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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

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NBS REPORT

8694

VAPORIZATION OF THERMIONIC REFRACTORY MATERIALS

Report written by

E. R. Plante

Work done by

N. J. Carrera

J. J. Diamond

R. F. Hampson

E. R. Plante

R. Szwarc

R. F. Walker

FINAL REPORT

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U. S. DEPARTMENT OF COMMERCE
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I. Introduction

The purpose of this final report is to summarize the objectives and accomplishments of the project over the last four years. A number of interim reports [1-14] have outlined general objectives and accomplishments at the time of writing.

The objectives of the project have been to develop a reliable method for the determination of evaporation rates of refractory materials in high vacuum and to supply NASA with reliable rate of vaporization data on refractory materials having potential use as emitters in thermionic engines.

II. Method of Measurement

A. Discussion of Langmuir Method

The rate of vaporization of a material into a high vacuum, m/at , is related to the equilibrium vapor pressure by the relation

$$m/at = \alpha \sqrt{\frac{M}{2\pi RT}} P_{eq} \quad (1)$$

In this equation, m is the mass of material sublimed, t is the duration of the experiment, a is the projected sample area, M is the molecular weight of the evaporating species, R is the gas constant and α is the vaporization coefficient. To determine the rate of vaporization at some temperature, one need measure only the quantities on the left hand side of equation (1) and the temperature. However, if the rate of vaporization at constant temperature is to be constant with time, certain other conditions must be fulfilled. Two sets of requirements must be met. First, the material must be undergoing univariant-congruent vaporization. Otherwise the rate of vaporization

may not be the rate determining step but the process observed may depend on changing surface conditions or the concentration of evaporating molecules in a non-volatile surface layer.

The second set of conditions can be summarized as follows:

- (1) The ambient pressure in the system is sufficiently low so that the number of collisions between the effusing vapor and the background gases are negligible;
- (2) The distance between the walls of the container and the evaporating surface is small compared to the mean free path of the vapor molecules;
- (3) The walls of the container are sufficiently cool so that no significant reflection or re-evaporation of the evaporated molecules can take place.

All three of these latter conditions say the same thing; namely, that a molecule having "evaporated" must not get back to the sample surface.

Usually these conditions are not too difficult to satisfy except that condition (3) may be violated if a susceptor is used to heat a non-conductor by radiation and both (1) and (3) may be violated in the case of compounds such as nitrides in which one of the vaporization products is a permanent gas.

The Langmuir method has sometimes been criticized on the grounds that it is difficult to determine the evaporating area with a reasonable degree of certainty owing to surface irregularities but this criticism is probably valid only under special circumstances. Melville [15] has concluded, for example, that the projected geometrical area is the correct one to use and that surface irregularities will have no effect on the observed rate of

vaporization if the vaporization coefficient is unity. Of course, it is always possible to envision a surface which is so irregular that it is not possible to determine its surface area accurately. The type of surface considered and used in this work is one of a common shape such as a cylinder in which the surface irregularities are small in comparison with the dimensions of the sample so that one can readily measure the geometrical area.

B. Equipment Used

At the time of initiation of this research contract with NASA, a microbalance apparatus was being used to carry out rate of vaporization measurements on some of the platinum metals. However, it was believed that the vacuum system used with this apparatus was not adequate and that measurements were subject to possible error because of contamination of the sample. This could take place by reaction of the sample with vapors backstreaming from the oil diffusion pump. Evidence for this was obtained during studies carried out on platinum [16]. It was noted that during the early part of these experiments, data believed to be reliable was obtained at temperatures as low as 1916°K while during the latter part of the experiments, data points obtained below 1975°K did not agree with the curve believed to represent the rate of vaporization of pure platinum. Among the possibilities suggested to explain this behavior was that the sample surface had become contaminated by its environment.

Hence, at the beginning of the NASA contract, a new vacuum system making use of ion pumping was designed for use with the old microbalance. The principle advantage of this new system was that it allowed rate of vaporization data to be obtained at ambient pressures in the 10^{-7} to 10^{-9}

torr range and greatly reduced the possibility of sample contamination or reaction with background gases during the measurements.

The microbalance used with this system has been in use in this laboratory for some time and has been described in detail by Walker [17]. Briefly, weight changes are determined by measuring balance beam displacement with a cathetometer. Sample weights used with this balance are usually in the range of 1 to 2 grams for which the balance sensitivity is about 0.5 micrograms/micron. Reproducibility of rest points is usually within ± 2 microns. Beam displacements have been determined at various times with the balance either magnetically damped or undamped. The principle advantage of damping is that measurements of the displacement can be made more rapidly than with the balance undamped. On the other hand, indications that the balance rest point might depend slightly on the position of the damper with respect to the magnet, have made it appear advantageous to use the balance undamped. However, the precision of the rest points using either method appears to be about the same.

One of the major problems involved in determining accurate mass changes appears to be the accumulation of static charge on various parts of the vacuum apparatus which results in temporary changes of the rest point. Although it has appeared from time to time in the past that this problem has been eliminated, drifts in the observed rest point of 20 to 30 microns have occasionally been noted. It is not known whether these drifts are due to static charge on the interior of the apparatus resulting from heating the specimen or whether they might be on the exterior of the glassware.

Some work on the possibility of modifying the microbalance to allow one to record rate of vaporization as a function of time was reported by

Carrera and Walker et al [18]. However, over the period of the contract, the microbalance and the method of using it have remained essentially unchanged.

III. Treatment of Experimental Data

Rates of vaporization of well characterized materials are usually related to an equivalent equilibrium pressure by assuming that the vaporization coefficient in equation (1) is equal to unity. This enables one to calculate a heat of sublimation by two methods which will give consistent results if the vaporization coefficient is equal to unity as assumed and there are no important systematic errors in the measured rates of vaporization.

In the second law method, one makes use of the Clausius-Clapeyron equation

$$d \ln P = \frac{\Delta H^\circ}{RT^2} dT \quad (2)$$

and some assumption concerning the variation of ΔH° with temperature to arrive at an equation relating the pressure and temperature. For most high temperature studies, the random scatter is sufficiently great so that no appreciable error is introduced by assuming that ΔH° is independent of temperature and integration of equation (2) yields;

$$\ln P = - \frac{\Delta H^\circ}{RT} + C \quad (3).$$

The significance of the integration constant can be seen by comparison of (3) with the relation

$$-\frac{\Delta G_T^\circ}{RT} = \ln P = -\frac{\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R} \quad (4).$$

Ordinarily, the values of ΔH_T° and ΔS_T° are evaluated by least squares of the experimental data.

The alternative way of treating rate of vaporization data is to make use of the third law of thermodynamics and absolute entropies for the gaseous and condensed phases. In the third law method, one can use equation (4) and substitute tabulated ΔS_T° 's based on heat capacity data to obtain third law heats of sublimation at each experimental temperature. These values can then be extrapolated to a reference temperature by use of heat capacity data. In practice, use is generally made of free energy functions which allow one to calculate a value for the heat of sublimation at the reference temperature, usually 298.15°K according to the equation,

$$\Delta H_s^\circ(298) = T \left[\left(\frac{G_T^\circ - H_{298}^\circ}{T} \right)_c - \left(\frac{G_T^\circ - H_{298}^\circ}{T} \right)_g - R \ln P_{atm} \right]$$

where $\left(\frac{G_T^\circ - H_{298}^\circ}{T} \right)$ is the free energy function. Differences between $\Delta H_s^\circ(298)$ obtained by the second law and third law methods can give information concerning the consistency of the vapor pressure data obtained, the free energy function data used, the sublimation reaction assumed, or the existence of a vaporization coefficient other than unity. Frequently, a lack of trend in the heat of sublimation calculated as a function of the experimental temperature is taken as an indication that no important systematic errors are present in the data. Actually, because of random error in the data points and limited temperature ranges, it is usually easier to find a

discrepancy by comparing second and third law heats of sublimation or the experimental entropy change with that found from heat content and spectroscopic data.

After having evaluated second and third law entropies or heats of sublimation, one is in a position to ask if the assumption of a unit vaporization coefficient is consistent with the values derived from the rate of vaporization data when the rates are converted to equilibrium pressures. In most high temperature studies, conservative estimation of temperature errors ordinarily indicate an overall uncertainty in pressures or rates of vaporization of 20-30% so that one cannot ordinarily distinguish a vaporization coefficient of 0.7 to 0.8 from unity.

If some effect is discovered which indicates the possible existence of a vaporization coefficient, one is then faced with the difficult task of deciding if the coefficient is real or could be due to systematic error. However, it is not the purpose of this report to deal thoroughly with this problem. Paul [19] has compiled data on evaporation coefficients for a number of substances. The consensus is that for metals, the vaporization coefficient is unity within experimental error.

IV. Results

Over the period of this contract, useful rate of vaporization measurements were carried out on Ru, Os, W, and Re. In addition, measurements on samples reported to have nominal compositions of TaB and Ta₂N were attempted but did not yield reproducible results. Both of these samples were found to consist of more than a single phase. The measurements carried out on TaB

indicated a relatively high rate of vaporization which could be explained on the basis of the existence of several phases between TaB and Ta reported in the literature. This made it appear unlikely that the rate of vaporization would be low enough to allow its use as an emitter material. The same conclusion was reached with respect to the rate of nitrogen loss of the Ta_2N . In addition, it appeared unlikely that useful measurements could be made on the nitride because the ion pump used on the vacuum system is not capable of continued high gas loads without overheating.

Measurements on ruthenium and osmium were carried out and published as a research paper [20]. The results of these measurements agreed satisfactorily with results obtained in other laboratories [21,22]. [One observation of interest made during the ruthenium rate of vaporization measurements involved the gradual departure of the measured rate of vaporization at low temperatures from the curve predicted on the basis of measurements made at higher temperatures. This behavior had been noted previously in studies on platinum] [16]. It was suggested that this effect might be due to surface contamination of the sample but no definite proof of this was obtained.

Measurements on the rate of vaporization of polycrystalline tungsten were made and will be published shortly [23]. These measurements yielded rates of vaporization in good agreement with older data in the literature. Additional determinations of the rate of sublimation were carried out on a single crystal tungsten sample having a square cross section and an approximate (100) orientation. These results lacked the precision of the data obtained using polycrystalline tungsten and were summarized in NBS

Report 8508 [11]. It appeared that much of the difficulty with this sample resulted from its square cross section.

Four series of measurements of the rate of sublimation of rhenium were carried out. One surprising result of these measurements was that rather large changes in the window and prism correction took place during the first three series. Previous experience indicated that if reasonable care was exercised to minimize the length of time that the window was in line of sight of the specimen, no appreciable changes in the window correction factor took place during the measurements. However, one important difference between Re and other materials studied in the present apparatus is that Re has highly volatile oxides, Re_2O_7 (boiling point 634°K) or perhaps $\text{ReO}_2(\text{g})$, which once formed would tend to migrate away from the hot zone and could get past the shutter to the window. Hence, it appears likely that rhenium oxide vapor is implicated in this problem. Although a number of reasonable explanations can be put forward to account for the presence of rhenium oxide in the vacuum system, the actual cause of the difficulty could not be determined with certainty. One possible source of rhenium oxide not previously mentioned would be the reaction of the Re deposited on the quartz insert tube with the quartz to form $\text{ReO}_2(\text{g})$. Apparently, this reaction could take place to an appreciable extent if the insert tube-Re metal interface attained temperatures of about 1400°K or higher. However, evidence to support this possibility is lacking at present. It is our intention to complete the study on rhenium and publish the results as a research paper.

V. Summary

In this report, we have briefly discussed the objective, method of measurement, apparatus, treatment of experimental data and results obtained from research on the Langmuir vaporization of refractory materials performed in this laboratory with support from NASA over the past four years. The major results of this project are dealt with very briefly since these are presently available in the literature [18,20] or will be in the near future [23]. The microbalance technique as used in this laboratory is capable of yielding rate of vaporization data on one-component systems at least as reliable as that from any other method.

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