Chemical Studies by Means of Molecular Beams. VII.* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 1.

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Introduction. An incandescent tungsten filament, when placed in alkali metal vapour, emits ions. This is because the atoms of alkali metal which strike the filament are ionized and evaporated. Generally, perfect ionization takes place when the ionization potential of the atoms is considerably smaller than the work function of tungsten.

This phenomenon was first discovered by Langmuir and Kingdon⁽¹⁾ with caesium; and later it was reported by Killian⁽²⁾ with rubidium and potassium. In the case of sodium and lithium, the ionization can be effected with a tungsten filament whose surface is covered with a monoatomic layer of oxygen.

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* Preceding papers were published in Japanese in the *J. Chem. Soc. Japan*, **57** (1936), **58** (1937).

(1) I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc.* (London), A, **107** (1925), 61.

(2) T. J. Killian, *Phys. Rev.*, **27** (1926), 578.

In 1929, Taylor⁽³⁾ applied this phenomenon to the intensity measurement of an atomic beam of alkali metals. A fine tungsten filament surrounded by a cylindrical cathode is placed within the path of an atomic beam. The atoms which strike the filament are ionized and attracted towards the cathode. The ion current thus produced gives the intensity of that part of the atomic beam, provided the ionization is complete. This method of measurement with fine filaments has since been used to advantage but it has a drawback when it is desired to measure the total intensity or a large portion of the intensity of the current at one time. This is especially the case with a weak atomic beam of a large cross section.

This inconvenience may be avoided by using a ribbon of convenient width in place of a fine filament. The way of measurement is quite the same as with a fine filament, except that owing to a considerably larger evolution of heat a suitable additional device around the ribbon is necessary. However, this undesirable heat effect may be reduced to minimum, if we use the method of flashing. The whole cross section of a weak atomic beam is received by an unheated ribbon surface for a certain time, which is then electrically flashed for a short time and the ions thus formed are measured by a ballistic galvanometer.

The present investigation has been carried out with potassium atomic beams to learn the conditions of applicability of this method.

Apparatus. The apparatus used is shown in Fig. 1. F represents an oven for potassium made of nickel chrome steel, the construction being similar to that previously used by Nishibori⁽⁴⁾ in our laboratory. The tungsten filaments for heating, which are inserted from the left hand, are not shown in the figure. Potassium atoms gush through the circular orifice O into a highly evacuated space and are caught by the surrounding cooled walls except for those which pass through the second circular orifice Sl and advance as a beam. S at the left side of Sl is a shutter for the atomic beam to which is attached a piece of iron to be operated from outside by a small electromagnet. The movement of the shutter is accurately controlled with a stop-watch electrically connected with it. A copper tube T_1 is cooled by liquid air contained in L_1 and serves to catch all atoms which have failed to pass through Sl. The diameter of O is 0.1 mm. and that of Sl 1.7 mm. The detector chamber is shown on the right

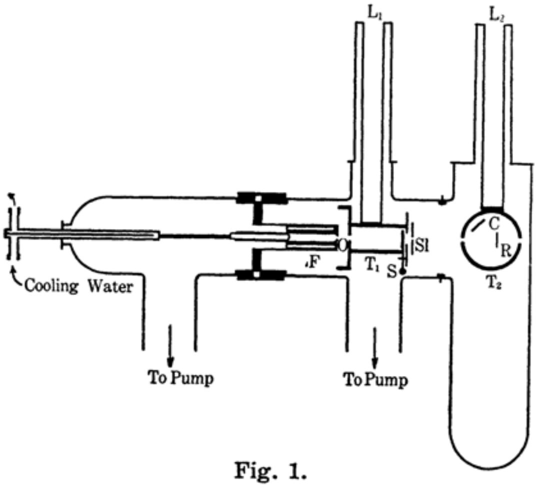

Fig. 1.

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(3) J. B. Taylor, *Z. Physik*, **57** (1929), 242.

(4) E. Nishibori, *J. Chem. Soc. Japan*, **58** (1937), 22.

hand. R is a tungsten ribbon 5 cm. long, 5 mm. wide and 0.13 mm. thick and C is a nickel cathode for collecting ions. T_2 is a copper tube cooled by liquid air in L_2 and protects the tungsten ribbon from harmful vapours given off by such as sealing wax.

Galvanometer circuit. This is shown in Fig. 2. The cathode C is kept at 120 V. negative against the tungsten ribbon. G is a ballistic galvanometer made in the Institute of Physical and Chemical Research and has a sensitivity of 3.77×10^{-10} coulombs. The protecting copper tube T_2 is kept at 6 V. positive against the ribbon to prevent ions from coming to it. The ribbon was heated with an alternating current of 10–42 A. taken from the sources of A. C. 100 V. and 200 V. through a step-down transformer. The temperature of the ribbon was measured with a Siemens optical pyrometer.

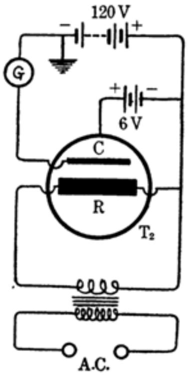

Fig. 2.

The treatment of the tungsten ribbon. As the surface of ordinary tungsten is always stained with alkali salts, it emits their ions when heated. The ribbon must therefore be freed from these by heating repeatedly for about 10 seconds in high vacuum at 1400–1500°C. until practically no ions could be detected by the galvanometer. It may be desirable to heat the tungsten at much higher temperatures but in the present case, heat thus generated causes an undue heating of the apparatus. At any rate the above treatment proved quite satisfactory for the purpose.

Purification of potassium. Potassium used in this experiment was carefully distilled in high vacuum into a long glass tube of appropriate diameter and kept dry for occasional use. When wanted, a short piece of the tube is cut out and immediately introduced into the oven and then the whole apparatus is evacuated without delay.

Method of measurement. When the evacuation is complete a required constant temperature is applied to the oven to produce an atomic beam of a definite intensity. With the shutter kept closed, the ribbon is flashed to remove any freshly adsorbed alkali atoms, left to cool for some time, and then the shutter is opened for a definite time to fire potassium atoms upon the ribbon surface, which is then flashed and the deflection of the ballistic galvanometer is recorded. The time of exposure of the ribbon to the beam is accurately measured with the stop-watch mentioned above. In this measurement we must be sure that all colliding potassium atoms are completely adsorbed by the ribbon. This was ascertained by Taylor and Langmuir(5) in the case of caesium. They showed that as long as the temperature of tungsten is below about 800°K., the impinging atoms are entirely fixed on the tungsten, until a mono-atomic layer is formed. It may be, therefore considered that it is the same in the present case.

Results. *Uniformity of the ribbon surface.* The ionizing power of the hot ribbon surface may differ near the two ends because of unequal

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(5) J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44** (1933), 423.

temperature distribution. Therefore, at least the uniform ionizing power of the portion which is uniform in temperature must be ascertained, if that part should be used for the intensity measurement. For this purpose the middle part of the ribbon which was to receive the atomic beam was shifted sideways by a special device not shown in the figure, exposing thereby different parts of the surface to the beam. The result obtained is shown in Fig. 3. The abscissa shows the displacement of the ribbon, while the ordinate represents the relative galvanometer deflections referred to position 2. All values agree with one another within a few per cent, showing that the uniformity is well rendered.

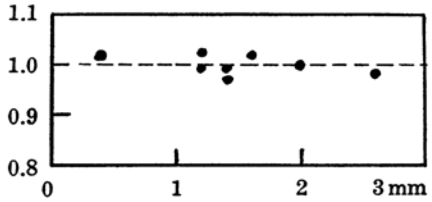

Fig. 3.

Relation between the ribbon temperature and the ionization efficiency. Fig. 4 illustrates the results of our measurements made with the aim to obtain this important relation. The ribbon was exposed to the atomic beam in each case for a definite time. The deflections of the galvanometer resulted by the flashing at different temperatures are shown in the ordinate and the flashing temperature and the corresponding electric current used for the flashing, are indicated in the abscissa. Curve I was obtained with the oven temperature 136°C. and the time of exposure 40 sec., while curve II, with 232°C. and 30 sec. respectively. Obviously the surface concentration of adsorbed atoms is lower in the former case. In both cases the curves rise rapidly until about 800°C., which implies the rapid increase of the ionization efficiency with the rise of temperature. Above 800°C., curve I shows a constant value which suggests the complete ionization of adsorbed atoms, while curve II has a maximum. This may be explained by the combined effect of the high surface concentration of adsorbed atoms and the surface migration which will be fully described in the next report.

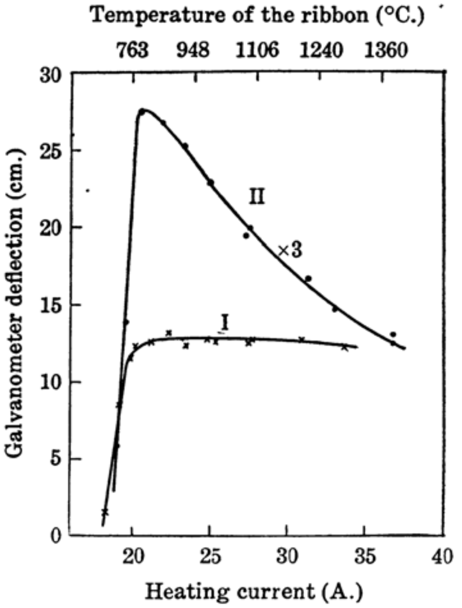

Fig. 4.

Relation between the surface concentration of adsorbed atoms and the ionization efficiency. When applying this method of flashing to the intensity measurement of an atomic beam, it is of the utmost importance to know the influence of the surface concentration of adsorbed atoms upon the ionization efficiency. The following experiment will make this point clear.

An atomic beam of a constant intensity was produced and the time of exposure of the ribbon to it was varied. The surface concentration of adsorbed atoms thus obtained is proportional to the time of exposure, since the condensation coefficient may be assumed to be unity. The ribbon with adsorbed atoms was then flashed and the deflection of the galvanometer was noted. The results obtained are shown in Figs. 5 and 6, where the time of exposure is indicated in the abscissa and the galvanometer deflections in the ordinate. Curves I–V represent the results obtained with five different beam intensities, corresponding to respective oven temperatures. Each curve rises linearly until the galvanometer deflection becomes about 19 cm. This suggests that the ionization efficiency is 100 per cent in this range of surface concentration. (Curve III shows a slight deviation from a straight line, but this was found to be due to a small change in the oven temperature in the course of measurement.)

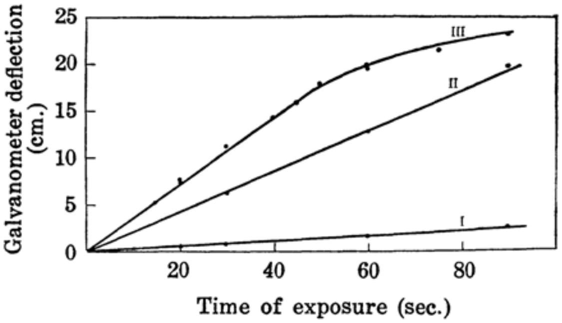

Fig. 5.

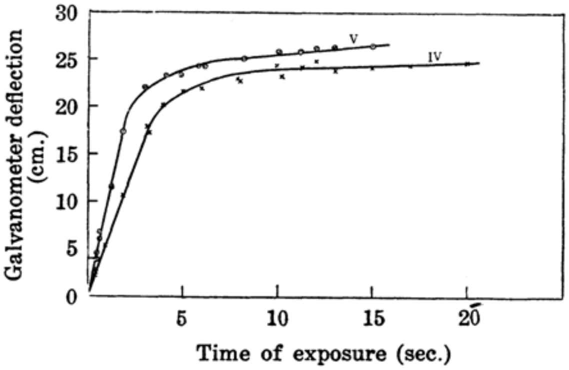

Fig. 6.

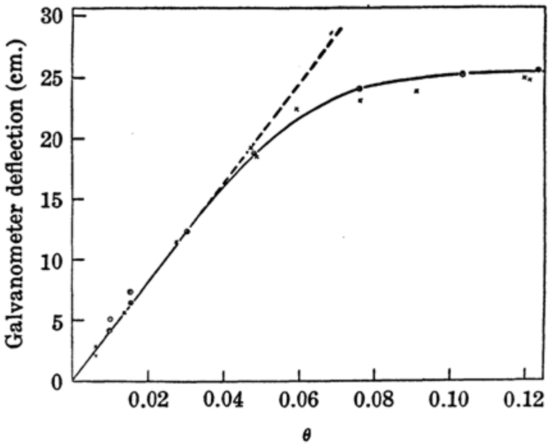

Fig. 7.

In reality, however, if the two curves in Fig. 6 is arranged to one with a smaller inclination (cf. Fig. 7), we see that the straight portion extends hardly to 15 cm. From this value, the highest surface concentration which still permits the perfect ionization of adsorbed atoms may be calculated. The results shown in Figs. 5 and 6 were obtained with deposits from a slightly divergent beam which has passed the last defining hole 3.45 mm. in diameter, perforated in the protector tube, so that the circular deposits formed on the ribbon is a little larger than the hole, namely 3.76 mm.

in diameter corresponding to the area of 0.111 cm.^{2}. According to Taylor and Langmuir$^{(5)}$ the number of caesium atoms in the mono-atomic layer on tungsten is 4.8×10^{14} per cm.^{2} of the apparent surface. This number is also applicable in the case of potassium. If we assume that the maximum surface concentration allowable for perfect ionization corresponds to 15 cm. of the galvanometer deflection, the number of ions which causes this deflection will be

$$\frac{150 \times 3 \times 3.77 \times 10^{-10} \times 2}{1.6 \times 10^{-19}} = 2.12 \times 10^{12} ,$$

where 3.77×10^{-10} is the sensitivity of the galvanometer which was used at 1/3 of its full sensitivity by means of an Ayrton shunt and the mirror-scale distance was one half of the normal, 1.6×10^{-19} is the ionic charge expressed in coulomb. Since so many ions were adsorbed on the apparent surface of 0.111 cm.^{2}, the fraction θ covered by the mono-atomic layer must be

$$\theta = \frac{2.12 \times 10^{12}}{0.111 \times 4.8 \times 10^{14}} = 0.040 .$$

According to Langmuir,$^{(6)}$ if ν_p and ν_a are respectively the numbers of ions and atoms evaporated in unit time from unit area of the surface which is in equilibrium with the impinging atoms, their ratio may be given by

$$\frac{\nu_p}{\nu_a} = \frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT} \right] \qquad (1).$$

V_w is the work function of pure tungsten and V_i the ionization potential of potassium and V_c the contact potential of tungsten covered with potassium against pure tungsten. V_c varies with θ. Now in the course of flashing at a temperature T, the surface concentration and consequently the contact potential, change continuously. Equation (1) holds only for a minimum amount of potassium atoms evaporated. Let us define the differential ionization efficiency for the surface with a certain θ and V_c by equation (2), where $N = \nu_p + \nu_a$:

$$\frac{d\nu_p}{dN} = \frac{\frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT} \right]}{1 + \frac{1}{2} \exp. \left[\frac{\varepsilon(V_w - V_i - V_c)}{kT} \right]} \qquad (2).$$

This equation shows that the ionization efficiency is highest when V_c is nil and decreases as V_c increases.

The total ionization ν_p which is proportional to the galvanometer deflection may be obtained by integrating equation (2) with respect to θ from θ to zero, N and V_c being expressed in terms of θ. N is obviously equal to $N_0\,\theta$, where $N_0 = 4.8 \times 10^{14}$ is the number of atoms in 1 cm.^{2} of the mono-atomic layer on tungsten. If V_c is assumed to be proportional to

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(6) I. Langmuir, *J. Am. Chem. Soc.*, **54** (1932), 2825.

θ, i.e. $V_c = c\theta$, as will be discussed below, the integration gives

$$\nu_p = A N_0 \frac{kT}{c\varepsilon}\Big[\log\,(1+\frac{1}{2}\,\mathrm{exp.}\,[\varepsilon(V_w - V_i)/kT]) - \log\,(1+\frac{1}{2}\,\mathrm{exp.}\,[\varepsilon(V_w - V_i - c\theta)/kT])\Big] \qquad (3),$$

where $A = 0.111$ cm.^{2} the area of the deposit.

We see from this equation that the total ionization will show a linear increase for a considerably wide range of θ, if $V_w - V_i$ is so large that 1 can be neglected against the expotential term, for in this case equation (3) is reduced to $\nu_p = N_0\,\theta$. This means the complete ionization for this range of θ.

The general form of the curve is determined solely by the second term, which can be put in the form $\log(1+e^x)$ and is graphically represented in Fig. 8. The comparison with the experimental curve (Fig. 7) shows that its linear portion corresponds to the range of x from 4 to 2, an appreciable deviation from the linearity beginning at about 2, or at

$$\varepsilon(V_w - V_i - V_c)/kT = 2.$$

Now if we put in equation (2) $V_w = 4.52$ V. $V_i = 4.32$ V. $T = 1.379$°K. and $V_c = 0$, the ionization efficiency will be found considerably less than 100 per cent:

$$\frac{\nu_p}{N} = 0.804\,.$$

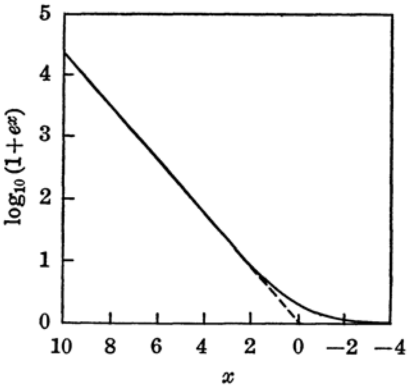

Fig. 8.

Thus the value of $V_w - V_i$ is not large enough to explain the straight portions of the curves shown in Figs. 5 and 6.

In their experiments on the surface ionization of potassium by tungsten, Copley and Phipps⁽⁷⁾ found that the values of ν_p/ν_a which they found could be brought into conformity with equation (1) if the factor ½ was omitted.

As they pointed out, a factor $(1-r_p)/(1-r_a)$ has been omitted in equation (1), where r_p and r_a are the reflection coefficients of ions and atoms. This factor is usually supposed to be unity but they assumed that it happened to cancel the factor ½. This argument may not be accepted as it stands but the omission of ½ has the favourable effect of increasing the ionization efficiency. According to equation (3) the differential ionization efficiency is calculated to 89.2 per cent at $\theta = 0$. This value is, however, still too low to explain the experimental results. Further considerations in this point will be discussed in the next report.

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(7) Copley and Phipps, *Phys. Rev.*, **45** (1934), 344.

Summary.

In these experiments on the measurement of the intensity of potassium atomic beams with a tungsten ribbon, the following results have been obtained:

(1) The ribbon was used to catch potassium atoms at room temperature and the positive ions formed by flashing were measured with a ballistic galvanometer.

(2) The ribbon surface is uniform for the ionization of potassium atoms.

(3) For the evaporation in the form of ions of adsorbed potassium atoms, the ribbon must be heated higher than 800°C.

(4) When the ionization of adsorbed potassium atoms is effected by flashing, the ionization is complete, when the surface concentration is below 0.04; otherwise, the ionization is incomplete.

(5) The ionization efficiency as a function of the surface concentration of potassium atoms was calculated on simple assumption and was found to deviate from the value observed.

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