

*Thermionic Effects caused by Vapours of Alkali Metals.*

By IRVING LANGMUIR and K. H. KINGDON, of the Research Laboratory,  
General Electric Company, Schenectady, N.Y.

(Communicated by Prof. Sir E. Rutherford, F.R.S.—Received November 18, 1924.)

Early in 1923 it was shown\* that a tungsten filament heated to  $1200^{\circ}$  K or more in saturated caesium vapour converts all caesium atoms which strike it into caesium ions. Thus when the filament is surrounded by a negatively charged cylinder a positive ion current flows from the filament, which is independent of the filament temperature (above  $1200^{\circ}$  K) and independent of the applied potential, if this is sufficient to overcome the space charge effect of the positive ions. At lower voltages the currents follow the  $3/2$  power law, and the currents are smaller than the corresponding electron currents obtainable from the same filament in the ratio of the square roots of the masses of the electrons and caesium ions.

The reason that the caesium atoms lose their valence electrons so readily upon contact with the filament, is merely that the electron affinity of tungsten (Richardson work function) is  $4.53$  volts, while the electron affinity of a caesium atom (ionising potential) is only  $3.88$  volts. Experiments showed in fact that if the work function for the filament is lowered to  $2.69$ , by allowing a monatomic layer of thorium atoms to accumulate on the surface (by diffusion from the interior of a thoriated tungsten filament), the positive ion emission becomes negligible.

The positive ions must be attracted to a tungsten surface because of the electron image force. Thus it is that below about  $1200^{\circ}$  K the caesium ions evaporate so slowly from a tungsten surface that this becomes partly covered by adsorbed caesium ions. The presence of these ions, however, lowers the electron affinity of the surface, so that when about 20 per cent. of the surface is covered, the work function falls below the ionising potential of the caesium. With more caesium on the surface the caesium atoms which strike the filament no longer escape in the form of ions but remain in the atomic state. Thus the positive ion currents disappear below about  $1100^{\circ}$  K. But the lowering of the electron affinity raises the electron emission, and when the surface becomes more completely covered by caesium as the temperature is lowered, the electron

\* Langmuir and Kingdon, *Science*, vol. 57, p. 58 (1923), and *Phys. Rev.*, vol. 21, p. 380 (1923).

emission rises to a maximum (of about  $10^{-5}$  amps. per  $\text{cm.}^2$  at  $700^\circ$ ) and then decreases rapidly at still lower temperatures, in accordance with Richardson's equation.

By heating a tungsten filament in a low pressure of oxygen its surface may be covered by a monatomic film of oxygen ions, which does not evaporate appreciably below  $1600^\circ$  K and which raises the electron affinity of the surface to 9.2 volts. On this surface, atoms such as those of copper, which have ionising potentials below about 9 volts, can be converted into positive ions, although others (such as mercury) with ionising potentials of 10 volts or more, do not form positive ions.\*

Cæsium ions are held more firmly by the adsorbed oxygen film than by a surface of tungsten, so that with a cæsium vapour pressure (at  $30^\circ$  C.) of only 0.0029 bar, the surface remains practically completely covered by cæsium ions, up to a filament temperature of  $1000^\circ$  K, and thus the electron emission reaches the high value of 0.35 ampere per  $\text{cm.}^2$ .

Since these results were published, detailed experimental studies of these phenomena have been made and the theory has been further developed. Full presentation of the data and the derivation of the theoretical results will be reserved for a paper to be submitted to the *Physical Review*, while in the present paper the aim will be to outline the view-point which has been arrived at and to state conclusions.

#### *Thermal Ionisation of Cæsium Vapour.*

The degree of thermal ionisation of cæsium vapour may be calculated from the ionising potential by the modified form of Saha's equation given by Fowler and Milne (*Monthly Notices, Roy. Astron. Soc.*, vol. 83, p. 403 (1923)). The ionisation of cæsium vapour at a pressure of 0.001 bar and  $1200^\circ$  K should be 0.00095, or only one-tenth per cent. A similar calculation for the degree of thermal excitation (corresponding to the first resonance potential of 1.48 volt) is only  $6 \times 10^{-7}$ .

Saha (*Phil. Mag.*, vol. 46, p. 534 (1923)) has attempted to calculate the electric conductivity of cæsium vapour from the degree of thermal ionisation, but has obtained results only partly in accord with experiments.

Let us consider an enclosure at  $1200^\circ$  K, having walls of tungsten and containing cæsium vapour corresponding to a pressure (ions + atoms) of 0.001 bar. Our experiments have shown that practically all cæsium atoms which strike tungsten surfaces at this temperature are converted into ions and

\* Kingdon, *Phys. Rev.*, vol. 23, pp. 774, 778 (1924).



leave the surface in this condition. The normal free path of the caesium atoms, being of the order of  $10^4$  cm. at this pressure, is so great that, with an enclosure of reasonable size, practically every atom or ion in any element of volume will have collided with the walls many times since its last collision with another particle in the free space. It is thus clear that nearly all the caesium atoms in a small enclosure at  $1200^\circ$  K must be converted to ions.

At first sight this conclusion seems to be entirely inconsistent with the degree of ionisation of  $10^{-3}$  calculated from the Saha equation. But we must remember that in calculating the degree of ionisation it was assumed that the concentrations of electrons and ions in the ionised gas are equal.\* Since the walls of the enclosure give off electrons, there is no necessary relation between the concentrations of the ions and the electrons. What Saha's equation really gives is the equilibrium constant,

$$K_n = \frac{n_e n_p}{n_a}, \quad (1)$$

where  $n_e$ ,  $n_p$ , and  $n_a$  are respectively the number of electrons, of positive ions and of atoms per unit volume. The value of  $K_n$ , when  $n_e$ ,  $n_p$ , and  $n_a$  denote the numbers of particles per cm.<sup>3</sup>, is given by

$$\log_{10} K_n = 15.385 + \frac{3}{2} \log_{10} T - \frac{19530}{T}. \quad (2)$$

At  $1200^\circ$  K the value of  $K_n$  is 5340. The electron emission from any metal is given by

$$I = AT^2 e^{-b/T} \quad (3)$$

where, for pure tungsten,  $A = 60.2$  amperes per cm.<sup>2</sup> deg.<sup>-2</sup> and  $b = 52,600$  degrees. The electron density  $n_e$  is obtainable from the electron emission  $I$  by the relation

$$n_e = \left( \frac{2\pi m}{e^2 k T} \right)^{\frac{1}{2}} I = 4.034 \times 10^{13} \frac{I}{\sqrt{T}}, \quad (4)$$

being expressed in amperes per cm.<sup>2</sup> and  $n_e$  in electrons per cm.<sup>3</sup> Thus we find that  $n_e$ , the number of electrons per cm.<sup>3</sup> in equilibrium with tungsten at  $1200^\circ$  K, is 9.25. Inserting this value of  $n_e$  in equation (1) together with the above value of  $K_n$ , 5340, we obtain  $n_p/n_a = 577$ . Thus if 578 caesium atoms or ions strike a tungsten surface at  $1200^\circ$  K, an average of only one will leave the surface as a neutral atom, while 577 leave as ions. This conclusion is in accord with the experiments.

\* This tacit assumption in Saha's recent paper is largely responsible for the discrepancy between his conclusions and the experimental data.

Suppose, on the other hand, the walls of the enclosure are completely covered by a single layer of thorium atoms. The electron emission for the surface is then given by equation (3), with the constants  $A = 7.0$  and  $b = 31,200$ , so that by equation (4) we find  $n_e = 6.0 \times 10^7$ . Then by equation (1) we obtain  $n_p/n_a = 8.9 \times 10^{-5}$ . This means that only one atom of 11,000 striking a fully thoriated tungsten surface would leave it as an ion. This is in accord with the observation that the positive ion emission from a thoriated filament in caesium vapour is negligible compared with that from pure tungsten.

Table I.—Thermal Ionisation of Caesium Vapour in Contact with Pure Surfaces of Tungsten and Thoriated Tungsten.

T.	$K_{n_e}$	Tungsten.		Thoriated Tungsten.	
		$n_e$	$n_p/n_a$	$n_e$	$n_p/n_a$
500	$2.35 \times 10^{-20}$	$5.56 \times 10^{-27}$	4230000	$2.52 \times 10^{-9}$	$9.33 \times 10^{-12}$
1000	2.26	$1.10 \times 10^{-3}$	2060	$2.52 \times 10^5$	$8.96 \times 10^{-6}$
1200	$5.34 \times 10^3$	9.25	577	$6.00 \times 10^7$	$8.90 \times 10^{-5}$
1500	$1.34 \times 10^7$	$8.29 \times 10^4$	162	$1.52 \times 10^{10}$	$8.80 \times 10^{-4}$
2000	$3.72 \times 10^{10}$	$8.22 \times 10^8$	45.3	$4.25 \times 10^{12}$	$8.75 \times 10^{-3}$
2500	$4.67 \times 10^{12}$	$2.21 \times 10^{11}$	21.1	$1.34 \times 10^{14}$	$3.49 \times 10^{-2}$

Table I gives data for the thermal ionisation of caesium vapour in enclosures of tungsten and fully activated thoriated tungsten. These figures are based on the assumption that the electron emission is that which is characteristic of the material of the walls and is not altered by the presence of the caesium vapour. This assumption is only valid if the temperatures are so high, or the vapour pressure of caesium so low, that no appreciable adsorption of caesium occurs. From the table it appears that caesium vapour in contact with tungsten walls at  $500^\circ$  K should be practically completely converted to ions. That this does not occur can be due only to the presence of adsorbed caesium, which increases the electron emission of the walls.

The degree of ionisation  $n_p/n_a$  decreases with rising temperature with tungsten, whereas it increases with thoriated tungsten. The positive ion emission from a pure tungsten surface in presence of caesium vapour is practically always limited by the rate at which the caesium atoms arrive at the surface, so that it is not practicable to use measurements of the positive ion currents from pure tungsten surfaces to determine experimentally the value of  $K_{n_e}$  and thus to check the theory.



With pressures of caesium corresponding to room temperature (0.001 bar), the number of positive ions generated becomes small compared to the number of atoms that strike the filament, if the filament temperature is below about 1150° K, but the electron emission at this temperature is too small to measure. At the still lower temperature at which large electron emissions are obtained from the filament due to the adsorbed caesium, the positive ion currents are too small to measure. However, by raising the pressure of the caesium vapour to 0.1 bar or more, it becomes possible to measure the positive ion and the electron emissions at the same filament temperature, and thus obtain data for determining experimentally the degree of thermal ionisation of caesium.

A pure tungsten filament was heated to 1177° K in a bulb containing saturated caesium vapour at 70° C. By applying first positive and then negative potentials to the surrounding collecting electrode, the electron and the positive ion emissions were measured. The currents increased a little with increasing voltage, because of the Schottky effect, so that they were corrected by extrapolating to zero volts by plotting the logarithms of the currents against the square roots of the voltages.\*

The electron emission at 1177° K was  $2.22 \times 10^{-6}$  and the positive ion emission  $2.06 \times 10^{-6}$  ampere per cm<sup>2</sup>. The electron emission from a pure tungsten surface at this temperature in absence of caesium is  $3.25 \times 10^{-12}$ . On raising the filament temperature to 1300° K or more, the positive ion current increased to  $2.43 \times 10^{-3}$ , and was then independent of the filament temperature and applied voltage, if this voltage were high enough to overcome the positive ion space charge. This ion current is thus a measure of the rate at which caesium atoms strike the filament and corresponds to  $1.52 \times 10^{16}$  atoms per sec. per cm<sup>2</sup>, or a pressure of 0.122 bar of caesium vapour.

At the lower temperature (1177° K) the atoms still strike the filament at the same rate, although the positive ion current is only 1/1180 as great as at the higher filament temperatures. The conditions at the surface of the filament must be essentially the same as though it were surrounded by an enclosure at 1177° K, containing such a concentration of caesium vapour that  $1.52 \times 10^{16}$  atoms strike each square cm. per second. This concentration would be

$$n_a = 1.40 \times 10^{12} \text{ atoms per cm.}^3$$

which corresponds to a pressure of 0.226 bar.

If the filament were in an enclosure at 1177° K under equilibrium conditions

\* S. Dushman, *Gen. Electr. Rev.*, vol. 26, p. 157 (1923).

with this concentration of caesium, the filament would emit and absorb electron and ion currents equal to those measured in the bulb at 70° C. From these observed currents we may thus calculate by equation (4) the equilibrium concentration of electrons and ions. We obtain in this way

$$n_e = 2.60 \times 10^6 \text{ electrons per cm.}^3,$$

$$n_p = 1.19 \times 10^9 \text{ ions per cm.}^3.$$

Substituting these values of  $n_a$ ,  $n_e$  and  $n_p$ , in equation (1) we obtain, for the experimentally determined value of  $K_n$  at 1177° K,

$$K_n (\text{exp.}) = 2210 \text{ per cm.}^3,$$

while calculation from equation (2) at 1177° K gives

$$K_n (\text{calc.}) = 2500 \text{ per cm.}^3.$$

This difference in the two  $K_n$ 's corresponds to a very small change in temperature. To obtain  $K_n = 2210$  from equation (2), we need only to substitute  $T = 1174$  instead of  $T = 1177$ . The agreement between the observed and calculated values is thus as close as the accuracy of the temperature measurements.

A similar set of data was taken with the filament at 1254° K and the bulb at 80° C., giving a caesium vapour pressure of 0.266 bar. The electron and ion currents were  $3.74 \times 10^{-6}$  and  $2.03 \times 10^{-5}$  ampere per cm.<sup>2</sup> respectively. The value of  $K_n$  found from these measurements was 16,600, while equation (2) gives 28,700. The error is larger, but the experimental value corresponds to that given by equation (2) at  $T = 1236^\circ$ , which agrees reasonably well with the observed temperature of 1254°. These experimental determinations of the thermal ionisation of caesium vapour thus give results in full accord with Saha's equation, and verify the Sackur-Tetrode value of the chemical constant as applied to ionisation.

In these experiments the ion currents used in determining  $n_p$  corresponded to a negligible fraction of the atoms striking the surface ( $n_a$ ). When  $n_p$  calculated from the ion current is not negligible compared to the  $n_a$  corresponding to the caesium pressure, there will be an appreciable departure from the equilibrium conditions. An analysis of the kinetics of the positive ion emission has led to the following equation for calculating  $K_n$  under these conditions,

$$K_n = \frac{n_e n_p}{n_a - n_p}. \quad (5)$$

Thus the effective concentration of caesium is not  $n_a$ , but is  $n_a - n_p$ .



If the collecting electrode is made positive, the positive ion current and  $n_p$  fall to zero, so that the effective concentration corresponds to  $n_a$ . Thus the amount of adsorbed caesium will be greater when the collector is made positive. For this reason,  $n_e$  in equation (5) cannot be determined from measurements of electron emission unless it is known that the amount of adsorbed caesium is too small to influence the emission. This condition, however, seems to be fulfilled with partly activated\* thoriated filaments at high temperatures, for the electron emission at temperatures above  $1300^\circ$  is not altered when the caesium vapour pressure is raised from 0 to 0.008 bar.

A series of measurements were made of the positive ion currents and the electron currents from thoriated filaments in various states of activity. The ion currents for fully activated thoriated filaments were about 1 per cent. of those from a deactivated filament for which the current was limited by the supply of caesium atoms.

The currents from the less active filaments decreased as the filament temperature was raised, while those from the more highly activated filaments increased with temperature, quite in accord with the calculated temperature variations of  $n_p/n_a$  given in Table I. But the values of  $K_n$  calculated from these data by equation (5) came out from 4 to 50 times too great. It is probable that the discrepancy is due to lack of homogeneity of the adsorbed thorium film. A few minute regions having less than the normal amount of thorium would have little effect on the electron emission, but would increase the positive ion emission and thus give too large values for  $K_n$ . Further experiments will be made to investigate these effects in more detail.

*Space Charge Effects.*—Since in general the electron density  $n_e$  and the ion density  $n_p$  are not equal, there will be space charges around a heated body in caesium vapour. For example, in a large enclosure having tungsten walls at, say,  $1500^\circ$  K, there is a positive space charge, which makes the potential of the space in the enclosure higher than that of the walls. This field repels ions and attracts electrons, and thus makes the concentration of the particles of the two signs in the centre of the enclosure more nearly equal. At a considerable distance from the walls the space charge and the potential gradient thus disappear, but the potential in this region may differ by several volts from that near the walls. By simultaneous solution of the Boltzmann and

\* A thoriated filament is said to be *activated* when thorium is brought to its surface by diffusion from the interior, thus increasing its electron emission. A full discussion of the methods of activating these filaments and the theory of these effects was given by Langmuir, *Phys. Rev.*, vol. 22, p. 357 (1923).

Poisson equations, the potential distribution near a plane electrode can be worked out.\*

*The Adsorbed Film of Cæsium.*—Both electrons and ions, when they approach within less than about  $10^{-6}$  cm. of a metallic surface, are acted upon by strong forces (electric image forces) drawing them towards the surface, because of the charges of opposite sign which the particles induce in the surface. Each singly charged particle is thus attracted to the surface by a force equal to  $e^2(2x)^2$ , so that within the range of this force the particles are distributed *as though* they were subjected to a potential equal to  $\pm e/(4r)$  in addition to the potential resulting from space charge.

Since the former potential is a fictitious one, called into play only by the presence of the particular particle upon which it acts, much confusion will be avoided if the term *potential* is not applied to it. It is, in fact, what the electro-chemist calls "electromotive force." However, since it is measured in volts it is better not to call it a "force," it is therefore suggested that the term *motive* be used. The *motive* is thus defined as a scalar quantity whose gradient, in any direction and at any point, represents the force-component per unit charge which *acts on an electron or ion*. The motive thus includes the potential.

The concentrations  $n_e$  and  $n_p$  just beyond the range of the image force are given by equation (1), so that the product  $n_e n_p$  remains constant. But within the region of the image force both  $n_e$  and  $n_p$  increase as the surface is approached, the increase of concentration being calculated from the Boltzmann equation

$$n_1/n_2 = e^{Ee/kT} \quad (6)$$

where  $n_1$  and  $n_2$  are the concentrations in two regions between which the motive difference is  $E$ .† Thus close to the surface the product  $n_e n_p$  increases rapidly. This does not violate thermodynamic principles, because the ionising potential, which was used in calculating  $K_n$  according to equation (2), becomes a function of the distance of an atom from a surface when the atom is in the region of the image forces.

We believe that the formation of an adsorbed film of cæsium on a tungsten

\* Since deriving the equations for this case and applying them to cæsium vapour, we have found that the subject of space charge under equilibrium conditions in presence of positive ions and electrons in a metallic vapour has been treated mathematically in a recent paper by Laue, *Sitzber. Preuss. Akad. d. Wiss.* (December 6, 1923), p. 334.

† The signs of these quantities are omitted, for they are different for positive and negative charges and may be readily supplied when needed.



surface is largely the result of the high concentration  $n_p$  of ions within the region of the image force. The motive corresponding to the image force is equivalent (according to Poisson's equation) to a fictitious space charge,  $n_f$  (electrons per unit volume), given by

$$n_f = \frac{1}{8\pi x^3} = \frac{0.040}{x^3} \quad (7)$$

where  $x$  is the distance from the surface. The actual space-charge densities in the image region are enormous compared to those outside this region, but nevertheless they are usually negligible compared to  $n_f$  except when  $x$  is less than about  $2 \times 10^{-8}$  cm.

Thus there are no appreciable *potential differences*, such as would be necessary to alter the contact potential of a metal, except within atomic distances of the surface. Since changes in contact potential always accompany changes in electron emission, we conclude that a modification of the electron emission of a surface by caesium vapour is not due to an electron and ion atmosphere, as was suggested in our paper in *Science*, but can only be due to caesium ions or atoms in a monatomic layer on the surface.\*

The concentration of ions in the image region is dependent on that outside this region, and, in fact, will be proportional to it, if the concentration is not too high. Thus, considering the data of Table I, we may understand why caesium vapour does not appreciably raise the electron emission of a fully chlorinated surface at any temperature, whereas that of tungsten at  $700^\circ$  K may be increased  $10^{16}$ -fold. Each adsorbed ion on the surface draws electrons into its neighbourhood and this partly offsets its positive charge. Probably considerations apply to the distribution of electrons around the adsorbed ion somewhat similar to those that Debye and Hückel† have applied to solutions of strong electrolytes.

If the adsorbed atoms are relatively far apart they probably repel one another, because of their excess of positive charge. But as they become more closely packed, the electron concentration in the spaces between the ions, varying as it does exponentially with the potential (equation 6), must increase very rapidly, and thus, as we shall see, the ions tend to be drawn together and exhibit properties like those of the molecules of liquids.

We are thus led to the conception of an *equation of state* for the adsorbed

\* We shall show that in the adsorbed film no distinction can be drawn between atoms and ions.

† Debye and Hückel, *Phys. Zeit.*, vol. 24, p. 334 (1923).

cæsium atoms. It has been possible, by measurements of the electron emission of tungsten filaments in presence of cæsium vapour, to gain much quantitative information as to this equation of state, and also to determine the energy changes involved in the adsorption of cæsium on tungsten or on a film of oxygen ions. This work is still in progress, and it is hoped that it can be extended to give the complete equation of state for even concentrated (close-packed) adsorbed films. It would seem that a study of the growth of these films, from the dilute (2-dimensional gas) state to the concentrated (liquid or solid), should throw much light on the state of the electrons within metals.

Qualitatively we have very direct evidence of the existence of two "phases" in the adsorbed films by measurements already briefly described in the paper in *Science*. The positive ion emission from a tungsten filament in cæsium vapour increases discontinuously as the temperature is raised. At a certain temperature a large positive ion emission begins at one point of the filament and then spreads at a uniform rate along the filament until the whole filament gives the higher emission. If while this process is occurring the temperature is lowered, the rate of spreading of the active region is decreased, or the boundary may even be made to move back again. There are thus two distinct surface phases (a concentrated and a dilute phase) with a definite boundary between them.

*Electron Emission from Dilute Cæsium Films adsorbed on Tungsten.*

Consider a tungsten surface at such high temperature in cæsium vapour that only a small fraction of its surface is covered by adsorbed cæsium. The concentration  $n_p$  of ions just outside the region of the image force will be high compared to  $n_a$  the concentration of atoms. The ions strike the surface at a rate proportional to  $n_p$ . Since the adsorbed film is dilute, the ions on the surface evaporate independently of one another, and thus the rate of evaporation of ions is proportional to  $n_\theta$ , the number of adsorbed ions per  $\text{cm.}^2$ ; so we may place

$$n_p = cn_\theta. \quad (8)$$

Here  $c$  is a constant at a given temperature, which is proportional to the probability of evaporation per unit time for any adsorbed ion.

It has been shown by one of us,\* both theoretically and experimentally, that for dilute adsorbed films the logarithm of the electron emission is a linear function of  $n_\theta$ , so that

$$\frac{d \log n_e}{dn_e} = B, \quad (9)$$

\* I. Langmuir, *Phys. Rev.*, vol. 22, p. 364 (1923).



where B is a constant at a given temperature. Combining equations (8) and (9) with (1) and integrating, we find

$$n_e \log \frac{n_e}{n_{e0}} = \frac{BK_n}{c} n_a, \tag{10}$$

where  $n_{e0}$  is the value of  $n_e$ , which corresponds to  $n_a = 0$ , *i.e.*, a surface of tungsten without adsorbed caesium. We thus see that, as the caesium pressure varies,  $I \log (I/I_0)$  should increase in proportion to the pressure of caesium vapour, and that from the constant of proportionality, since we know  $K_n$ , we can determine  $B/c$ .

Experiments made for the purpose of testing this conclusion have given data in good agreement with this theory. Filament temperatures from 1450° to 1800° K were used and the caesium vapour pressures ranged from 0 to 4.07 bars (bulb at 120° C.). Filament temperatures of at least 1450° were needed to give sufficient electron emission, and the high caesium vapour pressures were required to give a sufficient increase in emission to test the theory. At 1470° the electron emission with 4.07 bars of caesium vapour was 1300 times, while at 1790° it was only 3.6 times, that of a pure tungsten surface.

The conclusions drawn from these experiments are—

(1) The quantity  $I \log (I/I_0)$  is proportional to the pressure of caesium vapour within the probable experimental error, except that at the highest pressures with the lowest filament temperatures the value is too high, probably because the surface film is no longer dilute. The agreement with the theory is in fact excellent for all cases where  $\theta$  does not exceed about 0.13. For  $\theta = 0.21$  the function  $I \log (I/I_0)$  is about 1.8 times the calculated value (at 1470° K).

(2) The pure number  $BK_n/c$  has practically no temperature coefficient, and has the value  $8.8 \times 10^{-4}$ .

(3) Since B is approximately inversely proportional to the filament temperature, the temperature coefficient of  $c$  is only slightly less than that of  $K_n$ . By the Clapeyron equation we can thus find the heat of evaporation of positive ions from the dilute adsorbed film and obtain a value corresponding to 3.97 volts.

(4) It has been found that the values of B defined by equation (9) range from about  $2.5 \times 10^{-13}$  at 1500° K to  $2.1 \times 10^{-13}$  cm.<sup>2</sup> at 1800° K. Thus the values of  $c$  are given by

$$\log_{10} c = 9.02 + 0.5 \log_{10} T - \frac{19530}{T}. \tag{11}$$

This equation gives data for the rate of evaporation of adsorbed caesium ions on tungsten.

The Gibbs equation for the adsorption isotherm may readily be put in the form

$$\frac{d\Gamma}{d \log n_p} = n_\theta kT, \quad (12)$$

where  $\Gamma$  represents the spreading force (in dynes per cm.) of the adsorbed film, which corresponds in the 2-dimensional film to a pressure in a 3-dimensional gas. An equation of state for the film is thus an equation which expresses  $\Gamma$  as a function of  $n_\theta$  and  $T$ . To obtain such an equation\* we merely need to obtain a relation between  $n_p$  and  $n_\theta$  in order to eliminate  $n_p$  from equation (12).

But in equation (8) we have such an equation between  $n_p$  and  $n_\theta$  for dilute films. Combining this with equation (12), integrating, and fixing the integration constant by the condition that  $\Gamma = 0$  when  $n_\theta = 0$ , we obtain as our equation of state for dilute films

$$\Gamma = n_\theta kT, \quad (13)$$

which corresponds exactly in 2-dimensional gases with the law  $p = nkT$  for ideal 3-dimensional gases. Since, at constant temperature, the assumption  $c = \text{constant}$  in equation (8) was verified by the experiments, we may take the foregoing analysis as proof that the dilute caesium films follow the laws of ideal gas films. This means that the spreading force of such films is due primarily to thermal agitation and not to repulsive forces between neighbouring adsorbed ions.

When the amount of adsorbed caesium became so great ( $\theta = 0.21$ ) that the film was no longer dilute, we have seen that the electron emission increased faster with the caesium pressure than it should according to the theory for dilute films. This means that  $\Gamma$  increased less rapidly than in proportion to  $n_\theta$ , and thus the adsorbed ions exerted *attractive forces* on one another. We shall find further support for this conclusion in our study of concentrated adsorbed films.

The energy changes involved in the formation of dilute adsorbed films throw considerable light on the mechanism by which adsorbed atoms are held on the surface. Since the energy required to remove an adsorbed atom in the form of a positive ion is approximately the same as the ionizing potential of the atom, it is probable that the relation between the positive kernel of an adsorbed atom (the  $\text{Cs}^+$  ion) and the electrons of the tungsten surface is substantially the same as that between the kernel and the valence electron of a free atom. Thus a

\* This method of obtaining an equation of state for adsorbed films has been applied to films on liquids by Langmuir, *Journ. Amer. Chem. Soc.*, vol. 39, p. 1888 (1917).



cæsium atom on a tungsten surface shares its valence electron with the tungsten very much as pairs of electrons are shared between atoms joined by the covalence bond. From this view-point there can be no real distinction between atoms and ions adsorbed on a metallic surface.

If we think of an adsorbed cæsium ion on a surface as having united with, or as sharing one of the "free electrons" of, the tungsten, it may seem at first as though these atoms should be capable of evaporating as such with relatively little energy change. A closer analysis, however, shows that this is not the case.

Let  $U_i$  represent the energy associated with the ionization of a cæsium atom in free space (*i.e.*, the ionizing potential). Let  $U_a$  be the energy required for the removal of an adsorbed cæsium atom (or ion) in the form of an atom. Let  $U_p$  be the energy used to remove an atom from the surface in the form of a positive ion, and finally let  $U_e$  be the work needed to remove an electron from the metallic surface. We can get an atom from the surface into the free space either by removing it as such or by removing an electron and an ion separately and then allowing these to combine in the free space. Thus we find the relation

$$U_a = U_p + U_e - U_i. \quad (14)$$

For a tungsten surface having very little cæsium on it  $U_e = 4.54$ ;  $U_p = 3.97$  and  $U_i = 3.88$  volts, and the equation then gives us  $U_a = 4.63$  as the energy involved in the evaporation of an atom as such. If  $U_p = U_i$  we see that  $U_a = U_e$ . Thus the energy adsorption of free atoms is determined principally by the electron affinity of the metal, and results from the fact that the metal is able to take the electron that is brought to it by the atom as one of its own electrons, even though this electron is shared by the atom. Of course, the electrons which are shared by a given atom may be, and probably are, continually changing, but the conception of shared electrons is not altered thereby.

*Concentrated Adsorbed Films of Cæsium on Tungsten.*—At sufficiently low temperatures a tungsten filament in presence of cæsium vapour becomes completely covered with a layer of adsorbed cæsium atoms ( $\theta = 1$ ). As the temperature is raised the emission increases, apparently in accord with the Richardson equation (equation 3), the logarithm of the electron current being practically a linear function of the reciprocal of the temperature. At a certain temperature (for each pressure of cæsium) the current reaches a maximum and then decreases as the temperature is raised, since the adsorbed cæsium evaporates at these higher temperatures and  $\theta$  becomes much smaller than unity.

The families of curves in fig. 1 give a summary of about 220 determinations of the electron emission of filaments in presence of caesium vapour. The curves have been drawn accurately from the experimental data and may be used for quantitative calculations if desired. The ordinates are the common logarithms of  $I_e$ , the electron current densities in amperes per cm.<sup>2</sup>, and the abscissas are the reciprocals of the absolute temperatures of the filament, multiplied by 1000 for convenience. The temperature of the bulb which fixed the vapour pressure of the caesium is given in degrees Centigrade on each curve. The two upper curves, which appear distinctly different from the rest, were obtained with filaments which were completely covered by a film of oxygen ions before admitting the caesium vapour. The other nine curves were obtained with pure tungsten filaments which had been flashed at high temperature to remove all impurities from the surface before the readings were taken. The caesium film condensed on them, of course, when the filament temperature was lowered to that at which the currents were read.

Considering now the curves obtained with the caesium adsorbed on the pure tungsten surface, we see that each curve consists of 3 parts :—

I. A low-temperature region where the emission apparently follows Richardson's equation, giving a straight line descending to the right in fig. 1.

II. An intermediate region where the plot in fig. 1 is curved, the current reaching a maximum as the temperature is raised and then falling. This region may be regarded as a transition curve between the straight portions I and III.

III. A high-temperature region, where the plot in fig. 1 becomes straight again, but the current decreases with rising temperature. An equation of the Richardson type may be used to represent these lines, but the quantity  $b$  would then have a negative value.

Fig. 1 shows that both in Regions I and II the straight lines at the various pressures are approximately parallel to one another. The envelope of the family of curves is a straight line, shown as the dashed line AB. All the curves of the family are, in fact, very nearly alike,\* and differ principally in being displaced in a direction parallel to AB. These displacements are found to be proportional to the logarithms of the pressures of caesium.

These conclusions may be summarized by saying that these electron emission data are given by the equation

$$\log I_e + M \log p = f(1/T + N \log p), \quad (15)$$

\* This is only approximate. It will be noticed that the curves for the higher pressures have the sharper curvature in Region II.



where  $M$  and  $N$  are constants and  $f$  denotes a function characteristic of the shape of the curves in fig. 1. From the data we find that the actual values of  $M$  and  $N$  are

$$M = -0.83; \quad N = 4.4 \times 10^{-5} \text{ deg}^{-1}.$$

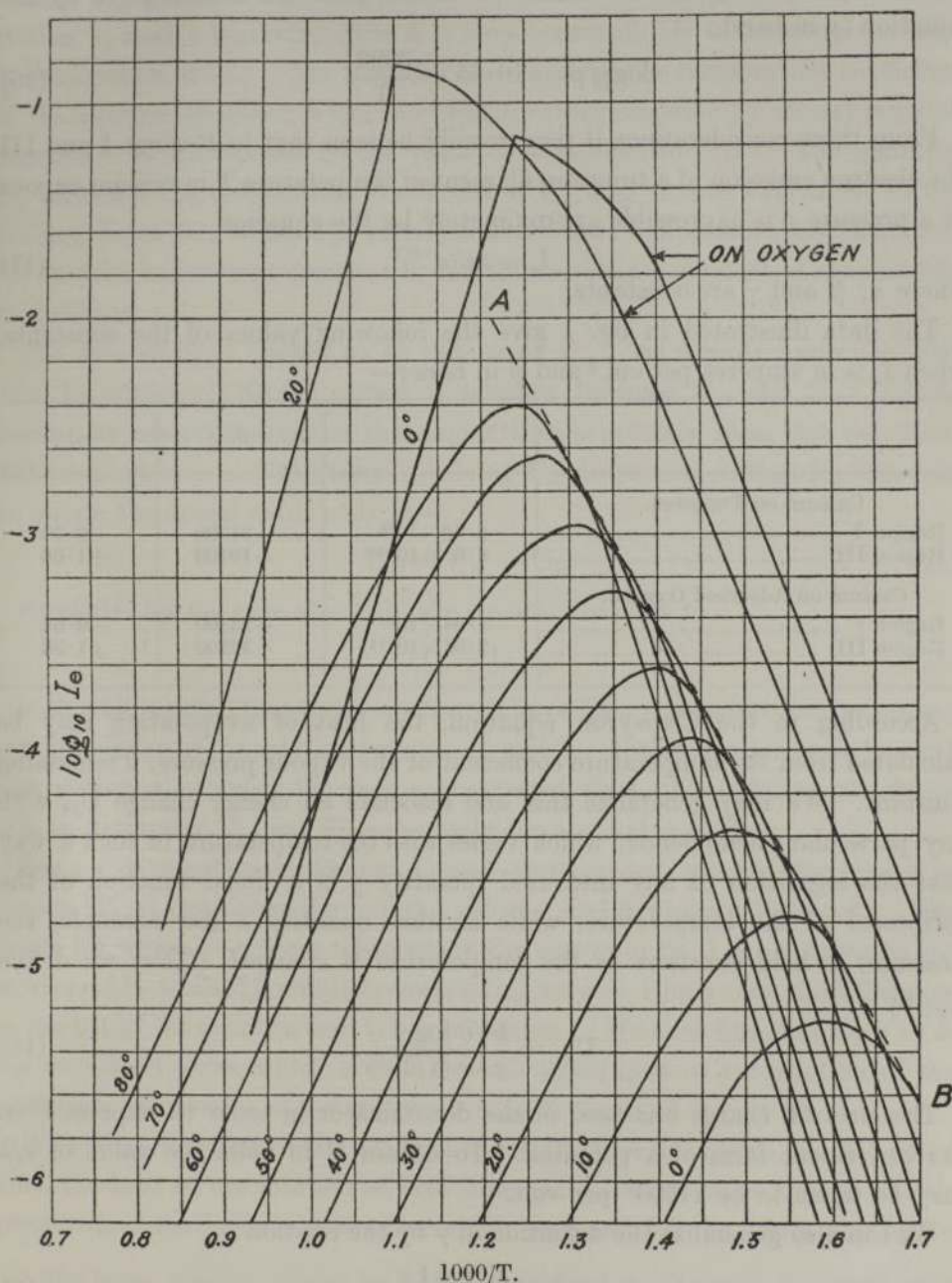


FIG. 1.—Electron emission from Tungsten filaments in Cæsium vapour at various pressures.

The pressures of caesium vapour used in these calculations were found by measurements of the positive ion currents obtained with filament temperatures of about 1500° K, where all the atoms that strike the filament are converted to ions. The vapour pressures obtained in this way are accurately given by the equation ( $p$  in bars)

$$\log_{10} p = 10.65 - \frac{3992}{T}. \quad (16)$$

From these considerations it may readily be seen that in Regions I and III the electron emission of a tungsten filament of temperature  $T$  in caesium vapour at a pressure  $p$  is expressible approximately by the equation

$$I_e = \alpha p^\gamma \varepsilon^{-\beta/T}, \quad (17)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants.

The data illustrated in fig. 1 give the following values of the constants, when  $I_e$  is in amperes per cm.<sup>2</sup> and  $p$  in bars :—

	$\alpha$ .	$\beta$ .	$\gamma$ .
Caesium on Tungsten.			
Region I .....	$6.65 \times 10^{14}$	+31300	-0.70
Region III .....	$8.6 \times 10^{-12}$	-19100	+1.66
Caesium on Adsorbed Oxygen.			
Region I .....	$1.04 \times 10^{10}$	+23400	-0.62
Region III .....	$2.95 \times 10^{-11}$	-32200	+1.96

According to the Clapeyron equation, the heat of evaporation may be calculated from the temperature coefficient of the vapour pressure,  $\theta$  remaining constant. We may generalize this and associate an energy change  $U_{yx}$  with any particular phenomenon, which varies with the temperature in such a way that the logarithm of any measured quantity  $y$  is a linear function of the reciprocal of the temperature, while another quantity  $x$  (for example, the pressure) is held constant as the temperature is changed. Thus we define  $U_{yx}$  by

$$U_{yx} = \frac{k}{e} \left( \frac{\partial \log y}{\partial (1/T)} \right)_x. \quad (18)$$

The electron charge  $e$  is used in the denominator in order to express  $U$  in the convenient form of a potential. To obtain  $U$  in volts the value of  $e/k$  may be taken to be 11600° per volt.

We can also generalize the definition of  $\gamma$  by the relation

$$\gamma = \left( \frac{\partial \log I_e}{\partial \log p} \right)_T, \quad (19)$$

which is consistent with equation (17).



In this way, by combination with equation (1), we may obtain the equation

$$U_{p\theta} = U_K - \frac{1}{\gamma} U_{ea} + \frac{1-\gamma}{\gamma} U_{e\theta}. \quad (20)$$

Here  $U_{p\theta}$  refers to the temperature coefficient of the *positive* ion concentration  $n_p$  near a filament, while  $\theta$  is kept constant. It is therefore the heat of evaporation of ions. The quantity  $U_{ea}$  measures the temperature coefficient of the electron emission, while the pressure (concentration of atoms) remains constant. It corresponds to the value of  $\beta$  in equation (17). The quantity  $U_K$  measures the temperature coefficient of  $K_n$ , and is thus equivalent to the ionizing potential, while  $U_{e\theta}$  corresponds to the temperature coefficient of the electron emission at constant  $\theta$ , and thus measures the heat of evaporation of electrons.

The data of fig. 1 enable us to determine  $U_{ea}$ ; we already know  $U_K$ , and thus by equation (20) we obtain a relation between  $U_{p\theta}$  and  $U_{e\theta}$ ; but in general we cannot determine these quantities separately from this equation. However, when  $\gamma = 1$  the term involving  $U_{e\theta}$  drops out, so that for this case we obtain the actual value of  $U_{p\theta}$  :—

$$U_{p\theta} = U_K - U_{ea}. \quad (21)$$

Similarly, for the case of  $\gamma = 0$ , the equation reduces to

$$U_{ea} = U_{e\theta}. \quad (22)$$

It should be noted that these conclusions have been reached without assuming any knowledge of the relation between  $I_e$  and  $\theta$ . If this relation were known\* with sufficient accuracy for very concentrated films ( $\theta > 0.9$ ), we should be able to determine  $U_{p\theta}$  and  $U_{e\theta}$  separately for any value of  $\theta$ .

Since  $\gamma$  is negative in Region I, and positive and greater than unity in Region III, it must pass through the values 1 and 0 while in Region II. The points for which  $\gamma = 0$  are those where the curves of fig. 1 are tangent to the envelope AB, while the points corresponding to  $\gamma = 1$  lie a very short distance to the left of the points where  $I_e$  is a maximum. We thus find that for  $\gamma = 0$ ,  $U_{e\theta} = -1.24$  volts, which is thus the calculated heat of evaporation of the electrons. This value of  $\gamma$  corresponds roughly to about  $\theta = 0.90$ .

With  $\gamma = 1.0$ , which occurs at about  $\theta = 0.87$ , the value of  $U_{p\theta}$  is  $-4.3$  volts. Thus the heat of evaporation of ions from these concentrated films is a little greater than the value  $-4.0$  volts, which we found for the dilute film by an

\* The linear relation between  $\log I_e$  and  $\theta$ , proposed by Langmuir, is a fairly good approximation up to  $\theta = 0.9$  or even higher, but is not sufficiently accurate for the present purpose. A fuller discussion will appear in the *Physical Review* article.

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entirely different method. The data are consistent with the assumption that  $U_{p\theta}$  varies gradually and steadily from  $-4.0$  to  $-4.3$  as  $\theta$  increases from 0 to 0.9. If we make this assumption, we may calculate  $U_{e\theta}$  by equation (20) for all values of  $\theta$  for which we know  $U_{ea}$ . Thus we find that  $U_{e\theta}$ , the heat of evaporation of the electrons in Region I, is about 1.5 volts and in Region III ( $\theta = 0.7$ ) is about 1.8 volts. These data for  $U_{e\theta}$  are only rough, but are in general accord with our knowledge that the heat of evaporation of the electrons is greatly decreased by adsorbed caesium and must vary roughly linearly with  $\theta$ . A thorough check of this part of the theory may require direct determinations of the heat of evaporation by its cooling effect. Contact potential measurements have been made with caesiated filaments and agree in general with these conclusions, but their accuracy is not yet as high as is desired.

For the caesium film on adsorbed oxygen, the heat of evaporation of ions  $U_{p\theta}$  comes out as 5.13 volts for  $\theta = 0.95$ . This is distinctly higher than that of ions adsorbed directly on tungsten and accounts for the much lower rate of evaporation of ions from the oxygen film.

An analysis of all these data from the thermodynamic standpoint by Gibbs' equation leads to the following conclusions:—

With very dilute caesium films ( $\theta < 0.15$ ) the spreading force  $\Gamma$  increases in proportion to  $\theta$ , and in this range  $\gamma$  increases slowly from 0 up to nearly unity. At  $\theta = 0.5$  to 0.8,  $\gamma$  is approximately 1.65; so somewhere between about  $\theta = 0.2$  and  $\theta = 0.5$ ,  $\gamma$  must be equal to unity. At this point  $\Gamma$  must reach a *maximum* value and then decrease as  $\gamma$  increases above unity. This means that strong attractive forces should render the film inherently unstable, and it should have a tendency to separate into two phases, just as has been observed in connection with the measurements of positive ion currents. However, in taking the data illustrated in fig. 1 (although in Region III  $\Gamma$  must decrease with rising  $\theta$ ), we have not observed any effects which would indicate separate surface phases.

At still higher values of  $\theta$  in Region II, in the neighbourhood of  $\theta = 0.87$ ,  $\gamma$  decreases again and passes through the value unity. Beyond this point  $\Gamma$  must again increase with rising  $\theta$ , indicating that repulsive forces are beginning to come into play as the film approaches saturation.

Finally, when  $\theta$  is about 0.90,  $\gamma$  becomes zero and then becomes negative. In this region the electron emission actually decreases as more caesium atoms become packed into the adsorbed film.



*Summary.*

1. From thermodynamic considerations involving the Saha equation, there must be a relation between the *positive* ion emission from a heated filament in the vapour of an alkali metal and the electron emission from this surface.

2. At high-filament temperatures and low pressures of the vapour, the electron emission is the same as in the absence of the vapour, so that the positive ion emission from different filaments in various vapours can be calculated.

Experiments with caesium and other metallic vapours, and with tungsten filaments and oxygen-coated and thorium-coated filaments, give results in accord with this theory. Measurements of the positive ion and electron emissions from tungsten filaments in caesium vapour give values for the thermal ionization of caesium vapour at about 1200° K in excellent agreement with the Saha equation.

3. At high-filament temperatures the positive ion emission becomes limited by the rate at which the vapour comes into contact with the filament, all atoms striking the filament being converted into ions. This permits quantitative measurements of the vapour pressure to be made. The vapour pressures of caesium (in bars) are given by

$$\log_{10} p = 10.65 - \frac{3992}{T}.$$

4. At lower filament temperature the electric image force causes a fraction  $\theta$  of the filament surface to be covered by a layer of adsorbed ions which share electrons with the underlying metal. The resulting double-layer causes an increase in electron emission and a corresponding decrease in positive ion emission. Electron emissions of over 0.3 ampere per cm.<sup>2</sup> at 1000° K may be obtained in caesium vapour at 30° C.

5. The theory of dilute adsorbed films ( $\theta < 0.2$ ) is developed and the equation of state for the adsorbed film is found to correspond to the ideal gas laws. For more concentrated films, attractive forces draw the ions together and under certain conditions cause separate 2-dimensional phases to appear.

6. The heat of evaporation of the adsorbed caesium atoms on tungsten in the form of ions corresponds to 4.0 volts for dilute and 4.3 volts for concentrated films. From adsorbed oxygen on tungsten the heat of evaporation of caesium ions is 5.1 volts.

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