points from the theoretical curve was more pronounced as is seen in Fig. 2(B). The resolution was not good enough to actually resolve a peak due to Li^6 but it can be assumed, as was originally done with the unresolved peak due to K^{41}, that the discrepancy between the experimental and theoretical intensities is due to an unresolved "zero moment" peak of Li^6. It follows from this that the nuclear spin of Li^6 is 2/2 or greater, and that the ratio of the magnetic moments of the two isotopes of lithium, μ_6/μ_7, can be put between the limits of 0.15 and 0.25, the value depending on the spin of Li^6. If a spin of 2/2 is assumed the magnetic moment of the Li^6 nucleus is calculated to be of the order of magnitude of that of the deuteron.

We are much indebted to Dr. Sidney Millman and other workers in the molecular beam laboratory for their able assistance in the course of these experiments.

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Positive and Negative Thermionic Emission from Molybdenum

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The positive and negative thermionic emission for molybdenum has been investigated. The electron work function has been found to be 4.17 volts and that of the positive ion 8.35 volts. The positive ion emission has been shown to agree with the Saha theory of ion formation to within the experimental limits of error.

IT has been shown by Smith[1] and by Wahlin[2] that when molybdenum is heated to a sufficiently high temperature, positive ions of the metal itself are emitted. The temperature variation of this ionic current has been studied by Smith[1] and by Barnes[3] with differing results. Smith, following the analysis used by Bridgman[4] in his derivation of the Richardson equation, has derived a positive ion thermionic equation which for molybdenum takes the form:

$$\log_{10} i + 0.453 \log_{10} T + 2.7\ \ 10^{-4}T = -\varphi_{0+}e/2.303kT + C, \quad (1)$$

neglecting any effect of the surface heat of charging. From this equation he computed φ_{0+} to be 6.33 volts. Barnes using the same equation obtains a value of 8.17 volts.

Because of these discordant results it was thought worth while to repeat the experiment with better outgassing conditions than have been used hitherto.

The thermionic tube used was one with a single guard ring and a U type filament. The tube, the potentials used and the outgassing treatment were similar to those described in a study of the positive ion emission from columbium by Wahlin and Sordahl.[5]

Extreme care was exercised in the baking and heating process to eliminate alkaline impurities as far as possible. The baking of the tube was continued for at least 500 hours with the filament at a temperature of about 1700°K and the furnace at a temperature of 450°C. The heat treatment of the filament was then continued at a temperature of 1900°K with occasional flashing to 2100°K or higher until a value for the electron work function, as measured at intervals from a Richardson plot, did not vary with heat treatment for at least 200 hours. After the baking and heat treatment the pressure remained lower than 3×10^{-8} mm when the filaments were varied over the temperature ranges used.

Three disappearing filament optical pyrometers were used in measuring the temperatures. These were calibrated in the usual manner by sectoring up and down from the gold point and then checked against the palladium point. None

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[1] L. P. Smith, Phys. Rev. **35**, 381 (1930).

[2] H. B. Wahlin, Phys. Rev. **34**, 164 (1929).

[3] L. L. Barnes, Phys. Rev. **42**, 491 (1932).

[4] P. W. Bridgman, Phys. Rev. **27**, 173 (1926).

[5] Wahlin and Sordahl, Phys. Rev. **45**, 886 (1934).

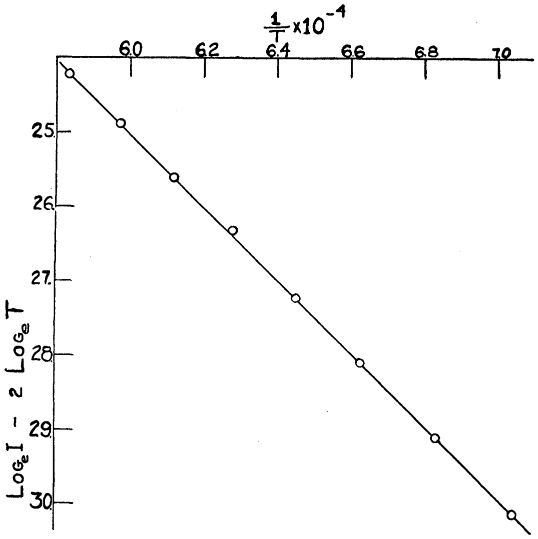

FIG. 1. Richardson plot for electrons.

were found to be as much as 1° in error at this temperature.

The emissivity used in calculating the true temperatures is the constant value 0.382 determined by Whitney.[6]

ELECTRON WORK FUNCTION

Two samples of pure molybdenum 1 mm wide and 0.05 mm thick, obtained from the Fansteel Company gave values for the electron work function of 4.17 volts with a constant $A=51$. These values were reached after 600 hours of heat treatment and did not change with further degassing up to 1100 hours at temperatures as given above. Fig. 1 shows a Richardson plot for one of these samples. A strip of the metal, of the same dimensions, kindly furnished by Dr. W. E. Forsythe was mounted in the tube after being rolled cold to a uniform thickness. This was given the same initial heat treatment as the others and after about 600 hours gave a work function of 4.25 volts. This value rose with further degassing and flashing to a final value of 4.38 volts in fair agreement with the value found by Dushman. The A for this specimen was found to be 175 amp.$\cdot$cm$^{-2}\cdot$degrees^{-2}. Flashing up to 2600°K did not change this value. A sample of the Fansteel specimen was then mounted after having been cold rolled lightly. This specimen gave a terminal value of 4.30 volts with $A=96$ amp.$\cdot$cm$^{-2}\cdot$degrees^{-2}.

Whether or not in the rolling process some impurity was introduced could not be determined. A spectroscopic analysis of the specimens failed to reveal any difference. There is a possibility as has been pointed out to the writer by Dr. W. P. Jesse that due to the cold rolling certain crystal faces may come up parallel to the surface of the strip and that these may persist with heat treatment in a vacuum. If this is the case, the difference in the specimens may be due to a difference in the crystalline orientation. However, since the first two specimens gave the most reasonable values for A, it is probable that 4.17 volts represents more nearly the correct value for a pure polycrystalline molybdenum surface. This value, furthermore, is in good agreement with the photoelectric and thermionic value (4.15) obtained by DuBridge and Roehr.[7]

If one assumes a roughness factor for the well outgassed molybdenum surface of 1.25 the true value of the experimental A is 41.0. The deviation of this value from the theoretical 120 is probably due to a temperature variation of the electron work function. Reimann[8] has computed this temperature variation on the assumption that it is due to a change in the zero-point energy of the electrons caused by a change in the number density of the free electrons; this change being due entirely to the expansion of the metal. From his calculation he estimates that the experimental A should be in the neighborhood of 41. However, with the present uncertainty in the roughness factor, the agreement with the determined value may be fortuitous.

POSITIVE ION EMISSION

After steady conditions as indicated by the electron work function study had been obtained, the potential was reversed and the positive ion variation with temperature obtained within the temperature range 2150°K to 2630°K. The currents at low temperatures were measured with a quadrant electrometer and those at high temperatures by means of a sensitive galvanometer.

Fig. 2 shows plots of the log $i+f(T)$ against

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[6] L. V. Whitney, Phys. Rev. **48**, 458 (1935).

[7] DuBridge and Roehr, Phys. Rev. **42**, 32 (1932).

[8] A. L. Reimann, Nature **133**, 833 (1934).

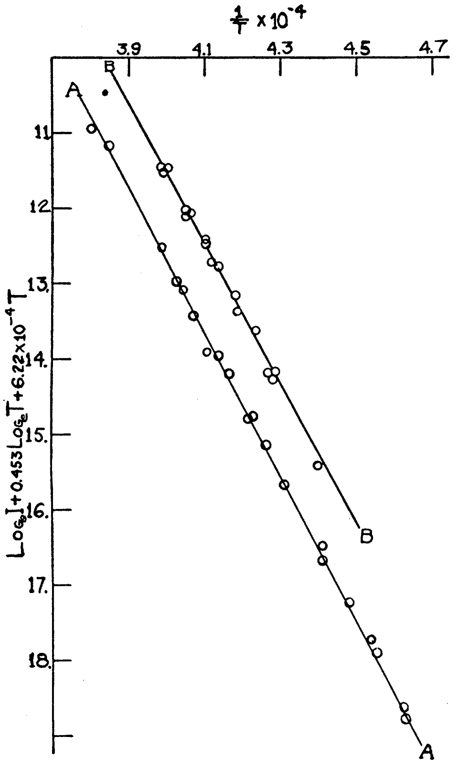

FIG. 2. Richardson plot for positive ions.

$1/T$ for the positive ion current, using Smith's equation. As will be noticed the curves are linear within the limits of experimental error over the entire temperature range. Barnes' plots show a definite curvature thus indicating the presence of an ionic impurity. Curve A is the plot for a specimen with electron work function of 4.17 volts and curve B for one with an electron work function of 4.38 volts.

The positive ion work function computed from the slope of these curves is 8.3 volts for curve A and 8.21 for curve B. These values are only slightly higher than the value found by Barnes (8.17 volts). This would seem to indicate that the impurity which acted to produce the curvature in his results did not greatly affect the slope at the higher temperatures. The points on the two curves in Fig. 2 represent data taken intermittently over a period of at least 100 hours of flashing and heat treatment. No progressive change in the current at a given temperature could be noticed during this time. One can conclude therefore that a steady condition had been reached.

It is to be noted that the positive ion current from the specimen with the higher electron work function is greater than the other by a factor of nearly 3. At first it was thought that this was due to the presence of an impurity ion but a mass spectrograph analysis failed to reveal the presence of a measurable amount of any such contamination.

The difference is, however, readily explainable on the basis of the difference in the electron work functions of the two specimens. Moon[9] has shown that according to the Langmuir-Kingdon-Saha theory of positive ion emission from hot metals, the following relation should hold.

$$n_p/n_a = \sigma_p/\sigma_a \exp - 11{,}600(U - \varphi_-)/T, \quad (2)$$

where n_p and n_a are the rates of evaporation of positive ions and neutral atoms, respectively, σ_p and σ_a are the statistical weights of the two, U is the ionization potential and φ_- the electron work function.

If we assume that n_a is independent of φ_- within the limit of experimental error, we see on taking the ratio of two equations with different electron work functions, that everything except the ratio of the n_p's, the difference in the electron work functions and the temperature, drops out. This is on the assumption that the abnormally high value of A observed for the high work function specimen is due to some other cause than simply a temperature variation in φ_- and that this temperature variation is the same for both specimens. Taking this ratio we see that with the observed difference of 0.2 volt the ratio of the + ion currents should be 2.6 at 2300°K. This agrees within the limits of error with the experimental ratio particularly in as much as the exponent is very sensitive to a small error in φ_-.

In Table I, the computed and observed ratios

TABLE I. *Observed and computed values of* n_p/n_a.

$1/T$ 10^4	OBSERVED RATIO	COMPUTED RATIO
4.0	1.89	1.82
4.2	1.94	1.88
4.4	1.97	1.94

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[9] P. B. Moon, Proc. Camb. Phil. Soc. **28**, 490 (1932).

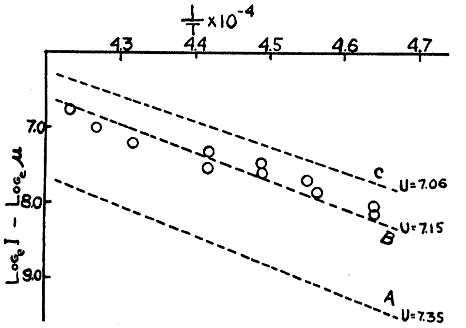

FIG. 3. Comparison of Langmuir-Saha equation with experiment.

for two samples with electron work functions of 4.17 and 4.30 volts are given for three values of $1/T$.

This variation of the positive ion current with φ_- shows, incidentally, that a stable condition giving a constant electron work function is essential for an accurate determination of the positive ion work function.

In order to compare Eq. (2) more directly with the experimental results it is convenient to write it in the form:

$$i_p/\mu = e/m\sigma_p/\sigma_a \exp -11{,}600 \times[U-(\varphi_{0-}+\alpha T)]/T. \quad (3)$$

Where α is the temperature coefficient of φ_-. This according to the discussion of the electron work function given above reduces to

$$i_p/\mu = e/m\sigma_p/\sigma_a 2.9 \exp -11{,}600(U-\varphi_{0-})/T, \quad (4)$$

where i_p is the positive ion current/cm^2, μ is the loss of mass/cm^2 per sec. and e/m is the specific charge for molybdenum.

Unfortunately the ionization potential of molybdenum is not known with sufficient accuracy to make a good comparison of this equation with experiment possible. Bacher and Goudsmit[10] give a value of 7.35 volts for U and Catalan and Magariaga[11] in a more recent determination give a value of 7.06±0.03 volts. The estimated error in this determination may, however, be too low. An earlier estimate by Catalan[11] yielded a value of 7.15 volts.

Fig. 3 shows a plot of $\log i_p - \log \mu$ against $1/T$ for the above equation with a statistical weight of 6 for the ion and 7 for the neutral atom where the statistical weight is taken as $2j+1$. φ_{0-} is here taken as 4.17 volts. Curve A is with $I=7.35$ volts. Curve B with $I=7.15$ and C with a value of 7.06 volts. The points are experimental, using evaporation data obtained in this laboratory by Mr. E. R. Piore and which will be published soon. The temperature range used in the plot is limited by the range of temperature used in obtaining the evaporation data.

As may be seen from the above plot the experimental data definitely favor an ionization potential of 7.15 volts. In order to agree with the 7.06 value the ratio of i_p/μ would have to be increased by a factor of 1.4. There is of course an uncertainty in the 2.9 factor but it does not seem likely from the value for the constant A given above that this can be 40 percent in error.

If in Eq. (3), we substitute

$$\mu = Bf(T) \exp -11{,}600H/T, \quad (5)$$

where H is the heat of evaporation of neutral atoms in volts, we get

$$i_p = Cf(T) \exp -11{,}600(U+H-\varphi_{0-})/T.$$

This is essentially the form of Smith's equation (Eq. (1)) and we see that $\varphi_{0+} = U+H-\varphi_{0-}$. Piore's vapor pressure data give $H=5.75$ volts computed from the slope of the Jones-Langmuir-Mackay[12] vapor pressure equation. With $U=7.15$ volts and φ_{0-} as 4.2 volts the value of φ_{0+} should be 8.7 volts. The average of all the experimentally-determined values is 8.35 volts. The lack of agreement may be due to a combination of a number of possible errors. There is an uncertainty of approximately 1/10 volt in the determined value of φ_{0+} and a somewhat greater possible error in H. In addition there is an uncertainty in the temperature factor in Eq. (1) due to the neglect of the effects of the surface heat of charging which might influence the experimental value of φ_{0+} appreciably. For the present, therefore, we must conclude that the agreement between the computed and experimental values of the positive ion work functions is as good as can be expected.

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[10] Bacher and Goudsmit, *Atomic Energy States*.

[11] Catalan and Magariaga, Anales soc. espan. fis. y. quim **31**, 707 (1933).

[12] Jones, Langmuir and Mackay, Phys. Rev. **30**, 201 (1927).