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LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Mobility of Caesium Atoms Adsorbed on Tungsten

A heated tungsten filament in presence of Cs vapor adsorbs Cs atoms. The number of atoms per unit area, σ, can be measured (if $\sigma < 3.6 \times 10^{13}$ cm^{-2}) by suddenly heating the filament (surrounded by a negatively charged cylinder) and observing the ballistic kick on a galvanometer, since every atom escapes as a positive ion.

Three cylinders placed end to end surrounded a straight filament. With all three cylinders at positive potential (22 volts) a Cs film was formed with the filament at low temperature. The Cs vapor was then frozen out by immersing the bulb in liquid air. The filament was next heated to a temperature (848°K) at which σ was reduced below 3.6×10^{13} and the temperature was then lowered to T_1 at which the rate of evaporation of atoms was very low. The potential of the central cylinder was then changed to -22 volts leaving the other two at $+22$. This allowed the Cs on the central part of the filament to escape as ions. The current to this central cylinder gave the rate of evaporation. After the removal was nearly complete, the potential of the central cylinder was altered to -44 volts and because the accelerating field for ions then reached into the end cylinders, an additional length a was freed from Cs. The current-time integral permitted the total length of cleaned filament to be measured.

In this way a *standard* Cs *distribution* was obtained in which the central part, free from Cs, extended at each end a distance of 0.165 cm into the end cylinders, while the two end sections were uniformly coated with Cs to a concentration of $\sigma = 2.73 \times 10^{13}$.

With the filament in this standard condition the temperature was changed to T_2 for a time t_2 while all three cylinders were at $+22$ volts so that no ions could evaporate. T_2 was chosen so low ($<848°$) that there was no appreciable change in σ by atom evaporation during the time t_2. During this time, however, the Cs migrated to some extent from the end sections into the central section. The number of atoms which had arrived were then measured by flashing the filament while the three cylinders were put at -22 volts, but the current to the central cylinder only was measured.

The migration of the Cs may be looked upon as a surface diffusion, the number of atoms per unit time crossing each unit of length of a line on the surface being $Dd\sigma/dt$. Treating the problem as one of diffusion, assuming as usual that D is independent of σ, it is then possible to calculate D from the foregoing experiments.

Measurements of the migration were made at $T_2 = 654°$, 702°, 746°, and 812°K with times from 200 to 4000 seconds. At each temperature the values of D obtained were approximately independent of t_2 (slight increase with t_2). The values of log D plotted against $1/T$ gave a straight line so that

$$\log_{10} D = -0.70 - 3060/T. \qquad (1)$$

At 812° this corresponds to $D = 3.4 \times 10^{-5}$ cm^2 sec.$^{-1}$.

A few experiments were made in which the Cs concentration on the end sections in the standard condition was altered to 1.74×10^{13}. At 812° a value of D of 1.4×10^{-5} was found. Thus D varies considerably with σ so that the experiments have given as yet only a kind of average value of D over the range from $\sigma_{\max}$ to 0.

Determinations of D at higher concentrations have been made by another method. In presence of a given pressure of Cs, the Cs film on a filament at about 1000°K surrounded by a negatively charged cylinder can exist in two phases, separated by a definite boundary. From the more concentrated phase (α phase) Cs evaporates as atoms while from the dilute β phase Cs evaporates as ions; both of these rates being equal to the rate of arrival from the vapor phase. At a given filament temperature there is only one pressure p_0 at which these two phases can coexist. If the pressure is changed to p_1, the phase boundary moves with a definite velocity v along the length of the filament, causing either one or the other phase to disappear.

At the phase boundary there is a sharp concentration gradient. The resulting surface migration is balanced by differences between the rates of evaporation into and arrival from the vapor. The rates of evaporation of atoms and ions, ν_a and ν_p, both depend on T and σ, but the rate of condensation μ is fixed by the Cs vapor pressure. The total evaporation rate $\nu = \nu_a + \nu_p$ rises from 0 at $\sigma = 0$ to a maximum at about $\sigma = 7 \times 10^{12}$, falls to a minimum at 43×10^{12} and then rises indefinitely. The curve $\nu - \mu$ as a function of σ thus intersects the σ axis at three points and forms two closed areas A_1 and A_2, enclosed by the curve and the σ axis. A recent article [I. Langmuir, J. Am. Chem. Soc. **54,** 1252 (1932)], gives data from which such curves can be prepared. Mathematical analysis shows that the condition for a stationary phase boundary is that $A_1 = A_2$.

If at any temperature the rate of arrival of Cs is changed from μ_0 to μ_1, the velocity of the movement of the boundary is given by

$$v = (D/2A)^{1/2}(\mu_1 - \mu_0).$$

This was derived on the assumption that D is independent of σ and that v is small.

The experiments show in fact that $A_1 = A_2$ and that v varies in proportion to $\mu_1 - \mu_0$. From measurements at 967°K a value of $D = 6 \times 10^{-4}$ was obtained. The concentration of the α phase was 7.3×10^{13}. From Eq. (1) for this temperature we calculate $D = 1.1 \times 10^{-4}$. The higher concentration is the probable reason for the higher observed value of D by this method.

The strong repulsive forces between the adatoms explains the variation of D with σ. It is planned to develop a quantitative theory of this effect. The coefficient of the last term of Eq. (1) corresponds to an activation energy for diffusion amounting to 0.61 volts. The atoms are normally held in definite positions with respect to the underlying tungsten lattice, but by acquiring thermal energy of agitation of 0.61 volts or more, may hop into adjacent vacant spaces. With definite knowledge of the lattice and the forces acting on the atom, it is hoped that the average life τ in each elementary space may be determined.

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Relative Abundance of H^1 and H^2 in Natural Hydrogen

Urey, Brickwedde and Murphy[1] have shown that an isotope of hydrogen of atomic weight 2 exists in ordinary hydrogen and that its abundance relative to H^1 is increased in liquid hydrogen by fractional distillation of liquid hydrogen near its triple point. By using the relative exposure times required to record the Balmer lines with a grating the relative atomic abundances were estimated as 1:4000 in natural hydrogen and 1:800 (or more) in the concentrated samples. Bleakney[2] found that the relative abundance in one of the same concentrated samples was 1:1100 ± 10 percent using a mass spectrograph method. The abundance as estimated by the relative exposure times agreed as closely with this as could be expected considering the approximate character of this method as compared with that used by Bleakney. However his estimate of the abundance in ordinary hydrogen reported at the Boston meeting, of 1:30,000 is in very marked disagreement with that given by Urey, Brickwedde and Murphy. Moreover Kallman and Lasareff[3] also using a mass spectrograph method conclude that H^2 must be less abundant than 1:40,000.

In order to explain these discrepancies we have searched for possible sources of error in the spectrographic estimates. The change of intensity of the H^2 Balmer lines relative to the H^1 Balmer lines depending upon whether the ordinary hydrogen or concentrated samples

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[1] Urey, Brickwedde and Murphy, Phys. Rev. **39,** 164 (1932); **40,** 1 (1932).

[2] W. Bleakney, Phys. Rev. **39,** 536 (1932).

[3] Kallman and Lasareff, Naturwiss. **12,** 206 (1932).