NOTE

The Rate of Evaporation of Electrons from Hot Filaments.—In a preceding paper[1] the author has derived an equation from statistical mechanics for rate of evaporation. Apparently the most critical test of this equation would be a calculation of the rate of evaporation of electrons from a hot filament. Preliminary calculations did not give a satisfactory agreement with observed data. In these calculations E_0 was placed equal to ϕ the "thermionic work function." Richardson[2] has shown, however, that the electrons leave the filament with an average excess energy of $2RT$. Consideration shows that E_0 should be placed equal to $\phi + 2RT$.[3] According to Richardson, the number of electrons evaporating from a metallic filament per sq. cm. per second is given by the empirical equation

$$n = A\sqrt{T}\,e^{-\frac{b}{T}} \tag{1}$$

The equation derived by the author is

$$n = \frac{\mathbf{N}}{Nhe^2}\sqrt{\frac{E_0RT}{\pi}}\,e^{\frac{-E_0}{RT}}$$

If we set $E_0 = RB + 2RT$, then approximately

$$A = \frac{\mathbf{N}}{Nhe^2}\sqrt{\frac{E_0R}{\pi}} \tag{2}$$

Below are tabulated the values of A calculated from the careful measurements of Langmuir[4] on tungsten, tantalum and molybdenum, and the values of A calculated from Equation 2 at 2000° K.

	A obs.	A calc.
Tungsten..........	1.48×10^{26}	6.00×10^{26}
Tantalum..........	0.705×10^{26}	3.27×10^{26}
Molybdenum.......	1.32×10^{26}	5.50×10^{26}

In view of the assumption of 1 free electron per atom in the metallic surface, the agreement is as good as could be hoped for and the deviation is remarkably regular.

If we assume that this equation holds generally for the metals, we can then obtain at once from thermodynamics a relation between the thermionic-work function and the thermoelectric force. Tungsten and molybdenum are the only pair of metals for which the data are at hand to check this relation, and for them the agreement is good. It appears entirely

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[1] THIS JOURNAL, **45**, 606 (1923).

[2] Richardson, "The Emission of Electricity from Hot Bodies," Longmans Green and Co., London, **1916**, p. 164.

[3] In the calculation of the vapor pressure of mercury in the earlier paper it appears that better agreement with the experimental data would be obtained by similar considerations.

[4] Langmuir, *Trans. Electrochem. Soc.*, **29**, 125 (1916).

possible to calculate the thermionic-work functions, and hence contact potentials between metals, from thermoelectric data.

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QUANTITATIVE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS WITH ARSENIC AND WITH MERCURY

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Analysis of Arsenical Compounds

During the past 20 years, the method for the quantitative analysis of carbon and hydrogen in organic compounds has been both greatly simplified and improved through the introduction by M. Dennstedt of a new method to combustion in a current of oxygen, with platinum as a catalyst. With regard to the saving of time and energy, this method is superior to any other, and yields results as accurate as those obtained by the older Liebig method. The procedure has been further developed so that in organic substances containing nitrogen, sulfur and halogens these elements may be determined simultaneously with carbon and hydrogen. Organic arsenicals or mercurials, however, could not be analyzed in this way, because of "poisoning" of the platinum catalyst by the arsenic oxide or mercury vapors formed. As the authors have been engaged in the preparation of organic compounds containing these elements, it was considered essential to obviate the above difficulty. Not only has this been accomplished, but in addition, the method developed for the concurrent determination of mercury appears to be superior to the usual gravimetric method, in so far as accuracy and rapidity are concerned.

In order to prevent arsenic oxide from attacking the platinum, a boat B containing red lead is placed immediately after the boat A containing the substance to be analyzed (Fig. 1). The red lead reacts quantitatively with arsenic oxide, forming lead arsenate which does not decompose at high temperatures. If the combustion is not conducted too rapidly, the lead arsenate may be observed as a thin white coating at that end of the boat B nearest A, except in the case of sodium salts containing sufficient sodium to combine with all of the arsenic when no such coating is formed. The stability of the lead arsenate at high temperatures is of great convenience as carbonaceous matter, which frequently settles upon it, can be entirely removed by continued heating.