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Phil. Trans. R. Soc. Lond. A 1935 **235**, 101-124

doi: 10.1098/rsta.1935.0017

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IV—Characteristics of the Adsorption of Indium and Thallium Atoms on Tungsten Oxide

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(Communicated by A. M. TYNDALL, F.R.S.—Received January 14—Revised May 16, 1935)

I—INTRODUCTION

The subject of the adsorption of atoms on surfaces is of considerable theoretical and technical importance. A knowledge of the processes involved is essential, for example, before we can understand many industrial applications which depend for their success upon the catalytic activity of metallic oxides. It is of great advantage in making experiments in this field if the adsorbed atoms or molecules can be detected by electrical methods, and TAYLOR and LANGMUIR* have shown recently that these methods allow us to make an extremely accurate and detailed study of the adsorption of caesium atoms on a tungsten surface.

The object of the experiments described in this paper was to examine the extent to which the adsorption of atoms on the surface of a metallic oxide can be described in terms similar to those developed by TAYLOR and LANGMUIR in their work with metallic tungsten. There is a marked contrast between the behaviour of metal atoms adsorbed (*a*) on the surface of a metal, and (*b*) on the surface of a dielectric like glass, and this difference is to be associated with the difference in the electrical properties of the two types of materials. The metallic oxides are generally semi-conductors and we can form no *a priori* estimate of the characteristics of adsorbed films on their surface. In previous work, no precise observations have been possible, largely on account of technical difficulties.†‡ Experiments were made on comparatively large masses of oxide and it is very difficult to maintain a uniform temperature throughout such a mass, to measure this temperature accurately and to change it quickly in the conditions imposed by the experiment. Further, the capacity for adsorbed atoms of such an aggregate of micro-crystals, the number of adsorbed atoms which can be

* 'Phys. Rev.,' vol. 44, p. 423 (1933).

† BREWER, 'J. Chem. Phys.,' vol. 2, No. 3, p. 116.

‡ POWELL and BRATA, 'Proc. Roy. Soc. A,' vol. 141, p. 463 (1933).

accommodated in a complete monomolecular layer over the whole of the available surface, is inconveniently large and the results are complicated by the comparatively slow process of diffusion of the adsorbed atoms over the surfaces throughout the crystalline mass.

In the present experiments these difficulties have been largely overcome by using the thin skin of oxide which forms on tungsten when it is heated in air. This oxide can be heated by passing a current through the tungsten strip or filament on which it is formed. In these conditions the temperature of the oxide is uniform, it can be accurately measured and it can be quickly changed. The resulting "field" presented by the oxide for the adsorption of atoms is still "three dimensional,"* so that diffusion of the adsorbed atoms to and from the outer surface, on to which the atoms are deposited and from which emission takes place, is still an important feature of the behaviour of the adsorbed atoms. The oxide is sufficiently thin, however, to ensure that this factor does not introduce serious complications in interpreting the results, and in some experiments the comparatively large capacity is an advantage.

In addition to their bearing on the general problems connected with the adsorption of atoms on oxide catalysts the results are of interest in connexion with the problem of producing thermionic sources of positive ions in high vacua. They also enable us to extend to the metals indium and thallium the methods of measuring and detecting beams of atoms which have hitherto been available only for the heavier alkalis.

2—THE EXPERIMENTAL TUBE

The final form of the apparatus is shown diagrammatically in fig. 1. It consists essentially of three coaxial, cylindrical electrodes, the outer ones acting as guard rings to the central short one, and insulated from one another by the method shown in detail in fig. 1c. A tungsten strip 1.3 mm wide and 0.07 mm thick runs down the axis of the electrodes. This strip will in future be referred to as "the filament." The position of the filament relative to the electrodes is defined by quartz bushes in discs attached to the main frame supporting the electrodes. The filament is put in tension, so that it maintains its position when hot, by means of a tungsten spring. The heating current to the filament does not pass through this spring but reaches the filament through a flexible copper lead.

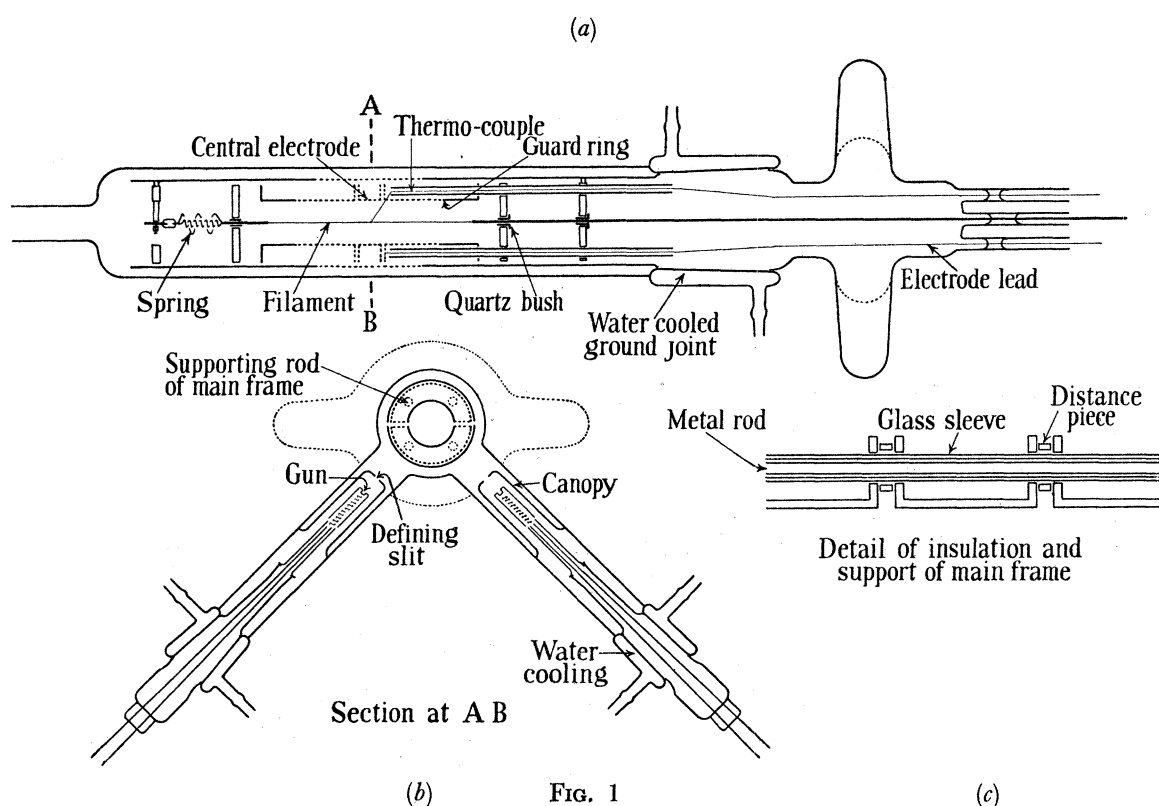
The temperature of the filament is measured by a platinum and platinum-rhodium thermocouple made up of No. 48 gauge wire. The ends of the two wires were welded together into a small blob in the oxygen-coal gas flame and the junction was then spot welded on to the centre of the filament. The thermocouple leads pass down the tube through small glass tubes supported by the flanges of the guard rings and then out of

* We use this expression not in the sense that the adsorbed atoms can migrate into the crystal lattice, but that the effective surface on which adsorption can take place is not confined to the outermost surface of the oxide immediately accessible to the bombarding stream, as with caesium on tungsten, but extends to the underlying crystal surfaces throughout the micro-crystalline aggregate.

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the end through ordinary glass seals ; *see* fig. 1*a*. Although the tube is of Pyrex glass, the gauge of the wire is so small that no difficulty was found in sealing the wire directly through the glass to make a vacuum-tight joint.

The electrode system is mounted in a glass tube supported by a large ground joint so that it can be rotated in vacuum. Two slits, diametrically opposite one another and parallel to the axis of the tube, cut the central electrode and two thirds of the length of the two guard ring electrodes. In addition, two slits, coplanar with the two in the electrode system, are cut in the supporting glass tube so that when the ground joint is suitably orientated, atoms from one or other of the two furnaces, fig. 1*b*, can pass through the slit system to bombard the filament. In fig. 1*a* the thermocouple lead



and its insulating tube together with the lead to one of the electrodes are drawn out of section in order to show the method of mounting. As shown in the diagram, they would shield part of the filament from the bombarding stream of atoms.

The furnaces were made by turning pieces of molybdenum to the shape shown in fig. 1*b*. They are heated internally by tungsten spirals placed inside thin quartz sleeves and the metals evaporate from the small cups in the top of the molybdenum. The slits in the glass canopies over the furnaces allow fan-shaped beams of atoms to pass through towards the filament. The general features of construction are sufficiently obvious in the diagram to need no further description.

The tungsten filament was made by thinning down from strip of about twice the required thickness*. The usual method of thinning by dissolving off the surface in molten sodium nitrite was found to be unsatisfactory and the strips were ground down on a surface plate by means of a fine stone. By this means they could be prepared of very uniform thickness and they were polished almost optically smooth. Before being mounted in the apparatus with the thermo-junction attached, they were aged for several hours at about 2700° C. The oxidation of the tungsten was carried out by heating in oxygen at a pressure of 3 mm of mercury for a few minutes. The temperature of the filament was gradually increased from 550° C until its colour, having passed through a series of characteristic changes due to interference effects in the film of oxide, reached a deep blue similar to that of tungsten wire as usually supplied by the makers. On heating to a temperature of 700° C *in vacuo* the oxide changes in colour to a reddish mauve. The film of oxide remains adherent to the underlying metal surface in spite of being repeatedly heated and cooled, and it is stable for an indefinite period in vacuum at temperatures below 780° C, and in air at room temperature. We estimate the thickness of the oxide film so formed to be 10^{-4} cm.

EXPERIMENTS WITH INDIUM

3—CALIBRATION OF THE ATOM STREAM

When pure indium metal is placed in the furnace and a given current is passed through the heating element, the temperature gradually rises to an equilibrium value and, with the ground joint suitably orientated, a constant stream of indium atoms then passes through the defining slits on to the filament. If the filament is now heated, positive ions leave it and a current passes to the collecting electrodes. In these experiments we measure only the current to the central collector. This positive ion current reaches an equilibrium value in a time which depends on the temperature of the filament and on the intensity of the bombarding stream of neutral atoms. The intensity of the bombarding stream depends very critically on the orientation of the tube, the positive ion current from the hot filament, in the steady state, being at a maximum at a particular setting of the ground joint and falling to half value at two degrees on either side of the optimum setting. The maximum current is sensibly the same whichever of the two sides of the filament is presented to the bombarding stream. In making experiments one of the settings corresponding to the maximum positive ion emission is always used.

With a given intensity of the bombarding stream and provided that the temperature of the filament is above a certain minimum, the equilibrium value of the positive ion current is independent of the actual value of the filament temperature. For a clean

* It is of importance to use strip of pure tungsten. We obtained some tungsten strip which contained impurities, probably silica which completely changed its oxidation properties from that characteristic of pure tungsten. We obtained pure tungsten strip through the courtesy of the British Thomson-Houston Company, of Rugby.

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tungsten filament bombarded with caesium atoms, a similar relation has been observed, the positive ion current being independent of the temperature of the filament provided that this temperature is above a certain minimum value. This fact has been interpreted by LANGMUIR and others as due to a dynamic equilibrium in which the number of neutral atoms reaching the filament per second is balanced by the number of positive ions leaving it.

In the present experiments, following LANGMUIR, let us suppose that the rate of emission of positive ions, v_+ , and of neutral atoms, v_n , from the filament, depends only on the temperature of the filament, $T^\circ\text{A}$, and on the population of the atoms on the oxide surface. Let us express this population as a fraction, θ , of the number of atoms which could be accommodated on the surface in a complete monomolecular layer.

Then $v_+ = f(\theta, T)$; $v_n = \psi(\theta, T)$.

In the equilibrium conditions which are set up when the filament, at a certain temperature, is bombarded with a constant stream of atoms, μ ,

$$\alpha\mu = v_+ + v_n \quad (1)$$

where α is the fraction of the atoms incident on the surface which is temporarily adsorbed by it. The coefficient of reflection of the surface for these atoms is then equal to $1 - \alpha$. In general we must regard α as a function of both θ and T .

In these 'equilibrium' experiments, if the temperature of the filament is decreased, we must expect the rate of emission of both positive ions and neutral atoms to fall temporarily. The rate of emission of atoms plus ions will then be smaller than the rate of condensation of atoms and the population of the surface will rise until a new equilibrium is set up. For caesium on tungsten, where the 'field' on which adsorption can occur is confined to the outermost surface of the metal*, the total capacity of the surface is so small that the change from one state of equilibrium to another follows the change in temperature very rapidly. In the present experiments this is no longer so; the capacity of the oxide is large enough to ensure, for example, that when the temperature is decreased, a time of the order of minutes is required before the population of the surface rises to a value corresponding to the new equilibrium. This effect is shown in fig. 2 in which the positive ion current to the central collection electrode is plotted against the time. In obtaining these curves the heating current in the furnace was maintained at a constant value. The temperature of the filament was kept constant for several minutes and then suddenly changed to a new value, the time required for the change in temperature to be completed being of the order of five seconds. At point "a" in fig. 2 the temperature was suddenly lowered from 765°C to 749°C . The positive ion current falls very rapidly to the value characteristic of the new temperature and the old equilibrium value of the surface concentration. We must therefore, suppose that the rate of emission of ions plus atoms is now lower than the rate of arrival of atoms so that the population of the surface rises, together with the positive ion emission, until a new equilibrium concentration is attained in which

* Compare however Bosworth, 'Proc. Roy. Soc.,' A, vol. 150, p. 58 (1935).

the rate of emission of ions plus atoms is once more equal to the rate of condensation of atoms. These results provide particularly direct evidence in support of the view that the constancy of the equilibrium positive ion current is a consequence of a dynamic equilibrium. Further, although the temperature range in the experiments we have described and, as we show later, the range in the values of θ involved, are small, the results do suggest that every incident atom is adsorbed by the surface and that none is reflected, *i.e.*, that the coefficient α is equal to unity. Otherwise, we must assume that the reflection coefficient has a value, different from zero, which is independent of the temperature of the surface and of the population of adsorbed atoms on it. Subsequently we give additional evidence in support of the view that α is

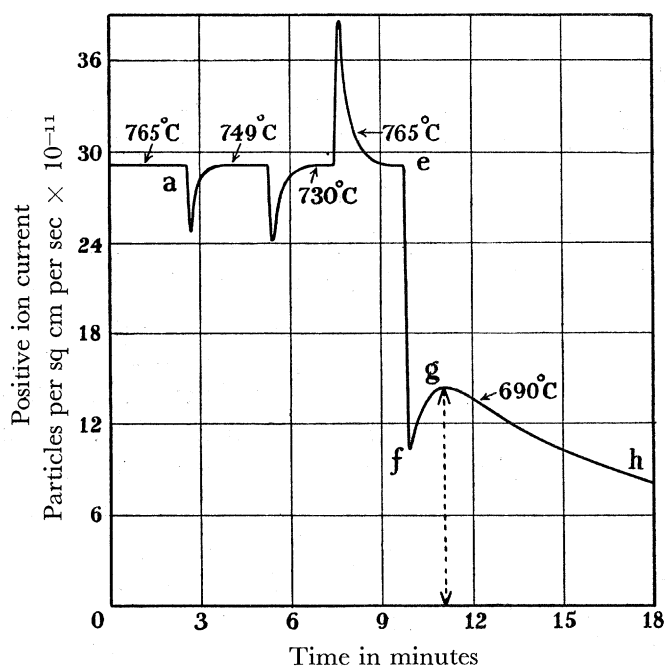


FIG. 2.—One side only of filament bombarded with constant stream of atoms.

equal to unity and we show further that with the low surface concentrations which occur when the filament temperature is sufficiently high the positive ion emission is accompanied by only a small emission of neutral atoms.

Equation (1) thus reduces to

$$\mu = \beta v_+, \quad (2)$$

where $\beta = \frac{v_+ + v_n}{v_+}$. β is a quantity nearly equal to unity, which we determine by a method described subsequently. When the filament temperature is sufficiently high the positive ion current gives, therefore, a measure of the number of atoms striking the filament per second and condensing on it.

If, with a given intensity of the bombarding atom stream, the temperature of the filament is suddenly reduced below a certain critical value, the change in the positive

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ion current with time is of a different form from that previously described. At point "e," fig. 2, for example, the temperature of the filament was suddenly reduced from 749° C to 690° C. The current falls rapidly as at point "a." Subsequently, it rises, reaches a value, *g*, less than that corresponding to the intensity of the bombarding stream, and again falls towards a new low equilibrium value. We defer analysis of this result to §5*b*, but we may note here that in using the positive ion emission as a measure of the intensity of the bombarding stream it is necessary to ensure that the temperature of the filament is so high that the equilibrium positive ion current from it is independent of this temperature.

4—DETERMINATION OF THE QUANTITY β

Applying the results described in the last paragraph a known number of atoms can be deposited on to the oxide by the following method. The furnace heating current is adjusted to a convenient value and the filament is maintained at a sufficiently high temperature to ensure that the positive ion current gives a measure of the intensity of the bombarding stream. When the value of the bombarding stream has been determined the filament is turned out of the stream and kept hot until the positive ion current has fallen to zero showing that all adsorbed atoms have been re-emitted from the oxide. The filament is then allowed to cool and the ground joint is rotated so that the atoms once more bombard the filament at a known rate. When a certain number of atoms have been deposited on the first face of the filament the ground joint is rotated through 180°, the same number of atoms is deposited on to the reverse side and the furnace is allowed to cool. By this method we must expect any element of area presented by the oxide film in the neighbourhood of the central collecting electrode to receive the same number of atoms per sq cm, although this population density must fall off slowly as we move outwards from the centre into the guard ring electrodes. When we speak of the number of atoms per sq cm, of oxide, we shall refer to the number of atoms per sq cm deposited on the oxide in the region of the central collecting electrode. This population density cannot be expressed numerically in terms of the quantity θ because, in contrast with the experiments with caesium on tungsten, which could be interpreted by assuming that the metal presented an almost perfectly uniform two dimensional field for adsorption, we shall show that the film of oxide consists of an aggregate of very small crystals and the total area of the "field" for adsorption which they provide is unknown.

When the deposition has been completed, for reasons given later, the filament is raised for half an hour to a temperature about 200° C below that at which the emission is to be studied. It is then raised to the desired emission temperature, a field is applied tending to drag ions to the collectors, and the way in which the resulting positive ion current varies with time is determined. In all the experiments described in this paper the accelerating potential dragging ions from the filament to the collecting electrodes has been maintained at 240 volts.

When a comparatively small number of atoms has been deposited on the filament, say, less than 3×10^4 per sq cm, the variation of the positive ion current with time when the filament is suddenly raised to the emission temperature is of the form shown in fig. 3, curve "a." The current quickly rises to a maximum and subsequently falls off exponentially. The area under this curve gives a measure of the number of the adsorbed atoms which leave the filament as positive ions during the emission. Let us assume that the total number of particles, atoms plus ions, leaving the filament during this period is β_1 times the number of positive ions. This number can be compared with the number of atoms originally deposited on the filament which depends on the quantity β of equation (2). If the number of atoms deposited on the filament is equated to the number of particles subsequently emitted it is found that $\beta = \beta_1$.

Let us assume that for a metal we can define a quantity ϕ , the electronic work function for the oxide surface when it is free from adsorbed atoms. The presence of

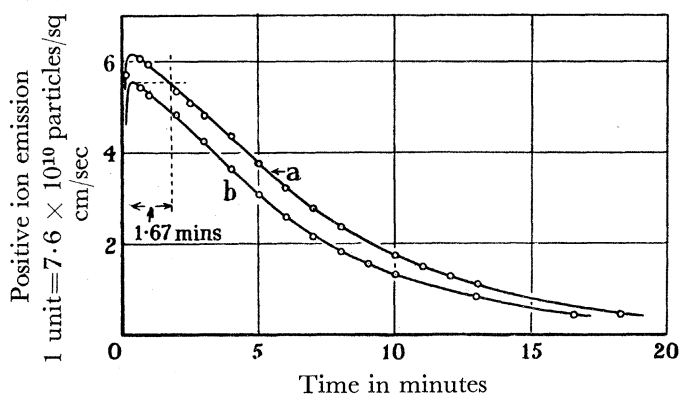


FIG. 3—Indium 656° C. Positive ion emission at constant temperature following deposition of a small number of atoms.

an adsorbed layer of atoms on the surface will give rise to an electrical double layer which will change the electronic work function.* With electro-positive atoms ϕ will be reduced by the presence of the double layer. We may expect the ratio of the positive ion to the neutral atom emission from the surface to vary with the electronic work function according to the relation

$$\frac{\nu_n}{\nu_+} = \epsilon^{-(\phi - I)e/kT} = \gamma \quad (3)$$

where I is the ionization potential of the adsorbed atoms in volts and the other signs have their usual significance. The quantity $\beta \left(= \frac{\nu_+ + \nu_n}{\nu_+} \right)$ in equation (2) is therefore equal to $1 + \gamma$.

The value of β ($= \beta_1$) can be determined experimentally in the following manner. The same number of atoms was deposited on the filament as in the experiment which gave the result illustrated in fig. 3a. After the deposition the filament was raised to the same emission temperature as before, but with the electric field between the

* See GURNEY, 'Phys. Rev.', vol. 47, p. 479 (1935).

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filament and the electrodes reversed, so that no positive ions could leave the filament and it was maintained in this condition for forty minutes. The field was then reversed and the variation of resulting positive ion current with time was measured as previously. The result is shown in fig. 3, curve "b." It will be seen that during the period of "ageing" with reversed field, when only neutral atoms could leave the filament, the number of adsorbed atoms which were lost was equal to the number leaving the filament in 1 min 40 sec, when both neutral atom and positive ion emission was allowed to proceed. We deduce, therefore, that at these low concentrations of adsorbed atoms,

$$\frac{v_+ + v_n}{v_n} = 24 ; \frac{v_+ + v_n}{v_+} = \frac{24}{23}$$

and that $\gamma = \epsilon^{-(\phi-1)e/kT} = 0.044$. Taking the ionization potential of indium to be 5.76 volts, this corresponds to a value of 6.13 volts for ϕ , the electronic work function of tungsten oxide.

For caesium on tungsten an adsorbed layer of 2.4×10^{14} atoms per sq cm, corresponding to $\theta = 0.5$, produces a change in the electronic work function of 2.7 volts. At 656° C with indium atoms on tungsten oxide, such a change in the electronic work function would change the ratio of positive ion to neutral atom emission by a factor of 10^{23} . The experimental determination of β_1/β in the present experiments shows that the quantity γ does not increase by more than 50 % when the concentration of atoms on the surface increases from very low values up to 3×10^{14} per sq cm. We may assume that the strength of the electrical double layer produced by a film of indium atoms on a surface of tungsten oxide is of the same order of magnitude as that of a layer of caesium atoms of the same concentration on tungsten. We therefore conclude that the source must be regarded as composed of small micro-crystals which offer a very large field for the adsorption of atoms. The deposition of a given number of atoms on to the outer surface of the oxide, on to the surface, that is, which is immediately accessible to the bombarding stream, results in the production of very much smaller values of θ than would occur if the atoms were deposited on to a tungsten filament. We show subsequently that the deposited atoms do not migrate over the crystal surfaces at room temperatures. At higher temperatures, however, they move comparatively freely so that we must expect them to migrate into the interior of the oxide film, from the surfaces into which they are directly deposited, immediately the source is heated. Otherwise we should observe very large losses of adsorbed atoms by evaporation as neutral atoms in experiments of the type illustrated by fig. 3 (b).

5—VARIATION OF POSITIVE ION EMISSION WITH SURFACE POPULATION θ

(a) *General Features of the Emission*—When the number of atoms deposited on the oxide is increased the form of the emission curves showing the variation of the positive ion current with time when the filament is subsequently heated is of an entirely

different character from that for small deposits shown in fig. 3. The results of a series of experiments made with successively increasing deposits are shown in fig. 4. It will be seen that the current starts at a certain value, which is smaller the larger the deposit, rises steadily to a pronounced maximum and subsequently falls abruptly. The peak in the positive ion current is sensibly constant whatever the value of the number of atoms originally deposited. Measurements show, further, that the proportion of atoms emitted as positive ions becomes progressively smaller as the number of deposited atoms is increased, corresponding to a rapidly increasing rate of evaporation of neutral atoms at high concentrations.

(b) *Uniformity of phase over the emitting surface*—In their work with caesium on tungsten, TAYLOR and LANGMUIR have observed a similar variation of the positive ion current with time when, following the deposition of caesium atoms, a tungsten filament is heated. In this type of non-equilibrium experiment, however, they show

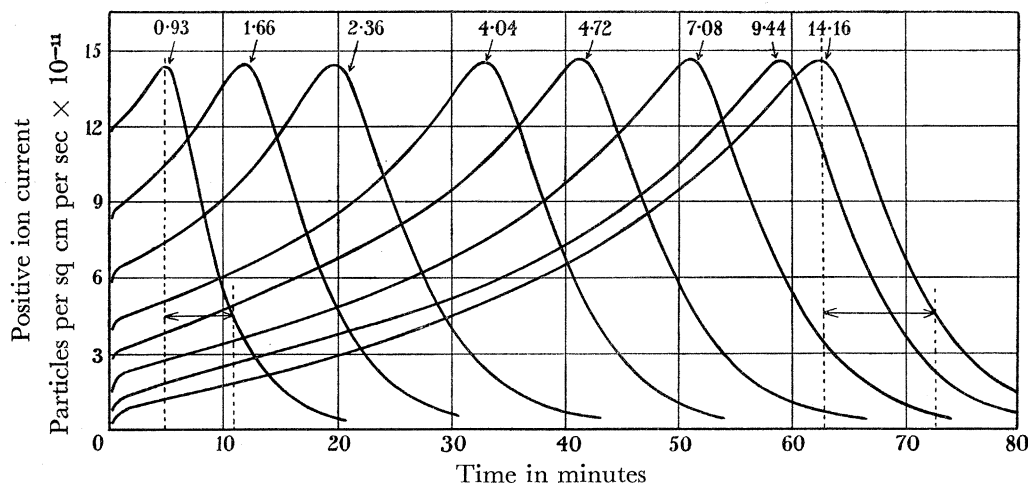


FIG. 4—Indium, 690° C. Positive ion emission following deposition of large numbers of atoms. Numbers represent atoms deposited per sq cm $\times 10^{-15}$.

that when the concentration falls below a certain critical value, the adsorbed layer breaks up into two phases, one dilute the other concentrated, and that the positive ions come largely from narrow regions of intermediate concentration between the two phases where the adsorbed atoms are migrating from the concentrated to the dilute areas. The areas of low concentration are regarded as practically devoid of atoms and the emission from them is negligible whilst the emission from the areas of high concentration consists almost entirely of neutral atoms. In the present experiments we show that in contrast with the behaviour of caesium on tungsten, the concentration of adsorbed atoms throughout the emitting surface is uniform at any stage in the emission. This conclusion is based upon the following observations. A large number of atoms was deposited on the filament and the heating current in the furnace was maintained at a value such that with the tube suitably orientated a known stream of atoms would bombard one side of the filament. Having started the positive ion

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emission in the usual way, the filament was suddenly turned into the atom stream, five minutes after the start of the run. The results are shown in fig. 5, the point at which the atom stream was allowed to bombard the filament being denoted by the arrow $\downarrow a$. It will be seen that the positive ion current is reduced as a result of the bombardment and that it rises again when the filament is turned out of the stream at the point marked $\uparrow b$. The filament was again bombarded at a time after the positive ion current had reached its maximum value and had commenced to fall, point 'c', fig. 5. In this case it will be seen that the positive ion current is very much increased by the atom stream. This definitely proves that above a small value of the concentration at which the positive ion current has a maximum value an increase in the population of the surface atoms leads to a reduction in the positive ion current at a given temperature. Further, we cannot assume that any patches of low concentration are present on the surface, before the maximum in the positive ion current is

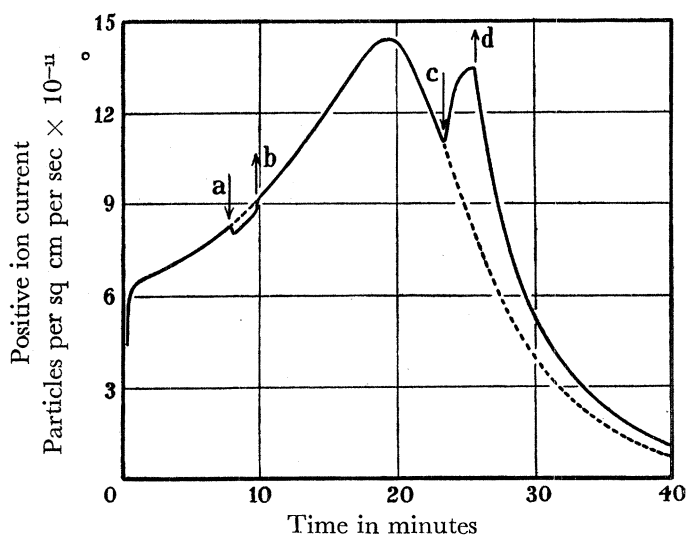


FIG. 5—Effect of bombarding filament at different stages during the emission.

reached, for they would give rise to large positive ion emissions when bombarded by neutral atoms.

Further and conclusive evidence for the uniformity of phase over the emitting surface is provided by the results of observations of the kind illustrated in fig. 2. In these experiments the temperature of the filament, bombarded by a constant stream of neutral atoms, is suddenly reduced from a high temperature, where the equilibrium concentration of atoms on the emitting surface is small, to one of the standard temperatures used in taking the non-equilibrium emission curves. The positive ion current falls, $e-f$ in fig. 2, rises to a maximum, g , as the population of the adsorbed atoms on the surface increases and subsequently falls towards a new equilibrium value, $g-h$. We can compare the maximum in the positive ion current at a given temperature in such an experiment with the maximum in the positive ion current in the non-equilibrium emission curves at the same temperature such as those

given in fig. 4. The ratio of the two peak currents is found to be one to two to within a few per cent. In the experiments in which the filament is being continuously bombarded by atoms we must expect the adsorbed atoms to be distributed in a uniform phase over the emitting surface. The fact that in these experiments only one side of the filament is being bombarded and that the peak current is one half that obtained in the non-equilibrium experiments when both faces of the filament are covered with adsorbed atoms shows quite definitely that in the non-equilibrium experiments also the adsorbed layer does not split up into two phases as it does with caesium on tungsten. In the results published by TAYLOR and LANGMUIR, the maximum positive ion current from a tungsten filament at a certain temperature when the whole of the emitting surface is bombarded continuously by caesium atoms is four times that observed when caesium is deposited and the filament is subsequently heated to the same temperature.

The fact that the emission curves, fig. 4, all rise to the same peak value shows that the thickness of the oxide is uniform to a high degree of accuracy, for otherwise we should expect that as the emission proceeded, different elements of the surface, covering different thicknesses of oxide, would reach the value of the surface concentration corresponding to the maximum rate of positive ion emission per sq cm at different times. In these circumstances, which actually arise if the oxidation is not carried out in appropriate conditions, the peak in the positive ion current is found to be lower and more diffuse the larger the number of atoms deposited on the filament. Since the peak current in these experiments attains a constant value in experiments with widely different numbers of deposited atoms we may assume that the concentration of adsorbed atoms remains accurately uniform over the whole of the emitting surface throughout the emission. At a given temperature a given positive ion current thus corresponds to a given concentration of adsorbed atoms on the emitting surface.

6—MIGRATION OF ADSORBED ATOMS

In an earlier form of the apparatus no provision was made for depositing the atoms onto both sides of the filament. It was then found that following the deposition of a standard number of atoms the variation of the positive ion current with time in the subsequent emission curves could be very much changed by maintaining the filament for different periods of time at the emission temperature but with reversed electric field so that the emission of positive ions from the oxide was prevented. In fig 6, a typical series of curves is drawn showing the change in the form of the emission curves after varying periods of this ageing process. It was found that the number of adsorbed atoms leaving the filament as positive ions, measured by the area under the emission curves, was becoming progressively smaller as the "ageing" period was increased and this was attributed to the uncontrolled evaporation of neutral atoms from the filament during the ageing. Experiments were therefore made in which the ageing was carried out at a temperature about 200° C below the emission

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temperature. If we assume the change in the emission curves to be due to the migration of atoms from the region of high concentrations, where they are deposited, round to the unpopulated regions on the other side of the filament, then we may expect to be able to allow this migration to proceed at temperatures low enough to ensure that the evaporation of neutral atoms is negligible.* We may expect the diffusion coefficient for any concentration of adsorbed atoms to vary less rapidly with temperature than the rate of emission of neutral atoms or positive ions since the energy required to enable an atom to hop from one to another of the available spaces on the surface lattice of the crystals must be less than that required to enable it to leave the surface completely. It was found that after ageing for a sufficiently long period at the lower temperature the positive ion emission curve in the subsequent emission experiment reached a constant form, which remained unaffected by further ageing

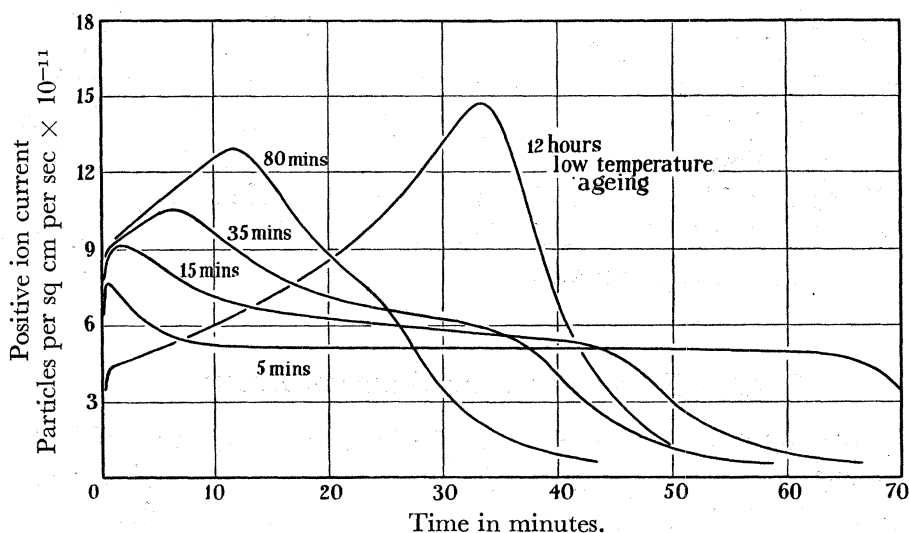


FIG. 6—Effect of ageing following deposition of atoms on one side of filament only.

and which was of exactly the same character as the curves shown in fig. 4. The forms of the curves shown in fig. 6 can all be explained by assuming that by migration different elements in the surface have achieved different concentrations of adsorbed atoms and that when the emission proceeds they make contributions to the variation of the positive ion current with time which is characteristic of their initial concentration. We thus have particularly direct evidence for the migration of the atoms over the oxide surface. The object of the thirty minutes ageing at a low temperature which is applied to the filament after making a deposition in the present experiments is to make use of the migration of the atoms to ensure that their distribution over the micro-crystals throughout the *thickness* of the oxide film is uniform. Although very long periods are required to produce equilibrium when the atoms have to diffuse distances of the order of one millimetre, the thickness of the oxide is

* BECKER. 'Phys. Rev.,' vol. 43, p. 428 (1933).

of the order of a thousandth part of this distance and equilibrium is attained in a correspondingly shorter time.

7—THE CONDENSATION COEFFICIENT α

The experimental result obtained earlier in the paper and expressed by the equation $\beta = \beta_1$ shows that the condensation coefficient α is constant from room temperatures up to the highest temperatures employed in these experiments, when the surface concentration is small. We use the migration of the adsorbed atoms to show that it has the same value when the surface population is high, for the emission curves from the surface corresponding to the deposition of a given *total* number of atoms, as calculated on the assumption that α is constant, is the same whether these are applied half to each side of the filament directly or whether all are applied to one face and the filament is subsequently aged to an equilibrium distribution. The form of the emission curves also remains the same if the filament during the deposition is maintained, with reversed field, at any temperature below that at which neutral atom evaporation becomes appreciable. These results show that α is independent of both θ and T over a wide range of values and strongly suggest that it is equal to unity. In what follows we shall assume that α is equal to unity under all conditions existing in these experiments.

8—THE EVAPORATION OF NEUTRAL ATOMS

Using the results of the previous paragraphs it now becomes possible to make determinations of the rate of evaporation of neutral atoms corresponding to different concentrations of adsorbed atoms on the emitting surface. This determination is, however, somewhat complicated at the higher temperatures by considerations which can be understood by reference to the emission curves shown in fig. 4. Starting with a uniform distribution of atoms over the crystal surfaces throughout the mass of the oxide, we must assume that as the emission proceeds the concentration of atoms at the emitting surface gradually falls with time, thus giving rise to the observed changes in the positive ion current. Let us assume that at the emission temperature the rate of diffusion is sufficiently rapid to ensure that the concentration of adsorbed atoms on the crystal surfaces is uniform throughout the *thickness* of the oxide right up to the actual emitting surface. The total number of atoms emitted from the oxide while the concentration changes from a value θ_1 , at which the positive ion emission has the value i_1 , to the value θ_2 at which the positive ion current equals i_2 , will then equal $N(\theta_1 - \theta_2)$, where N is the total number of atoms which could be accommodated as a complete monomolecular layer over the whole of the crystal surfaces, and this quantity will be constant whatever the number of atoms on the oxide at the beginning of the experiment. Similarly, the number of positive ions emitted during this same period will be the same in different experiments. From fig. 4 it will be seen that this

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condition is not fulfilled in the actual experiments. The total number of positive ions leaving the oxide when the positive ion current changes from one to another of two given values is increased by about 50% in going from the experiment with the smallest to that with the largest of the deposits. This result must be a consequence of the rate of migration being too small to maintain a uniform phase throughout the thickness of the oxide when atoms and ions are being emitted from the outermost surface. When, therefore, in any experiment, the surface concentration has reached a given value, the distribution of atoms over the surfaces throughout the interior of the oxide depends upon the number of atoms originally deposited. It will be seen, however, that the curves corresponding to a wide range of the heavier deposits are closely similar. At lower temperatures this range increases to include the experiments with low deposits and for these temperatures it is possible to determine the

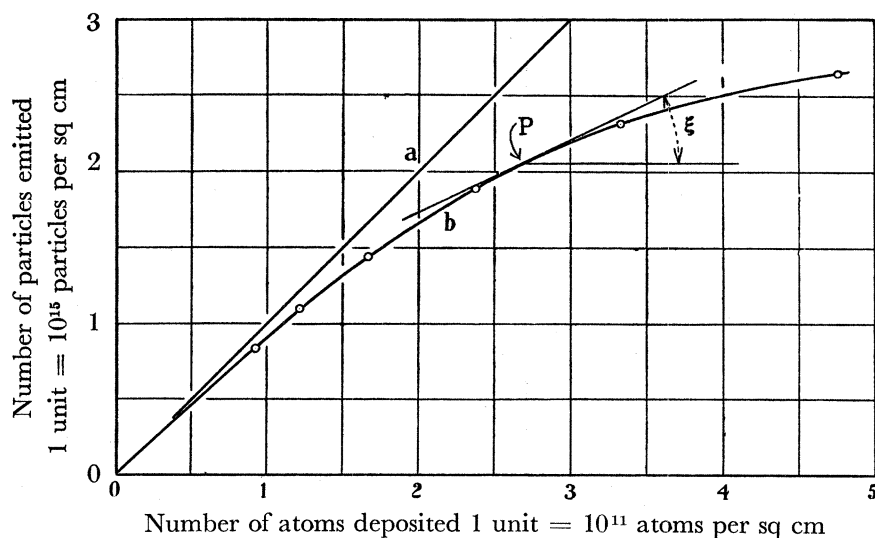


FIG. 7—Variation in total number of positive ions leaving filament with the total number of atoms deposited. (a) Total number of particles emitted; (b) Number of positive ions emitted.

neutral atom emission at different values of the surface concentration by the following method.

A curve is plotted showing the total number of positive ions leaving the oxide as a function of the number of atoms originally deposited on it. Such a curve is shown in fig. 7 for the results given in fig. 4. At any point, P, in this curve a tangent is drawn and the inclination of the tangent to the axis determined. If the inclination is ξ then we can write $\frac{v_+ + v_n}{v_+} = \cot \xi$, in the condition that the filament has the number of atoms deposited on it represented by the point P. The positive ion emission corresponding to this number of adsorbed atoms can be determined unambiguously from the experimental results and the neutral atom emission is then defined by the relation $v_n = v_+ (\cot \xi - 1)$.

The speed of migration varies with temperature less rapidly than the rate of emission of atoms, and we have seen that at the higher temperatures we cannot assume that the positive ion emission determines unambiguously the number of atoms left on the oxide. At these temperatures the above method leads to an error in the determination of the neutral atom emission. The method, however, gives an approximation which has subsequently to be adjusted. The final curve for the neutral atom emission corresponding to different positive ion emissions from the surface must have such a form that it fulfils the following conditions. In any experiment of the type represented by one of the curves in fig. 4, the variation in the neutral

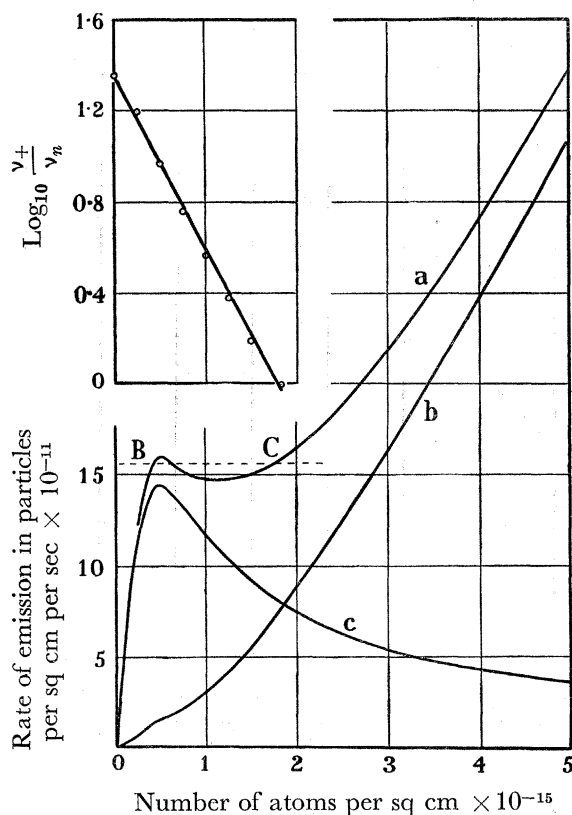


FIG. 8—Indium 690° C. Variation of rate of emission of positive ions and neutral atoms with surface concentration. (a) Total emission; (b) neutral atom emission; (c) positive ion emission.

atom emission with time is plotted by reference to the corresponding positive ion curve. The curve showing the variation with time of the rate of emission of atoms plus ions from the surface can then be drawn, and the area under this curve gives a measure of the total number of particles leaving the filament during the emission. The curve showing the variation of the neutral atom emission with surface concentration must be such that this number is equal to the number of atoms originally deposited on the filament, and this condition must be fulfilled for all the curves of a series at a given temperature corresponding to different numbers of deposited atoms. This

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gives a unique determination of the neutral atom emission accompanying any value of the positive ion emission.

In order to associate these values of the positive ion and neutral atom emission with the concentration of atoms in the emitting surface to which they correspond, we assume that at the beginning of any experiment, when the emission is started, the concentration of atoms over the crystal surfaces is sensibly constant throughout the whole mass of the oxide. In fig. 8 a curve is drawn showing the initial positive ion current following the deposition of various numbers of atoms on to the oxide, together with the corresponding values of the neutral atom emission. The sum of these curves gives the total rate of emission of atoms and ions, and it will be seen that this rate rises rapidly with increasing surface concentration, falls to a minimum and again rises sharply. Included in the figure is a curve showing the variation of $\log_{10} \nu_+/\nu_n$ with the number of deposited atoms. It will be seen that the electronic work function varies almost linearly with the surface concentration of adsorbed atoms in the range covered in the present experiments.

9—ALTERNATIVE METHOD OF DETERMINING THE NEUTRAL ATOM EMISSION

In another form of the apparatus the rate of emission of neutral atoms has been determined directly by employing a second oxidized strip parallel to the axis of the tube which intercepts a certain fraction of the atoms evaporating from the central filament.

If at any moment, during the emission of positive ions and neutral atoms from the main filament, the auxiliary strip is suddenly heated, the positive ion current to the central collecting electrode will be increased. This increase will in general be made up of two parts; that due to the atoms which have accumulated on the auxiliary strip, and that due to the continuous arrival of atoms on it. After the auxiliary strip has been at a sufficiently high temperature for a short time the increased positive ion current to which it gives rise will be due entirely to the bombarding neutral atoms. The number of these atoms can therefore be determined by switching off the heating current through the auxiliary strip and observing the resulting decrease in the positive ion current to the central collector. If the temperature of the auxiliary strip has been sufficiently high, the concentration of atoms on its surface will have been low, and the positive ion current from it will give a measure of the neutral atoms reaching it.

An example of the application of this method to the determination of the rate of evaporation of neutral atoms from the main filament is shown in fig. 9. At the beginning of the experiment, from *a* to *b*, the emission proceeds normally with the auxiliary strip cold. At point *b*, the main filament was allowed to cool, and the auxiliary strip was heated to drive off the atoms which had accumulated during the time *a-b*. With the auxiliary strip still hot, the main filament was again raised to the standard emission temperature and the positive ion current, and its variation with time was determined, *b-c-d*. The positive ion current is greatly increased by

the presence of the heated auxiliary strip. At the point d the auxiliary strip was suddenly allowed to cool, and the positive ion current dropped to the value e . The drop in the positive ion current $d-e$ gives a measure of the number of neutral atoms reaching the strip when the positive ion current from the main filament has the value $e-f$, and the corresponding value of the neutral atom emission from the main strip can be calculated. From results of this kind we can determine the variation in the neutral atom emission from the main strip with the concentration of deposited atoms on the oxide surface and the results are in agreement with those deduced by the previous method. This second method can only be applied in conditions where the neutral

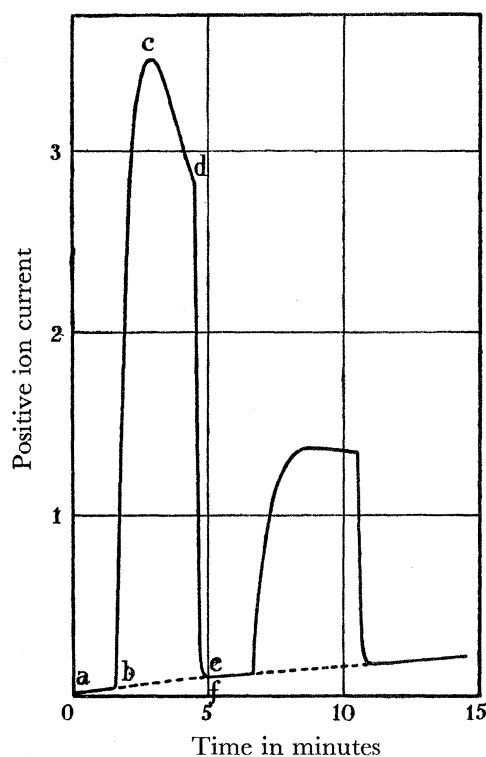


FIG. 9—Increase in positive ion current due to presence of auxiliary filament.

atom evaporation from the filament is large compared with the rate of emission of positive ions since the auxiliary strip only intercepts a small fraction, about one-thirtieth, of the neutral atoms leaving the filament.

10—THE POSITIVE ION WORK FUNCTION

The fact that the migration of the atoms is insufficient to maintain a uniform phase throughout the whole of the oxide when emission is taking place from the surface prevents the determination of the work function of the positive ions for a range of values of the surface concentration. For suppose that, with a given number of atoms

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on the surface the positive ion current is measured at a given temperature, on lowering the temperature to a new value the positive ion current will change not only as a consequence of the reduction in temperature of the oxide but because the concentration of atoms at the actual emitting surfaces increases as a result of the reduced rate of emission at the lower temperature. It was found that if measurements were made with a given number of atoms deposited on the oxide then the values of $\log \nu_+$ plotted against $1/T$, where T is the absolute temperature of the oxide, gave points lying accurately on a straight line. The gradient of this line could not, however, be regarded as a measure of the positive ion work function, because similar results in experiments with a wide range in the number of adsorbed atoms on the oxide gave a series of lines, all with the same gradient. In the experiments in which the variation of the positive ion current with time, following the deposition of atoms, is measured, fig. 4, the increase in the positive ion current as the emission proceeds can only be explained as a consequence of a decrease in the positive ion work function with decreasing concentration. The parallelism of the $\log \nu_+, 1/T$ curves must therefore be regarded as fortuitous, and due to the interplay of the various factors which together determine the emission.

If we assume that at different temperatures the maximum in the positive ion current corresponds to a given concentration of adsorbed atoms on the emitting surface, an assumption which must be very nearly true, then we can determine the value of the positive ion work function corresponding to this concentration. The value so found is 1.20 volts.

11—VARIATION IN THE TOTAL RATE OF EMISSION FROM THE SURFACE WITH CONCENTRATION OF ADSORBED ATOMS

The form of the variation of the total rate of emission of ions, plus atoms from the surface, given in fig. 8, has similar characteristics to that given by TAYLOR and LANGMUIR for caesium on tungsten. The emission rises to a maximum, falls to a minimum, and again rises sharply. It was first pointed out by BECKER that such a curve showed that either of two phases of the adsorbed layer, such as those represented by the points B and C, could be in stable equilibrium with a bombarding stream of intensity represented by OA. In non-equilibrium experiments with caesium on tungsten when the concentration of the adsorbed layer falls below a certain value the layer does break up into two phases. Although in the present experiments the depth of the minimum in the total emission curve is of a different order of magnitude from that for caesium on tungsten, the curve is of the form which might lead to the growth of two phases. The fact that the adsorbed atoms remain on the field in a uniform phase must be due to the rate of diffusion being sufficiently rapid to prevent the appearance of a dilute phase.

EXPERIMENTS WITH THALLIUM

12— ν_+/ ν_n FOR LOW CONCENTRATIONS OF ADSORBED ATOMS

The methods developed for the investigation of the adsorption of indium atoms on tungsten oxide have been extended to the metals thallium and gallium. The results for thallium will be described briefly, emphasis being given only to those points where there is a difference between the new results and those already described.

Experiments of the type illustrated for indium in fig. 3 *a* and *b*, show that with thallium the rate of emission of neutral atoms is no longer small compared with that of positive ions even at very low concentrations of atoms where the electronic work function of the surface must be almost identical with that for the clean surface. The mean value of the quantity ν_+/ν_n at low concentrations, in a series of experiments at a temperature of 656° C, was found to be 3·4. If we substitute these quantities in the equation

$$\frac{\nu_n}{\nu_+} = \epsilon^{-(\phi - I)e/kT}$$

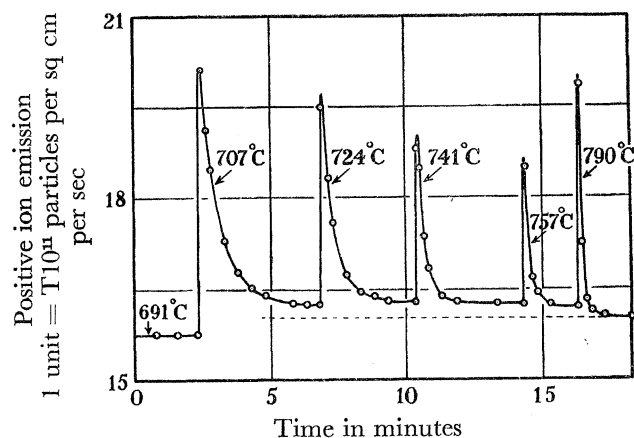


FIG. 10—Thallium. One face of filament bombarded with constant atom stream.

taking the ionization potential of thallium to be 6·08 volts, we deduce a value of ϕ equal to 6·25 volts, in fair agreement with the result in the experiments with indium. The appreciable value of the neutral atom emission has an influence on the equilibrium experiments of the type represented in fig. 2. With indium the positive ion current is sensibly independent of the temperature over a wide range when the filament is bombarded by a constant stream of neutral atoms. It is shown in fig. 10 that with thallium, if the temperature is sufficiently high, an increase in temperature produces a decrease in the positive ion emission. This result is easily explained since the ratio $\nu_+ / (\nu_+ + \nu_n)$ varies with the temperature. The ratio of the total to the positive ion emission is equal to $1 + \epsilon^{-(\phi - I)e/kT}$. Since the total emission is equal to the constant bombarding stream in these experiments, and since $\nu_+ / (\nu_+ + \nu_n)$ decreases with increasing temperature, we must expect ν_+ to fall as T increases. The

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actual fall observed is too small to enable an accurate value of ϕ to be calculated, but it is equal to that expected from the previously determined value of ϕ to within the limits of the experimental error.

13—VARIATION OF POSITIVE ION AND NEUTRAL ATOM EMISSION WITH SURFACE CONCENTRATION

A series of experiments was made, similar to those with indium in which a known number of atoms having been deposited on to the oxide the emission at a convenient temperature was studied. The curves show the same general features as in the

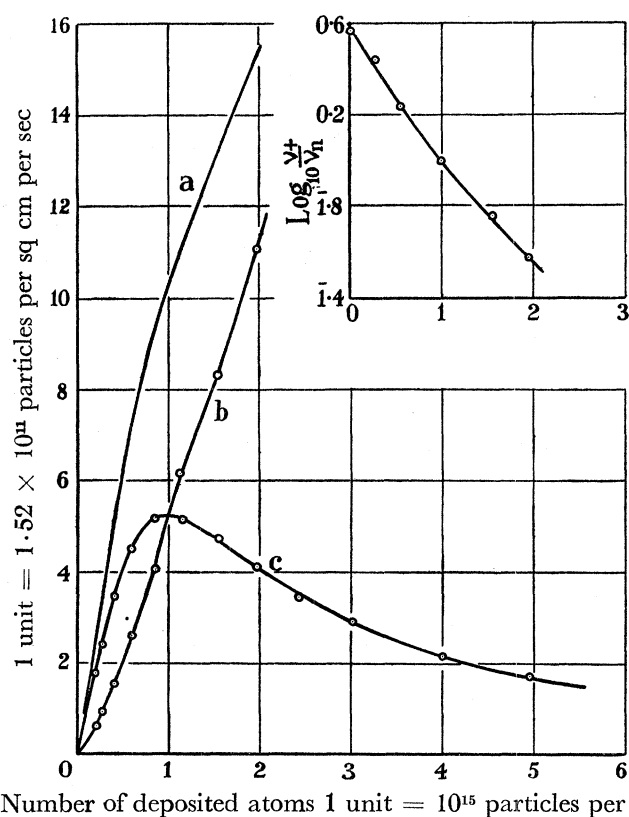


FIG. 11—Thallium 656° C. Variation of rate of emission of positive ions and neutral atoms with surface concentration. (a) $v_+ + v_n$; (b) neutral atom emission v_n ; (c) positive ion emission v_+ .

experiments with indium, and as with indium, it was shown that the phase at the emitting surface remained uniform throughout the emission. Fig. 11 shows the variation of the positive ion and the neutral atom emission at various surface concentrations of adsorbed atoms calculated by the methods previously described. It will be seen that with thallium the total emission increases steadily with increasing surface concentration, so that there is no possibility of the adsorbed layer splitting up into two phases. The variation of the electronic work function with the number of deposited atoms is also shown in fig. 11. This curve can be compared with the

corresponding curve for indium given in fig. 8. The results for the two metals shown in these figures were obtained with the same oxide film, and they therefore enable us to make a comparison between the dipole moment to be associated with a thallium and with an indium atom at low concentrations on tungsten oxide. The mean of a number of determinations of this ratio, thallium to indium, is 0.80.

14—EXPERIMENTS WITH GALLIUM

It has not been possible to extend the results obtained with thallium and indium to include gallium. The gallium atoms are much more tightly bound to the surface than indium or thallium. In order to obtain appreciable emissions of positive ions and neutral atoms it becomes necessary to heat the oxide to high temperatures where it starts to disintegrate, either by decomposition, or, more probably, by evaporation. At the temperatures at which the oxide is stable, the emission is very slow, and quite a small deposit requires a time of the order of three days before the atoms are completely re-emitted from the surface. If a deposit of gallium atoms is made the adsorption properties of the surface for indium or thallium atoms are completely changed. We may expect such a deposit to act as a catalytic poison. In a previous paper using iron oxide instead of tungsten oxide, a similar effect was observed, and it was suggested that in some instances catalytic poisoning may be regarded as due to the adsorption by the active surfaces of any substance which cannot be removed from the surface without heating to such a temperature that the catalyst itself is destroyed.

15—GENERAL REMARKS

Experiments have been made with a number of other oxides in an attempt to find the most satisfactory substance to serve as a base for the production of thermionic sources of positive ions. The ideal material for such a source would be a highly refractive oxide with a large electronic work function. So far we have examined nickel oxide, uranium oxide, iron oxide, and molybdenum oxide. The electronic work functions of nickel oxide and uranium oxide are lower than that of tungsten oxide, and only very small emissions of positive ions of the elements indium and thallium can be obtained. Molybdenum oxide is unsatisfactory because it evaporates at a low temperature. Iron oxide has an electronic work function very close to that of tungsten oxide, and the limiting temperature at which it can be maintained for long periods is of the same order as with tungsten oxide. Other oxides are being examined.

Tungsten or iron oxide, especially in the form of thin uniform layers produced by the oxidation of the metal in air, give very satisfactory "fields" on which to study the migration of the surface atoms, and, in particular, the variation of the diffusion coefficient with surface concentration. The comparatively large capacity of such a

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film enables one to work with much larger numbers of atoms than are adsorbed on a single surface, and with indium and thallium the interpretation of the results is not complicated by a tendency of the adsorbed layer to split into two phases. We may point out here that in the present experiments the observed migration cannot be explained as a movement of the atoms by evaporation from one crystal face to another in the interior of the crystalline mass. For if such a process were of importance then we should expect large losses of adsorbed atoms by evaporation from the outermost surface, whereas, even in the experiments in which the atoms are deposited on to one face of the oxide and migrate round to the back, the long "ageing" period produces no measurable loss of the deposit.

We are much indebted to Professor A. M. TYNDALL, F.R.S., for his interest throughout the course of these investigations and for numerous discussions; and to the Colston Research Society of the University of Bristol for a grant for the purchase of apparatus. We are also indebted to the skill of Mr. J. H. BURROW and Mr. H. F. TRESSIDER in the construction of the apparatus.

16—SUMMARY

A method is described for producing thin stable films of the metallic oxides of uniform thickness. The films can be heated uniformly, their temperature can be determined accurately and changed quickly. With a film of tungsten oxide an accurate and detailed study of the characteristics of the adsorption and emission of indium and thallium atoms on the "field" provided by the oxide has been made. These characteristics are compared with those of caesium on tungsten, and the extent to which the conceptions developed by TAYLOR and LANGMUIR can be applied to the case of atoms adsorbed on the surface of a metallic oxide is examined.

It is shown that of the indium or thallium atoms striking the surface a constant fraction is adsorbed, independent of the temperature of the surface and of the number of atoms adsorbed on it over a wide range of values. This fraction is probably equal to unity.

When the heated surface of the oxide is bombarded with indium atoms, a dynamic equilibrium is set up in which the number of atoms arriving at the hot surface is balanced by the emission of positive ions and neutral atoms. The ratio of the positive ion emission to that of neutral atoms enables a determination of the electronic work function of the surface when free from adsorbed atoms, to be made. The experiments with indium give the value 6·13 volts and with thallium 6·25 volts.

The variation of the positive ion, ν_+ , and neutral atom emission, ν_n , with surface concentration of adsorbed atoms has been measured. The ratio ν_n/ν_+ increases with surface concentration corresponding to a linear decrease of the electronic work function in the range of surface concentrations examined.

When a large number of atoms of the order of 10^{16} per sq cm are deposited on the surface and the oxide is heated, the positive ion current starts from a low value,

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increases with time to a pronounced maximum, and subsequently falls rapidly to zero. It is shown that the adsorbed layer remains in a uniform phase over the emitting surface throughout the emission.

The necessary characteristics of an oxide required to serve as a base for thermionic sources of positive ions is discussed, and the actual characteristics of a number of oxides are described.