Chemical Studies by Means of Molecular Beams. VIII.* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 2.

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Relation between the Surface Concentration of Adsorbed Atoms and the Ionization Efficiency. In the preceding report it was shown that the efficiency of ionization which was obtained by flashing the potassium atoms deposited on the tungsten surface differed considerably from what to be expected from the simple considerations as to the magnitudes of the work function and the contact potential of the tungsten used.

Now let us examine more closely the conditions of the tungsten surface and adsorbed potassium atoms. The tungsten ribbon was, as stated previously, heated to 1400–1500°C. This heat treatment is sufficient to get rid of the alkali contamination but not of the adsorbed oxygen, although it may completely eliminate the tungsten oxide. For the perfect removal of the adsorbed oxygen, the tungsten ribbon should be heated over 2900°K. In our experiments, therefore, we have always to do with a surface partly covered with oxygen, i.e. an incomplete W−O surface. The W−O surface has a very large electron work function, though its exact value has not yet been determined. Kingdon⁽¹⁾ takes the value to be about 9.2 V. and Reimann⁽²⁾ about 6.2 V. and Bosworth and Rideal⁽³⁾ about 6.3 V. At any rate in our experiments V_w must be valued at somewhat higher than 4.52 V.

Since our measurements indicate that the surface ionization curves show an appreciable departure from the linear course at $\theta = 0.04$, which corresponds to $x = \varepsilon (V_w - V_i - V_c)/kT = 2$, as we have already mentioned in the preceding report, we may estimate V_w if we know V_c, the contact potential of a potassium covered surface against the original surface. When potassium atoms are adsorbed on the W−O or W surface they are ionized there and adsorbed as ions, as long as θ is not too large. These adsorbed ions induce the negative charges under the metal surface and form the dipoles therewith. These dipoles produce the contact potential difference V_c according to the following equation:

$$V_c = 2\pi \sigma_0 \theta \mu , \qquad (1)$$

where $\sigma_0 = 3.56 \times 10^{14}$ is the number of atoms adsorbed per cm^2 of the true surface at $\theta = 1$ and μ is the average dipole moment. According

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

(1) K. H. Kingdon, *Phys. Rev.*, **24** (1924), 510.

(2) A. L. Reimann, *Phil. Mag.*, **20** (1935), 594.

(3) R. C. L. Bosworth and E. K. Rideal, *Proc. Roy. Soc.* (London), A, **162** (1937), 1.

to de Boer⁽⁴⁾ μ can be theoretically calculated by the equation:

$$\frac{\mu}{2} = \varepsilon r - \frac{\alpha \varepsilon}{(2r)^2}\,, \tag{2}$$

where ε is the electronic charge and r the radius and α the polarizability of the potassium ion. Their values are respectively 4.8×10^{-10}, 1.33×10^{-8} and 0.88×10^{-24} and equation (2) gives then the value of μ to be

$$\mu = 11.36 \times 10^{-18}\ \text{e. s. u.}$$

With this value of μ and $\theta = 0.04$, V_c is calculated from equation (1):

$$V_c = 300 \times 2\pi \times 3.56 \times 10^{14} \times 0.04 \times 11{\cdot}36 \times 10^{-18} = 0.305\ \text{V}\,.$$

As stated before, $V_w - V_i - V_c = 2kT/\varepsilon = 0.238$, when $\theta = 0.04$, so that $V_w - V_i = 0.543$ V or $V_w = 4.86$ V, since $V_i = 4.32$ V. On the other hand, Bosworth and Rideal⁽³⁾ found the dipole moment of potassium on W − O surface at $\theta = 0.04$ to be 20.5×10^{-18} e. s. u. which gives $V_c = 0.55$ V, so that $V_w = 5.11$ V.

These latter values of V_c and V_w seem to be more reliable than the former, since they are based on the actual experimental data of μ, but there is no definite evidence for this. Accordingly, we shall continue our discussion taking both values into consideration. In equation (1) V_c is proportional to θ. In reality, however, as θ increases, the mutual depolarizing force of anions begins to be operative and gradually causes to slacken the increasing rate of V_c, so that the $V_c - \theta$ curve will pass a maximum and decrease to approach a constant value of solid potassium. Since in our experiments the value of θ is small, we may use equation (1) or

$$V_c = c\,\theta\,, \tag{3}$$

where c is equal to $2\pi\sigma_0\,\mu$ and found to be either 7.6 or 13.8, according as the theoretical or the experimental value of μ is used.

With either of these values and $T = 1379$°K for the ribbon temperature or $\varepsilon/kT = 8.4$ and $A = 0.111\ \text{cm}^2$, the total ionization can be calculated numerically by means of equation (3) in the preceding report⁽⁵⁾ from which ½ is omitted:

$$\nu_p = AN_0\frac{kT}{c\,\varepsilon}\Big[\log\left(1+\exp.\left[\varepsilon(V_w - V_i)kT\right] - \log\left(1+\exp.\left[\varepsilon(V_w - V_i - c\theta)/kT\right]\right)\Big]$$

The total ionization curves are shown in Figs. 1 and 2 with full lines. The experimental points represented by × and ⊙ correspond to those in Fig. 6 in the preceding report.

The agreement of the experimental points with the theoretical curves is not good in either case, but in the region of larger values of θ, it is better in Fig. 2 than in Fig. 1.

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(4) J. H. de Boer, "Electron Emission and Adsorption Phenomena." 85, Cambridge (1935).

(5) K. Kodera, this Bulletin, **14** (1939), 114.

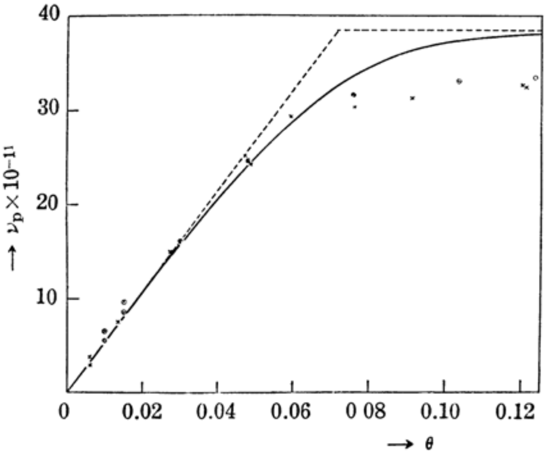

Fig. 1.

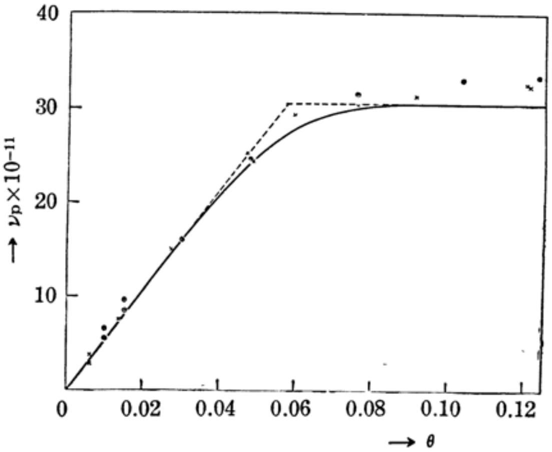

Fig. 2.

Now turning to our assumption $V_c = c\,\theta$, it must be noted that for larger values of θ this relation holds no longer good on account of the mutual depolarizing force. This argument makes plausible the deviation of the theoretical curves from the experimental points. It is therefore desirable to know a more precise relation between V_c and θ in this region of θ. Bosworth and Rideal⁽³⁾ have determined μ for a wide range of θ, from which V_c is obtained as a function of θ (Fig. 3). With these values of V_c the differential ionization is calculated by equation (2) in the preceding report⁽⁵⁾ with the factor ½ dropped:

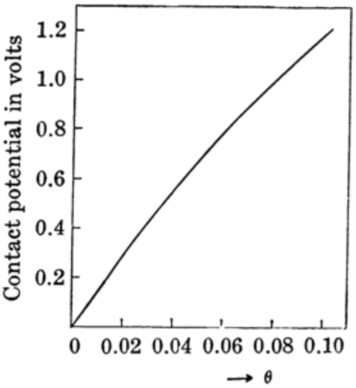

Fig. 3.

$$\frac{d\nu_p}{dN} = \frac{\exp.\,[\varepsilon(V_w - V_i - V_c)/kT]}{1 + \exp.\,[\varepsilon(V_w - V_i - V_c)/kT]}$$

The results is shown in Fig. 4. The total ionization curve may be obtained from Fig. 4 by graphical integration. The result (Fig. 5) is seen to be in sufficient agreement with the experimental values.

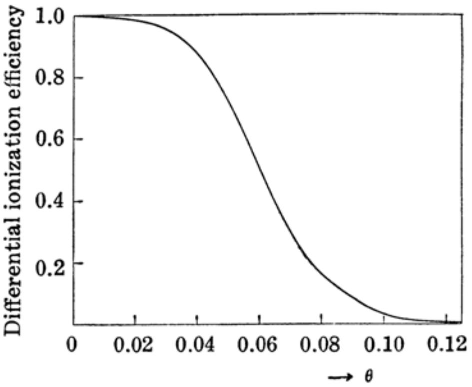

Fig. 4.

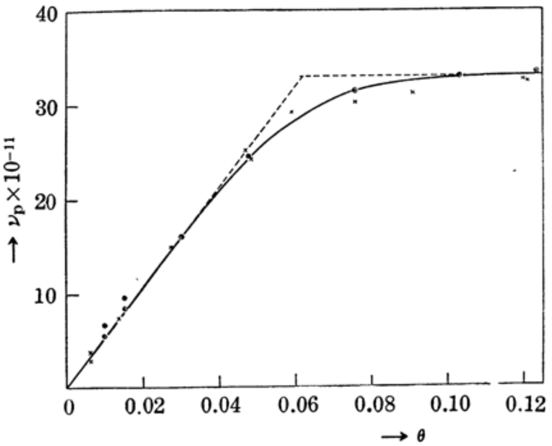

Fig. 5.

The Surface Migration of the Adsorbed Atoms. In our experiments, adsorbed atoms are at first confined to a very small portion of the ribbon surface. If the surface migration can take place, the site of the adsorbed atoms will gradually spread out and the surface concentration will accordingly become smaller. It must therefore be possible, by taking advantage of this phenomenon, to reduce a high surface concentration and bring about better or even complete ionization.

The phenomenon of surface migration is not significant when the ribbon is kept at room temperature but becomes noticeable at higher temperatures. (Bosworth and Rideal⁽³⁾ have, however, reported that even at room temperature they observed the migration to occur when θ was large.) To examine this effect, deposits having a certain θ larger than 0.04 were preheated to 600–700°C. for different intervals of time, the cathode being kept at a higher potential to suppress the evaporation of ions. If the surface migration has occurred, the flashing should give a larger ion current than without preheating.

The results obtained in these experiments are shown in Figs. 6 and 7 in which the ordinate represents the galvanometer deflection and the abscissa, the time of preheating. The existence of the surface migration is evident in all the curves. Curves I–IV in Fig. 6 were obtained respectively with the temperatures of 756, 704, 651 and 634°C. for preheating. Each of these curves has a maximum, the height of which decreases as the temperature of preheating rises. This is probably attributable to the fact that some fraction of the adsorbed atoms is evaporated while being preheated. That the rise of the curves is more rapid at a higher temperature of preheating is due to the greater migration velocity of the atoms. The dotted line in the figure represents the galvanometer deflection corresponding to the perfect ionization. The maximum of IV is equal to 94 per cent of that value. When the adsorbed atoms were heated at 580°C. for 6–7 minutes, a 100 per cent ionization was effected. In case θ was smaller than 0.04, the preheating caused no change in the ionization efficiency. This is self-evident since the ionization efficiency is 100 per cent from the outset.

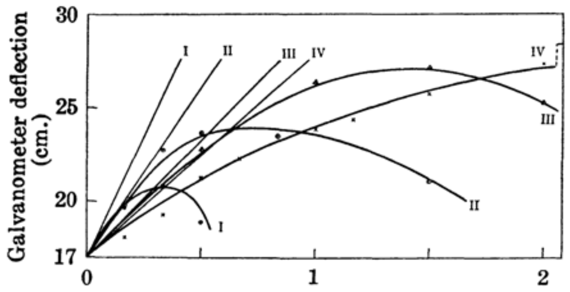

Fig. 6.

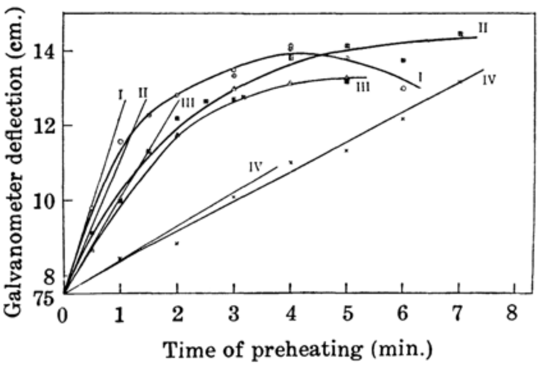

Fig. 7.

This surface migration explains also the behaviour of curve II in Fig. 4 in the preceding report.⁽⁵⁾ If a low flashing temperature of the ribbon is effected with a small electric current, the rise of the ribbon temperature is comparatively slow, so that there is ample time for the surface migration to take place and improve the ionization efficiency in the region $\theta > 0.04$. But the migration velocity increases as temperature rises, so that, as exemplified in curve II, an optimum will be reached at a temperature where these opposing effects just balance. Making use of the surface migration, the portion of the linear increase in the initial part of the curve in Fig. 6 in the preceding report may be extended to the larger values of θ.

Energy of Activation of the Surface Migration. It would be interesting to correlate the preceding experimental results with the migration velocity of the adsorbed ions, although the experiments were not undertaken for this special purpose. Especially it should be mentioned that the data relating to the temperature are inexact, for the range with which we are here concerned lies outside the limit of direct measurement with an optical pyrometer.

Let us assume that the migration or diffusion coefficient of the potassium ion on the tungsten surface is a function of the temperature only and not of the surface concentration, although this assumption is only approximately right(6).

If a certain deposit of potassium atoms begins to expand at a certain temperature, the distribution of the surface concentration after a time t will be given by a function in which the diffusion coefficient D and the time t occur everywhere in the form of product Dt.

If then equal deposits simultaneously start the migration at different temperatures, they will attain the identical distribution of concentration successively in time t given by the relation $Dt =$ constant. Although the total number of potassium atoms remains constant, every stage of expansion of the deposit is characterized by the corresponding amount of ions liberated upon flashing, since, as we have seen, the ionization efficiency is a function of the surface concentration. The same state of expansion to be attained at different temperatures may then be recognized by the equality of the galvanometer deflection obtained on flashing.

As to the actual determination of t from the curves in Figs. 6 and 7 use was made of the tangents drawn at the initial points with the purpose of avoiding the effect of the loss of potassium caused by evaporation during the preheating and of the change of contact potential with the surface concentration. The heat of activation Q for the migration may then be obtained from the inclination of the log $t - T^{-1}$ straight line, provided the diffusion constant is expressible in the form $Ae^{-\frac{Q}{RT}}$

The value of Q was thus detemined for two cases of different initial surface concentrations $\theta = 0.10$ and 0.20 of the deposit. Q was found greater for the smaller surface concentration. The magnitudes of Q are fairly similar to those obtained by Bosworth,(6) who, by following the expansion of the deposit by the photoelectric activity, determined D for different temperatures and different surface concentrations and then Q

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(6) R. C. L. Bosworth *Proc. Roy. Soc.* (London), A, **154** (1936), 112.

from the log $D-T^{-1}$ lines. Since, however, the probable error is large, it would be reasonable not to give our Q values but to associate to the curves the tangents whose relative inclinations were conversely determined from the value of Q as given by Bosworth, i.e. $Q = 0.59$ V. for $\theta = 0.10$; $Q = 0.53$ V. for $\theta = 0.20$. One will see in Figs. 6 and 7 that they are fairly in line with the curves.

Thus we see that the procedure we have just mentioned permits a convenient determination of the activation energy of surface migration though not the migration coefficient itself. Refined measurements would yield more accurate values.

Advantages of the Method of Flashing. This method of flashing with a tungsten ribbon has its own limit of application. If a measurement of the intensity at a point or along a line on the cross section of an atomic beam is required, it is more convenient to use a filament. On the contrary, for the measurement of the intensity of an atomic beam as a whole or of a very spacious portion of it, this method is preferable. One important precaution to be taken is to keep the specific surface concentration always below 0.04. Even if we take advantage of the surface migration, 0.1 would be the highest allowable surface concentration in practical use. For this reason, this method is more suitable for measuring weak atomic beams with a large cross section. An atomic beam of a high intensity can be measured with the ribbon kept at a flashing temperature, but this process generates much heat which may give rise to many troubles in the apparatus. Of atomic beams with the same total intensity, those with larger cross sections are more suitable for measuring than those with smaller cross sections.

An example will make this point clear. When a surface concentration of 0.04 is produced within a circle of radius 0.1 mm., the number of atoms adsorbed is:

$$4.8 \times 10^{14} \times 0.04 \times \pi (1 \times 10^{-2})^2 = 6.0 \times 10^9$$

where 4.8×10^{-14} is the number of atoms adsorbed on each cm^2. of the apparent area when θ is 1. The quantity of electricity to be obtained when all these atoms are ionized is:

$$1.6 \times 10^{-19} \times 6.0 \times 10^9 = 0.96 \times 10^{-9} \quad \text{coulombs,}$$

where 1.6×10^{-19} is the charge of an ion in coulomb. By dividing this value by the sensitivity of the galvanometer used, 3.77×10^{-10} coulomb per 1 mm. deflection, the value of the galvanometer deflection is found to be

$$0.96 \times 10^{-9} / 3.77 \times 10^{-10} = 2.55 \text{ mm.}$$

Thus we see that the maximum allowable surface concentration within a circle of radius 0.1 mm. can give rise to only 2.5 mm. deflection of the galvanometer.

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 ionization efficiency of adsorbed potassium atoms by flashing is found to be in good agreement with the calculated one, if the correct values of the work function and those of the contact potential of the tungsten surface are used.

(2) Adsorbed potassium atoms begin to migrate on the surface of the ribbon when the latter is heated to 500–700°C. This effect enables us to obtain a perfect ionization even with a concentration higher than $\theta = 0.04$.

(3) A simple method of determining the heat of activation of the surface migration is proposed.

From the above facts, it has been concluded that this method is the most suitable for measuring all at one time weak atomic beams of large cross sections.

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