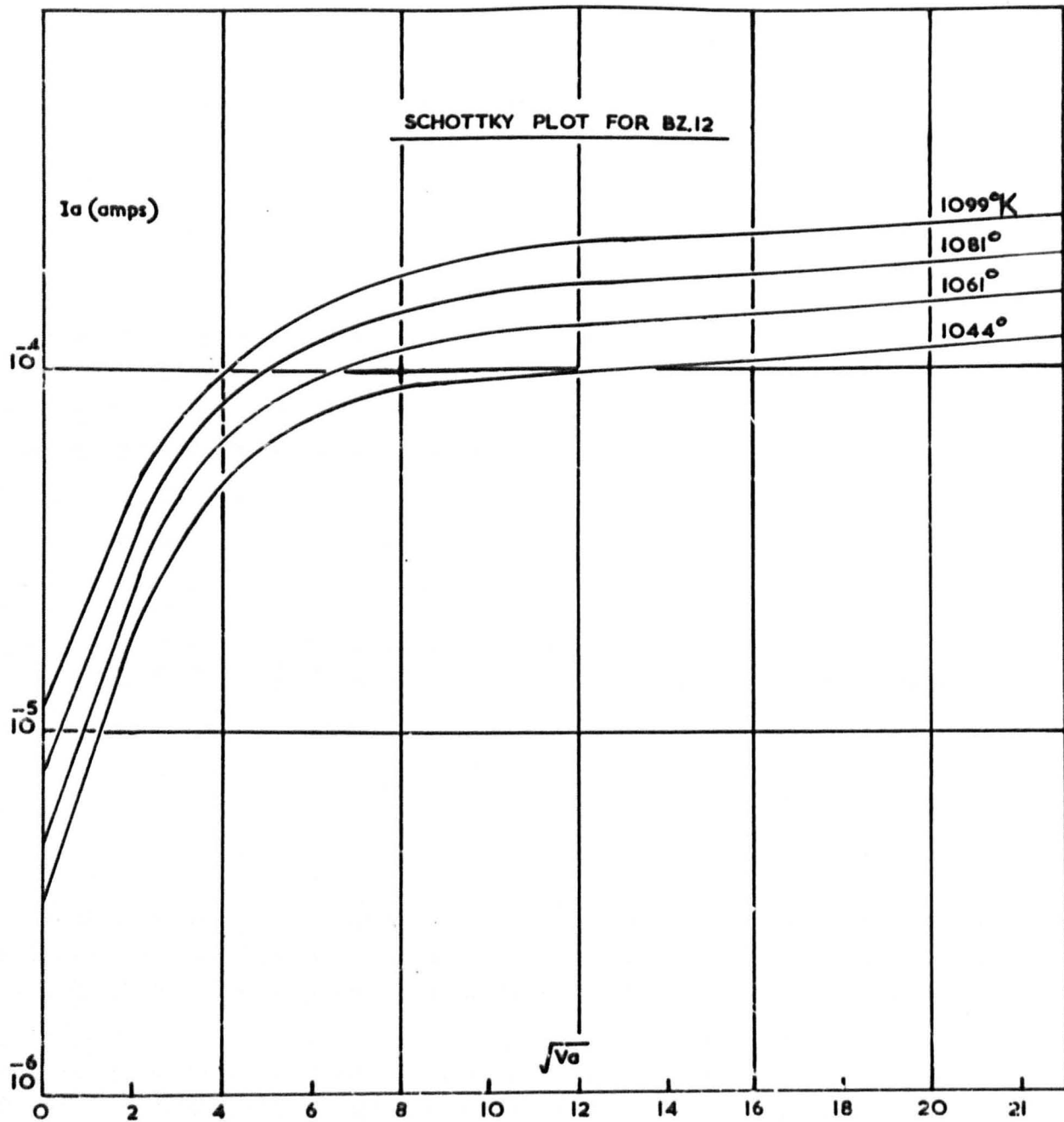


fig. 6. 17.

RICHARDSON PLOT FROM SCHOTTKY PLOT

FOR BZ 12.

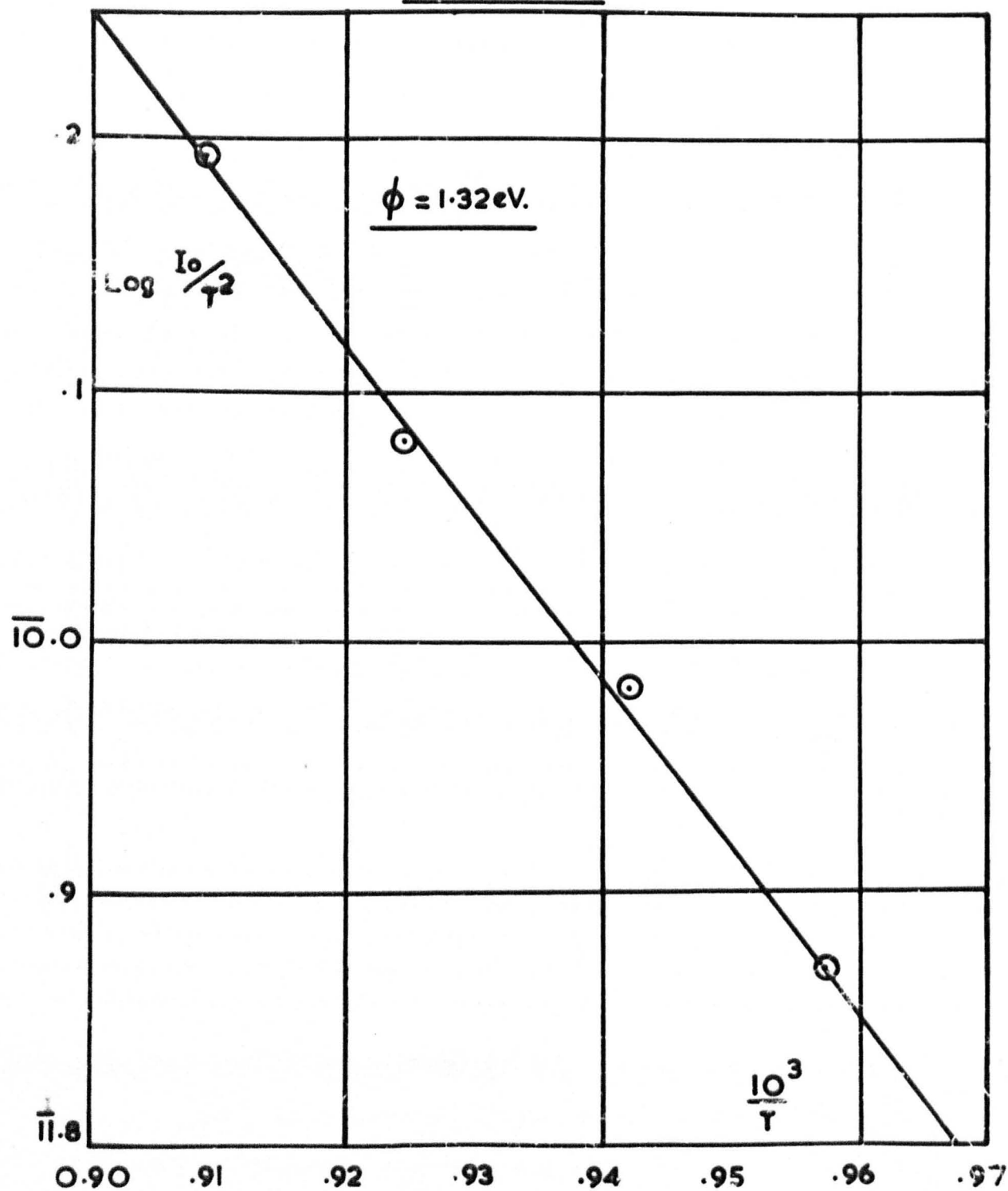


fig. 6. 18.

The contact potential difference between the electrodes which was 1.15 V from the first set of characteristics decreased rapidly until after 6 hours ageing it had reached 0.25 V, at which value it remained. This indicated that the anode had a work function of 3.67 eV after seal-off, not having the value for nickel of 5.0 eV due, presumably, to some material evaporated from the cathode and deposited upon the anode surface. The most probable evaporant would be barium. Since the c.p.d. decreased during the initial ageing, and the cathode work function was decreasing, the anode work function must have been decreasing at a greater rate than that of the cathode. The final value of the anode work function from the characteristics and knowledge of the cathode work function was 2.05 eV. The work function of barium is 2.51 eV so the anode had not more than a monolayer of barium upon it. All this reasoning assumed that the Richardson plot gives a value of the real work function.

With the cathode fully activated a Schottky plot was made on BZ12, the maximum voltage applied being 400 V. Fig (6.17) shows the results obtained from the cathode at four temperatures. Above an applied voltage of 100 V the plot is linear. This value of voltage, since the electrodes are 1 mm. apart, corresponds to an applied field of 1000 V.cm^{-1} . The deviation from the Schottky law at lower field strengths is due to the differences in work function over the cathode surface giving rise to surface fields as mentioned previously. A Richardson line was drawn from the Schottky plots (fig (6.18)) and this indicated a work function of 1.32 eV. This value is not the same as that obtained from a Richardson plot made from the I_a - V_a char-

acteristics. One would expect the value from a Schottky plot to be lower since the thermionic emission is supplemented by field emission.

Before completing measurements on BZ12 a final check was made on its work function as determined by a Richardson plot from its characteristics and this gave $\phi = 1.73$ eV in close agreement to those values obtained previously.

This was the final cathode worked upon in the preliminary work. The collected values obtained for the work functions are shown in table 6.3. This indicated that cathodes could be reproduced successfully if the same processing procedure was applied strictly to each.

Table 6.3

Cathode	Mixture	ϕ (eV)
BZ3	I	2.02
BZ8	II	1.65 - 1.75
BZ12	III	1.73

The conclusions drawn from the experimental work are given in the final chapter, but it may help if those drawn from the preliminary work are briefly outlined here. They are:-

1. cathodes can be reproduced within certain limits.
2. the work function of the 'M'-cathode as indicated by a Richardson plot is 1.7 - 1.8 eV.
3. such a cathode can be reactivated after exposure to the atmosphere several times.
4. there appears no difference between the properties of cathodes

sintered in hydrogen and those sintered in vacuum.

5. the particular reducing agent used, when in small quantities, has no noticeable effect upon the emission properties of the cathode.

Chapter VII

Results from a Study of the Effect of Oxygen and Sulphur upon the Thermionic Emission from 'M'-cathodes.

The second section of the work to be described in Part II is a study of the effect of oxygen and sulphur upon the thermionic emission from 'M'-cathodes. The procedure followed with a cathode after activation was to determine its work function by the Richardson plot method, these results indicating when the cathode was fully activated. The emission from the cathode was then 'poisoned' at a given temperature and anode voltage to 10% of its value. The recovery of emission was followed and plots of emission against time were made.

7.1. The effect of oxygen on the emission from 'M'-cathodes

The effect of oxygen upon six cathodes was studied. Four of these were prepared from mixture III and the other two from mixture IV.

7.1.1. Oxygen poisoning of cathodes containing 1% zirconium hydride

Oxygen poisoning of the emission from four cathodes made up from mixture III was studied. The usual work function estimations were made after activation of the cathodes and table 7.1 shows the results which were obtained. The values of ϕ confirmed the conclusions drawn from the preliminary work.

Valve BZ13 was the first used for the study of poisoning. The cathode was pressed from mixture III, in exactly the same manner as were previous cathodes. It was mounted in a valve assembly which, in addition to the usual components, contained a filament coated with barium peroxide provided by Hopkin and Williams. The assembly

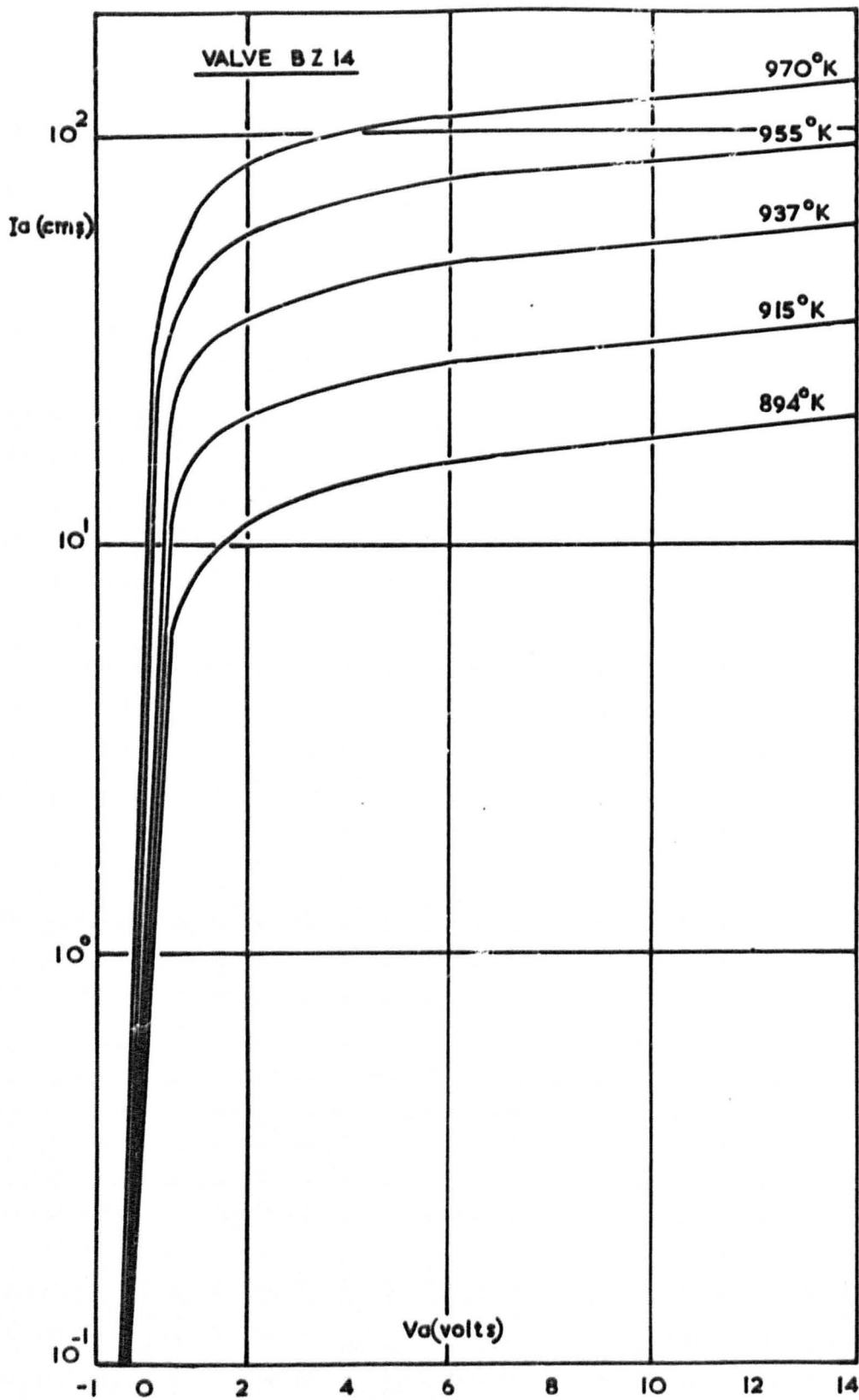


fig. 7. 1.

RICHARDSON PLOT FOR BZ 14.

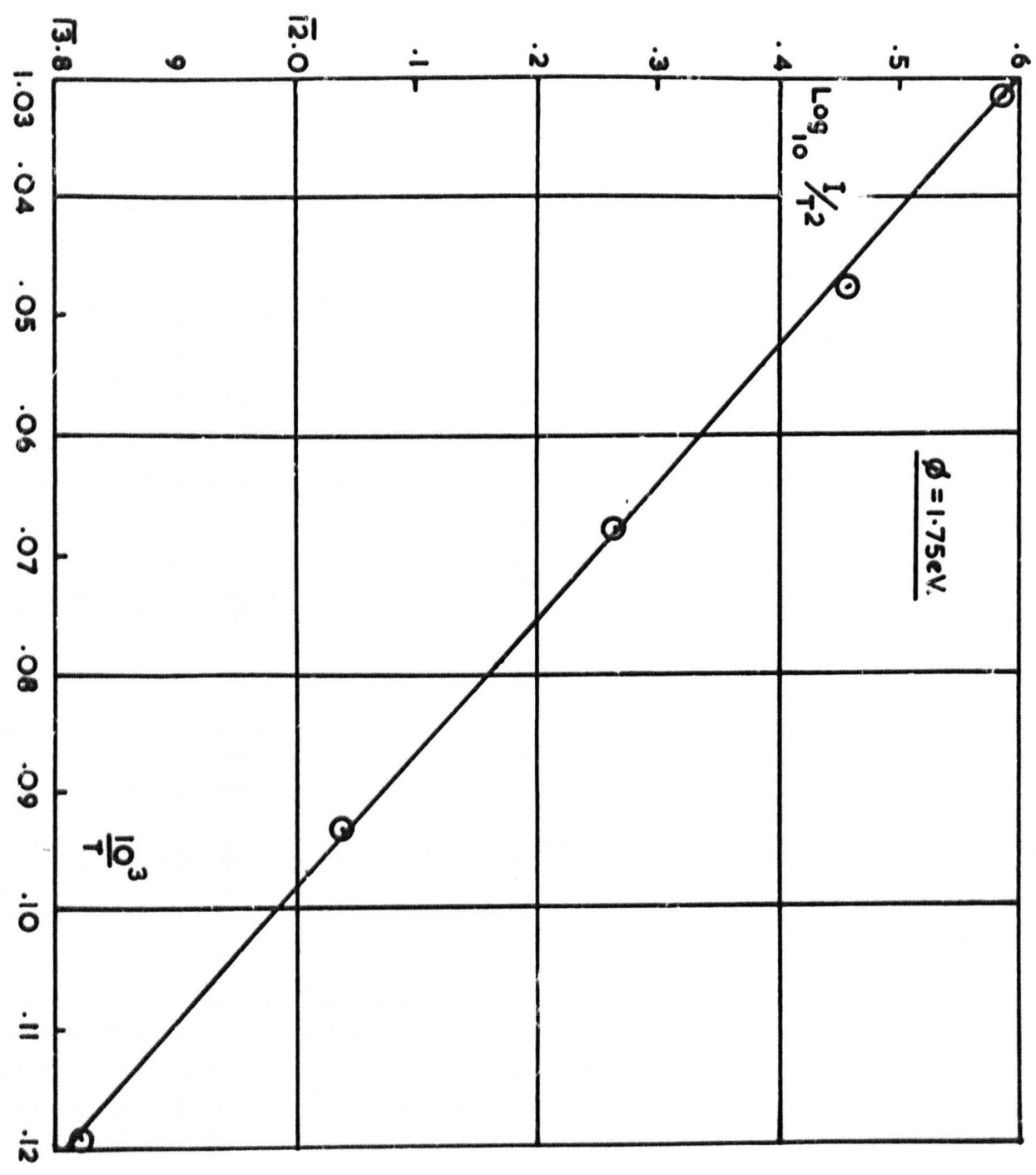


fig. 7. 2.

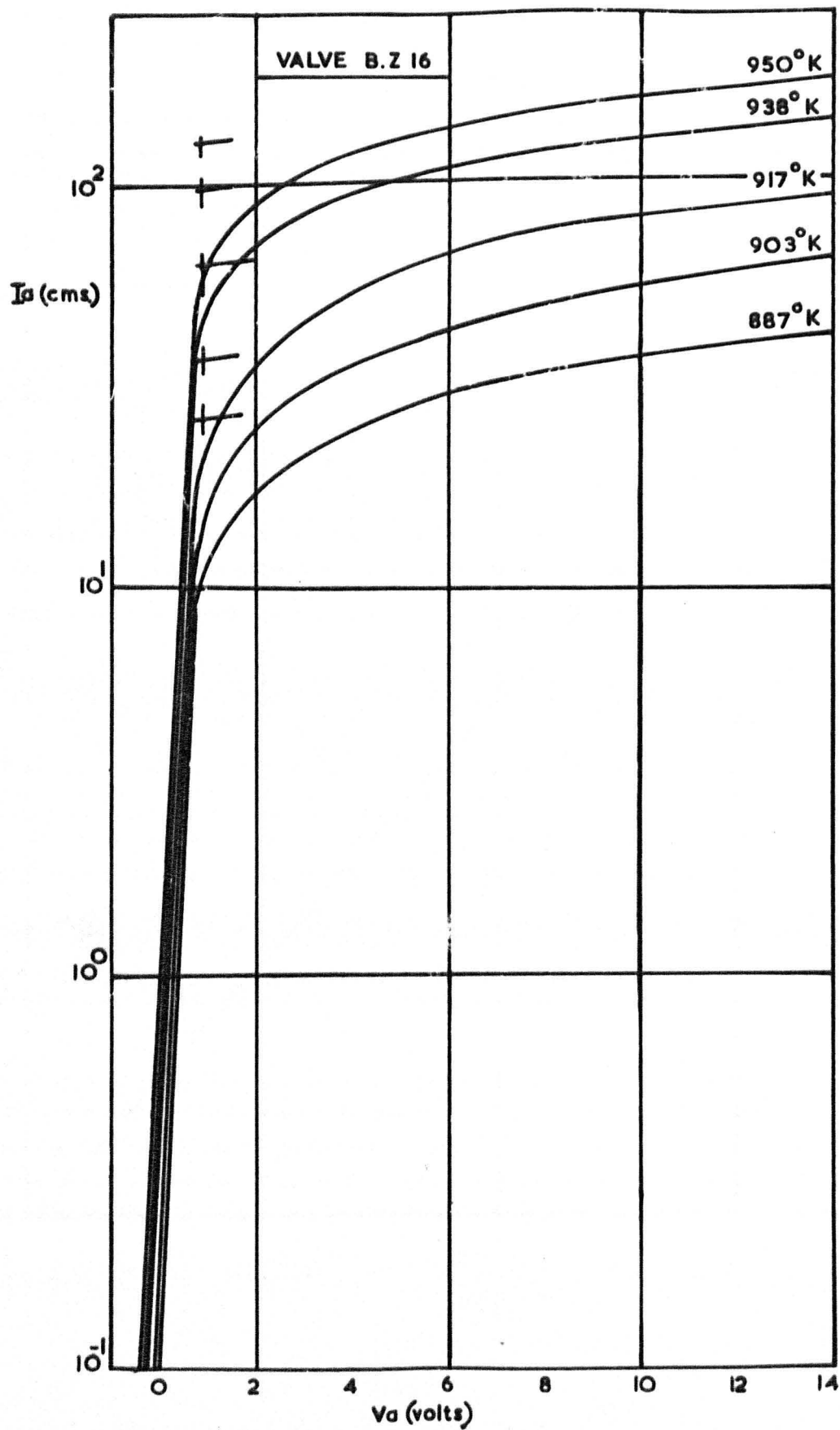


fig. 7. 3.

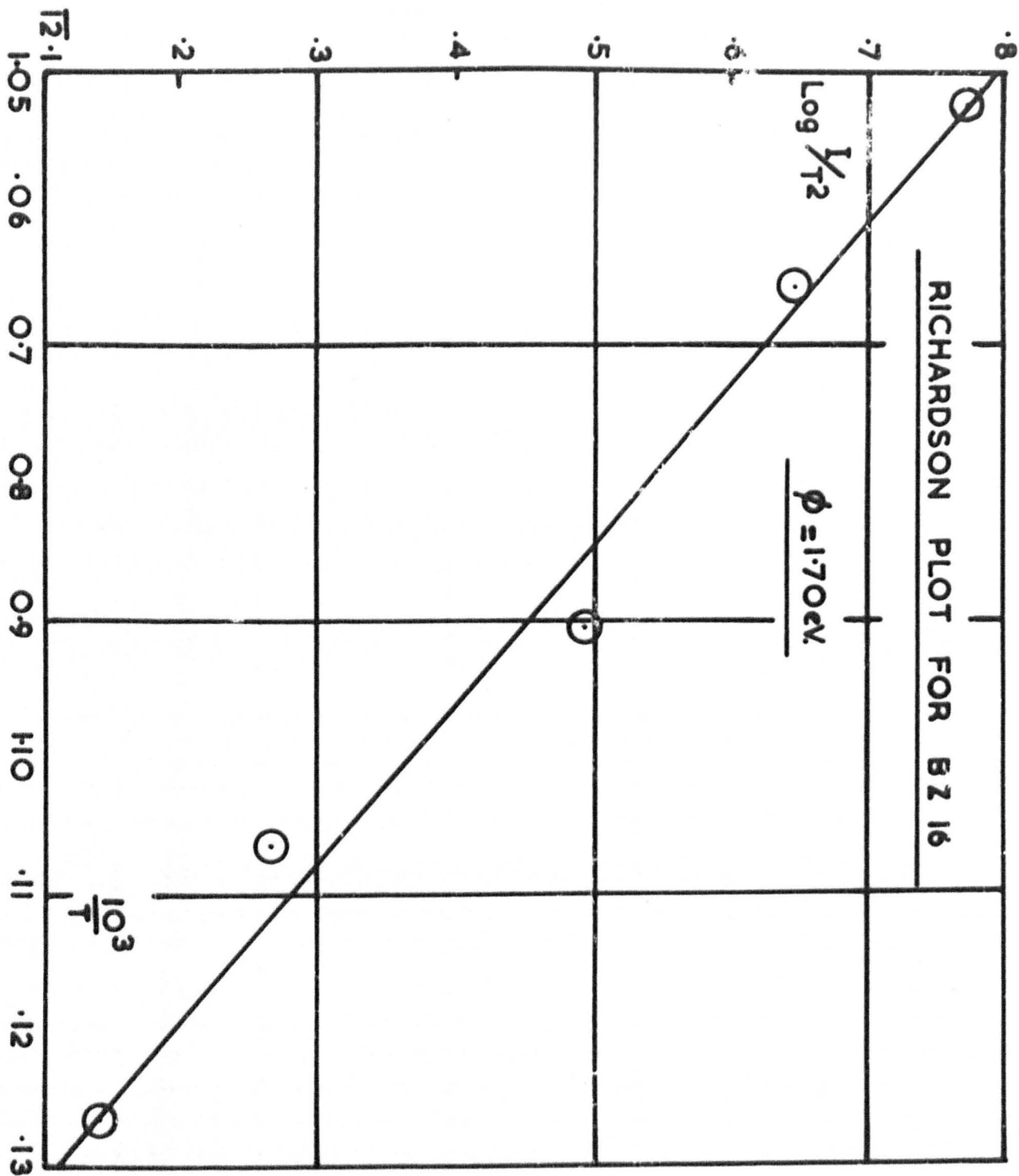


fig. 7. 4.

OXYGEN POISONING OF BZ 16

<u>I — $V_a = 8v$</u>	<u>PT=20s</u>	<u>T=946°K</u>
<u>II — $V_a = 8v$</u>	<u>PT=40s</u>	<u>T=946°K</u>
<u>III — $V_a = 8v$</u>	<u>PT=60s</u>	<u>T=948°K</u>

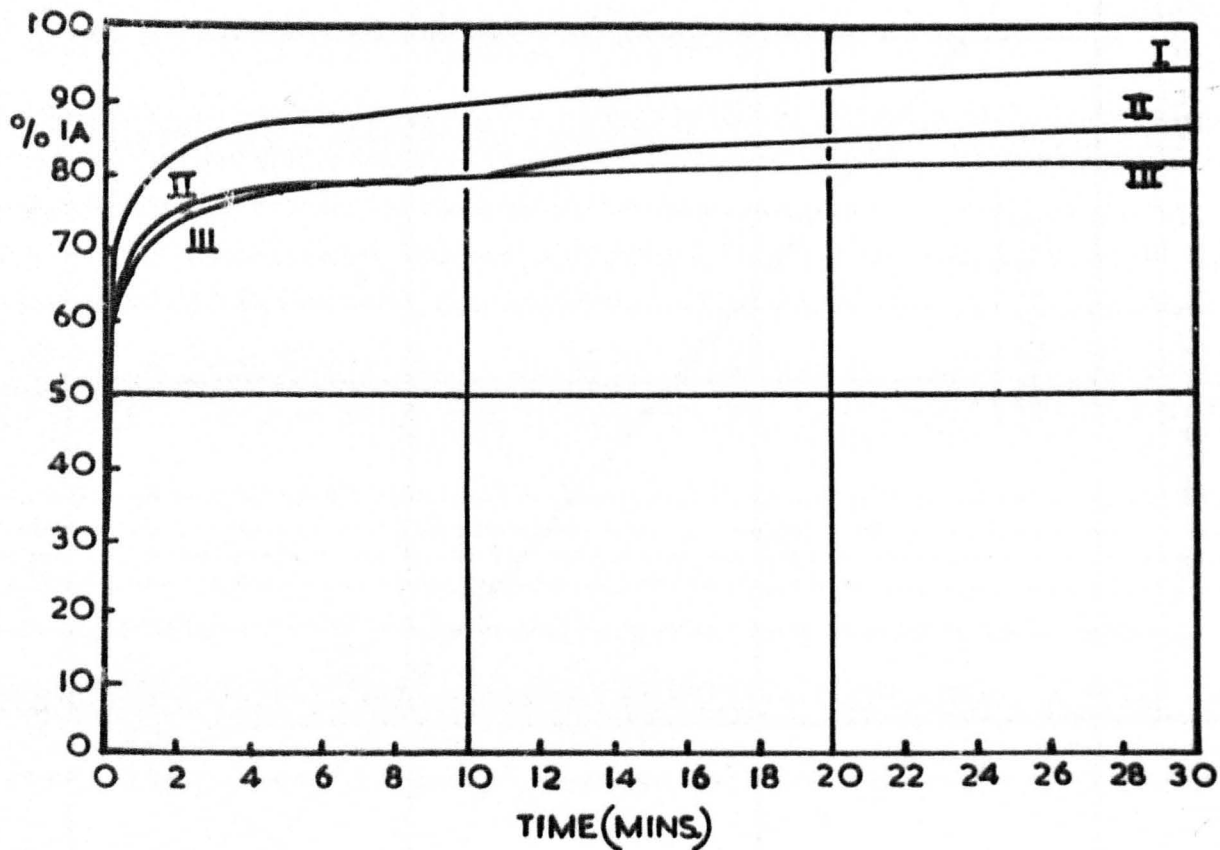


fig. 7. 5.

OXYGEN POISONING OF BZ 16

I — $V_a = 12v$ PT = 30s T = 1067°K

II — $V_a = 12v$ PT = 30s T = 1017°K

III — $V_a = 12v$ PT = 30s T = 967°K

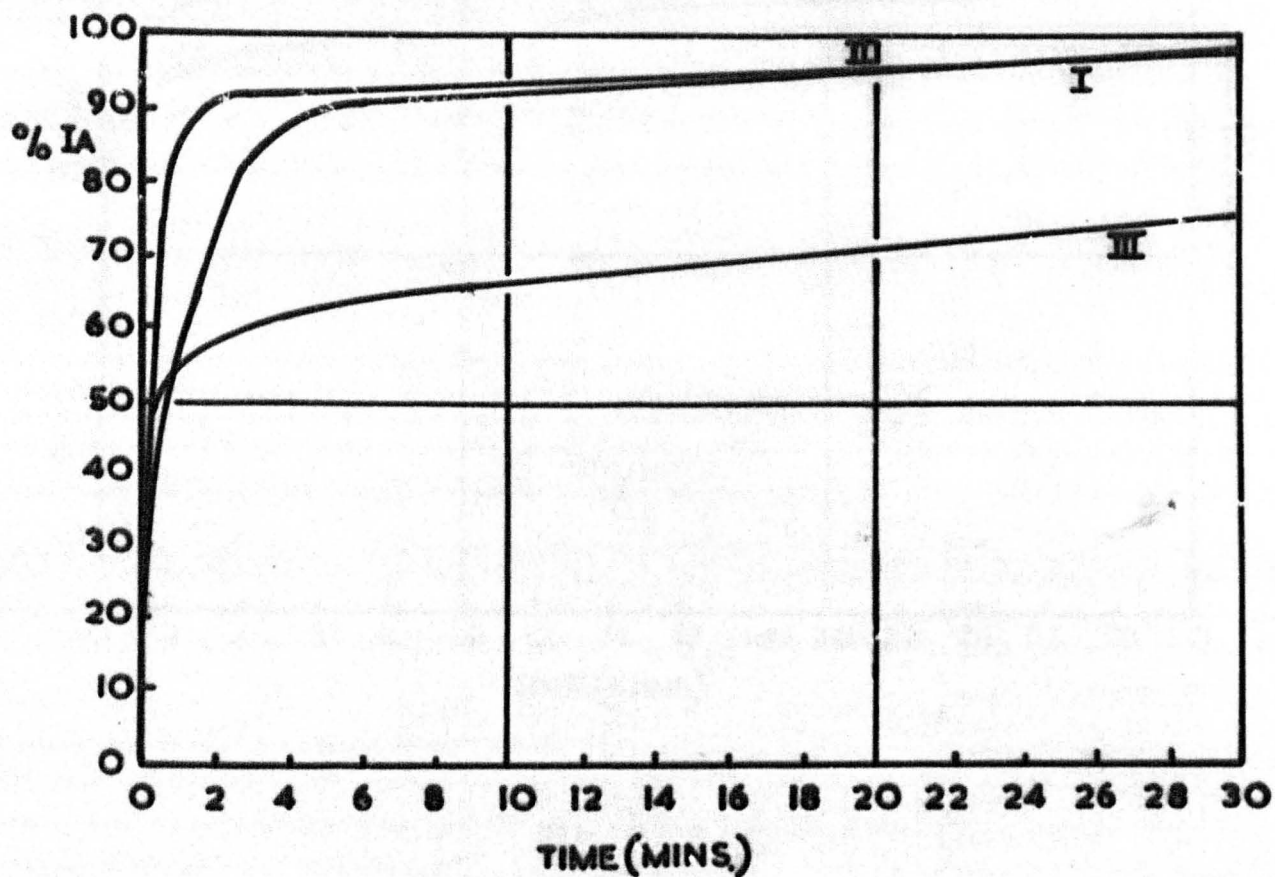


fig. 7. 6.

OXYGEN POISONING OF BZ.16

<u>I</u>	<u>$V_a = 8v$</u>	<u>$PT = 30s$</u>	<u>$T = 1064^{\circ}K$</u>
<u>II</u>	<u>$V_a = 8v$</u>	<u>$PT = 30s$</u>	<u>$T = 1014^{\circ}K$</u>
<u>III</u>	<u>$V_a = 8v$</u>	<u>$PT = 30s$</u>	<u>$T = 965^{\circ}K$</u>

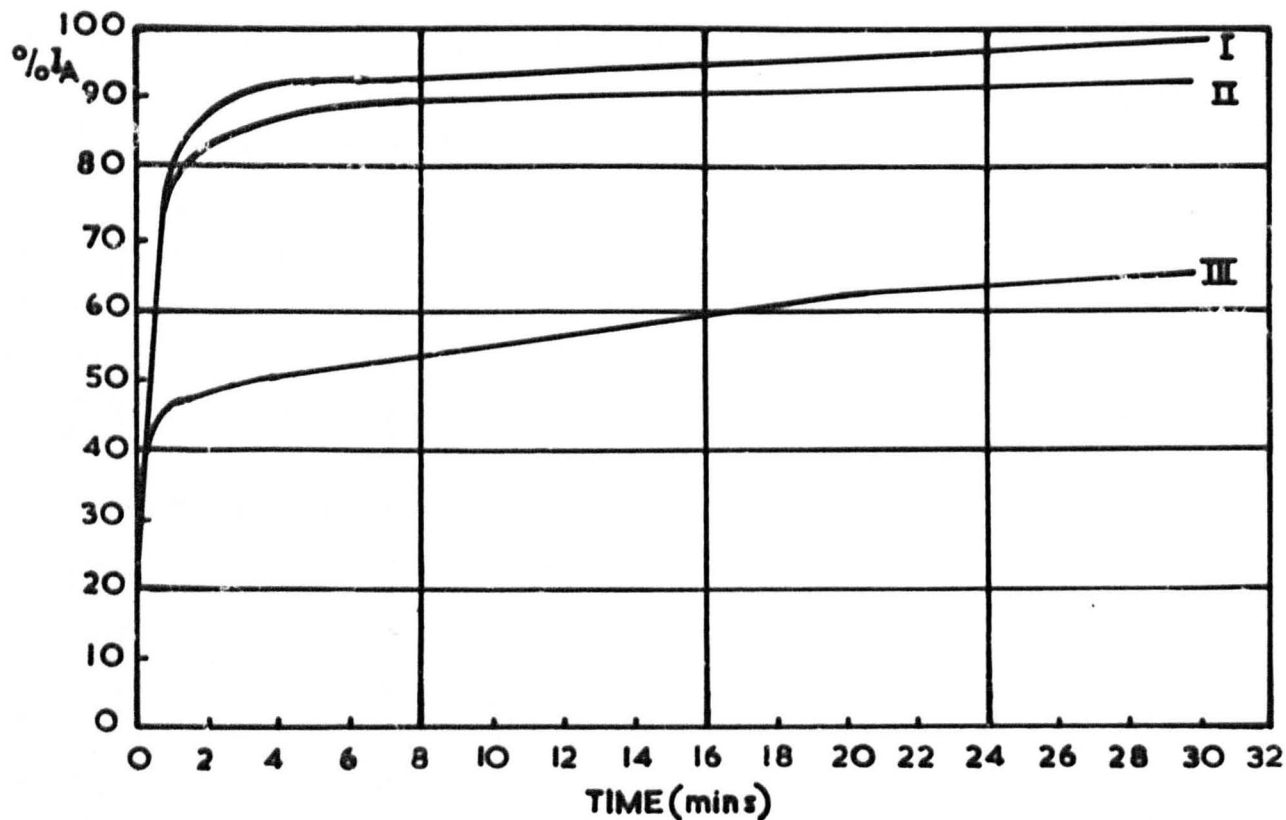


fig. 7. 8.

The cathode was activating until the time of the second set after seal-off. Again the value of A decreased with decrease in work function. A set of characteristics of BZ14, and the corresponding Richardson plot are shown in figs (7.1) and (7.2). These are typical examples of this group of cathodes.

An attempt was made to poison the emission from BZ13. The cathode temperature was constant at 1028°K and with 10V applied to the anode the emission was poisoned to 10% in 30 secs. Recovery was complete in 13 mins. A second poisoning was made but not enough control over the liberation of the oxygen was exerted and the emission poisoned to 1%. The recovery took about 30 mins. A third poisoning was completed successfully at a cathode temperature of 1041°K and $V_a = 10\text{V}$. A series of poisonings were then made using $V_a = 4, 8$ and 12V at cathode temperatures of 975° , 1025° and 1075°K , and poisoning times of 30, 45 and 60 secs. Typical recovery curves are shown in figs (7.5) to (7.8). The anode voltage was not taken above 12V as the first ionisation potential of oxygen is 13.55eV and it was desired to avoid any complications produced by ionising the oxygen.

It was found from this cathode that poisoning was reversible, as suggested by previous cathodes which had been exposed to the atmosphere. The recovery was dependent upon cathode temperature, being very rapid if the cathode was above 1100°K . Variation of the anode voltage between 0 and 12V appeared to have little effect upon the rate of recovery. The recovery curves, as seen from the graphs, could be divided into two portions, the first being a rapid increase in emission and the second part, a much slower recovery to

OXYGEN POISONING OF B.Z 16

I - $V_a = 12v$

PT = 30s

T = 1017°K

II - $V_a = 8v$

PT = 30s

T = 1014°K

III - $V_a = 4v$

PT = 30s

T = 1016°K

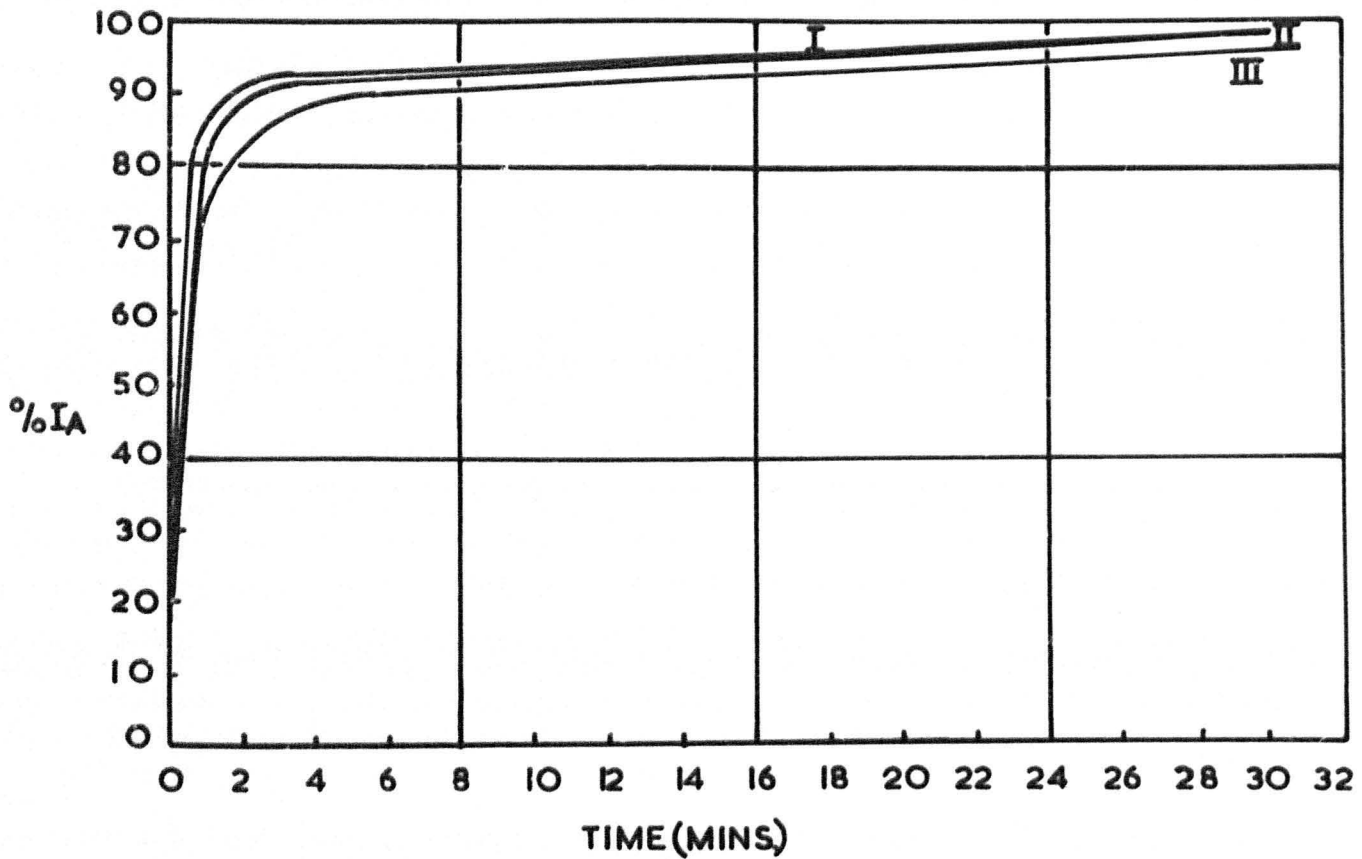


fig. 7. 7.

the initial value. The first portion took about two minutes to complete and it was noticed that the shorter the poisoning time the more rapid was this initial recovery rate. The cathode could be completely reactivated rapidly by application of 150V to the anode or by raising the temperature of the cathode to 1200°K.

Cathode BZ16 was also made from 0.1 gms of mixture III and the processing followed exactly the same procedure as BZ13. Only one set of characteristics was taken before seal-off. After seal-off one set was taken after twelve hours ageing and another set after a further three hours. The results are shown in table 7.3. A set of characteristics and Richardson plot for BZ16 are shown in figs (7.3) and (7.4). The set of characteristics taken with the valve on the system gave a contact potential difference of 1.2eV which indicates an anode work function of 5.1eV. It seems that the anode at this stage was clean and that subsequent reduction in the anode work function was due to material evaporated from the cathode.

Table 7.3.

Valve BZ16		
Measurement	ϕ (eV)	$A(\text{amps.cm}^{-2} \cdot \text{K}^{-2})$.
Before seal-off	3.90	9.9×10^8
After seal-off (1)	1.70	0.4
" " " (2)	1.70	0.013

Four poisonings of BZ16 were made at 965°K with $V_a = 12, 8$ and 4V in the first three and 4V again in the fourth, but in this case the voltage was reversed in polarity after $\frac{1}{2}$ min, 5 mins and then at every

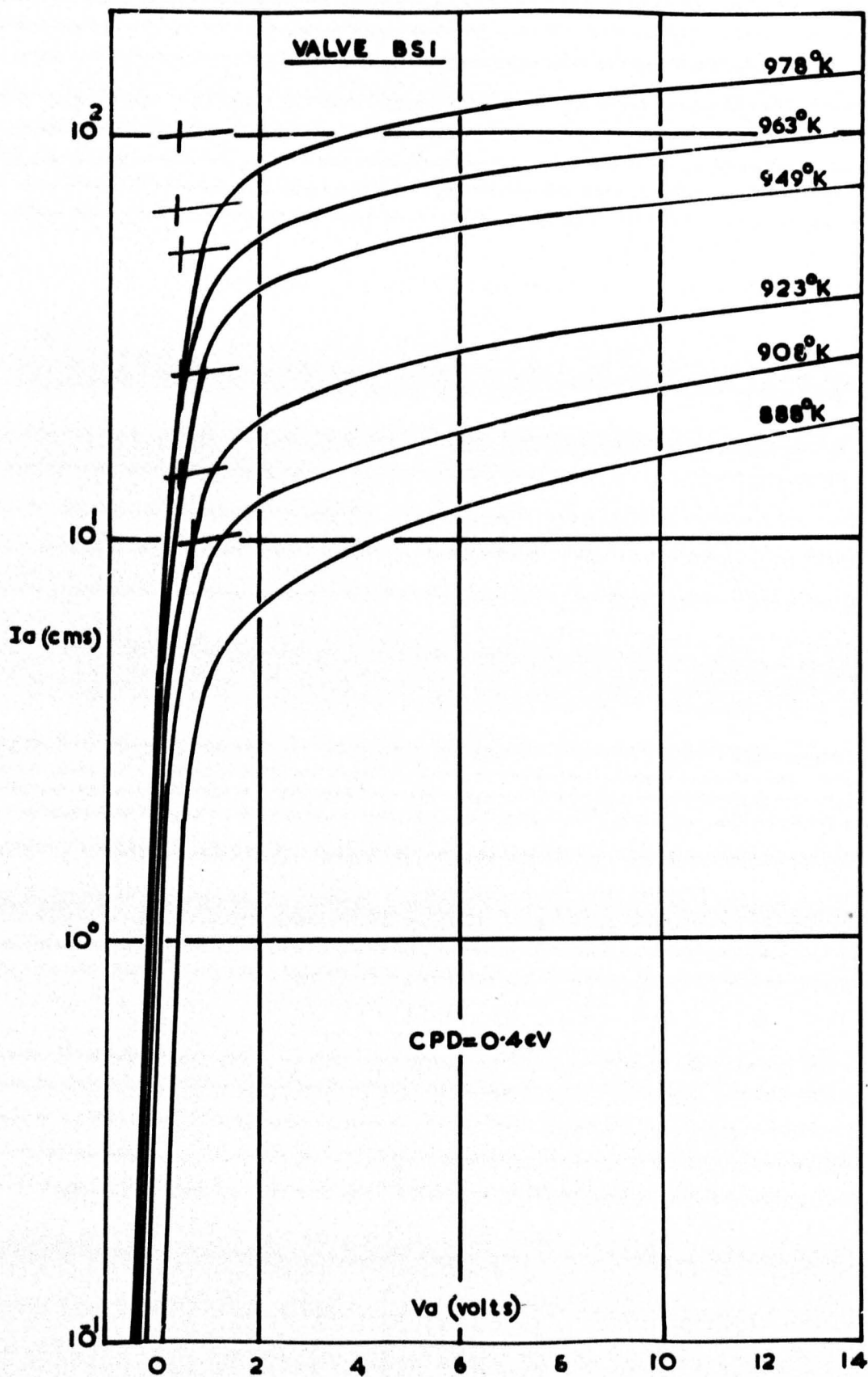


fig. 7. 9.

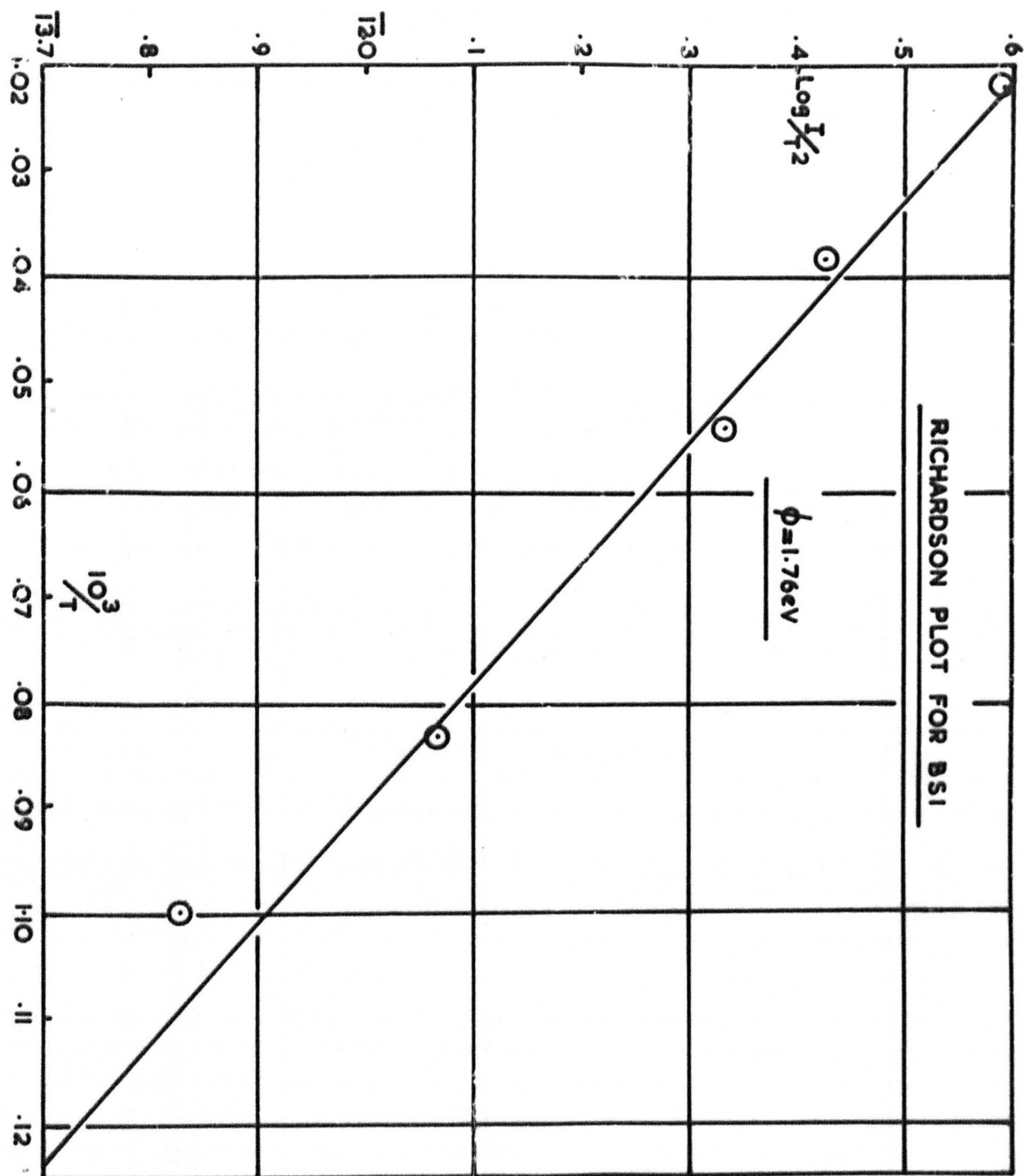


fig. 7. 10.

5 mins up to a total time of 30 mins. This was done in an attempt to see if the oxygen leaving the cathode during reactivation was ionised. The type of curve obtained was similar to that in fig (7.12) although the re poisoning during the period when negative voltage was applied was not so pronounced with $V_a = 4V$ as with $V_a = 12V$.

Three more poisonings were made at $1037^{\circ}K$ with $V_a = 8V$ and the poisoning time varied at 20, 40 and 60 seconds. These were repeated at 988° and $948^{\circ}K$. The nine poisonings were then repeated for $V_a = 4V$ and $V_a = 12V$. Some of the results obtained are shown in figs (7.5) to (7.8). Recovery with V_a periodically reversed was studied for $V_a = 12$ and $8V$. A series of recoveries were then followed after poisoning the emission to 10% over a given period and others after poisoning the emission at 10% for a given period. The initial recovery was slower from the latter type of poisoning, but after about 30 mins recovery from both types of poisoning had proceeded to about the same extent.

7.1.2. Oxygen poisoning of cathodes containing 0.1% silicon

Two cathodes were produced from mixture IV and oxygen poisoning was carried out upon their emission and the recovery studied. The values of their work functions obtained from Richardson plots completed the comparison of values of ϕ for cathodes prepared from the four mixtures. The two cathodes behaved very similarly as is apparent from their work functions which were 1.75 and 1.73 eV over the same temperature range. The corresponding values of A were 0.03 and 0.01 amps. $cm^{-2} \cdot ^{\circ}K^{-2}$. (see figs (7.9) and (7.10)).

OXYGEN POISONING OF B.S.2

$V_a = 12v$

$PT = 60s$

$T = 922^\circ K$

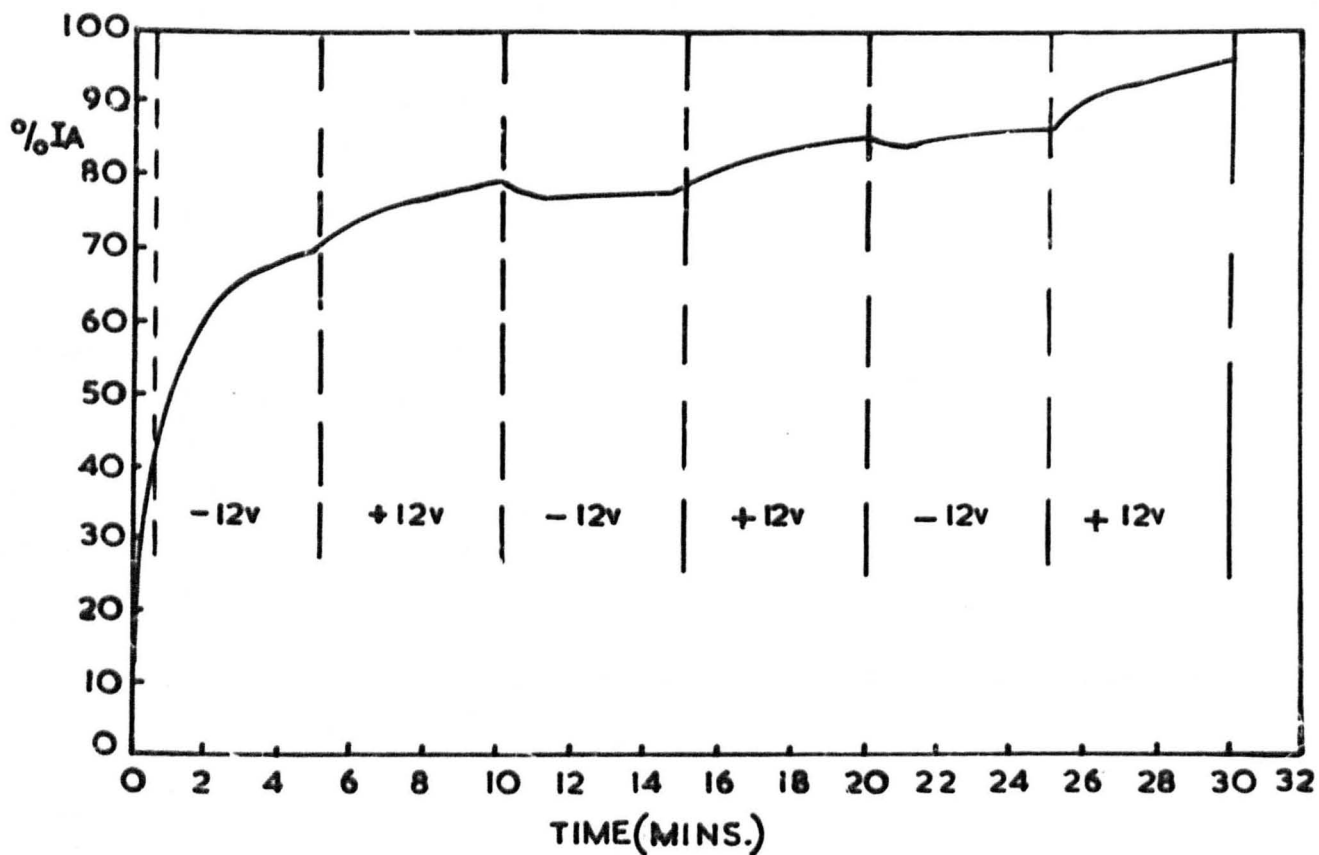


fig. 7₁₂.

OXYGEN POISONING OF BS.2

$V_g = 12v$

$PT = 60s$

$T = 963^{\circ}K$

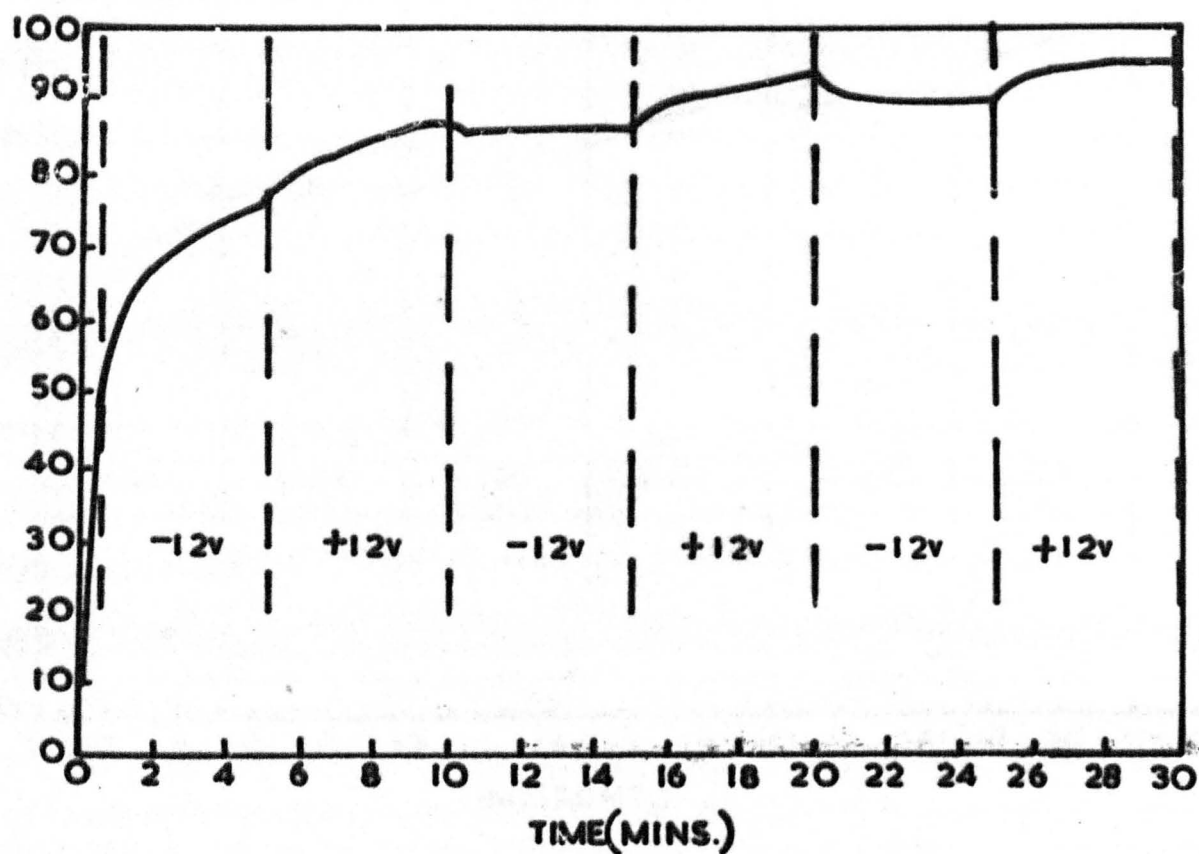


fig. 7. 13,

Cathode BS2 was made from 0.1 gas of mixture IV. It was mounted and processed in exactly the same way as BZ16. After activation and six hours ageing a Richardson plot was made, giving $\phi = 2.24$ eV. The valve was baked, etc. and sealed off. The cathode was aged for a further eight hours when a Richardson line gave $\phi = 1.73$ eV, a value from which it did not change on further ageing.

The first poisoning of the emission was made and the recovery was followed with the polarity of the anode voltage (6V.) reversed each 5 mins, as with BZ16. Repoisoning of the cathode during negative anode voltage again took place. The cathode emission was poisoned a second time and with $V_a = 12V$ the anode voltage was reversed at 5 minute intervals. The re-poisoning was even more noticeable in this case, as shown in fig (7.12). The procedure was repeated (fig (7.13)). Poisoning was effected at 920° , 970° and $1020^\circ K$ with $V_a = 4, 8$ and $12V$. and the poisoning time was varied between 20, 40 and 60 secs. (see fig (7.11)). The recovery curves were of the same form as ones obtained previously, the two sections of the curve again being very apparent.

Since the recovery of the emission from poisoning by oxygen as studied with several cathodes followed the same form in each case, no more oxygen poisoning was carried out. The conclusions drawn from the work are listed at the end of this chapter and are discussed in the final chapter.

7.2. The effect of sulphur on the emission from 'M'-cathodes

As an interesting comparison with the effect of oxygen upon the emission from the 'M'-cathode it was decided to use sulphur. Since

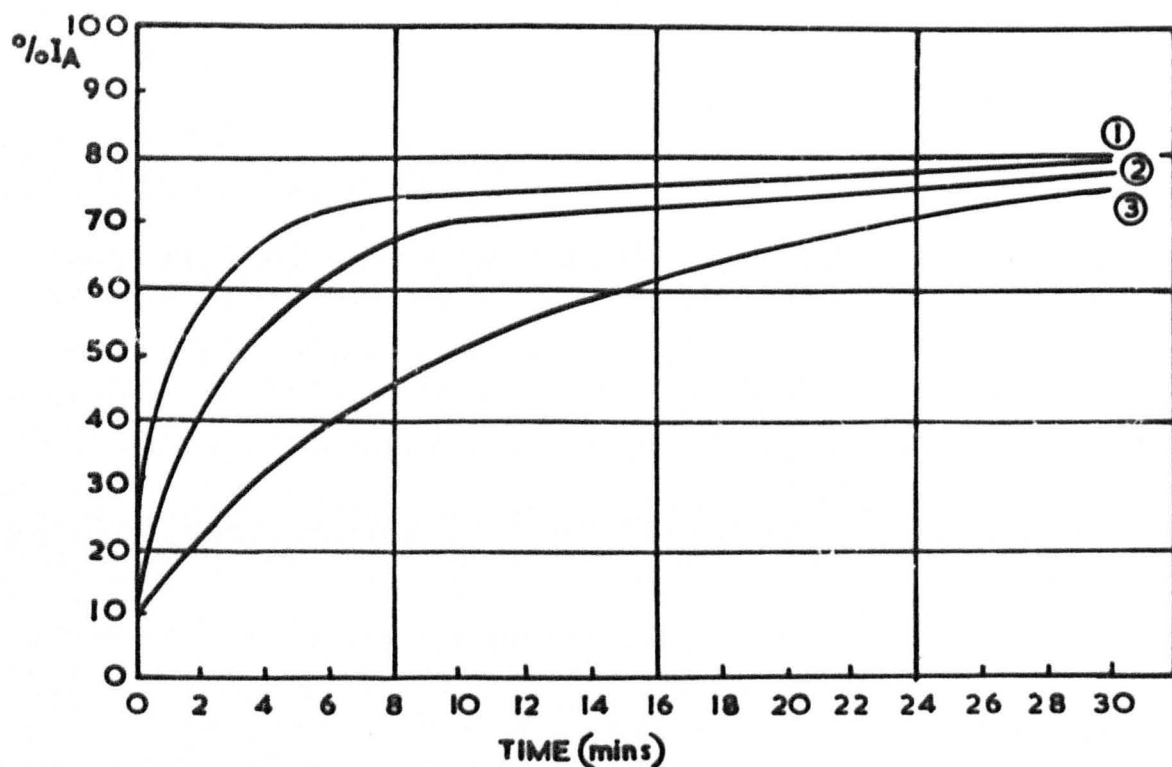
sulphur is a larger atom or ion, whichever particle is important in the poisoning process, it was expected that the poisoning due to sulphur would be slower, i.e. that sulphur would not be such an efficient poisoning agent. Any difference between the two may also be attributed perhaps, in part, to the greater electronegativity of oxygen. Two cathodes were made, one each from mixtures III and IV. The sulphur was obtained from a filament coated with molybdenum disulphide from which it was released by passage of a current. One cathode is described in more detail, the results from the second one being very similar.

Cathode BZ17 was made from 0.1 gms of mixture III in exactly the same way as previous cathodes from this mixture. The processing, too, followed closely that of the other cathodes. There was one difference. The valve was only baked to 250°C as above that temperature the sulphur was liberated from the poisoning filament. The baking time was increased to 8 hours at this temperature.

After seal-off the cathode was aged for 15 hours. A set of characteristics was taken and the resultant Richardson line gave 1.85 eV as the work function. After a further 6 hours ageing the work function had reached its minimum and final value of 1.80 eV.

The first ionisation potential of sulphur is 10.3 eV, so all recovery studies were carried out with $V_a < 10\text{V}$. A set of poisonings were made with $V_a = 8$ and 4V . at temperatures of 1075° , 1025° and 975°K . The poisoning time in each case was 60 secs., this time being taken to poison the emission to 10%. Another set of recoveries from poisoning at 10% for 60 secs were followed. Typical

SULPHUR POISONING OF CATHODE BZ.17



- ① $V_a = 8v$ $T = 800^{\circ}C$ POISONED SLOWLY TO 10% I_A OVER 1 MIN.
- ② $V_a = 8v$ $T = 750^{\circ}C$
- ③ $V_a = 8v$ $T = 700^{\circ}C$ POISONED AT 10% I_A FOR 1 MIN.

fig. 7. 14.

results are shown in fig (7.14).

Recovery from poisoning with the polarity of the anode voltage regularly reversed was then studied. No re-poisoning of the cathode during negative anode voltage was detectable. The second cathode behaved in exactly the same way. This is a difference from the oxygen poisoning, but as the method of detection is not very sensitive it could well be that the re-poisoning was taking place but remained undetected.

The normal recovery curves were very similar to those obtained using oxygen, the main difference being that recovery under any given conditions was slower with sulphur. The recovery at 1100°K which was very rapid with oxygen, was only 80% complete in 30 minutes with sulphur. By poisoning at 10% for 60 seconds the initial recovery rate was much lower than the rate when poisoned to 10% in 60 seconds, just as with oxygen.

7.3. Conclusions

The conclusions drawn from this work will be briefly outlined here and discussed in the final chapter. The first point made was that the results confirmed the conclusions drawn at the end of the preliminary work. A table of the work functions obtained from Richardson lines for the cathodes worked with is shown below.

The results show that poisoning of the emission by oxygen and sulphur is reversible. The recovery from sulphur poisoning is slower than that from oxygen poisoning. Sulphur is a less effective poisoning agent than oxygen but no quantitative work has been carried out on this aspect as yet. The recovery curves indicate that the poisoning is due to two processes. One is the sorption of poisoning material

on the cathode surface and the second is by diffusion of material into the cathode. As reactivation occurs the surface material is lost quite readily, giving the rapid initial increase in emission, whereas the material in the cathode diffuses out comparatively slowly, giving the gradual return to complete activation. This indicates that the pores must, in some way, contribute directly to the emission. More material will diffuse into a cathode, the longer the poisoning period and so it will reactivate more slowly, as the results show. These results appear compatible with the fact that the sulphur atom or ion is larger than the oxygen atom or ion and hence would be more difficult to diffuse into or out of the matrix. The recovery rate may also be influenced by the gas pressure in the region near the cathode surface.

Table 7.4.

Cathode	Mixture	ϕ (eV)	$A(\text{amps.cm}^{-2}.\text{°K}^{-2})$
BZ3	I	2.02	2
MV1		1.4	0.09
MV2		1.7-1.8	0.6
BZ8	II	1.65-1.75	0.02
BZ12	III	1.78	0.04
BZ13	III	1.80	0.02
BZ14	III	1.75	0.01
BZ15	III	1.71	0.02
BZ16	III	1.70	0.01
BZ17	III	1.80	0.02
BS1	IV	1.75	0.03
BS2	IV	1.73	0.01
BS3	IV	1.73	0.04

The re-poisoning of the cathode by oxygen when the voltage across the valve is reversed could be due to either the oxygen leaving the

cathode as negative ions, or some material leaving the anode and moving to the cathode. The former reason is supported by the observation that an increase in anode potential increases the recovery rate. From energy considerations sulphur should be able to ionise to about the same extent as oxygen. That such an effect has not been observed with sulphur may be due to the insensitiveness of the method employed.

PART III

Evaporation and Diffusion Rates in 'M'-cathodes

Chapter VIII

Evaporation Rates from Dispenser Cathodes

This chapter deals with work previously reported on evaporation rates from dispenser cathodes and the following chapter with diffusion rates.

A knowledge of the evaporation rate of the active material from any given cathode is essential if any estimate is to be made of its useful life. Similarly, improvements in the construction and composition of cathodes leading to increased life may be obtained only by study of the variation of evaporation rates with cathode composition and porosity. In the last two years such work on dispenser cathodes with a tungsten base has been reported from several laboratories.

8.1. The evaporation of materials

The rate of evaporation is related to the equilibrium pressure of the gas phase of the product over the solid phase by kinetic theory equations. The rate of evaporation in grams per square centimetre per second, m , from an open surface, is given by

$$\alpha m = \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} p = 43.74 \times 10^{-6} p \sqrt{\frac{M}{T}}$$

where M is the molecular weight of the evaporant, R is the gas constant in ergs.deg⁻¹, p is the vapour pressure in dynes/cm⁻², T is the temperature in °K and α is the accommodation coefficient which takes into account the mechanism of condensation of gas molecules striking the solid-gas interface. If r is the reflection coefficient, $\alpha = 1/(1-r)$.

In the case of Knudsen evaporation from an opening in a closed system in thermal equilibrium the evaporation rate is given by

$$n = \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} p = 43.74 \times 10^{-6} p \cdot \sqrt{\frac{M}{T}}$$

From thermodynamical considerations the rate of evaporation can be represented by an equation of the type

$$n = A \exp \left(- \frac{B}{T} \right)$$

where A is a constant which depends only slightly on temperature and B is a constant which is equal to ϕ_E/k , where k is the Boltzmann constant and ϕ_E is the activation energy for evaporation in electron volts. This equation may be rewritten

$$\log_{10} n = \log_{10} A - \frac{5.040 \phi_E}{T} \quad \text{--- (1)}$$

A plot of $\log_{10} n$ against $1/T$ then yields a slope from which ϕ_E may be calculated. This equation is very similar in form to the Richardson thermionic emission equation.

8.2. Measurement of evaporation rates from cathodes

The activation energy of evaporation is conveniently determined by use of equation (1). One method of measuring the evaporation rate is to collect the evaporant over a known angle in a given time and analyse the material chemically to determine the amount collected. A similar method is to include in the evaporant some radioactive material and using counting techniques estimate the amount of material evaporated. Another way is to use a mass spectrometer to measure the

the change in a given ion current when the cathode temperature is altered. A fourth technique, due to Becker,⁽⁷⁸⁾ is most commonly used to measure the evaporation of the alkaline earths from cathodes. In outline, it depends upon the evaporant being collected upon a tungsten wire from which the thermionic emission may be measured. The evaporant on the wire lowers its work function and since the wire has a minimum work function for complete or almost complete monolayer coverage, a fairly accurate estimation of the evaporation rate can be made provided that the amount of material in a monolayer is known.

The details of this method are as follows. Above the cathode is stretched a thin tungsten wire (about 0.1 mm. diameter) and between this wire and the cathode a moveable shutter is interposed. By exposing the wire to the cathode some of the evaporant from the cathode is collected on the wire. If the shutter is closed and used as an anode with the wire as cathode, the emission from the wire may be measured. The evaporant is collected for a short, measured, time, the shutter is closed and the emission from the wire is measured. This is repeated until a maximum is obtained in the plot of emission against the time for which the evaporant has been collected. This maximum corresponds to a minimum in the work function of the wire and so gives the time taken to collect a monolayer of evaporant, assuming that monolayer coverage gives a minimum work function.

This measurement is repeated for various cathode temperatures, the tungsten wire being thoroughly cleaned between each run by flashing at over 2000°C. Since the geometry of the cathode-wire

system remains unchanged and the percentage of the total evaporant collected must be the same in each case, the time for a monolayer to be collected at each temperature is directly proportional to the evaporation rate from the cathode at that temperature. Thus a plot of the times to attain monolayer coverage against the reciprocal of the cathode temperature is a straight line, if equation (1) obtains, from the slope of which the activation energy of evaporation can be found. If a minimum work function is not obtained at complete monolayer coverage, provided it always occurs at the same degree of coverage, no error is introduced in finding the activation energy since only the time to reach a minimum is used.

The Becker method affords a simple but quite accurate means of finding the activation energy of evaporation, ϕ_g . Sources of error in the experimental work are in the measurement of the cathode temperature and in the loss of activating material from the wire by re-evaporation during the measurement of the thermionic emission from the wire. This method of determining ϕ_g for the evaporants from dispenser cathodes has been used by Brodie and Jenkins,⁽⁷⁹⁾ Rittner et al.,⁽¹⁷⁾ Du Pre and Rittner⁽¹⁵⁾ and by Schaefer and White⁽¹⁴⁾ with 'L'-cathodes while Brodie and Jenkins⁽⁸⁰⁾ and Rittner et al.⁽⁵⁵⁾ have employed it with impregnated cathodes.

In the early published work on the 'L'-cathode, Schaefer and White⁽¹⁴⁾ reported measurements of the evaporation rate from these cathodes using the Becker method. For a monolayer coverage of the wire they obtained a work function of the wire of 1.58eV which agreed with the value of 1.56eV for a monolayer of barium on pure tungsten.⁽⁵³⁾

If the evaporant had been barium oxide they would have expected a work function of 1.0eV ⁽⁸¹⁾. The evaporant was collected on the wire until it was many atomic layers thick and the value of the work function obtained was 2.02eV , as compared with 2.1eV for bulk barium.⁽⁸²⁾ Hence they concluded that the evaporant was barium with no more than insignificant quantities of barium oxide.

This conclusion has been questioned by Rittner et al⁽¹⁷⁾ who suggest that the value in the literature for the work function of a monolayer of barium on pure tungsten, which is 1.56eV , is in error and should be 2.15eV , which is the value they obtained as a mean of many determinations.

In discussing the mechanism of barium transfer in the 'L'-cathode, Schaefer and White dismiss the rate of production of free barium by reduction of the oxide as the process controlling the evaporation rate since similar reductions are known to be very efficient.⁽⁸³⁾ To distinguish between the two other possibilities, the rate of Knudsen flow of barium oxide vapour into the pores of the tungsten and the rate of surface diffusion of the barium, they studied the activation energy of barium transfer. From their evaporation rate measurements they obtained an activation energy of 2.61eV per atom and since the latent heat of evaporation of barium oxide is 3.91eV ⁽⁸⁴⁾ it was concluded that the surface diffusion of barium was the limiting process. However, from the published results of the evaporation measurements the value of ϕ_g , the activation energy, is not 2.61eV but 2.83eV . This error in calculation of a value upon which the reasoning was based nullifies Schaefer and Whites argument and coupled with the more recently deter-

mined value for the work function for barium on pure tungsten as compared with the value which they used leads to their proposed mechanism of operation of the 'L'-cathode lacking general support.

Du Pre and Rittner⁽¹⁵⁾ proposed that Knudsen flow through the pores and surface diffusion played important roles in the transport mechanism. The findings of Rittner's group were published after extensive work had been carried out⁽¹⁷⁾. The Becker method was used to determine the evaporation rate from an 'L'-cathode containing barium oxide only. The wire was calibrated as an absolute detector of barium by chemical methods, firstly by acidimetric titration and then by means of a manual polarograph. From a high porosity cathode (28% porous) the activation energy obtained was 3.25 eV and for a lower porosity cathode (17% porous) the activation energy was 3.00 eV. Addition of strontium oxide led to a reduction in the mass evaporation rate by a factor of 17.5.

A polarographic analysis of the evaporation products revealed barium as the only metallic constituent. By measuring the reducing power of a sample of the evaporant by determining the chemically equivalent quantity of hydrogen evolved on exposure to water vapour, the content of free barium was found. The total barium content was then measured acidimetrically and polarographically and from the difference between these results and that from the reducing power the barium oxide content was determined. It was found to be from 33-44 mole% with the 28% porous cathodes and 52 mole % with the 17% porous cathodes. The presence of strontium did not alter the large oxide content of the evaporant. For a 24.5% porous cathode the oxide content computed as barium oxide was 50%.

These results do not agree with those of Schaefer and White⁽¹⁴⁾. The value of ϕ_g is higher and the evaporant is found to contain up to 50% of barium oxide where Schaefer and White found only negligible amounts.

The conclusions reached by Brodie and Jenkins⁽⁷⁹⁾ are similar to those of Rittner et al.⁽¹⁷⁾ In their work on evaporation from the 'L'-cathode, Brodie and Jenkins determined the cathode temperature by means of an optical pyrometer and correcting for absorption by the glass for various heater currents before starting measurements. The cathode was aged for several hours and was held at the measuring temperature for half an hour prior to taking readings. The mass per unit area of monolayer of evaporant was estimated by an electrolytic method and a value of $3.5 \times 10^{-8} \text{ gm.cm}^{-2}$ was obtained. This is slightly greater than the value obtained by De Boer⁽⁵²⁾ of $2.3 \times 10^{-8} \text{ gm.cm}^{-2}$, but may be due merely to a difference in composition of the evaporants.

Two types of tungsten discs were used in the measurements. One type was 25% porous and the other 45% porous. Measurements were made on cathodes containing barium oxide only and on others containing barium and strontium oxides. The results obtained from the barium oxide cathodes are interpreted as revealing that in some circumstances the evaporation rate is not limited by the transport mechanism, as suggested by Schaefer and White⁽¹⁴⁾ and by Rittner,⁽¹⁸⁾ but by the chemical reaction rate. This is based upon the result that with 45% porous tungsten the evaporation rate was the same for 0.5 mm. and 1.0 mm. thick discs. The observed activation energy was 3.5eV compared with 3.25eV obtained by Rittner.⁽¹⁷⁾ With 25% porous discs the evaporation was found to be

limited by the transport mechanism. The observed value of ϕ_R for these cathodes was 3.1eV. By comparing the evaporation from a cathode made with a 2 mm. thick, 45% porous disc and that from 1.25 mm. thick, 25% porous disc, the evaporation rates are about 3.5:1 and indicate that Knudsen flow is the predominant transport mechanism. The authors suggest that had the evaporation rate been limited by surface migration then the ratio would have been 1:3.

With cathodes containing the double-oxide the evaporation rates are higher in each case, in contradiction to Rittner et al⁽¹⁷⁾, and it is concluded that all these cathodes have their evaporation limited by Knudsen flow since the activation energies and evaporation rates are in the ratio of the Knudsen flow rates. Strontium oxide has little effect on the equilibrium reaction vapour pressure of barium but increases the maximum reaction speed at a given temperature. This makes it possible to maintain the equilibrium pressure even with 45% porous tungsten which was not possible with barium oxide alone.

The rate of evaporation from the impregnated cathode, in contrast to the 'L'-cathode is strongly time-dependent. Almost all of the total barium evaporates at a rate given by a $t^{-\frac{1}{2}}$ law. Levi⁽²⁴⁾ was the first to report on the evaporation from the impregnated cathode. He found that the addition of 5 moles of calcium oxide to the eutectic barium aluminate mixture gave a fourfold reduction of barium evaporation at a given temperature. Over the first 2000 hours of life the evaporation averaged 2×10^{-10} gms.Ba.cm⁻².sec⁻¹ at 1465°K. Brodie and Jenkins⁽⁴⁾ reported that the addition of $\frac{1}{2}$ mole of calcium oxide caused an almost negligible reduction in the barium evaporation rate. The authors

suggest that the variation from Levi's ⁽²⁴⁾ results is possibly due to the greater porosity of the tungsten disc together with the lower proportion of calcium oxide. This would also account for the fact that the barium evaporation from these cathodes was $1.7 \times 10^{-9} \text{ gm.cm}^{-2} \cdot \text{sec}^{-1}$ at the beginning of life at 1465°K compared with Levi's value of $2 \times 10^{-10} \text{ gm.cm}^{-2} \cdot \text{sec}^{-1}$.

In a later paper, ⁽⁸⁰⁾ Brodie and Jenkins reported further work on the evaporation from impregnated cathodes using various impregnants. The evaporant from barium aluminate cathodes behaved, as far as emission and migration characteristics were concerned, as if it consisted of barium with only a small proportion of barium oxide. The value of ϕ_E was 3.70-3.96 eV. With cathodes impregnated with barium-calcium aluminate it was found that the initial report that calcium oxide did not reduce the evaporation rate was in error and that further results had confirmed Levi's work ⁽²⁴⁾. With an impregnant of composition $3 \text{ BaO} \cdot \text{Al}_2\text{O}_3 + \frac{1}{2} \text{ CaO}$, the value of ϕ_E was 4.21 eV, the same value also resulting when an impregnant of $3 \text{ BaO} \cdot \text{Al}_2\text{O}_3 + 1 \text{ CaO}$ was used. These values of ϕ_E show an increase of 0.25 eV over the value of 3.96 eV obtained when an impregnant of $3 \text{ BaO} \cdot \text{Al}_2\text{O}_3$ was used. Another set of measurements was made on cathodes containing impregnants of $2\frac{1}{2} \text{ BaO} \cdot \text{Al}_2\text{O}_3$ together with 0 CaO , $\frac{1}{2} \text{ CaO}$ and $1\frac{1}{2} \text{ CaO}$. The values of ϕ_E obtained were 3.81 eV, 4.18 eV and 4.48 eV. respectively. The final batch employing the aluminate were made up from $3.7 \text{ BaO} \cdot \text{Al}_2\text{O}_3$ with 0 CaO and $\frac{1}{2} \text{ CaO}$, giving values of ϕ_E of 3.70 eV and 3.80 eV respectively. Measurements were made on silicate cathodes, the impregnant consisting of $3 \text{ BaO} \cdot \text{SiO}_3$ with 0 CaO and with $\frac{1}{2} \text{ CaO}$. ϕ_E

was 4.21eV in each case, although the accuracy of the result for the pure silicate is suspect as the evaporation rates at the higher temperatures were decaying quite rapidly with time and repetition of measurements gave poor reproducibility. It appeared that the calcium oxide decreased the evaporation rate to about twice that for the aluminates cathodes at a given temperature. The life of the pure silicate cathodes was quite short, probably due to the barium-producing reaction being inhibited by the reaction products. The addition of calcium oxide eliminated this and gave enhanced emission.

The evaporation rates from cathodes of various thicknesses impregnated with $3\text{BaO} \frac{1}{2}\text{CaO} \text{Al}_2\text{O}_3$ were measured and the results showed that, at the beginning of life at least, the barium produced is proportional to the disc thickness and the reaction, therefore, must take place uniformly through the disc. Thus barium must be leaving the site of the reaction fairly freely. The conclusion drawn by the authors is that since the impregnant closes the pores the transport of barium must be by migration along the interface between the tungsten and not by Knudsen flow as in the 'L'-cathode. As the barium is leaving the reaction site freely, the reaction rate must be limited by reaction kinetics and not by the production of an equilibrium reaction pressure of barium.

Rittner, Rutledge and Ahlert⁽⁵⁵⁾ have studied the evaporation from the barium aluminate impregnated cathode. The evaporant was first analysed by use of a manually operated polarograph. Barium was the only element detected in front of the plug and the evaporant from the rear of the plug contained some aluminium as well, presumably

from the heater coating. 60% of the total barium evaporated came from the front of the plug. The method of Rutledge and Milch⁽⁸⁵⁾ was used for determining the absolute instantaneous evaporation rate of total barium and the average fraction of barium oxide. At several stages during life evaporant from a cathode at 1190°C was collected on a tungsten wire and the time for maximum emission from the wire to be obtained was found. At the end of life the evaporant from the front of the cathode was analysed polarographically and acidimetrically for total barium. Results indicated an average barium oxide content of 44%.

By plotting the logarithm of the barium evaporation rate against the logarithm of time a straight line was obtained up to a time of 2000 hours. The slope of this line was $-0.52 \text{ gm.cm}^{-2}.\text{sec}^{-2}$. Beyond 2000 hours the data lay below this line and at 7,500 hours the evaporation rate fell rapidly towards zero. From emission tests the life of the cathode was found to be 7,500 hours. The time dependence of the evaporation rate is in marked contrast to that from the 'L'-cathode. Brodie and Jenkins⁽⁸⁰⁾ made their measurements at the beginning of life so this effect was not noticed.

Rittner et al.⁽⁵⁵⁾ obtained a much greater evaporation rate from their impregnated cathode over the first few hundred hours of life than from the 'L'-cathode. Over this initial period ϕ_E was 3.1eV; this value did not appear to be a function of cathode age. The impregnant used in these cathodes had the composition $5\text{BaO}.2\text{Al}_2\text{O}_3$, for which composition Brodie and Jenkins obtained a value of ϕ_E of 3.81eV. Rittner and his co-workers conclude that since the observed evaporation rate is large compared with the evaporation rate from a completely

covered tungsten surface and since the evaporation rate decreases rapidly with time despite constant barium oxide coverage, as implied by constant emission during life, the dominant process is Knudsen flow rather than surface migration of adsorbed barium oxide. The observed time dependence of the evaporation rate is then accounted for by assuming that the reaction zone sinks from the cathode surface as material is evaporated out of the pores leaving partially blocked lengths of pores which increase with time. This produces an increasing impedance to the transport of barium from the reaction site to the cathode surface giving a decreasing evaporation rate and ensuring maintenance of equilibrium conditions in the reaction zone.

The authors then derive an expression for the rate of flow of material by Knudsen flow through the partially blocked pores. The mass rate of flow is given by

$$\frac{dm}{dt} = K_1 (r_e/L) P^{(M/T)^{1/2}} \quad \text{--- (1)}$$

where M is the molecular weight of the material, T is the absolute temperature, K_1 is a geometric constant, r_e is the effective pore radius, L is the length of this pore and P is the equilibrium pressure of $(Ba + BaO)$. P , M and T are time independent and r_e is to a first approximation. L is proportional to the total mass, m , evaporated

$$\text{therefore } m = K_2 L \quad \text{--- (2)}$$

$$\text{therefore } \frac{dm}{dt} = K_3 / m \quad \text{--- (3)}$$

$$\text{where } K_3 = K_1 K_2 r_e P^{(M/T)^{1/2}}$$

Integrating for initial conditions $t = 0, m = 0$

$$m = (2K_3 t)^{\frac{1}{2}} \text{ --- --- --- --- --- } (4)$$

and from (3) $dm/dt = \left(K_3/2t\right)^{\frac{1}{2}}$

Hence, if this holds, a plot of the logarithm of the evaporation rate against the logarithm of the time should give a straight line with a slope of $-\frac{1}{2}$. A slope of -0.52 was obtained between 1 and 2000 hours. The fall in points below this line after 2000 hours is attributed to a decrease in the value of K_2 or of r_e .

In their work on the pressed cathode Hughes and Coppola⁽³³⁾ find that the addition of molybdenum to tungsten reduces the evaporation rate from the cathode. The evaporation rate of barium and barium oxide from a cathode with a 100% molybdenum matrix was $30 \mu\text{gas.cm}^{-2}.\text{hr}^{-1}$, and for a 100% tungsten cathode the value was $100 \mu\text{gas.cm}^{-2}.\text{hr}^{-1}$. The relationship between evaporation rate and the molar concentration of tungsten was linear and the authors assumed that the evaporation product in the case of pure molybdenum was almost pure barium oxide while the increase due to the presence of tungsten consisted of barium.

No results have been reported for evaporation rate measurements from dispenser cathodes having a nickel base, but it is useful to consider briefly the main points arising from similar work on oxide-coated cathodes. One of the earliest workers in the field was Becker⁽⁷⁸⁾ who obtained values of the evaporation rate of barium from an oxide cathode of $0.1 \mu\text{gas.cm}^{-2}.\text{hour}^{-1}$ at 1200°K and $14 \mu\text{gas.cm}^{-2}.\text{hour}^{-1}$ at 1400°K . These measurements were made on cathodes on platinum-iridium cores in which there were no reducing agents to provide excess barium.

A higher evaporation rate would be expected from a cathode on a nickel base and this has been found by Kawamura⁽⁸⁶⁾ who used Becker's method and found an evaporation of $7.5 \mu\text{gms.cm}^{-2}.\text{hour}^{-1}$ at 1200°K . The rate of evaporation was found to be independent of the thermionic current drawn but to depend on the secondary structure of the crystal and upon the core material. The value of ϕ_g was 2.9 eV for equimolecular barium-strontium oxide and 3.9 eV for barium oxide. It was concluded that molecular barium oxide was evaporated from the cathode.

To distinguish between metallic barium and barium oxide Jenkins and Newton⁽⁸⁷⁾ used a chemical which excluded the oxide and they obtained a value of $4 \mu\text{gms.cm}^{-2}.\text{hour}^{-1}$ at 1225°K for the evaporation rate of barium. Plumlee and Smith⁽⁸⁸⁾ used mass spectrometric techniques to study the evaporation products from oxide coated cathodes. They found that the thermal evaporation depended upon the thermal history of the cathodes. In early stages of life the evaporation from triple oxide cathodes was largely of barium compounds, some barium atoms and less strontium. The barium compounds were barium oxide and barium chloride, the evaporation of the latter gradually dying away. The largest Ba^+/BaO^+ ratio observed was 2:1 and this decreased after several hours. Cathodes on nickel bases had a strontium evaporation rate almost as high as that of barium. A small calcium evaporation was also noticed.

Aldrich⁽⁸⁹⁾ studied the evaporation products of barium oxide heated on ribbon filaments of platinum, tantalum, nickel, molybdenum and tungsten and of strontium oxide on platinum using a high resolu-

tion mass spectrometer for positive ion analyses. The ratio Ba^+/BaO^+ was measured for each base material as a function of temperature and of the energy of the ionising electrons to determine the origin of each ion peak observed. The results indicated (a) only on systems barium oxide on platinum, barium oxide on nickel and strontium oxide on platinum were the evaporation processes reproducible without particular attention to procedure; (b) the two systems barium oxide on platinum and strontium oxide on platinum differ markedly in their evaporation mechanisms; (c) at high temperatures peaks are found due to Ba_2O^{++} , Ba_2O^+ , Ba_2O_2^+ and other barium compounds depending on the base metals used; (d) a measurable ion current was found due to Sr^+ ions evaporated from platinum.

In some later work, Pelchowitch⁽⁹⁰⁾ used a mass spectrometer to study the evaporation from alkaline-earth oxides coated on various metal ribbons. The evaporant was mainly barium oxide when this oxide was coated on nickel or platinum, or with the other alkaline-earth oxides on platinum. Barium peroxide is evaporated from the BaO/Pt system at high temperatures. It was found that plots of the logarithm of the evaporation rate against reciprocal temperature gave two straight lines in some cases, indicating two activation energies, one predominating at higher temperatures and the other at lower temperatures. This applied to the evaporation curve for barium oxide from all the systems on platinum containing barium oxide. The junction of the two slopes was at a temperature of 1250°K . This was not found with barium oxide on nickel but the author suggests that the nickel base metal evaporates through the

porous barium oxide and that the evaporation rate curve of nickel behaves critically at 1250°K . Resistance measurements of the systems were then made using oxide layers pressed between metal electrodes. The previously discovered transition points were found to appear quite definitely in resistance against temperature plots.

The evaporation products found by Pelchowitch agree both with Aldrich⁽⁸⁹⁾ and Plumlee and Smith⁽⁸⁸⁾. No explanation is suggested of the transition phenomena reported in the work. Leverton and Shepherd⁽⁹¹⁾ used a different technique. They employed radioactive tracers to study the evaporation of the alkaline earths from oxide coatings on passive nickel bases. A few percent of the total cathode barium, strontium and calcium was found to leave a triple oxide cathode during processing and ageing. The rates of transfer of these elements from the cathode during life tests of 118 hours at cathode temperatures from 1175° to 1279°K obeyed the normal evaporation rate equations. The mass of barium transferred in 118 hours at 1123°K was $2.9 \times 10^{-6} \text{ gm.cm}^{-2}$, and from a cathode containing barium oxide only was $1.4 \times 10^{-5} \text{ gm.cm}^{-2}$ at this same temperature. The masses of strontium and calcium evaporated from the triple-oxide cathode were 2.1×10^{-7} and $1.2 \times 10^{-8} \text{ gm.cm}^{-2}$, respectively. The evaporation was reduced by breakdown and flashing in argon at a pressure of a few millimetres Hg.

Peterson,⁽⁹²⁾ too, used isotopes of barium and strontium to measure the evaporation rate from oxide-coated cathodes. A collector was shielded from the cathode by a removable electrode during activation and ageing. Cathodes were run at 855°C for 118 hours. It

was found that over a range of molar compositions of barium from 20% to 50% the evolution of barium was independent of composition Affleck and Holroyd⁽⁹³⁾ used Ba^{140} in barium oxide cathodes and found that the time rate of deposition for a given cathode temperature was constant. This was achieved by use of a tube with several moveable collectors.

Wooten, Ruchle and Moore⁽⁹⁴⁾ measured the rates of evaporation of barium and strontium from oxide cathodes during life-tests up to 20,000 hours. The conclusions reached were that the product evaporating under normal conditions is largely barium metal with less than 5% strontium, less than 2% barium oxide and less than 0.01% strontium oxide. The chemical reducing agents present in the nickel support were found to play an important role in determining the barium evaporation rate. Another factor which affected the rate markedly was the composition of the anode and grid. This had not previously been closely controlled. No correlation was found between the barium evaporation rate and the thermionic activity of individual cathodes and no effect on the evaporation rate was produced by the space current.

The conclusions drawn from this review are that the evaporant from dispenser cathodes containing barium oxide alone consists of barium oxide as well as barium, despite the suggestion of Schaefer and White⁽¹⁴⁾ to the contrary. Results from the 'L'-cathode indicate that the percentage composition of the evaporant does vary with cathode porosity, the more porous the cathode the less the oxide content of the evaporant. The evaporation rate, too, increases with cathode porosity up to a porosity of about 45% when it is

limited by the chemical reaction rate. If strontium oxide is present, this limitation does not occur. Evaporation from impregnated cathodes obeys a $t^{-\frac{1}{2}}$ law over the first few thousand hours of life. The addition of calcium oxide to the impregnant reduces the evaporation rate. Rittner et al.⁽⁵⁵⁾ report that the average barium oxide content of the evaporants is 44%, while Brodie and Jenkins⁽⁸⁰⁾ find that the oxide content is only a small proportion of the total evaporant. The barium producing reaction is found to occur uniformly throughout the tungsten disc. The evaporation rate from the impregnated cathode is much greater over the first few hundred hours of life than from the 'L'-cathode.

Results are thus leading to a conception of the forms in which active material is lost from cathodes. With a knowledge of the variations of the evaporation rate and the thermionic properties with both composition and porosity a stage will be reached when cathodes may be produced to serve economically any particular requirements and so replace the culinary art which has existed in the manufacture of cathodes.

Chapter IX

Diffusion Rates through Dispenser Cathodes

No previous work on the direct measurement of the diffusion rates of the alkaline earth metals through dispenser cathodes has been published. However, values of the diffusion rate have been estimated from evaporation rate measurements and have also been measured for oxide-coated cathodes by several workers. The diffusion rate of the activating material through the metal to the surface is of major importance if, at any stage during cathode life, it is the controlling factor of the emission or of the evaporation from the cathode. The measurement and interpretation of its effects upon the cathode performance are fairly straight-forward for dispenser cathodes in which the reservoir is below the porous metal disc, but for cathodes in which the reservoir of activating material is actually in the pores of the disc, the problem is more complex since the initial boundary conditions cannot be defined. In this chapter such work as has been reported is considered.

9.1. Diffusion in metals

The initial diffusion theory was based upon the realisation that for diffusion to occur between two points there must exist a difference in concentration between them. The analogy with the transfer of heat by conduction was recognised by Fick⁽⁹⁸⁾ who adapted Fourier's equation for heat conduction to give the two well-known diffusion equations (see (95), (96), (97)).

The equations are based on the hypothesis that in isotropic substances the rate of transfer by diffusion through unit area of cross-section is proportional to the concentration gradient normal

to the section. This gives the first equation directly

$$F = -D \frac{\partial C}{\partial x} \quad \text{---} \quad (1)$$

where F is the rate of transfer per unit area of section, C is the concentration of diffusing substance, x is the space co-ordinate measured normal to the section and D is called the diffusion coefficient. The negative sign indicated that diffusion takes place down the concentration gradient.

The second and more general equation is derived from this

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad \text{---} \quad (2)$$

where $\frac{\partial C}{\partial t}$ is the rate of accumulation of the diffusing material at a point where the concentration gradient is $\frac{\partial C}{\partial x}$. If the assumption is now made that D is independent of concentration, equation (2) becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{---} \quad (3)$$

This equation is found to be strictly valid only for self-diffusing systems. Equation (2) is the one applicable to interdiffusing metal systems and the one most suitable for representing diffusion processes. If D does vary with concentration the equation may be written

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 f(C)}{\partial x^2} \quad \text{---} \quad (4)$$

where a suitable form for the function of the concentration is found so that D_0 is a true constant.

By integration a solution of equation (3) is found. It is

$$C = \frac{A}{t^{\frac{1}{2}}} e^{-x^2/4Dt} \quad \text{--- (5)}$$

where A is an arbitrary constant. If M_d is the total amount of substance diffusing in a cylinder of infinite length and unit cross-section, it is given by

$$M_d = \int_{-\infty}^{\infty} C \cdot dx.$$

If the concentration distribution is given by equation 5, on writing

$$\begin{aligned} x^2/4Dt &= y^2 & dx &= 2(Dt)^{\frac{1}{2}} dy \\ \text{then} & & M_d &= 2AD^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-y^2} dy \\ & & &= 2A (\pi D)^{\frac{1}{2}} \quad \text{--- (6)} \end{aligned}$$

Substituting for A from (6) in (5)

$$C = \frac{M_d}{2(\pi Dt)^{\frac{1}{2}}} e^{-x^2/4Dt} \quad \text{--- (7)}$$

In the problem involved, the diffusion through cylindrical metal bodies, the cathode approximates to a semi-infinite cylinder extending over the region $x > 0$ with an impermeable boundary at $x = 0$. The solution for negative values of x is taken to be reflected in the plane $x = 0$ and superposed on the original distribution in $x > 0$. The concentration for the semi-infinite cylinder is given by

$$C = \frac{M_d}{(\pi Dt)^{\frac{1}{2}}} e^{-x^2/4Dt} \quad \text{--- (8)}$$

The observed temperature dependence of the measured diffusion coefficient is found to follow the form

$$D = D_0 e^{\frac{-\phi_D}{RT}} \quad \text{--- (9)}$$

where D_0 is practically independent of temperature. If it is not, then two or more mechanisms of diffusion are usually operative. The value of ϕ_D , the activation energy, is found by measuring the slope of a plot of $\log D$ against $1/T$. Both D_0 and ϕ_D depend upon the concentration so it is important to plot for a series of values of $1/T$ values of $\log D$ measured all at the same concentration. Very many measurements give some mean value of D over a range of concentration so that the activation energies calculated from these data will also be mean values over the same range.

9.2. Measurement of diffusion rates in cathodes

To determine the activation energy of diffusion, ϕ_D , diffusion is allowed to take place for a known time at a fixed temperature and then the concentration of the diffusing substance is estimated at successive distances from its point of origin. If the logarithm of the concentration is plotted against x^2 , then from equation (8) the slope of the resulting curve is equal to $-1/4Dt$. Thus D can be found. If this is repeated for several temperatures a plot of $\log D$ against $1/T$ gives a slope from which ϕ_D may be calculated by use of equation (9).

There are several methods of determining diffusion coefficients. In all of them successive thin layers of material parallel to the original interface are removed in some way and their composition determined by a convenient method such as chemical, quantitative spectrographic, X-ray analysis, mass spectroscopic analysis or micro-

radiography. The change in certain properties such as ionic emission, photoemission, reflectivity, electrical resistance, the X-ray diffraction pattern and changes in the Curie point may also be utilized. The method employed with cathodes is that generally used for self-diffusion. This involves the diffusion of a radioactive isotope from a known point of origin into the cathode which is then sectioned and the abundance of active material in each section is determined by use of a Geiger-Müller or similar counter. Knowing the percentage by which the radioactive isotope is present in the total diffusible material and assuming that the radioactive atoms behave in exactly the same way as the unactive material then the concentration of material in each section can be calculated from the count. If only a value of D is required, since this is determined from the slope of the graph, it suffices to plot the logarithm of the activity of each section against x^2 .

The diffusion of materials in oxide cathodes was invoked to explain several observed effects before any direct measurements were made and the diffusion of barium plays a major role in several proposed theories to explain the mechanism of such cathodes. Becker and Sears⁽⁹⁹⁾ suggested that barium diffused through an oxide cathode to maintain an optimum concentration of barium at the cathode surface. Hermann and Wagener⁽⁶⁰⁾ calculated the diffusion coefficient for an alkaline earth oxide coating from the ionic mobility and obtained $D \approx 2.5 \times 10^{-11} \text{ cm}^2 \cdot \text{sec}^{-1}$ at 1225°K .

Some of the earliest direct measurements applicable to the oxide cathode were made by Redington⁽¹⁰⁰⁾ who measured the diffusion rate

of barium in single crystals of barium oxide over the temperature range $550^{\circ} - 1520^{\circ}\text{K}$ and the surface diffusion rate of barium in the same temperature range. A radioactive tracer technique, employing ^{140}Ba , was used. The crystals were sectioned by means of a microtome for the internal diffusion measurements. For the surface diffusion measurements a movable slit system was used to scan the distribution of the surface. It was found that the barium diffusion took place by two defect mechanisms. Only the combination of the interstitial atom and the barium vacancy defects gave a correct phenomenological account of the observations. The energy required to form an interstitial barium atom and a barium vacancy was $23^{\pm} 5\text{eV}$ assuming that the identification of the barium vacancy was $1.7^{\pm} 0.3$ electronic charges. The value obtained for the activation energy of surface diffusion was $0.16^{\pm} 0.03\text{eV}$. Redington suggests that in oxide cathodes of particle size less than 0.2μ diameter surface diffusion can be expected to be the predominate diffusion process at about 1000°K .

These results were used by Sproull, Bever and Libowitz⁽¹⁰¹⁾ in conjunction with their own results to determine the diffusion process which gives the blue colouration to barium oxide crystals. They concluded that this process does not transfer barium and that the principal lattice defects in barium oxide with excess metal are oxygen vacancies.

A continuation of Redington's work using an oxide-coated cathode in place of a single barium oxide crystal was carried out by Bever⁽¹⁰²⁾. The results from this work indicated that two diffusion processes

were operative, one predominating above 1280°K and the other below that temperature. The activation energy was $4.1 \pm 0.6\text{eV}$ for the higher temperature mechanism and $0.40 \pm 0.07\text{eV}$ for the lower one. D lay between $3 \times 10^{-9}\text{cm}^2.\text{sec}^{-1}$ at 1490°K and $1.5 \times 10^{-12}\text{cm}^2.\text{sec}^{-1}$ at 740°K . There is a difficulty in applying these results to elucidate the theory of the oxide cathode since a barium excess in the cathode can also be created by the diffusion of oxygen vacancies.

The diffusion rates of various elements in nickel have been measured. Lander, Kern and Besch⁽¹⁰³⁾ used carbon in nickel and obtained the relationship between D and temperature

$$\ln D = 0.909 - 20,200/T$$

over the temperature range $700 - 1,300^{\circ}\text{C}$. The diffusion was measured by finding the rates of evolution of carbon monoxide and carbon dioxide liberated by carbon from nickel oxide coatings.

Peterson, Anderson and Shepherd⁽¹⁰⁴⁾ have reported on the importance of the diffusion rates of reducing agents from the base nickel in the chemical activation of oxide cathodes and found that the strontium evaporation rate provides a direct indication of the rate of reduction of the coating. The values of D_0 and θ_D obtained for the various metals are summarised in table I. The full description of the diffusion rate measurements in this work was given by Swalin and Martin⁽¹⁰⁵⁾.

In a later paper⁽¹⁰⁶⁾ a model of the cathode was proposed to explain these results. One interesting conclusion drawn by Peterson from this work was that a bulk diffusion process occurs in the oxide crystals during chemical activation and that either the surface ad-

Table I

Reducing Agent	$D_0(\text{cm}^2.\text{sec}^{-1}.)$	$\phi_D(\text{eV})$
Al	1.87	2.78
Mg	0.44	2.46
Ti	0.86	2.67
Mu	7.50	2.92
W	11.10	3.34
Mo	3.00	2.99
Si	1.50	2.68

sorption energy for free barium on the oxide crystals is 3.3eV or that the bulk diffusion coefficient is much less than the value given by Redington⁽¹⁰⁰⁾ for barium in barium oxide.

The diffusion of tungsten in nickel has recently been measured by Allison and Moore⁽¹⁰⁷⁾. They used ¹⁸⁵W in single and polycrystalline nickel over a temperature range 1,100 - 1,275°C. Radioautographs were used to observe grain boundary diffusion. For volume diffusion the value of ϕ_D obtained was 3.09eV and $D_0 = 1.13 \text{ cm}^2.\text{sec}^{-1}.$, compared with Swalin and Martin's 3.34eV and $11.1 \text{ cm}^2.\text{sec}^{-1}.$ Only two measurements were made on diffusion through polycrystalline nickel and these indicated a diffusion rate higher by a factor of 3 than volume diffusion at temperatures above 1100°C. Radioautographs showed clearly grain boundary diffusion. Attempts to measure surface diffusion were unsuccessful.

As previously mentioned no measurements of the diffusion rates through dispenser cathodes have been made although in the theories proposed for the mode of operation of these cathodes diffusion of barium along the pore walls, together with Knudsen flow through the

pores, is suggested as the transport mechanism. In the following chapters the attempt to make such measurements is described.

Chapter X

Techniques

The experimental work on evaporation and diffusion is divided into six sub-sections. Different types of tube were constructed in an attempt to measure:- (a) the evaporation and diffusion rates in the 'M'-cathode matrix using ^{140}Ba , (b) the evaporation from the cathode using the Becker method⁽⁷⁸⁾ to ascertain if the results agreed with those from the use of the isotope, (c) the surface diffusion rate of the isotope over nickel, (d) the diffusion rate through the cathode matrix in the presence of argon at a pressure of about 400 mm.Hg., and (e) the effect of a deflecting electrostatic field upon the evaporation rate. The sixth section concerns an autoradiographic study of the barium distribution through a cathode and at the cathode surface.

The construction of the various tubes is described and the method of making measurements on each type is outlined. The initial section deals briefly with the precautions taken when working with the radioactive material to prevent any risk of contamination and this is followed by a short section on the chemical preparation of the 'labelled' barium carbonate.

10.1. Protective precautions

The use of radioactive isotope, ^{140}Ba , in the experimental work necessitated the removal of apparatus to an isolated room, so positioned that other personnel and apparatus were unaffected by any radiation inside the room. This room was converted into a tracer laboratory. The maximum amount of ^{140}Ba present in the laboratory at any one time

RADIATION DATA



BARIUM 140:—

Half Life 12·8 days.

Type of radiation:

Energy in MeV:

beta	gamma
0·48 (40%)	0·03
1·02 (60%)	0·13
	0·16
	0·30
	0·54

decays to La^{140}

LANTHANUM 140:—

Half Life 40·2 hours.

beta	gamma
0·42 (16%)	0·33 (24%)
0·86 (12%)	0·49 (46%)
1·15 (20%)	0·82 (26%)
1·36 (30%)	0·89 (1%)
1·62 (14%)	1·60 (96%)
2·20 (8%)	2·57 (4%)

was 1 millicurie but a large safety factor was allowed in taking the described precautions.

The floor of the laboratory was coated with Perreko floor paint (British Paints Ltd.) to fill all cracks and pores and to facilitate washing down in the case of a spill. The bench at which the necessary chemistry was carried out was covered by a single sheet of aluminium to avoid cracks in which active material could accumulate and for the ease of washing down. The room was well ventilated to give an adequate air-flow rate.

The decay scheme for ^{140}Ba is shown in fig (10.1.1) the principal radiation emitted from the protection point of view being the γ -radiation. The active material was stored in a lead castle which, in turn, was surrounded by lead blocks $1\frac{1}{2}$ inches thick. This ensured that there was very little chance of any activity from the isotope not in immediate use being detected in the laboratory. All measurements on the activities of samples in the experimental work were carried out in a separate counting room. The high toxicity of ^{140}Ba , if present in the human body, is due to its accumulation in the bone marrow and the possible malignant consequences of its presence in such a vital region. Strict precautions were taken to avoid it being ingested or entering the body through cuts or abrasions.

Rubber gloves were worn whenever active material was handled. They were washed with soap and water after use while still on the hands and the 'surgical technique' was applied in putting on the gloves or removing them. A pair of CeeVee reachers, 3 ft. long, were employed to handle the millicurie of material whenever possible. An overall buttoning to the neck was worn. A film, supplied and developed

fortnightly by the Radiological Protection Service, was always carried. A quartz fibre electroscope was also carried to give an idea of the accumulated γ -radiation to which the body had been exposed. The laboratory was monitored daily, when working with the isotope, with a hand radiation monitor, type 1118A, to check for any spills or residual activity. All waste was stored for at least 100 days, i.e. 8 times the isotope half-life, and then monitored before disposal by burial.

A difficulty arose in mounting valves containing 'active' cathodes on the pumping system. No glass blowing using a mouth-operated blow tube was possible. This was overcome by the use of a foot-operated bellows which proved an adequate substitute. When the valves were on the pumping system or on the bench they were screened by lead shielding.

10.2. Preparation of the barium carbonate

The radioactive material was obtained from the Isotopes Division, A.E.R.E., Harwell, in the form of barium chloride in 0.1N. hydrochloric acid. Immediately the isotope was received it was diluted by making up its volume to 150 mls. with 0.1N. hydrochloric acid in which 27.8 gms. of Analaar barium chloride was dissolved. This gave 10^{-10} gms. of active material in 0.2 gms. of barium chloride. From this it follows that 1 count per minute was equivalent to 5.5×10^{-9} gm. barium before the active material began to decay.

25 mls of the barium chloride solution were taken by means of a pipette, using a filter pump to draw the active solution into the pipette. The remainder of the solution was placed in a lead castle, until required. To the 25 mls of solution 85 mls, a slight excess,

of a normal solution of ammonium carbonate were added. Barium carbonate was precipitated and the filtrate was removed using a filter pump. The precipitate was washed thoroughly several times with distilled water and dried. The carbonate was then placed in an airtight container in a lead castle and used as required. The only impurity of consequence liable to have been left in the carbonate was chlorine but adding excess ammonium carbonate and the thorough washings should have reduced chlorine present to a negligible amount.

10.3. Evaporation and diffusion rate measurements using ^{140}Ba .

The type of valve used for these measurements is shown in fig (10.3.1). A normal 'M'-cathode was not used in this work since it would have been very difficult to have carried out any diffusion measurements upon a cathode in which the active material was initially evenly distributed throughout the nickel matrix. Instead, the barium carbonate was pressed on to the back of a nickel disc containing 0.1% silicon which had been processed in exactly the same way as an 'M'-cathode. After breakdown of the carbonate and activation the thermionic properties of this type of cathode are very similar to those of the 'M'-cathode and it was assumed that when fully activated the two types are identical in their mode of operation. The validity of this assumption is discussed in Chapter 12.

The valves took the form of simple, planar diodes with an anode consisting of a 2 cm. diameter 'O'-nickel disc which could be rotated to one side of the tube by use of an external magnet acting on a magnet slug fixed on the opposite end of an arm to the anode. This exposed a second 2 cm. diameter 'O'-nickel disc to the cathode. The second disc was fixed about 1 mm. above the anode such that when the

anode was in position the fixed collector was completely shielded from evaporant from the cathode. This arrangement was much more convenient than a moveable collector only as it enabled thermionic measurements to be made on the valve. The anode-cathode separation was about 1 mm. as in previous valves. The separation between cathode and collector was measured with a cathetometer. All metal components were hydrogen furnace before use.

The cathode was produced by pressing nickel powder into one end of a weighed, 0.5 cm. internal diameter '0'-nickel tube to give a plug about 3 mm. thick. The tube plus powder was weighed to determine the mass of the powder. Onto the back of the disc was then pressed 0.25 gm. of the 'labelled' carbonate. A piece of thin '0'-nickel sheet was pressed on to the back of the carbonate to protect the heater which was inserted in the remaining cavity. The cathode, heater and thermocouple were mounted on a 7 pin, FK 10, C9 glass pinch supplied by Edison Swan, Ltd. The moveable anode was supported on one end of an 18 S.W.G. '0'-nickel arm 1.5 cm. long on the other end of which a magnetic slug encased in C9 glass was held by means of an '0'-nickel strip around it. Across the centre of this arm, and perpendicular to it, was spot-welded 2 cm. of 1.0 mm. diameter tungsten rod. This assembly formed the rotatable part of the valve structure.

The ends of the tungsten rod rested in small glass cups constructed so that the tungsten had no lateral motion but was rotatable. The glass cups had narrow '0'-nickel bands around them which were spot-welded to 18 S.W.G. nickel supports. These supports were spot-welded to the pinch leads. A piece of 0.25 mm. diameter '0'-nickel

wire coil was welded at one end to the anode arm and at the other to one of the nickel supports to serve as an anode lead. The fixed collector was also supported from the pinch by 18 S.W.G. '0'-nickel wire. Two barium getters were attached to the assembly near the pinch and the whole assembly sealed into a C9 glass envelope, type T64/195.

The valve was sealed onto the pumping system, pumped out and baked for 4 hours at 420°C as in the previous experiments. A 24 hour breakdown of the carbonate was also carried out as before. Activation consisted of running the cathode at 950°C for another 24 hours with 250 volts applied between cathode and anode, after which the thermionic emission from the cathode was constant at a few milliamperes. The supplies were then switched off, the valve re-baked for 4 hours at 420°C and the metal parts eddy-current heated. The getters were outgassed and then fired and the valve was sealed off from the system.

On the bench the cathode was held at a fixed temperature for 25 hours, no emission being drawn, with the collector exposed to the cathode for a known period of this time in short intervals to prevent the collector becoming too heated and losing material by re-evaporation. After 25 hours the cathode heater was switched off, the valve was opened and the collector was carefully removed. Several counts were then made on the collector with the apparatus described in Chapter IV.

The absolute value of the count from the collector was found in order to determine the evaporation rate in $\text{gas.cm}^{-2}.\text{sec}^{-1}$. The counting rate recorded on the scaler, N , is connected with the disintegration rate,

GROWTH CURVE FOR SYSTEM $^{140}\text{Ba}-^{140}\text{La}$

↑
COUNTS / SEC

$$D = \frac{0.693N_0}{T_1} \left[2^{-t/T_1} + \frac{T_1}{T_1 - T_2} \left(2^{-t/T_1} - 2^{-t/T_2} \right) \right]$$

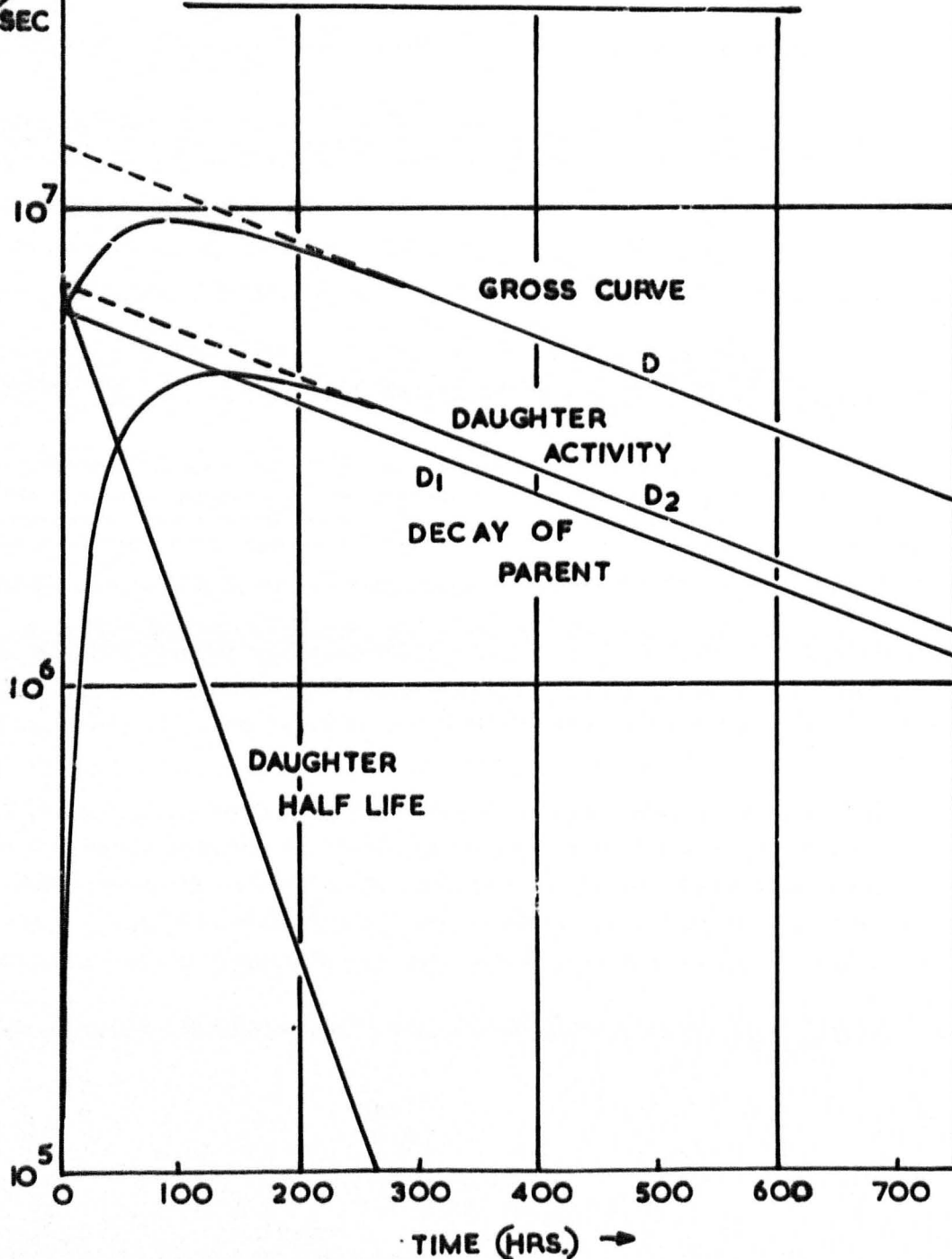


fig. 10. 3. 2.

D_1 by

$$N = D_1 E_c f_t f_B f_w f_s$$

where E_c is the efficiency of the counter, f_t is the correction factor for the dead time of the counter, f_B is the correction factor for back-scattering, f_w is the correction factor for absorption in the air and in the counter window and f_s is the correction factor for self absorption in the sample.

If a very thin sample is used, f_s may be neglected. The value of the term $E_c f_B f_w$ was determined by use of a standard β -ray source, ^{36}Cl , in the same position with respect to the counter and in the same sample holder as the samples to be counted were placed. 10 counts of 10,000 were made with the standard source which gave a standard deviation $< 1\%$. The standard source was accurate to only $\pm 3\%$. The backscattering and absorption in the air and the counter window were then the same for all cases and could be included with the counter efficiency. The value of this factor for the Geiger-Müller tube used was 2.11%. The only factor which had to be calculated each count was that correcting for the dead time of the counter. A value of D_1 could then be obtained from the observed value, N . From this the actual amount of barium on the collector could be calculated since the degree of decay of the material was read off from the decay chart shown in fig. (10.3.2) and the mass equivalent to 1 count min^{-1} was known.

The percentage of the total evaporant from the cathode which had been collected was determined theoretically. If a is the distance between the cathode and collector, b is the radius of the collector and c is the radius of the cathode, the fraction C' , of the maximum solid angle,

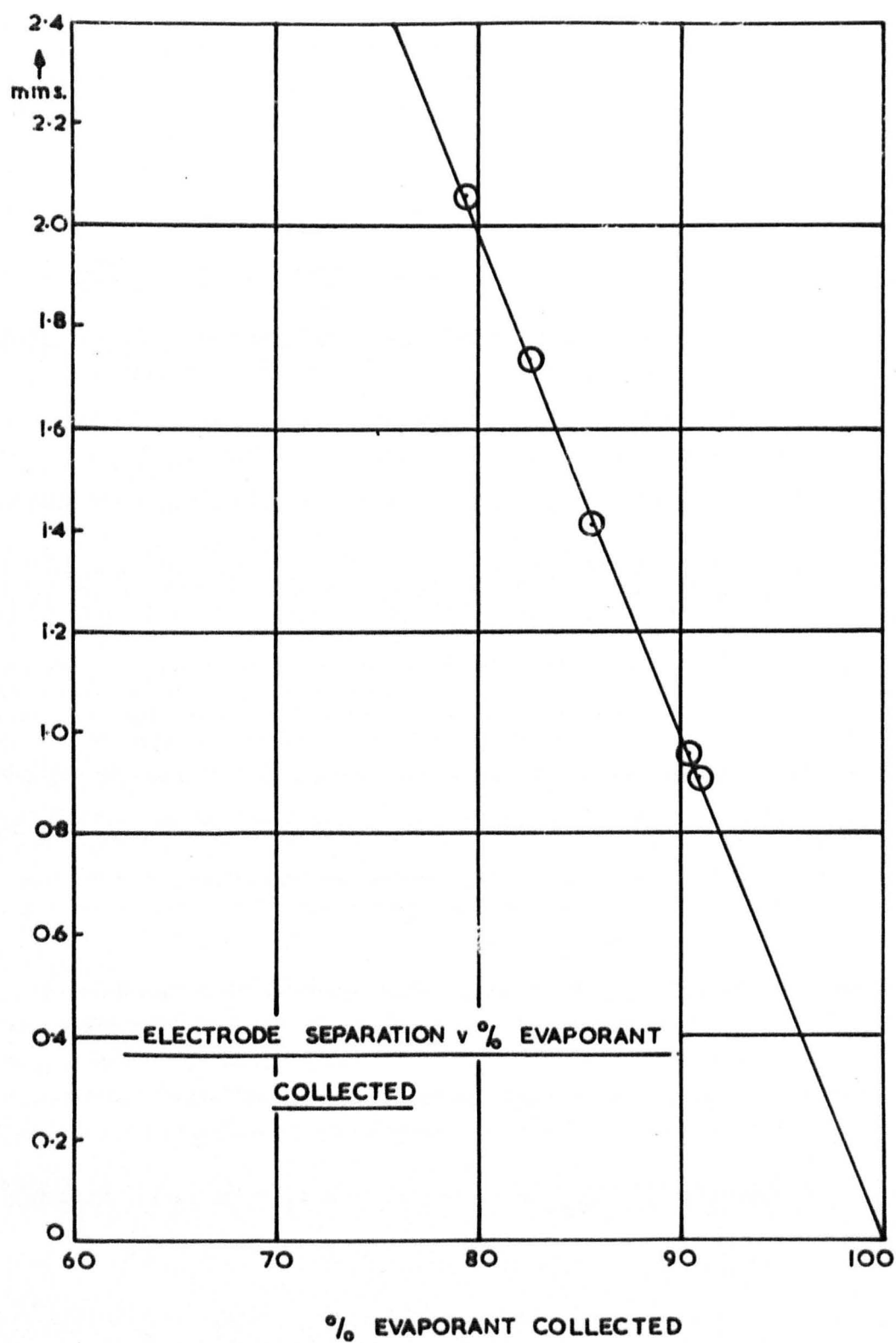


fig. 10. 3. 3.

2π , between cathode and collector is given by

$$G' = 0.5 \left[1 - \frac{1}{(1+\beta)^{1/2}} - \frac{3}{8} \frac{\gamma \beta}{(1+\beta)^{5/2}} - \gamma^2 \left(-\frac{5}{16} \frac{\beta}{(1+\beta)^{7/2}} + \frac{35}{65} \frac{\beta^2}{(1+\beta)^{9/2}} \right) - \gamma^3 \left(\frac{35}{128} \frac{\beta}{(1+\beta)^{9/2}} - \frac{345}{256} \frac{\beta^2}{(1+\beta)^{11/2}} + \frac{1155}{1024} \frac{\beta^3}{(1+\beta)^{13/2}} \right) \right]$$

where $\beta = b^2/a^2$ and $\gamma = c^2/a^2$. In the arrangement used the collector radius was 1.0 cm. and the cathode radius was 0.25 cms. in all cases, so a graph, fig (10.3.3), was plotted of G' in percentage of evaporant collected against the cathode-collector separation so that the percentage of the total evaporant collected in any tube could be read off directly. The evaporation rate from the cathode was thus found and the result gave a point on a plot of the logarithm of the evaporation rate against the reciprocal of the temperature. The results from several such valves run at different temperatures gave a straight line from the slope of which the activation energy of evaporation, β_E , was found.

The cathode was carefully removed from its cylinder and all active material remaining between the cathode and the nickel disc at the rear was cleaned away. The outer layers around the sides of the cathode were skimmed off on a lathe to remove any material which had diffused along the surface between the cathode and the cylinder. The thickness of the cathode was measured with a micrometer screw gauge and from this, together with the mass of powder used and knowing the cathode diameter and the density of nickel, the porosity of the cathode was calculated from the formula stated in section 3.3.

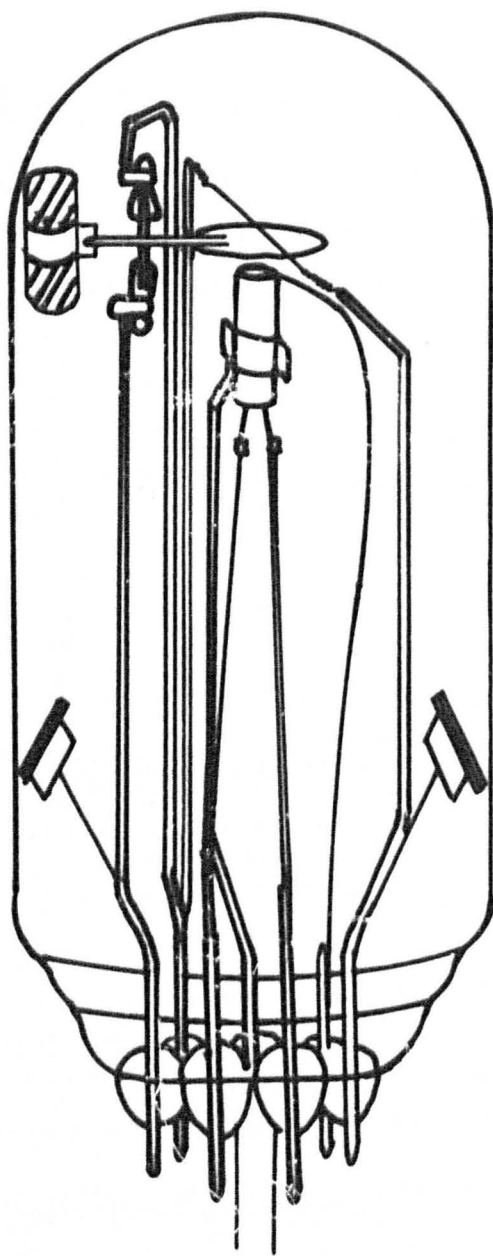


fig. 10. 4. 1.

A lathe ($\frac{1}{2}$ " Boxford Precision lathe) was used to section the cathode and sections as thin 0.01 mm could be cut. With the first two cathodes a microtome was tried but it was impossible to cut a section of even thickness due to the hardness of the nickel. The section thickness was determined by measuring the cathode thickness before and after taking the section. The turnings were collected as each section was cut and after the whole cathode had been sectioned counts were made on each section to determine the amount of barium present in each. The mean of five counts on each sample was taken. A graph was plotted of the logarithm of the counting rate against x^2 , where x was the distance from the base of the cathode to the centre of the section. A profile of the distribution of barium throughout the cathode thickness resulted. The slope of this graph gave the value of the diffusion coefficient for that particular temperature. The diffusion coefficients for cathodes at various temperatures were obtained and by plotting the logarithm of the diffusion coefficient against the reciprocal of the temperature the activation energy of diffusion, ϕ_D , was obtained from the slope. Each valve of this type yielded one point on the graph for ϕ_D and one point on the graph for ϕ_D .

10.4. Measurement of evaporation using the Becker method (note)

Tubes were built to measure the evaporation rate by the Becker⁽⁷⁸⁾ method, described in Chapter 8, to verify the results obtained by use of the isotope. A diagram of such a tube is shown in fig (10.4.1). The cathode was constructed in the same manner as described in the last section except that Analar barium carbonate was used instead of the 'labelled' carbonate. This was mounted on an FK10 pinch and a moveable

shutter, the same as described in section 10.3, was positioned about 1 mm. above the cathode. A 0.18 mm. diameter tungsten wire about 2.5 cms. long with a short length of tungsten spring at each end to keep the wire taut when at higher temperatures was mounted between two 18 S.W.G. nickel supports horizontally and symmetrically over the cathode above the shutter. A tungsten-nickel thermocouple was used, as before, to measure the cathode temperature. Two barium getters were inserted near the base of the assembly which was sealed in a C9 glass envelope, mounted on the pumping system and baked at 420°C for 4 hours.

The breakdown and activation procedure followed the same pattern as with the previous tubes. After ageing the valve was again baked, the metal parts were eddy-current heated, the getters outgassed and fired and the valve was sealed off. The tungsten wire was flashed at a temperature over 2000°C to clean it. The cathode was held at some fixed temperature and after 30 minutes the shutter was opened for 2 minutes and then closed. The tungsten wire had a current passed through it which had been predetermined to give a wire temperature of 600°C as measured by an optical pyrometer. 12 volts were applied between the wire (cathode) and the shutter (anode) and the emission from the wire was measured by means of a sensitive galvanometer, ($1\mu\text{amp} = 417\text{ cms}$) lamp and scale and a universal shunt. The current through the wire and the voltage supply were cut off, the wire was exposed to the cathode for another two minutes and another emission measurement was made. This was repeated until the emission from the wire passed through a maximum. The maximum emission cor-

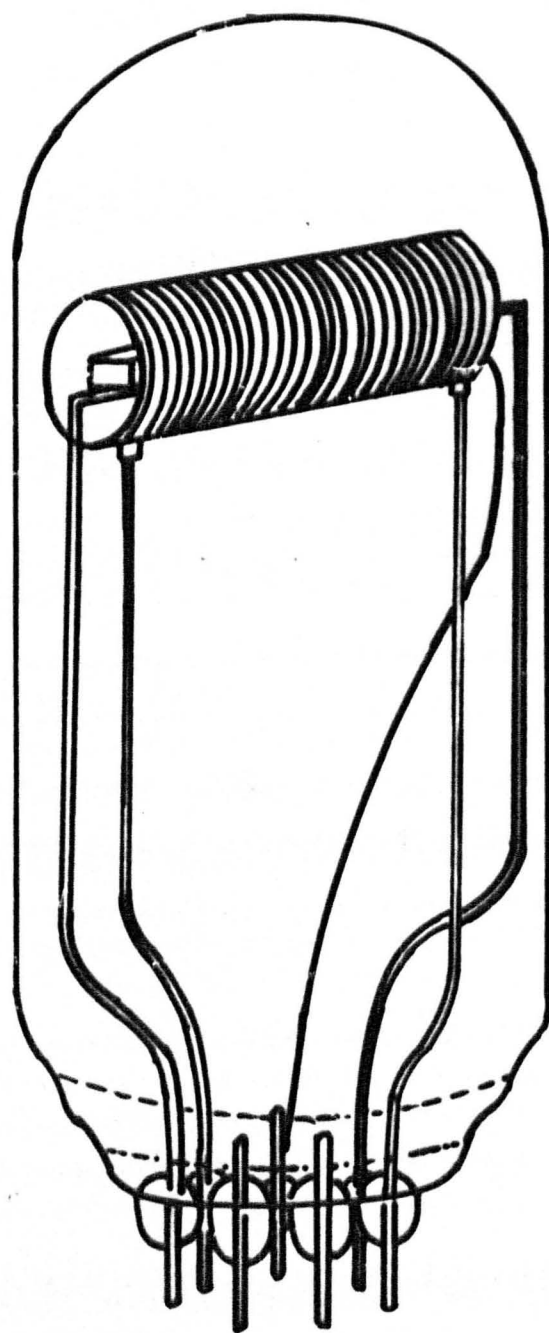


fig. 10. 5. 1.

responded to total or almost total monolayer coverage of the wire. Knowing the time to obtain this and assuming Brodie and Jenkins⁽⁷⁹⁾ value for the mass per area of monolayer, the evaporation rate could be calculated.

The wire was then cleaned by flashing several times, the cathode was raised in temperature and the procedure repeated. Thus with one tube it was possible to carry out a range of measurements at different temperatures to obtain a value for ϕ_E . To obtain ϕ_E it was only necessary to plot the logarithm of the time taken to obtain monolayer coverage against the reciprocal of the temperature, the slope of the graph giving ϕ_E .

10.5. Surface diffusion measurements.

The surface diffusion rate of ^{140}Ba over nickel was measured in the type of tube shown in fig (10.5.1). The nickel bar was manufactured by pressing the 4 - 5 μ cathode nickel powder into bar form by means of a punch and die. The pressure was applied by a fly-press, as for the cathodes. A weighed amount of nickel powder was used. The nickel was sintered in a tubular furnace in an atmosphere of hydrogen at 1100°C for an hour. The bar dimensions were taken and its porosity calculated. Bars of about 12% porosity were selected to correspond with the porosity of the cathodes. A selected bar was machined to give a rectangular cross-section 6 mm. wide by 3 mm. deep. The length of the bar was about 3.0 cm. A small step was cut in one end of the bar on which the active barium carbonate was placed. The edge of this step was clearly defined as all distance measurements were made from it. A retaining strip of 'O'-nickel was

welded around the edge of it to prevent any active material from spilling.

The bar was inserted centrally in a ceramic tube of internal diameter 1.2 cm and length 5 cm. The wall thickness was 1.5 mm. These tubes were supplied by Messrs. Bullers, Ltd. On the outside of the tube was wound a coil of nichrome strip, $1/32 \times 0.0124$ ins. and resistance $4.20 \text{ ohms.yd}^{-1}$. As much wire as possible was used. Two 18 S.W.G. nickel supports held the ceramic tube in place and served as leads to the coil. The temperature of the nickel bar was measured in the usual way by a tungsten-nickel thermocouple, the tungsten wire being spot-welded as near to the surface of the bar as possible to the step. The whole assembly was mounted on an FK10 pinch and sealed in a C9 envelope.

All diffusion was carried out with the valve on the pumping system. The valve was baked for 4 hours at 420°C and, after cooling, an alternating current was passed through the heater coil, control being exerted by means of a Variac transformer running off the mains. The maximum bar temperature that was attained was 650°C . The bar was heated at a constant temperature for 48 hours. The pressure in the system was always less than 10^{-6} mm.Hg. during the diffusion run. Some of the nichrome evaporated in this time onto the inside of the envelope but the bar was protected from this evaporant by the ceramic tube.

After 48 hours running the heater was switched off, the valve removed from the system and opened. The step was machined off after any radio-active material was cleaned away. The surfaces on the sides

and bottom of the bar were skinned to remove any active material which may have diffused over them. Sections across the top surface of the bar were taken by means of the lathe. These could be cut to a width of 0.01 mm. The depth to which they were taken was 0.5 mm. All turnings were collected and five counts made on each sample, the mean being taken. A graph was then plotted of the logarithm of the activity of the sample against the square of the distance of the sample centre from the step edge. The slope of the resulting plot gave a value of the diffusion coefficient at that particular bar temperature. By obtaining the diffusion coefficients at various temperatures and plotting the logarithm of them against the reciprocal of the temperature, the activation energy of surface diffusion, ϕ_s , was obtained from the slope.

10.6. Diffusion in the 'M'-cathode in the presence of argon.

To elucidate the results obtained from the measurement of the diffusion rate of barium in the 'M'-cathode, described in section 10.3., it was decided to repeat these measurements when the cathode was in argon at a pressure of some hundreds of mm.Hg. The mean free path of argon at 400 mm.Hg. is 0.2μ which is much smaller than the expected average pore diameter in the cathode. The valves were made in the same way as described in section 10.3. except that the moveable anode was dispensed with and the fixed collector was moved to within about 1 mm. from the cathode.

Two tubes were made up and a side arm containing a constriction and a breakable internal seal was put on each envelope. The tubes were mounted on the pumping system with the side arms parallel and

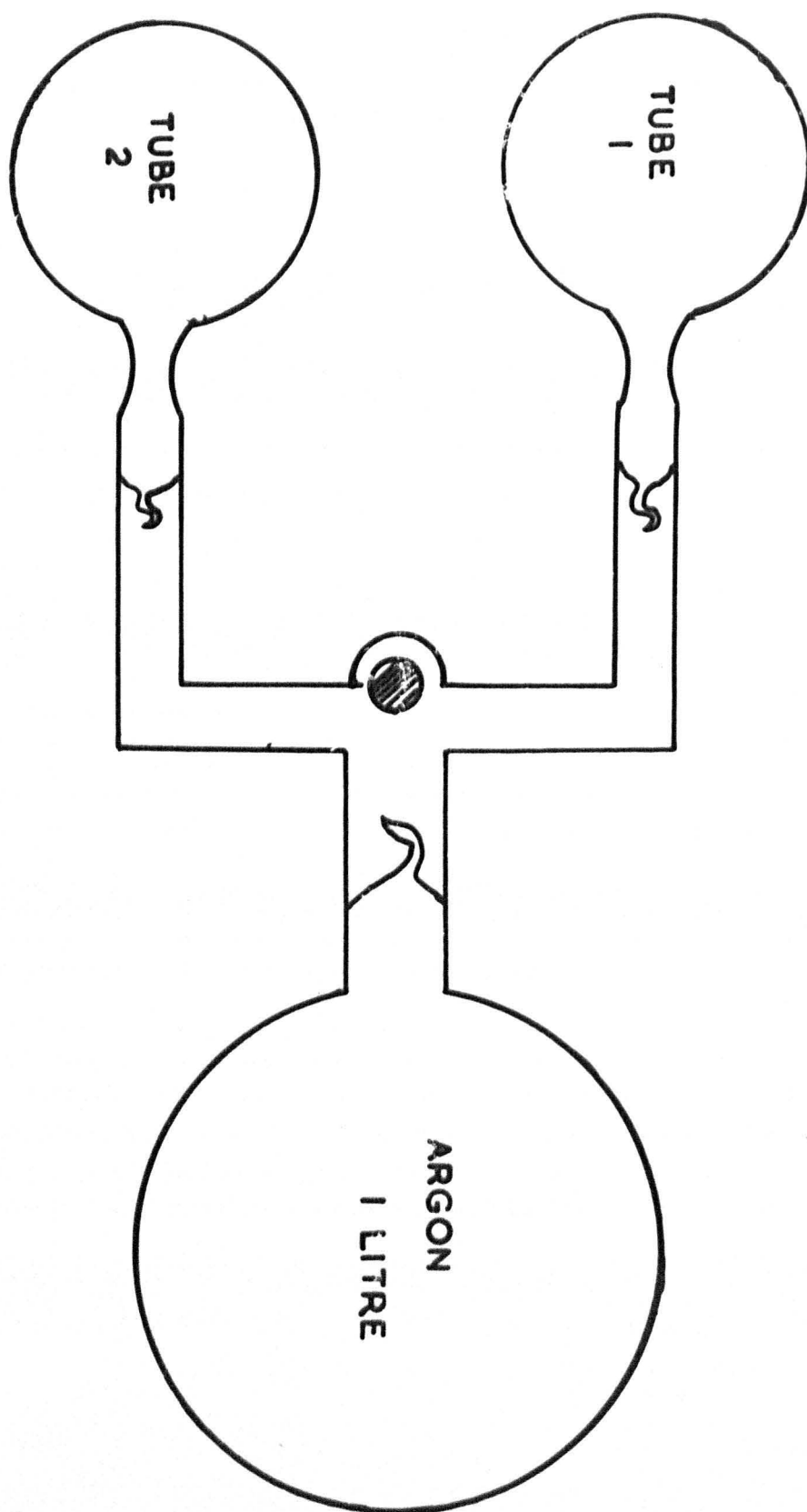


fig. 10. 6. 1.

about 10 cm. apart. The tubes were linked to a litre flask of argon at atmospheric pressure, as shown in fig (10.6.1), by means of a T-piece of glass tubing. A breakable internal seal was included in the neck of the argon flask. A magnetic ball was placed in this T-tube to serve as a breaker. The two seals in the side arms on the tubes were broken to pump down the tubing between the valves and the argon. This system was baked for 4 hours at 420°C and the metal parts then eddy-current heated. The carbonate was broken down and the cathode activated in exactly the same way as described in section 10.3. The tubes were rebaked at 420°C for 4 hours, the metal parts were eddy-current heated, the getters in each tube were cut-gassed and fired and the two tubes were sealed off from the pumping system.

The internal seal to the argon flask was broken releasing gas into both tubes. Each tube was then sealed and drawn off from the argon system at the constriction. The cathodes were heated to a fixed temperature and left for 25 hours. The maximum temperature obtainable with argon in the tubes was just over 1000°C . After 25 hours the heaters were switched off, the valves opened and the cathodes sectioned as before. The diffusion coefficients were found in the usual way. The pressure of the argon in the valves was estimated to be just over half an atmosphere i.e. about 400 mm.Hg., since the volume of the two valves and connecting glass tubing was not quite one litre.

10.7. The effect of an electrostatic field on the evaporation rate

To obtain information as to whether any of the evaporant was in an ionised form it was decided to study the effect of an electric

field on the evaporation rate. The field necessary to produce a deflection of 1.0 cm. in a distance of 0.5 cm on a beam of singly charged barium ions when the deflecting plates are 5.0 cm. apart is 60 volts.

The type of tube used in these experiments was the same as those for the Becker measurements described in section 10.4, (fig.(10.4.1)), but in addition two rectangular '0'-nickel plates 4.5 cm by 3 cm. were positioned 4 cm. apart, one on each side of the cathode-wire system. The cathodes were processed in exactly the same way as before and after seal-off two measurements were made of the evaporation rate at a given temperature, as before. A voltage was then applied between the two deflector plates and the evaporation rate measured twice more. This procedure was repeated for several temperatures. Any difference with and without the applied field in the evaporation rate must then be due to ions being deflected away from the collecting wire.

10.8. Autoradiographs of the barium distribution in an 'M'-cathode

Cathodes were produced as described in section 10.3. and mounted with a fixed anode 1 mm. away from their surface. The valves made up from these cathodes were processed in the same way as those for the diffusion measurements. Valves were opened at various stages during activation of the cathodes and after complete activation. The cathodes were removed and very carefully placed face downwards on a piece of stripping emulsion from a Kodak autoradiographic stripping plate AR50 resting on a glass slide. This arrangement was placed under a portable X-ray machine and exposed to a 2/5 second burst of 10KV X-rays which outlined the cathode on the film. The cathode, film

and slide were fastened firmly together by means of cello tape, wrapped in black paper and put in a dark place. The times of exposure ranged from several hours up to a week. At the end of the exposure time the film was unpacked in the dark and developed in undiluted Kodak developer, D196 for 6 minutes. The film was immersed in clean water for a minute, fixed for 15 minutes, washed in running water for 15 minutes and then allowed to dry in a dust free atmosphere.

Prints could be taken off the negative using whatever enlargement was required. The manufacturers quote the optimum resolution obtainable with the AR50 emulsion as being of the order of 12 microns. As well as obtaining a picture of the cathode surface by this method an idea of the distribution of barium through the cathode was obtained by sectioning a cathode down the centre and placing both semi-cylinders face downwards on the film which was then developed. The active parts of the cathode showed white on the prints.

This section concludes the description of the various techniques employed in the evaporation and diffusion studies and the results obtained from the use of these are now considered.

Chapter XI

Results

The results from this work are conveniently divided into two main sections, the first containing the results of evaporation rate measurements and the second those of diffusion rates. The former section is sub-divided to cover three types of measurements; the evaporation rate as determined by use of ^{140}Ba and by the Becker method, and the effect of an applied electrostatic field on the evaporant. The latter section deals with the diffusion of ^{140}Ba through 'M'-cathodes both in vacuum and in argon and with the surface diffusion of ^{140}Ba over nickel. The techniques involved in making these measurements were given in the last chapter so this chapter consists of a summary of the results obtained.

11.1.1. Evaporation rate measurements using ^{140}Ba .

The type of tube used for these measurements is described in section 10.3 and shown in fig (10.3.1). Since the half-life of ^{140}Ba is 13 days it meant that for each delivery of isotope the experimental work had to be completed 3 weeks after receiving the tracer. The tubes were prepared prior to receiving the isotope so that all that was necessary was to press the active material onto the back of the cathode disc and mount the cathode in the assembly, evacuate and seal off the tube. The first batch of tubes built differed from those described in section 10.3 in that the collector was rotatable, no shutter being incorporated. The cathode-collector separation was about 1 mm. in these tubes. In table I are shown the results for the evaporation rate obtained from the first eleven tubes which were all made using the first delivery of the isotope.

Table I

Tube	Temp °C	Evaporation Rate ($\text{cm. cm}^{-2} \cdot \text{sec}^{-1}$)
T7	1030	1.62×10^{-8}
T11	1020	1.44×10^{-8}
T9	1000	7.29×10^{-9}
T12	1000	2.30×10^{-8}
T.6	950	9.10×10^{-8}
T.5	925	1.60×10^{-8}
T.4	900	6.52×10^{-9}
T.8	900	1.66×10^{-8}
T.2	875	7.25×10^{-9}
T.3	875	6.56×10^{-9}
T15	850	7.12×10^{-9}

The values obtained for the evaporation rates had quite a large scatter for cathodes running at the same temperature and the dependence upon temperature when the logarithm of the evaporation rate was plotted against $1/T$ was only vaguely apparent. The best line through the points indicated an activation energy of evaporation of 0.96eV. With one of the later tubes of this group a thermocouple was included on the centre of the lower face of the collector and its temperature measured when over the cathode. With the cathode running at 1000°C the collector temperature was almost 600°C. This suggested that the inconsistency in the results may be due to an appreciable amount of the collected material being re-evaporated. To overcome the heating of the collector it was decided to have a fixed collector at twice the distance from the cathode and to interpose a moveable shutter between the two. The type of tube shown in fig (10.3.1) was therefore made. The shutter was opened for short, timed periods to expose the collector to the cathode. This method was found very ef-

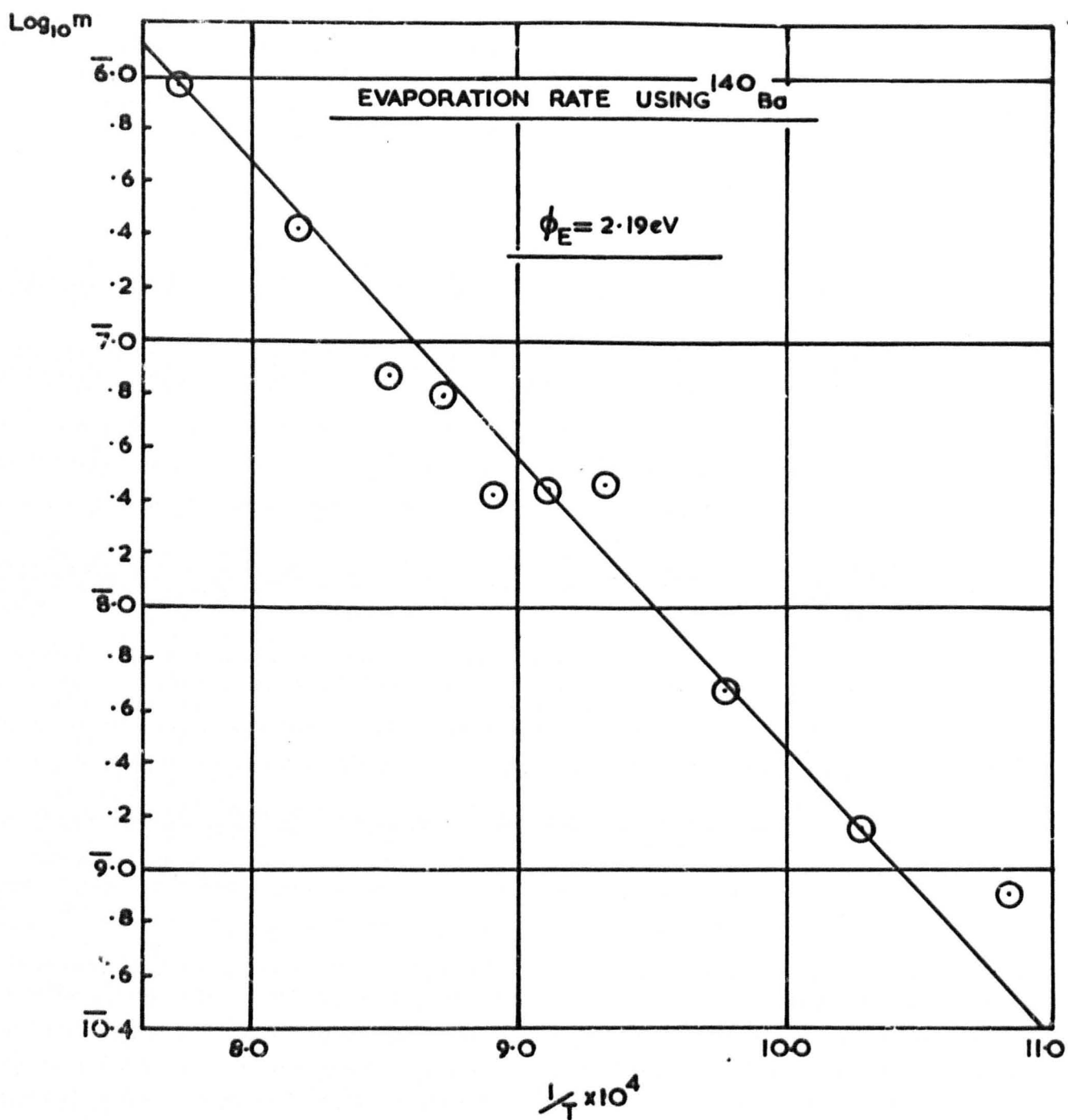


fig. 11. 1. 1.

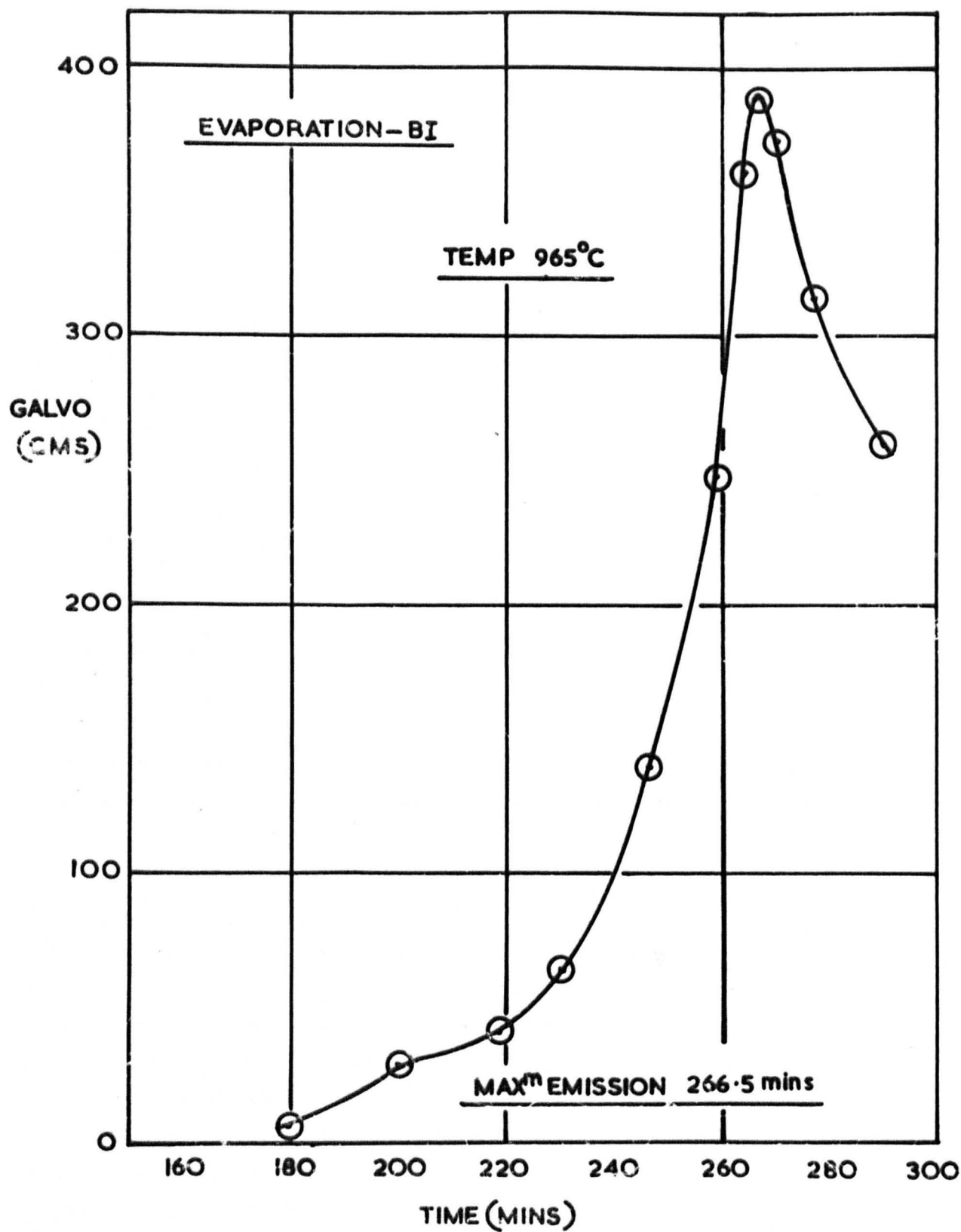


fig. 11. 1. 2.

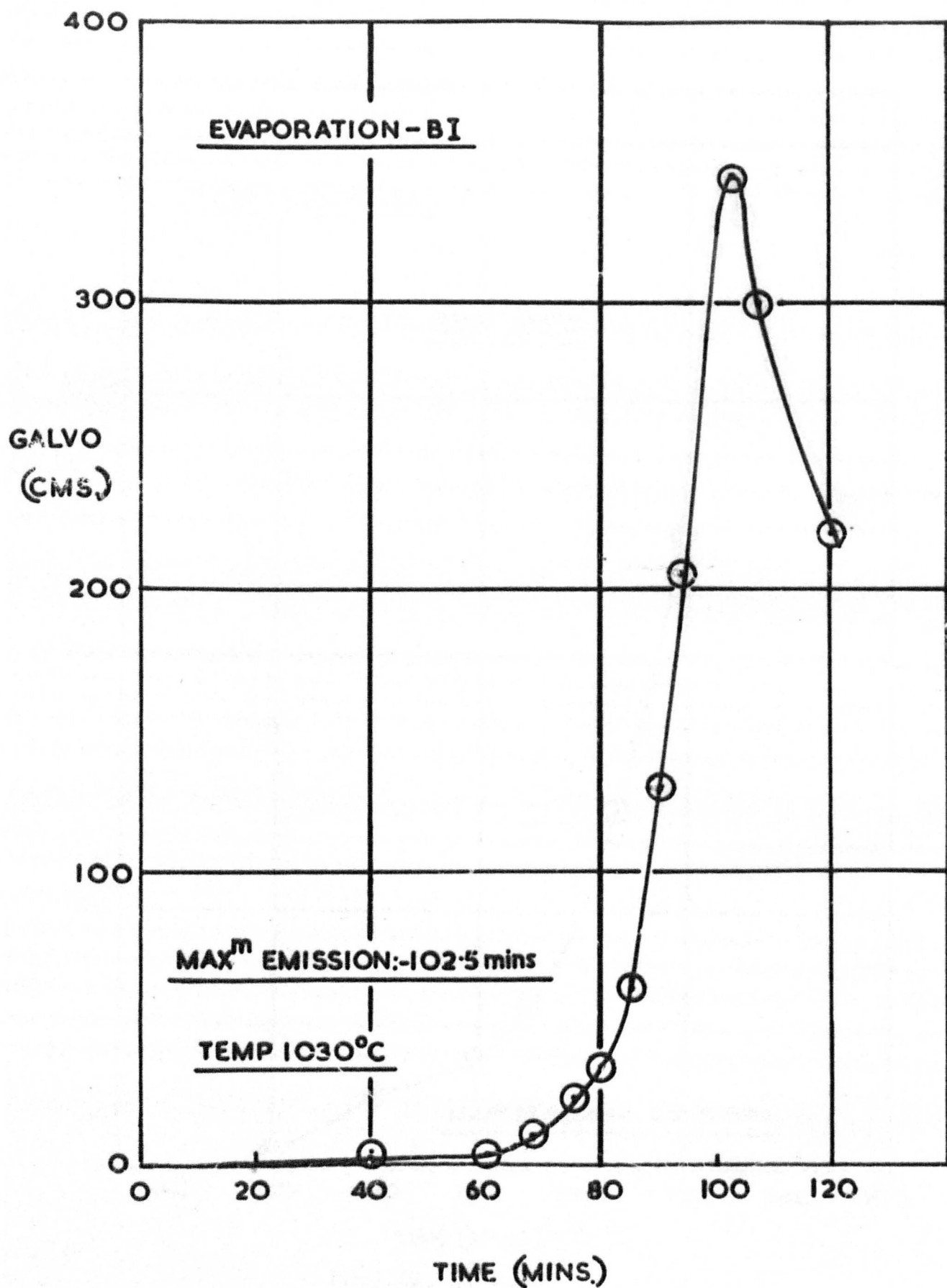


fig. 11. 1. 3.

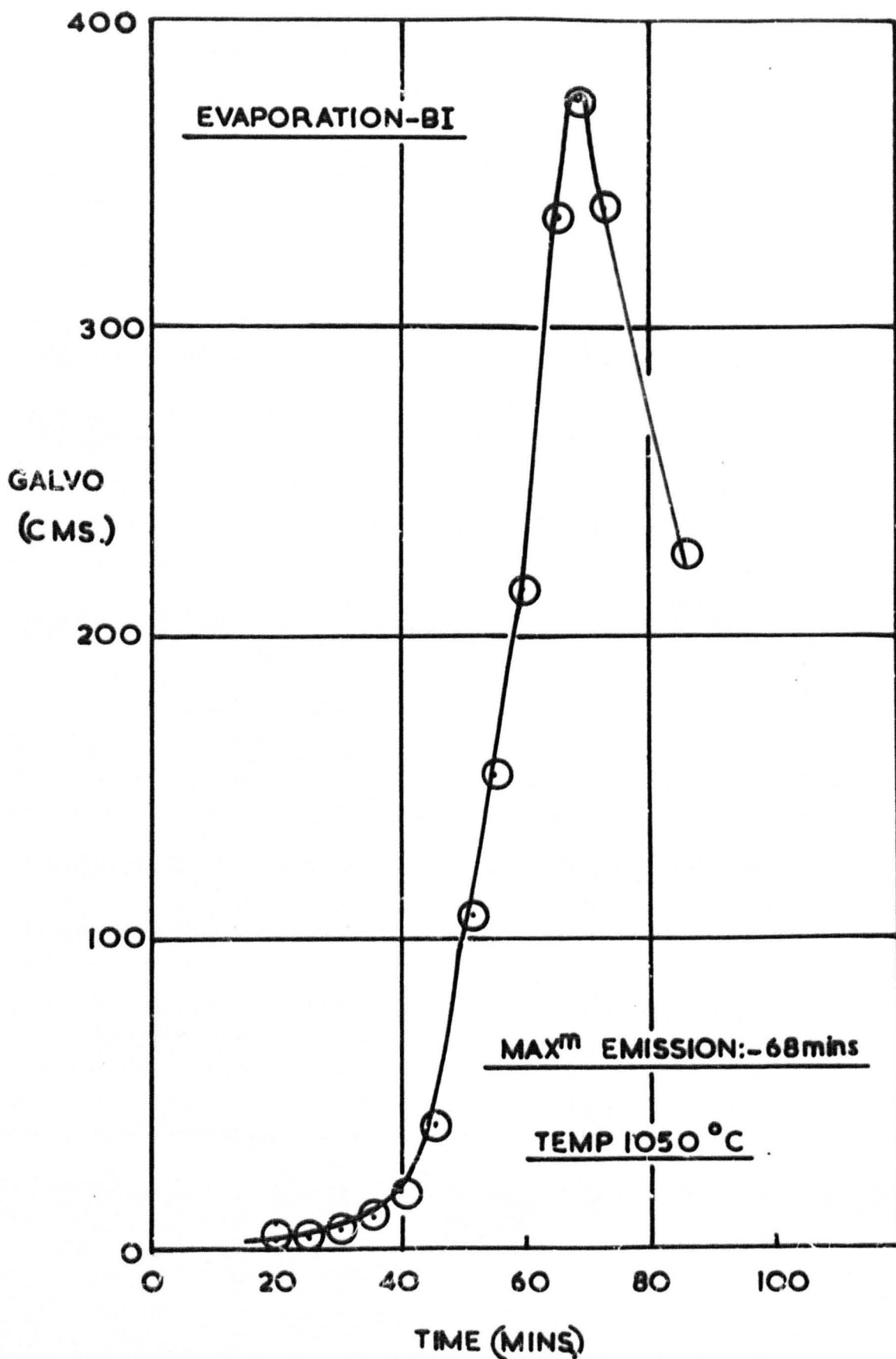


fig. 11. 1. 4.

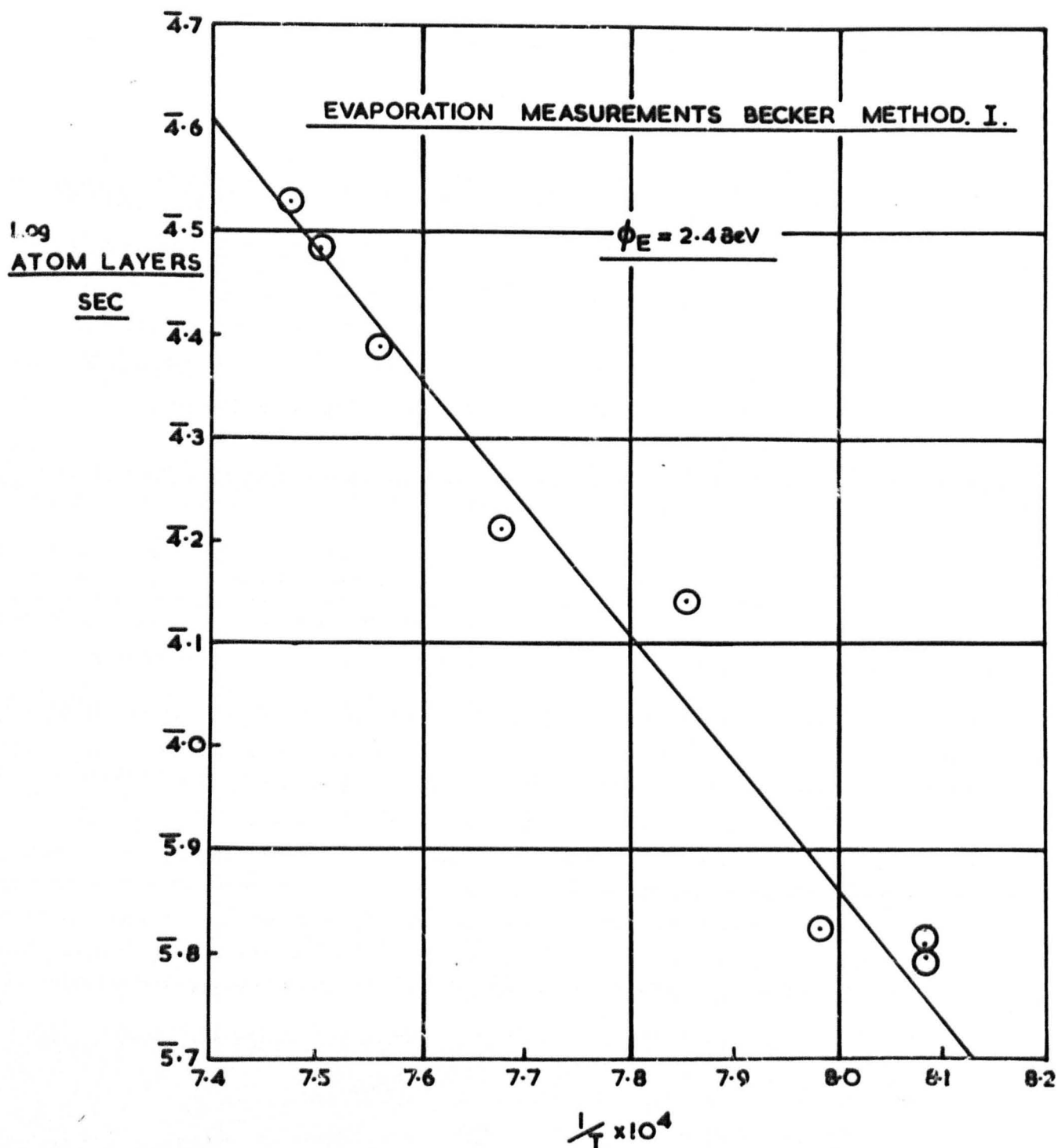


fig. 11. 1. 5.

fective in keeping the cathode temperature down.

The second and succeeding groups of tubes were made with the moveable shutter. Ten more tubes in all were constructed for evaporation rate measurements. The results obtained from them are given in table II. The temperature range covered by the measurements was from 650 - 1020°C. The results are plotted in fig (11.1.1) and fit well to a straight line from which $\phi_E = 2.19\text{eV}$. The points between 800° and 900°C show the greatest divergence from the line.

Table II

Tube	Temp. (°C)	Evaporation Rate ($\mu\text{m.cm}^{-2}.\text{sec}^{-1}.$)
T19	1020	9.173×10^{-7}
T22	950	2.63×10^{-7}
T18	900	7.42×10^{-8}
T27	875	6.26×10^{-8}
T24	850	2.68×10^{-8}
T26	825	2.84×10^{-8}
T21	800	2.90×10^{-8}
T23	750	4.81×10^{-9}
T20	700	1.39×10^{-9}
T25	650	8.04×10^{-10}

11.1.2. Measurement of the evaporation rate by the Becker method

Two tubes, as shown in fig (10.4.1) were constructed and used for evaporation measurements in the manner described in section 10.4. With the first tube, after two trial runs, eight measurements were made. Typical examples of the curves obtained by plotting emission from the wire against time are shown in figs (11.1.2)-(11.1.4). The results were plotted as $\log (\text{atom layers. sec}^{-1}.)$ against $1/T$, as shown in fig (11.15). From the slope of the resulting straight line

EVAPORATION MEASUREMENTS-BECKER METHOD II

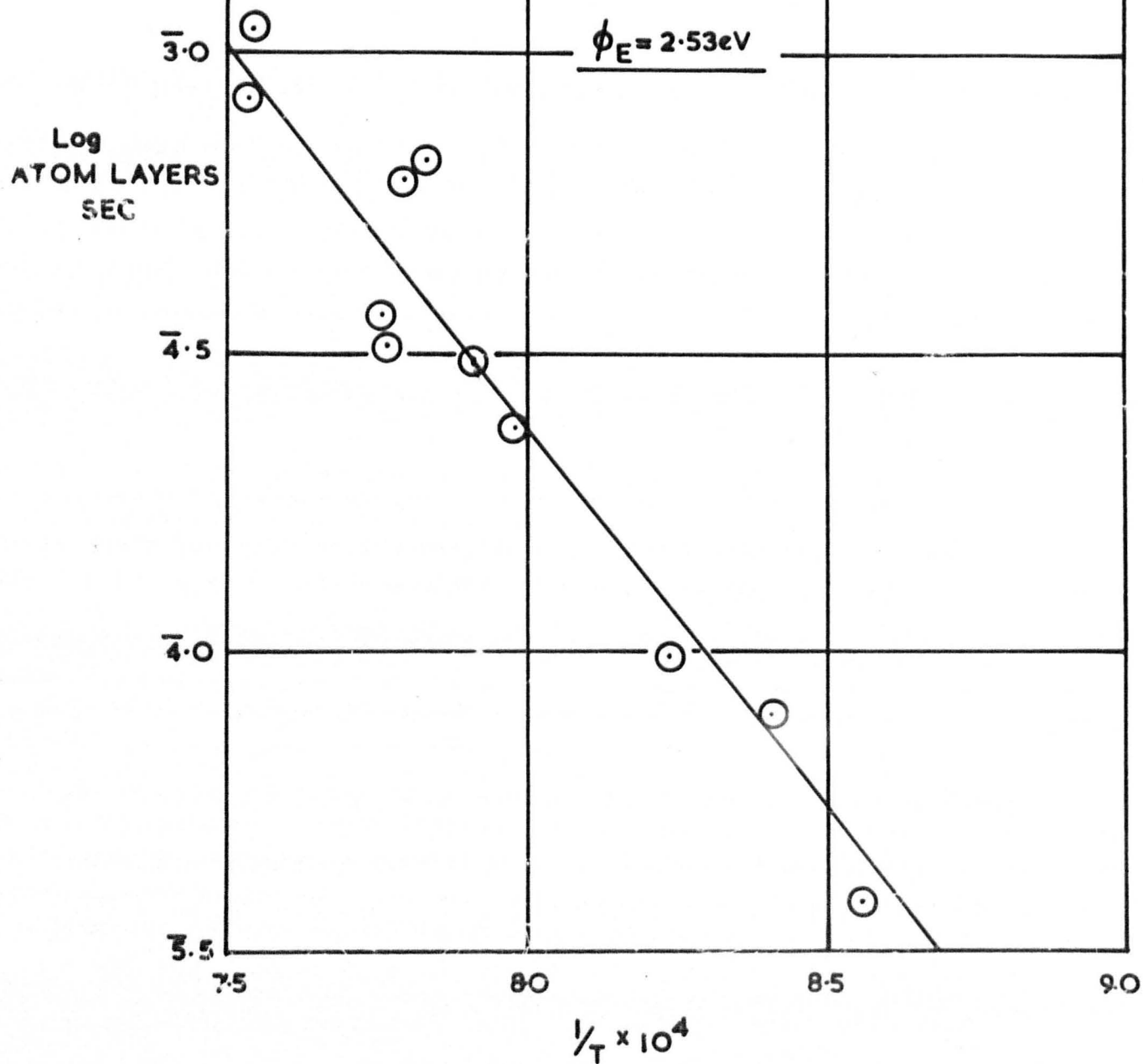


fig. 11. 1. 6.

an activation energy of evaporation of 2.48 eV was obtained. This was 0.3eV higher than the value obtained using ^{140}Ba . A second tube was built and eleven readings taken over a range of temperature 900 - 1050°C. The activation energy plot is shown in fig (11.1.6) and this gave a value of $\phi_g = 2.53\text{eV}$. This was in good agreement with the result from the previous tube.

The discrepancy between the results from the Becker method and that from use of the isotope is not large and could be due to loss of collected evaporant still occurring by re-evaporation in the latter case, although this had been considerably reduced by use of a shutter.

11.1.3. Effect of an applied field upon the evaporant.

A study of the effect of an applied electric field on the evaporation rate was made using the tube described in section 10.7. Two runs were made with no field applied and two runs were made with 250 volts applied. This was done at a cathode temperature of 1000°C. The results are shown in table III.

$T = 1000^\circ\text{C}$	Time for monolayer coverage
Without field	2.1 mins
" "	229 "
With field	2.3 "
" "	232 "

Table III

A second attempt was made to detect any effects of the field. This time the cathode was run at 1012°C and the measurements without and with an applied field were alternated. The results are shown in table IV. Again no effect was observed indicating that the evaporant from the cathode is not ionised.

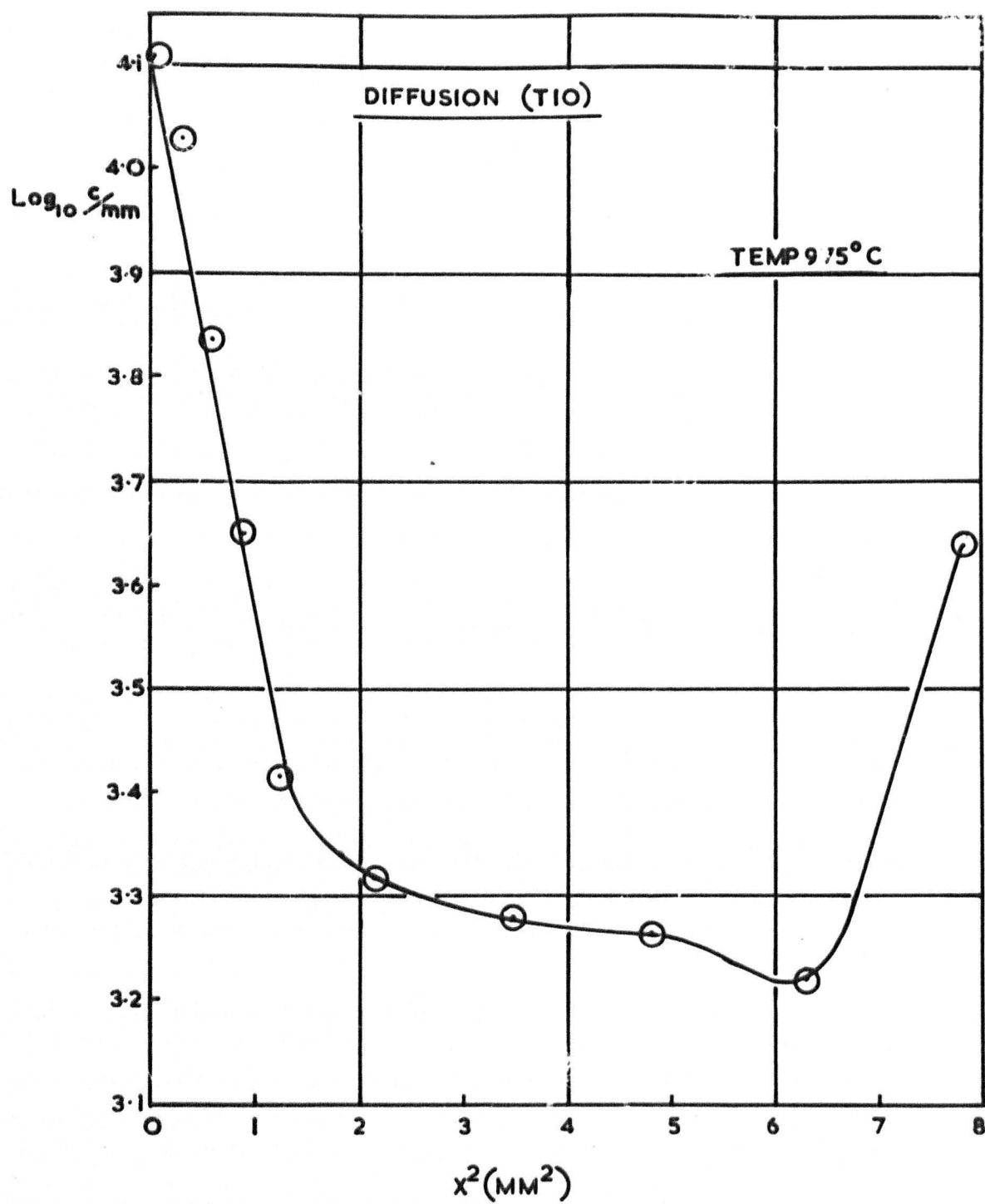


fig. 11. 2. 1.

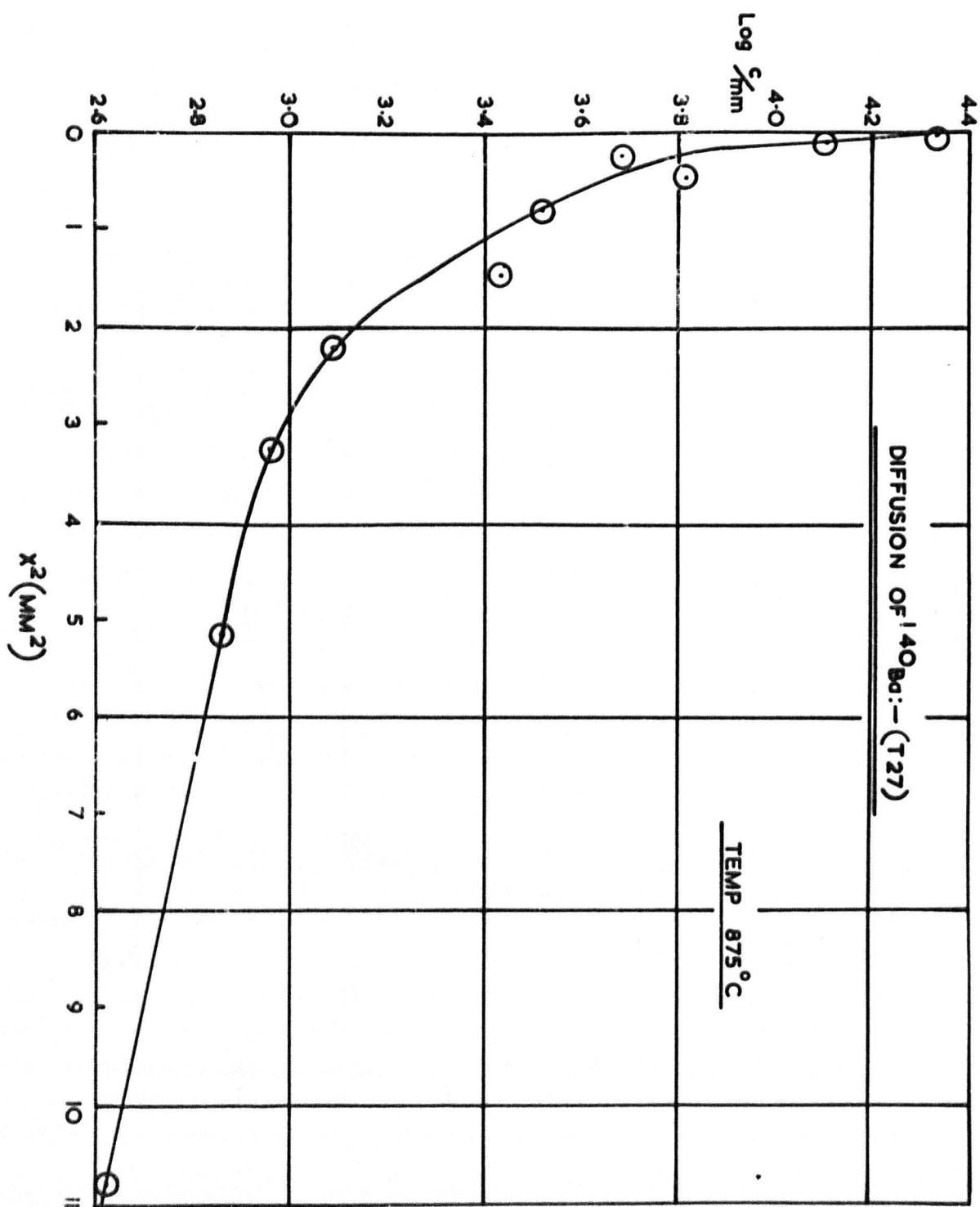


fig. 11. 2. 2.

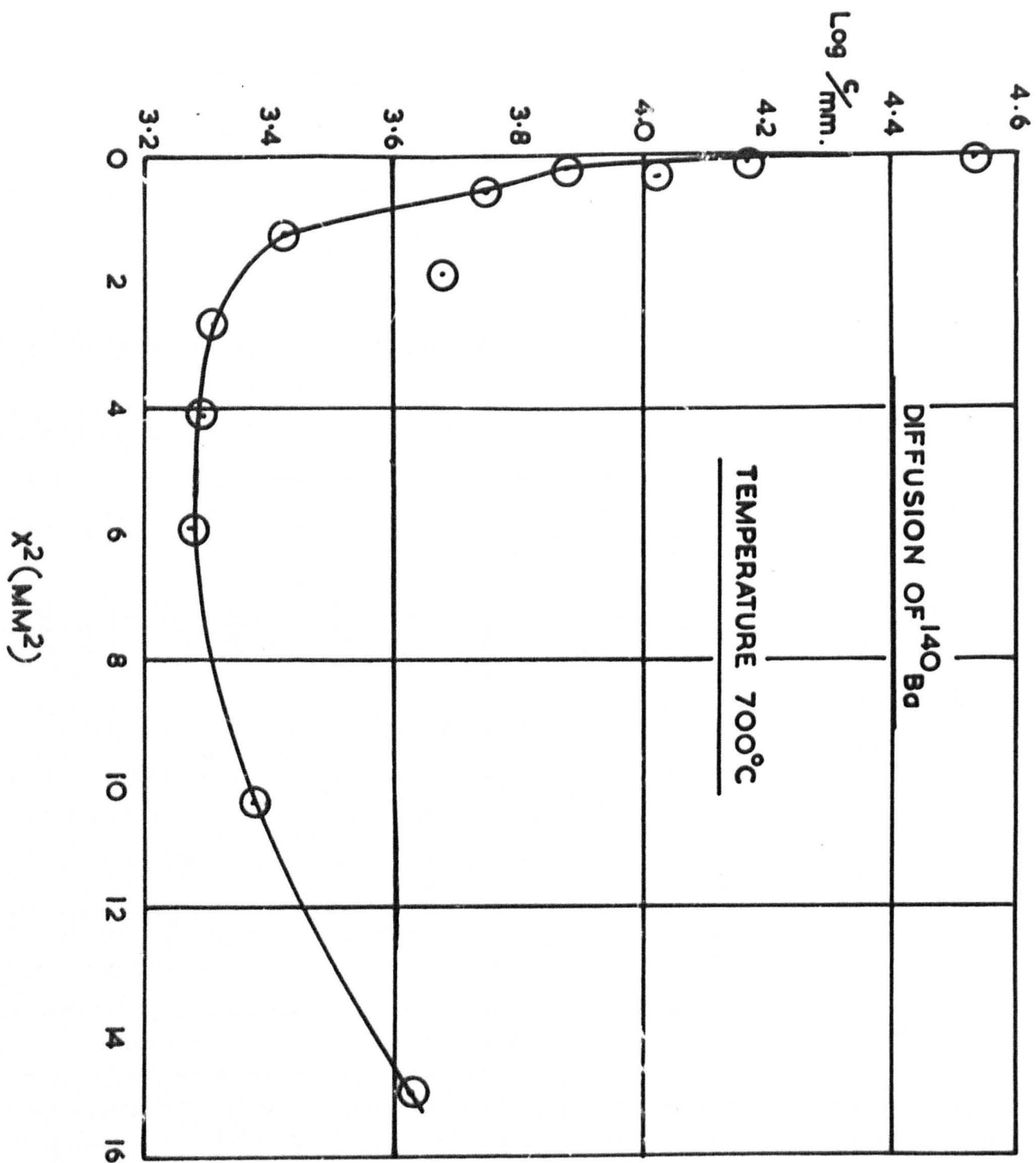


fig. 11. 2. 3.

<hr/> T = 1012°C Time for monolayer coverage <hr/>	
Without field	202 mins
With field	193 "
Without field	198 "
With field	207 "

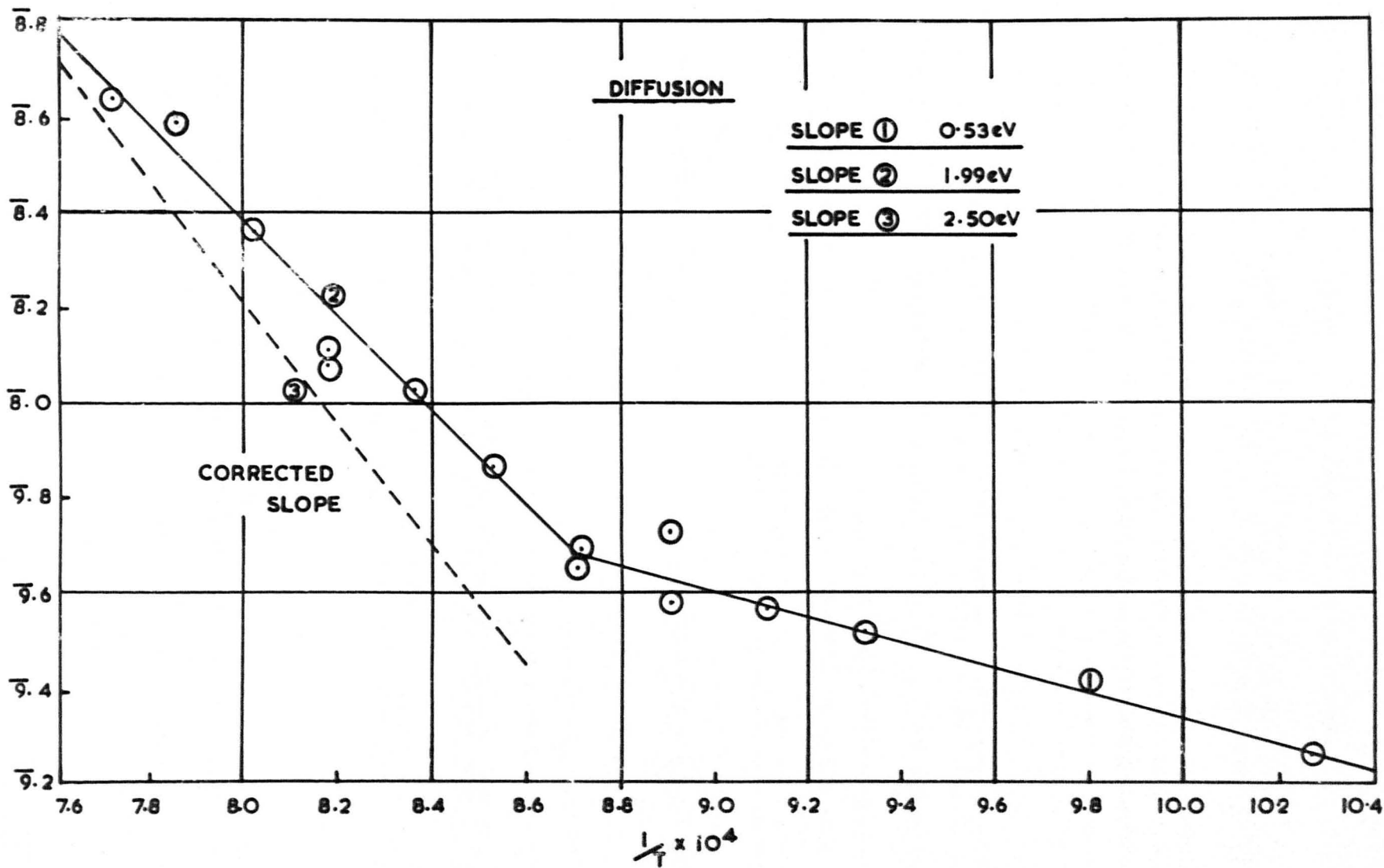
Table IV

11.2.1. The diffusion of ^{140}Ba through a nickel matrix in vacuum

The diffusion rate of ^{140}Ba was measured through fifteen cathodes in vacuum. A diagram of the tube arrangement is shown in fig (10.3.1). Typical examples of the diffusion profiles obtained are shown in figs (11.2.1)-(11.2.3). It was apparent from the profiles that the activating material had diffused through the cathode and that a concentration had built up at the cathode surface. This was a confirmation of previous indications that barium, in some form, over the surface of the cathode was responsible for the efficiency of this type of emitter. It also signified that the diffusion rate of barium through the matrix was greater than the evaporation rate from a normal, activated cathode.

An analysis of the diffusion profile presented two difficulties. The first was that some barium diffused into the cathode matrix during the breakdown of the carbonate so that at the instant from which the diffusion was timed the active material was not all confined below the base of the cathode. However, provided that each cathode was subjected to exactly the same treatment before the start of the timed diffusion, then the initial conditions for the measured period should be approximately the same in each cathode. From the profile a value of D was obtained, the logarithm of which was then plotted against

fig. 11. 2. 4.



$1/T$ to give a slope from which ϕ_D was found. Since no absolute value of D is required to find ϕ_D it was assumed that the difference in the initial slopes of the diffusion profiles was proportional to the difference of the diffusion coefficients.

The second difficulty was due to the build-up in concentration of barium at the cathode surface. This increase would give rise to some diffusion back to the regions of lower concentration nearer to the centre of the matrix thus tending to make the profile more shallow. The second assumption made was that this back diffusion had a negligible effect upon the initial slope of the diffusion profile.

The results obtained from the cathodes studied are listed in Table V and the plot to determine ϕ_D is shown in fig (11.2.4). The temperature range covered was from $700^\circ - 1020^\circ\text{C}$ and the diffusion coefficients ranged from 1×10^{-9} to $5 \times 10^{-8} \text{ cm}^2.\text{sec}^{-1}$ over this range. The $\log_{10} D \text{ v } 1/T$ plot fitted very well to two straight lines intersecting at a temperature of about 875°C . The slope of the line over the lower temperature portion gave a value of $\phi_D = 0.53 \text{ eV}$ and that over the higher temperature range of 1.99eV . When the latter was corrected for the lower temperature slope the value obtained for ϕ_D was 2.50 eV .

These results show that two diffusion processes must be in operation in the temperature range studied, one predominating below 875°C and the other above that temperature. At this stage it was decided to make a few diffusion measurements with the cathodes in argon at a comparatively high pressure to determine if the diffusion rate was affected. This decision was based upon the idea that one of the

processes operating may be Knudsen flow of material through the cathode pores and if this was so then this process would be affected by a change in the gas pressure in the valve. The results obtained are given in the next section.

Table V

Cathode	Temp. ($^{\circ}\text{C}$)	D ($\text{cm}^2.\text{sec}^{-1}.$)
T20	700	1.82×10^{-9}
T17	800	3.27×10^{-9}
T16	825	3.70×10^{-9}
T26	825	3.70×10^{-9}
T15	850	3.79×10^{-9}
T24	850	5.30×10^{-9}
T14	875	4.46×10^{-9}
T27	875	4.81×10^{-9}
T18	900	7.40×10^{-9}
T5	925	1.07×10^{-8}
T22	950	1.23×10^{-8}
T6	950	1.27×10^{-8}
T10	975	2.29×10^{-8}
T12	1000	3.90×10^{-8}
T19	1020	4.35×10^{-8}

Another four cathodes of different porosities were made and run at 900°C to see how diffusion varied with porosity. The results, together with that from the previous cathode are given in Table VI. These show clearly that increase in porosity gives an increase in diffusion rate in the region above 875°C .

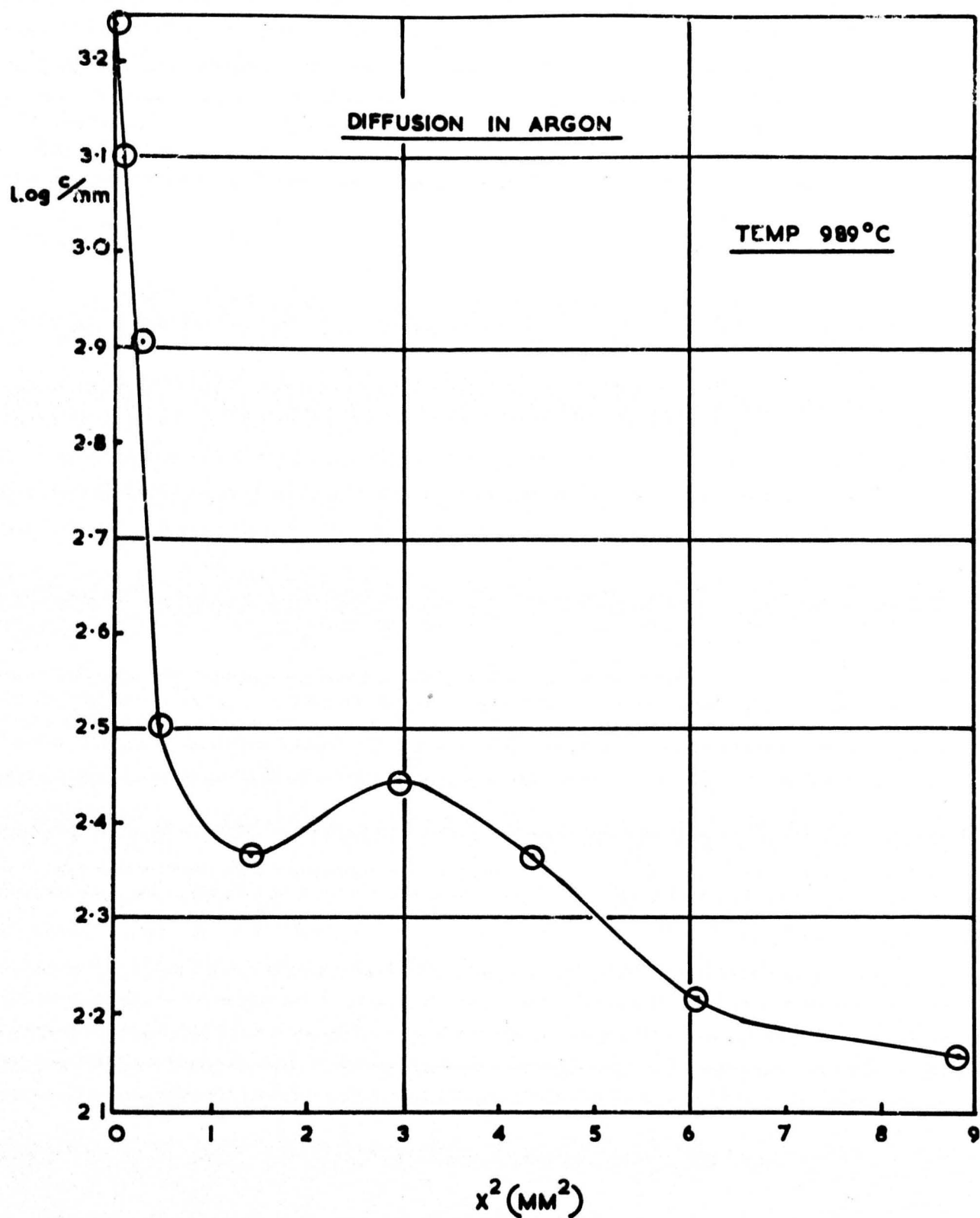


fig. 11. 2. 5.

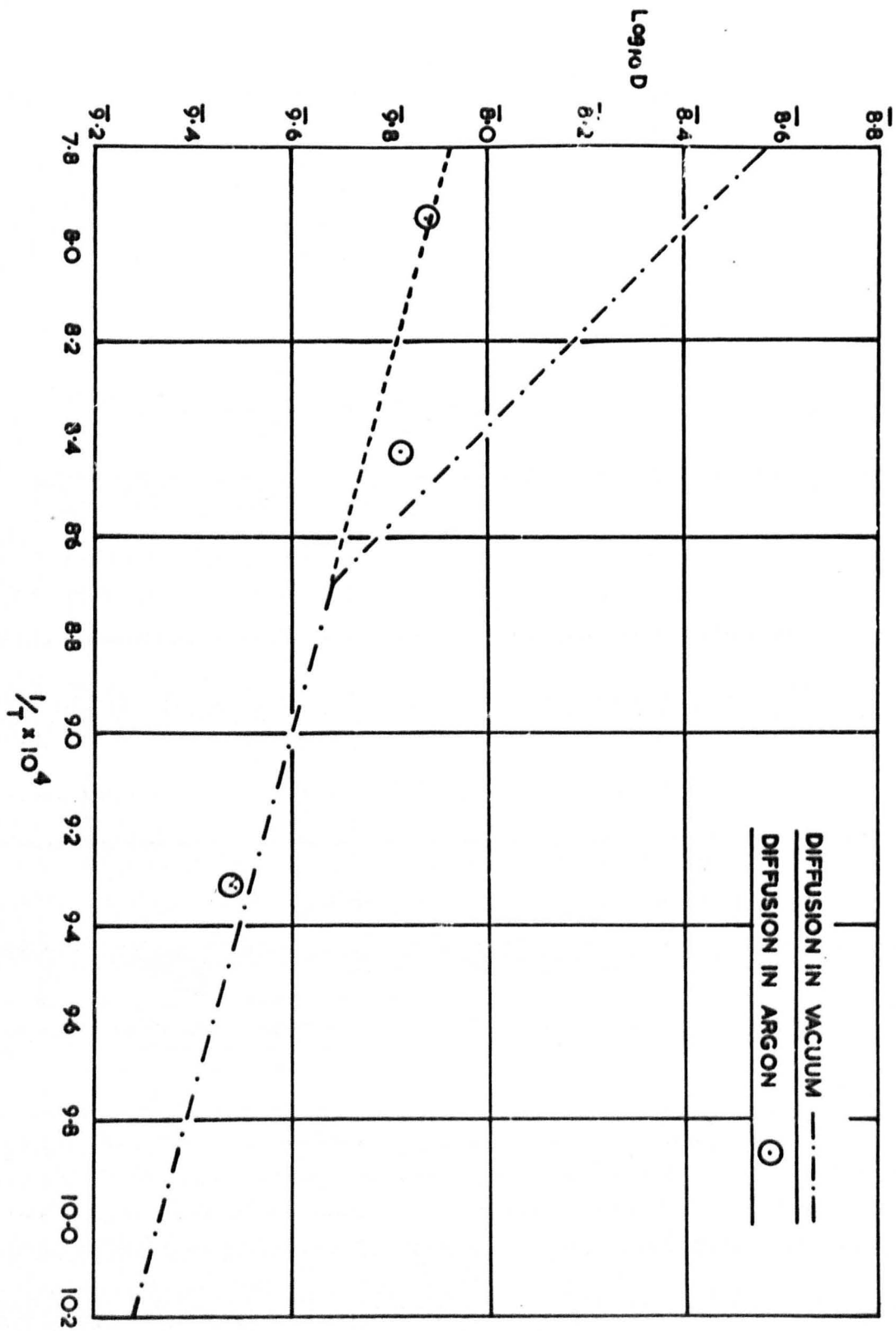


fig. 11. 2. 6.

Temperature 900°C	
Porosity %	D (cm ² .sec ⁻¹ .)
10.65	5.3×10^{-9}
12.10	7.3×10^{-9}
12.76	9.8×10^{-9}
17.20	1.35×10^{-8}
29.66	1.72×10^{-8}

Table VI

11.2.2. The diffusion of ¹⁴⁰Ba through a nickel matrix in argon

The technique employed to introduce argon into the valves at a pressure of about 400 mm.Hg. was explained in section 10.6. Measurements were made upon three such tubes. The results obtained are presented in table VII and an example of the type of diffusion profile obtained is shown in fig (11.2.5). The points on a plot of $\log D \sqrt{t}$ compared with the graph obtained for the diffusion through cathodes in vacuum is given in fig (11.2.6). From the graph it is seen that

Cathode	Temp (°C)	D (cm ² .sec ⁻¹ .)
A1	989	7.5×10^{-9}
A2	920	6.62×10^{-9}
A3	813	2.98×10^{-9}

Table VII

if the lower temperature slope of the diffusion with the cathode in vacuum is extrapolated to higher temperatures then the two values of D obtained with the cathodes in argon at temperatures above 875°C both lie very close to this line. This is interpreted as implying that the mechanism of diffusion predominating at higher temperatures

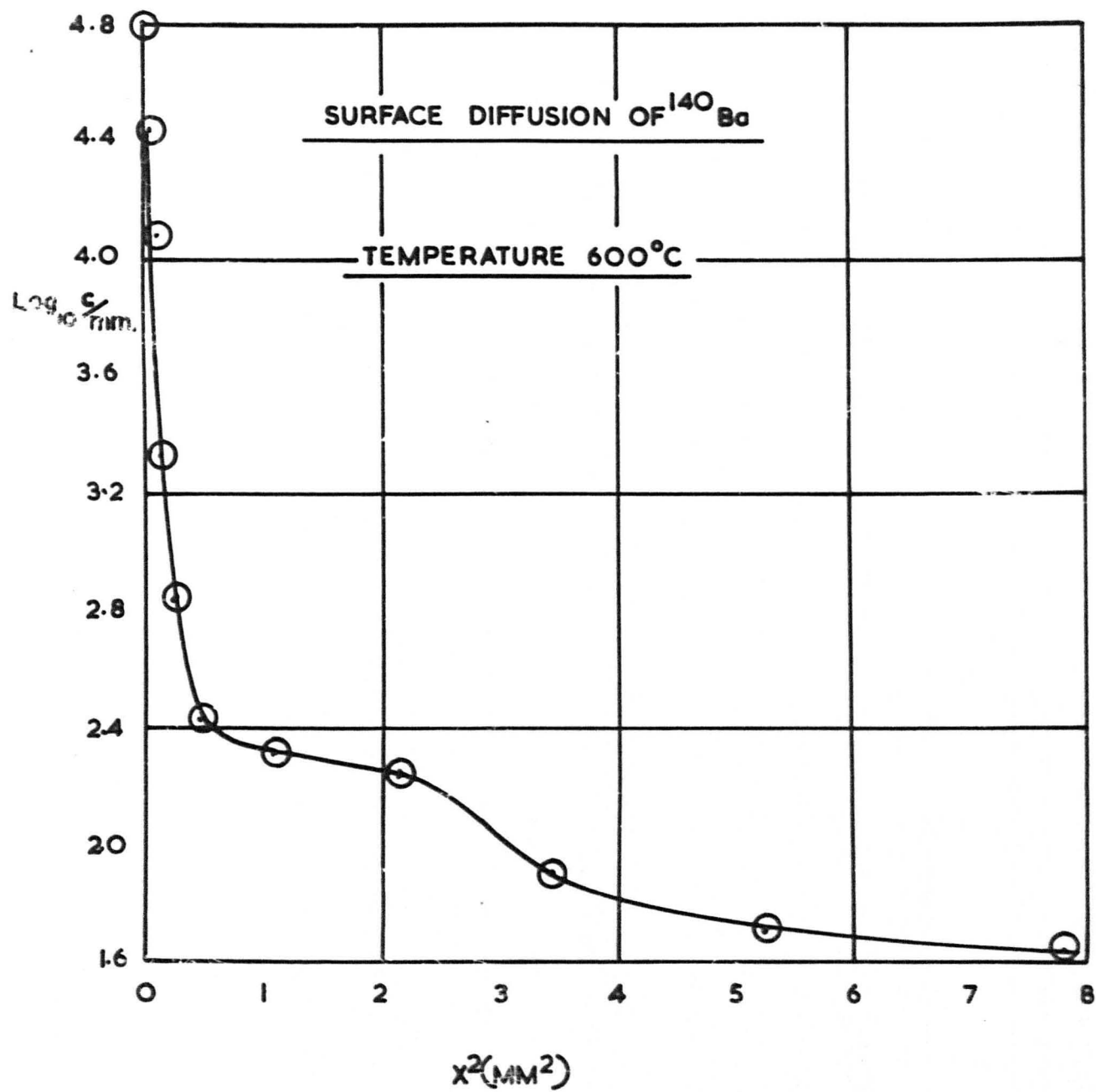


fig. 11. 2. 7.

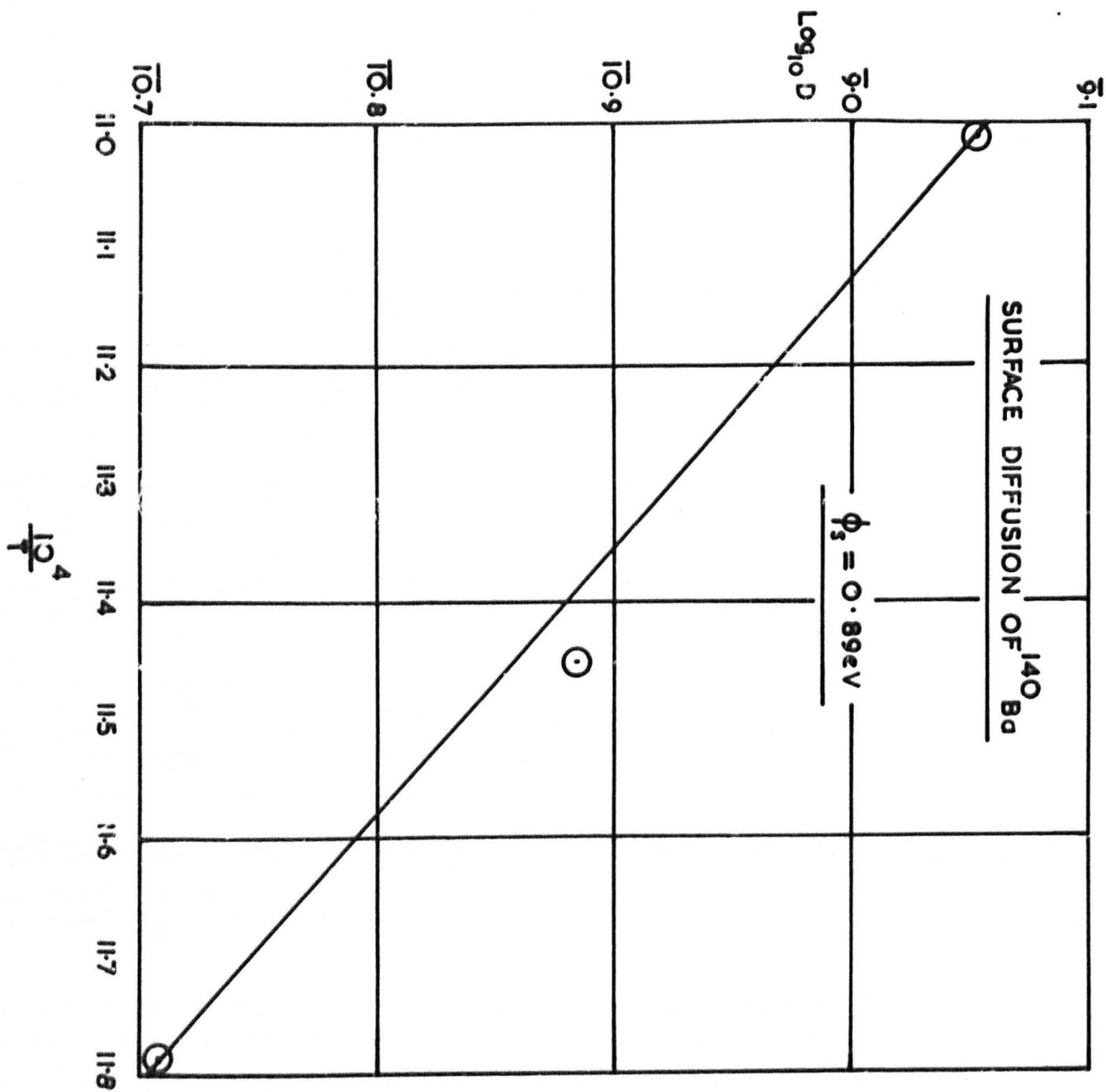


fig. 11. 2. 8.

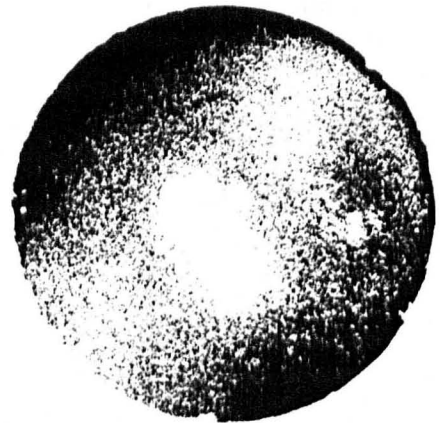
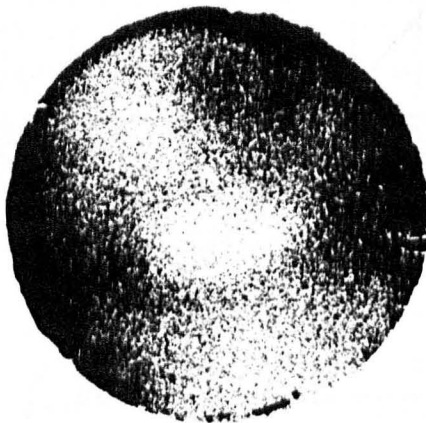
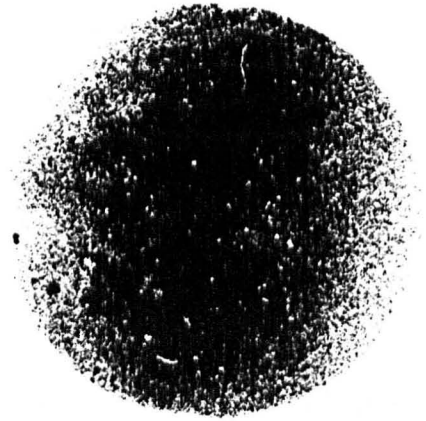
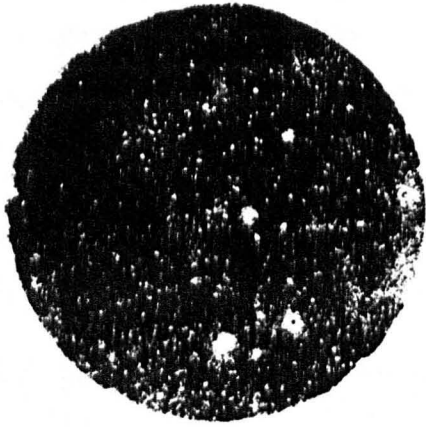


fig. 11. 3. 1.

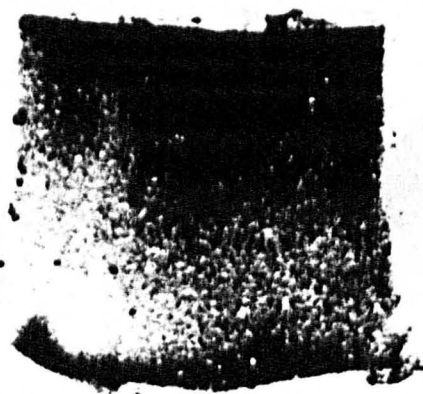
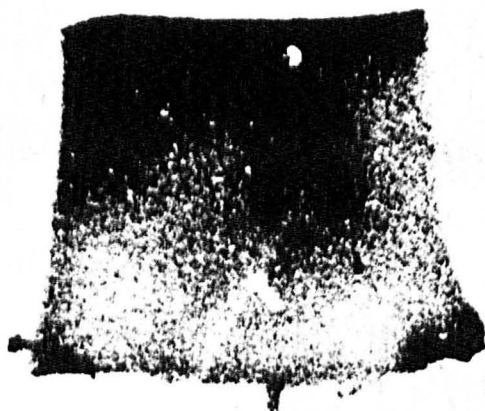


fig. 11. 3. 2.

has been reduced to a negligible factor by the inclusion of the inert gas in the tube.

11.2.3. Surface diffusion of ^{140}Ba over nickel.

Three tubes were built for surface diffusion measurements. The temperature range over which measurements could be made was limited due to the inability to heat the nickel to a high temperature. The results obtained are shown in table VIII and a typical profile in fig (11.2.7.) The profiles obtained were not straight lines, probably due to the fact that a large depth of surface on the atomic scale had to be taken off for the samples and so some internal diffusion was measured as well. The graph shown in fig (11.2.8) is the resultant $\log_{10} D v^1/T$ plot from these data. The slope gives a value for the activation energy of surface diffusion of 0.89eV. This is only a very approximate value since it is based only upon three points on the graph.

Tube	Temp ($^{\circ}\text{C}$)	D ($\text{cm}^2 \cdot \text{sec}^{-1}$)
1	635	1.14×10^{-9}
2	600	7.65×10^{-10}
3	576	5.09×10^{-10}

Table VIII

11.3. Autoradiographs

The autoradiographs shown in figs (11.3.1) and (11.3.2) were taken to obtain some qualitative idea of the cathode surface and the distribution through the cathode. Those of the surface were taken at various stages during activation and show that material moves out over the surface from the pores but does not give 100% coverage.

Chapter XII

Discussions of Results

In this chapter the results obtained are discussed and the conclusions drawn from the work are presented. A mechanism of operation of the cathode is proposed and further work to test this hypothesis is suggested.

12.1 .Composition of the cathode

In practice 70% by weight of nickel is employed in the 'M'-cathode slight variations being made depending upon the cathode required. The composition varied between 70:30 to 75:25 in this work. The cathodes have all been robust and machinable and no difference in their emission properties is evident. No life tests have been carried out but presumably a difference would be detected here. It would seem that under the same operating conditions the cathodes containing 25% of barium carbonate would have shorter lives.

The chief disadvantage of the cathodes containing 30% carbonate was that during sintering the difference in shrinkage between these and the 25% carbonate cathodes was appreciable. If this shrinkage is likely to lead to movement of the cathode in its containing cylinder then it is necessary to sinter the cathode before enclosing in the final valve assembly. This should not be deleterious in any way since any poisoning which occurs after sintering is reversible and the cathode is easily reactivated. The effect of water vapour on the cathode may produce adverse effects but the cathode could be maintained in a dry atmosphere.

A reducing agent is necessary in the cathode materials. In the cathodes made zirconium, zirconium hydride and silicon were

added in various mixtures. No measurements were made on the rate of activation of the various cathodes in an attempt to correlate this with the reducing agent used. The resultant cathodes all had the same work function and gave very similar emission, so the thermionic properties of the cathodes did not depend on the particular reducing agent used. This indicates that with each reducing agent barium was produced at a rate equal to or greater than that which is required for the most efficient operation of the cathode.

With silicon a difficulty may arise in that barium silicate could be formed as an interface compound in the matrix. Eisenstein, John and Affleck⁽³²⁾ have shown by X-ray analysis that the silicate exists at the interface in the oxide-coated cathode, so presumably it will also be formed in the 'M'-cathode. The only adverse effect of the silicate would be that it blocks some of the pores of the matrix. Cathodes are now made by using barium silicate instead of the carbonate as discussed below.

Silicon is much easier to handle than zirconium, with which care must be taken. Of the other possible elements aluminium and magnesium are the most convenient to use, although the latter would probably evaporate too quickly, but no reports have been made of the use of these as reducing agents. The cathodes of Levi⁽²⁴⁾ and of Brodie and Jenkins⁽⁴⁾, amongst others, employ the alkaline earth aluminates in place of carbonates, and the latter workers have also used the corresponding silicates. This provides a means of introducing a barium source which has air stability and produces barium at a rate much closer to that which is required to replenish barium lost from the cathode surface. The tungsten of the cathode acts as

reducing agent.

The problem of producing free barium at such a rate that it is just sufficient to replace that lost from the surface, without production of excess, is important in determination of cathode life. Since nickel is inert it may be that an optimum rate of production of barium could be achieved by using a barium source such as the aluminate together with a reducing agent.

12.2. Effect of the sintering atmosphere

The conclusion drawn from a comparison of the results of cathodes sintered in hydrogen and those sintered in vacuum is that the cathodes differ very little in their thermionic properties. This conclusion is only an approximation since the results upon which it is based cannot be compared to a high degree of accuracy. Very little work has been performed on the chemistry of the matrix cathode. When more knowledge of the possible reactions in the 'M'-cathode is at hand, the choice of sintering atmosphere can then be based upon more fundamental concepts.

During sintering in hydrogen the barium carbonate will dissociate to give the oxide and carbon dioxide, the latter being swept out in the stream of hydrogen passing the cathode. The hydrogen could then act as a reducing agent to give barium from its oxide. The reaction involved is straightforward



The computed barium pressure is given by

$$\log P_{\text{Ba}} (\text{mm}) = -12,300/T + 6.81 + \frac{1}{2} \log P_{\text{H}_2} (\text{atm})$$

For a pressure of one atmosphere, hydrogen is a moderately active reducing agent, but at low pressures the reducing power is much less⁽¹⁰⁸⁾. During sintering in hydrogen some of the barium oxide is probably reduced to barium by the hydrogen as well as by the added reducing agent.

Since minute quantities of impurities may play an important role, obtaining information from experimental results is difficult. (see Appendix I). The presence of several impurities is possible which would complicate the chemical reactions in the cathode and so conflicting results between workers could emerge. A theoretical analysis based upon thermochemistry to determine what reactions are possible, and using thermodynamics and the diffusion theory to determine any limits upon the reaction speed, would be most helpful.

12.3. The work function of the cathode

The work function of the 'M'-cathode as determined by Richardson plots over the temperature range 600 - 900°C is 1.7 to 1.8 eV. The validity of employing this method for the determination of work functions is doubtful and an investigation into this is being made in this laboratory. The values obtained compare quite well with those obtained by the same method by Beck⁽²⁾ and are higher than those obtained by Mehnard and Uzan⁽³⁷⁾. Assuming that the values obtained are approximately the real values then it is obvious that the cathode surface consists of an electropositive element upon the nickel which reduces the work function from 5.0eV to 1.7eV. That this element is barium is fairly well established and the autoradiographs obtained confirm this and indicate that the surface coverage by barium is less than a complete monolayer. This confirms Beck's⁽²⁾ results from his

electron microscope images, but the surface is almost certainly more complex than the above explanation. There is evidence from other cathodes that oxygen plays a role on the cathode surface i.e. the surface is actually barium on oxygen on nickel. Further work is necessary to help in providing evidence on this aspect.

12.4. Poisoning of the emission by oxygen and sulphur.

The results show that poisoning of the emission by oxygen and sulphur is reversible. The recovery from sulphur poisoning is slower than that from oxygen poisoning. Sulphur is a less effective poisoning agent than oxygen but no quantitative work has been carried out on this aspect.

The recovery curves indicate that the poisoning is due to two processes. One is the sorption of poisoning material on the cathode surface and the second is by diffusion of material into the cathode. As reactivation occurs the surface material is lost quite readily, giving the rapid initial increase in emission, whereas the material in the cathode diffuses out comparatively slowly giving the gradual return to complete activation.

More material will diffuse into a cathode the longer the poisoning period and so it will reactivate more slowly as the results show. The gas pressure existing in the region of the cathode surface may also play an important part in determining the reactivation rate. The results appear compatible with the fact that the sulphur atom or ion is larger than the oxygen atom or ion and hence would be more difficult to diffuse in or out of the matrix.

The re-poisoning of the cathode by oxygen when the voltage across

the valve is reversed could be due to either the oxygen leaving the cathode being in the form of negative ions or to some material leaving the anode and moving to the cathode. It has been found that with oxide-coated cathodes⁽⁷⁶⁾ the oxygen which leaves the cathode after poisoning is in the form of O_{16}^- ions. It is hoped soon to use a mass spectrometer in this laboratory to study the recovery process to determine if this observed effect is due to ionised oxygen.

That the formation of negative oxygen ions from the poisoning gas at cathode surfaces is possible may be seen from the following considerations. The energy required to form two O_{16}^- ions is 8.6eV. The energy gained in the process is 11.6eV. Hence the formation of O_{16}^- ions during poisoning seems probable. Applying this reasoning to sulphur the energy required is 6.3eV and the energy that would be gained is 8.3eV. Thus the ionisation of sulphur seems probable to about the same extent as oxygen. That such an effect has not been observed with sulphur may be due to the insensitiveness of the method employed in the preliminary experiments.

12.5. The evaporation from 'M'-cathodes

The activation energy of evaporation of the material evaporated from an 'M'-cathode is between 2.2 and 2.5 eV, most probably closer to the latter value. This is very similar to the activation energy of the high temperature diffusion process. The exact nature of the evaporant was not determined but it did contain barium and from previously reported work⁽¹⁸⁾ it would seem that both barium and barium oxide are present in the evaporant.

The experiments indicate that the evaporant from the cathode was not ionised. This is in agreement with the results of Rittner⁽⁵⁵⁾ who found that the evaporant from an impregnated cathode was not ionised. The period over which the cathodes were investigated did not exceed 100 hours of life so no conclusions can be drawn about the relationship between evaporation rate and cathode life. The evaporation over this initial period of life was constant at a given temperature. Since the cathodes used for these measurements were similar in construction to the 'L'-cathode it is not surprising that this result agrees with similar measurements on 'L'-cathodes.⁽¹⁷⁾ The normal 'M'-cathode, however, is more similar in construction to the impregnated cathode and it has been found with the latter that the evaporation rate is given by a $t^{-\frac{1}{2}}$ law. It seems probable that the evaporation rate from an 'M'-cathode would obey a similar relationship. It is hoped to make measurements on a cathode over a substantial fraction of its life to ascertain if this is correct.

The evaporation rate from the cathodes is quite high. By assuming that the nickel surface of the cathode is covered by a complete monolayer of barium atoms and assuming the pores to be open, then the number of barium atoms on the cathode surface will be of the order of 10^{14} . This is about 3×10^{-8} gms. of barium. At 1000°C the evaporation rate was found to be 7×10^{-7} gm.cm⁻².sec⁻¹, which means that 1.4×10^{-7} gms. are lost from the cathode per second. On the average this needs a new monolayer formed every 0.22 seconds. As the cathode is 12% porous, assuming that the surface has the same structure and using the activation energy of surface diffusion which was found to be

0.89eV it is seen that surface diffusion could not provide sufficient barium at this rate to cover the surface. Thus a large percentage of the evaporant must come directly from the pore ends without ever being sorbed on the surface. Whether this barium serves any useful purpose in the operation of the cathode depends upon whether the pore ends contribute to the emission. If it does not, then reduction of this evaporation would lead to a more economical cathode.

12.6. Diffusion through 'M'-cathodes

Two diffusion processes were found to operate in the temperature range $700^{\circ} - 1020^{\circ}\text{C}$. The one predominating up to 875°C has an activation energy of 0.53eV. The activation energy of surface diffusion was found to be approximately 0.89eV. It is suggested that this low temperature process is diffusion along the pore walls. If this is so, then increasing the porosity of the cathode would increase the wall area and so the diffusion rate at any temperature below 875°C should increase with porosity.

The process operating above 875°C has an activation energy of 2.50eV. The introduction of argon into the valves at 400 mm.Hg. pressure suppresses this process. It is proposed that the higher temperature mechanism is the flow of barium, either free or as the oxide or both, through the cathode pores by Knudsen flow. The vapour pressure of barium at 900°C is 1 mm.Hg. and that of barium oxide 3×10^{-8} mm.Hg., so argon at 400 mm.Hg., since it can penetrate the pores of diameter greater than 0.2μ readily, would suppress such flow. This also indicated that the majority of pores are greater than 0.2μ in diameter.

The diffusion rate at any temperature is greater than the evapor-

ation rate, so a build-up in concentration of barium in some form is obtained near the surface, as shown in the diffusion profiles. If the two proposed processes in fact obtain, the barium and barium oxide must accumulate in the pores, blocking them up to a large extent but not affecting the evaporation rate if the temperature of the material is still the same. This would then give emission from the pore ends which would behave, presumably, as small oxide-coated cathodes, as suggested by Brodie and Jenkins.⁽⁹⁴⁾ If the high temperature diffusion is predominantly Knudsen flow then an increase in porosity should increase the diffusion rate. This is what was found in the four cathodes studies at 900°C.

12.7. Mechanism of operation of the 'M'-cathode.

In the previous discussion all the following points have been made but they are now gathered together to form a summary of the conclusions reached.

- (i) the barium carbonate in the cathode is broken down by heat treatment to give barium oxide and carbon dioxide. Some of the barium oxide is reduced by the agent present (silicon) to give the free metal.
- (ii) barium and barium oxide move to the cathode surface by two mechanisms; one, which predominates below 875°C, is by diffusion along the pore walls and the other, which predominates above 875°C, is by Knudsen flow through the pores.
- (iii) on arrival at the cathode surface a high percentage of the Knudsen flow material is lost by evaporation. The nickel surface of the cathode is covered, although not completely, by a monolayer of barium. Oxygen is probably present on the nickel surface below the barium.

The surface material is continuously evaporating and being replaced from the interior.

(iv) during the activation of the cathode the pore ends become blocked to some extent with barium and barium oxide. The pore ends may then contribute to the emission.

(v) the work function of the cathode is 1.7-1.8eV. The activation energies are as follows, (a) of evaporation 2.2-2.5 eV, (b) of surface diffusion is 0.89eV, (c) of the low temperature bulk diffusion process is 0.5eV, and (d) of the higher temperature diffusion process is 2.5eV.

12.8. Summary of suggestions for further work.

(1) the part played by oxygen at the cathode surface and its presence in the evaporant.

(2) the use of barium aluminate instead of barium carbonate

(3) the use of a mass spectrometer to study recovery from poisoning

(4) the relationship between evaporation rate and cathode life.

Appendix 1.

Comparison of the equilibrium reaction pressures obtained from thermochemical data and from the results

All the thermochemical data employed in the following theory is obtained from Kubaschewski and Evans, 'Metallurgical Thermochemistry,' London, 1956. The symbols used are explained at the beginning of the thesis.

The change in free energy, ΔG , taking place during a reaction governs the reaction rate. The Gibbs-Helmholtz equation defines the change in free energy by

$$\Delta G = \Delta H - T \Delta S$$

If only one of the products is gaseous then the change in free energy is proportional to the logarithm of the equilibrium reaction pressure.

$$\log_e p = - \frac{\Delta G}{RT}$$

$$\text{therefore } \Delta S = -4.574T \log_{10} p$$

Substituting for ΔG , we obtain

$$\log_{10} p = 0.2193 \left[\frac{-\Delta H}{T} + \Delta S \right] \quad \text{where } p \text{ is in atmospheres}$$

$$\text{or } \log_{10} p = 0.2193 \left[\frac{-\Delta H}{T} + \Delta S \right] + 2.8808 \quad \text{where } p \text{ is in mm.Hg.}$$

For values at temperatures above 298°K, for which values of ΔH and ΔS are tabulated, heat capacities must be considered.

$$\text{It is known that } \Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p dT$$

and also
$$\Delta S_T = \int_0^T \frac{\Delta C_p}{T} dT$$

therefore
$$\log_{10} p = 0.2193 \left[- \frac{\Delta H_{298}}{T} - \frac{1}{T} \int_{298}^T \Delta C_p dT + \Delta S_{298} + \int_{298}^T \frac{\Delta C_p}{T} dT \right] + 2.8808$$

The reduction of barium oxide by silicon is now considered. The equation is



ΔH_{298} in cal. mole⁻¹ is given by

$$(2 \times -133,000) + 0 = (\frac{1}{2} \times -46,000) + 0$$

therefore
$$\Delta H_{298} = + 243,000 \text{ cal. mole}^{-1}. \quad \text{--- (1)}$$

ΔS_{298} in cal. deg⁻¹. mole⁻¹. is given by

$$(2 \times 16.8) + (\frac{1}{2} \times 4.5) = (\frac{1}{2} \times 43.5) + 41$$

therefore
$$\Delta S_{298} = 26.9 \text{ cal. deg}^{-1} \text{ mole}^{-1}. \quad \text{--- (2)}$$

If the reaction is studied at a temperature of 1300°K corrections are now applied to bring ΔH_{298} to ΔH_{1300} . The heat capacity of the reactants is given by:

$$C_p (2\text{BaO}) = 25.48 + 2.08 \times 10^{-3}T + 3.968 \times 10^{-5} T^2.$$

$$C_p (\frac{1}{2}\text{Si}) = 5.55 + 0.88 \times 10^{-3}T + 0.91 \times 10^{-5} T^2.$$

$$\underline{31.03 + 2.96 \times 10^{-3}T + 4.878 \times 10^{-5} T^2. \quad \text{--- (3)}}$$

Since the silicates form a co-ordination lattice, the heat cap-

acity at room temperature is $6.2 \text{ cal.deg}^{-1}.\text{gm. atom}^{-1}$. The molar heat capacity is $6.2 \times \text{no. atoms in the molecule}$. Thus for Ba_2SiO_4 , $C_p = 43.4 \text{ cal.deg}^{-1}.\text{mole}^{-1}$. The heat capacity at the transition point is given by $7.25 \times n = 50.75 \text{ cal.deg}^{-1}.\text{mole}^{-1}$ for Ba_2SiO_4 . Assuming a linear increase in C_p with temperature and since the first transition point of Ba_2SiO_4 is its melting point, 2033°K , there is a difference in C_p values of $(50.75 - 43.4) = 7.35$ over a temperature range of $(2,033 - 298) = 1735^\circ\text{K}$.

Therefore the slope of a C_p v T graph is 4.237×10^{-3} . The intercept of such a graph at $T = 0^\circ\text{K}$ is given by $43.4 - (4.237 \times 10^{-3} \times 298) = 43.26$

$$\text{Therefore } C_p = 43.26 + 4.24 \times 10^{-3} T$$

Thus the heat capacity of the products is given by :

$$C_p \left(\frac{1}{2} \text{Ba}_2 \text{SiO}_4 \right) = 21.63 + 2.12 \times 10^{-3} T$$

$$C_p (\text{Ba}) = \frac{5}{26.63 + 2.12 \times 10^{-3} T} \quad - - - - (4)$$

Subtracting C_p (reactants), given in equation (3) from this we have

$$C_p = -4.40 - 0.84 \times 10^{-3} T + 4.878 \times 10^{-5} T^2 \quad - - (5)$$

By integration of this equation and substitution of $T = 298^\circ\text{K}$ and $T = 1300^\circ\text{K}$ expressions are obtained for substitution in

$$\log_{10} p = 0.2193 \left[- \frac{\Delta H_{298}}{T} - \frac{1}{T} \int_{298}^T \Delta C_p dT + \Delta S_{298} + \int_{298}^T \Delta C_p dT \right] + 2.8808$$

and we obtain

$$\log_{10} p(\text{mm}) = 7.74 - 5.25 \left(\frac{10^4}{T} \right) - - - - (6)$$

From the experimental results, using those from the first Becker tube shown in fig (11.1.5), the straight line obeys the equation

$$\log_{10} m = 0.017 - 1.45 \left(\frac{10^4}{T} \right) - - - - (7)$$

Air flow measurements through a 12% porous cathode gave a flow of $0.6 \text{ cm}^3 \cdot \text{sec}^{-1}$ at unit pressure for unit pressure difference across the matrix.

Therefore for barium vapour at 1300°K

$$\text{flow} = \sqrt{\frac{1300}{298} \times \frac{29}{137}} \times 0.6 = 0.577 \text{ cm}^3 \cdot \text{sec}^{-1}.$$

$$\text{therefore } m = \frac{137}{22.4 \times 10^3} \times \frac{298}{1300} \times 0.577 \times \frac{p}{760}$$

$$\text{or } p = 9.4 \times 10^5 m$$

Substituting in (7)

$$\text{therefore } \log_{10} p = 5.99 - 1.45 \left(\frac{10^4}{T} \right) - - - - (8)$$

Equations (6) and (8) do not correspond closely. This is probably due to other impurities in the nickel serving as reducing agents as well as the silicon.

Appendix II

The effect of oxygen and sulphur on the
thermionic emission from matrix cathodes.

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PART I

THE 'M' - CATHODE

Chapter I

The Dispenser Cathode

1.1. Introduction

The term dispenser, or sintered, cathode is used to include all those cathodes in which the metallic base of the cathode is formed by sintering from the powdered metal and in the operation of which the 'activating' material is dispensed to the surface of the metal to give a lower work function. The nomenclature in use in the existing literature for the numerous variations of this type of cathode is not rigidly standardised. The work to be described is especially concerned with a cathode made by milling together nickel powder and one or more of the alkaline earth carbonates. The mixture is then pressed to the desired shape, sintered and activated. This type of cathode has been termed the 'moulded' or 'M' - cathode⁽¹⁾ and also the 'B-N' - cathode.⁽²⁾ In the following chapters it will be referred to as the 'M' - cathode.

1.2. General Properties

The dispenser cathode consists of a porous metal base with a reservoir of the emissive material somewhere below the surface of the cathode, to which it diffuses to give enhanced thermionic emission. The reservoir may be either incorporated

where

$$A_0 = \frac{4\pi m e k^2}{h^3} = 120 \text{ amp.cm}^{-2} \text{ deg}^{-2} \text{ --- (4)}$$

The reflection coefficient r is much less than unity if the barrier is described fairly well by the image-force potential. This was shown by Nordheim (49) on the basis of wave mechanics. With this simplification (3) may be written

$$I = A_0 T^2 \exp \left[-\frac{\phi}{kT} \right] \exp \left[-\sqrt{E} \cdot \frac{e^{3/2}}{kT} \right] \text{ --- (5)}$$

The relative dependence of I upon field strength has been found to obey this equation very closely for clean metal surfaces. A does not have the theoretical value and in a few cases by a very large factor. The reasons for these deviations lie in the assumptions made in the derivation of the equation. These have been discussed at length by Seitz. (41) — 47?

If a weak applied field produces saturation, a plane just outside the range where image forces are appreciable will still be at a potential practically the same as that just outside the surface of the conductor, hence the equation (5) reduces to

$$I_0 = A_0 T^2 \exp \left[-\frac{\phi}{kT} \right] \text{ --- (6)}$$

Assuming this equation, if the emission current is measured at very low applied voltages for various temperatures and the emission is plotted as a function of the applied voltage then a set of

was sealed into an envelope and the cathode was processed as were earlier cathodes. The emission drawn from the valve during ageing was 2mA with $V_a = 100V$. After baking and eddy-current heating two sets of characteristics were taken with a period of three hours between the two measurements. During this interval the cathode was aged at $850^{\circ}C$. The valve was baked and eddy-current heated again and the getters fired, after which the valve was sealed off. Four more sets of characteristics were taken at three hourly intervals and the values of ϕ obtained are shown in table 7.2.

Table 7.1.

Cathodes containing 1% Zirconium Hydride		
Cathode	$\phi(eV)$	$A(amps.cm^{-2}.^{\circ}K^{-2})$
BZ13	1.80	0.02
BZ14	1.75	0.01
BZ15	1.71	0.02
BZ16	1.70	0.01

Table 7.2.

Valve BZ13		
Measurement	$\phi(eV)$	$A(amps.cm^{-2}.^{\circ}K^{-2}).$
Before seal-off (1)	2.66	690
" " " (2)	2.28	4.3
After seal-off (1)	2.06	0.6
" " " (2)	1.80	0.02
" " " (3)	1.88	0.05
" " " (4)	1.80	0.02