

NATIONAL BUREAU OF STANDARDS REPORT

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UNPUBLISHED PRELIMINARY DATA

VAPORIZATION OF THERMIONIC
REFRACTORY MATERIALS

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NBS REPORT

8670

VAPORIZATION OF THERMIONIC

REFRACTORY MATERIALS

E. R. Plante

Fourteenth Status Report for the period December 1, 1964 - February 28, 1965
to the National Aeronautics and Space Administration

NASA Order No. R57 Amendment 2
(Extension of Order No. R6)

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The last report (1) listed preliminary data obtained in two series of measurements on the rate of sublimation of rhenium. At the time of writing that report, it was believed that the cause for a difference in the average rates of sublimation of rhenium of about 50% obtained from the series I and series II data was due largely to error in obtaining the window correction factor for the series I data. In both of these series, differences in the window and prism correction factors of about $5.7 \times 10^{-6} \text{K}^{-1}$ corresponding to differences in temperature of about 42°K at 2700°K were noted on the basis of measurements of the window factors made before and after each series. However, the precision of the measurements in the individual series was good and no significant difference was observed between the second law heats of sublimation. These two factors appear to be at odds with a change in the window factor as large as that observed. Also, it was noted that better agreement between second and third law heats of sublimation was obtained if the window correction obtained at the end of the series was used to calculate the third law heats. It appeared that all the difficulties could be resolved if it was assumed that in both of these series, a rapid change in the window factor occurred. It was suggested, therefore, that contamination during series I had taken place during the first experiment when rhenium metal was deposited on the window because of the selection of too high an operating temperature while the window had become contaminated in series II during the preliminary outgassing procedure by one of the highly volatile rhenium oxides. It was supposed that this oxide had gotten into the vacuum system during glassblowing procedures by oxidation of rhenium metal.

On the basis of these assumptions, the microbalance apparatus was carefully cleaned to remove any remaining rhenium oxide in the hot zone of the vacuum system and a third series of measurements was undertaken. The results of this third series of measurements were practically the same as in the first two series in that the correction factor for the window again increased although by a little less than in the first two series.

Since a change in the window factor of the magnitude observed makes it impossible to treat the experimental data in a reliable fashion it was decided to attempt to isolate the cause of the change. The most likely sources of contaminant were considered to be;

1. Deposition of rhenium on the window during temperature measurements;
2. Evaporation of contaminant from the shutter;
3. Contamination of mirror or prism with dust during experiments and during measurements of the window factors;
4. Evaporation of contaminant from the platinum-plated, vycor insert tube.

The possibility that other sources of a contaminating vapor were important were considered unlikely because of unfavorable geometry. There is an additional possibility that rhenium oxide could come from the sample itself but this would require a relatively temperature independent diffusion process and would appear to be ruled out by the manufacturers estimate of 12PPM oxygen impurity.

An attempt to rule out each of the items considered was made but none yielded results which indicated that it would be responsible for the change in the window correction factor observed during the first three series of measurements.

Examination of the residuals, $|\log P_{obs}| - |\log P_{calc}|$, from the least squares treatment of the series II and series III data shows a preponderance of positive residuals (pressures too low) for the experiments at the beginning of a series and a preponderance of negative residuals (pressures too high) for the experiments at the end of the series. This shows that there was some change in the window and prism correction factor during the vapor pressure measurements contrary to our previous assumptions. The residuals, expressed as percentages are, +8, +6, +5, -1, 0, -7, -3, +2, -7 for the series II data and +19, 0, 0, +1, 0, +2, +1, -3, -11, -14, +9, -6 for the series III data. However, on the basis of the observed changes in the window and prism correction factor one would expect to see a range of $\pm 34\%$ in the residuals for series II and $\pm 28\%$ for the series III data. Thus, while some change in the window correction factor may have occurred during the series II and series III measurements, it is questionable that the trend is sufficient to force one to conclude that all of the change took place during the measurements and the original assumptions made may have some validity.

One final series of measurements has been undertaken. In these measurements it was planned to carry out all experiments at a temperature of about 2650°K where

the precision of the measurements would be sufficiently good to easily detect a change in the window correction as large as those occurring in the series II and series III measurements. After seven experiments of 20 minutes duration each with a total weight loss of 1900 micrograms the apparatus was opened and the prism and window recalibrated. No change in the window calibration was observed and no change was predicted by the data obtained. If it turns out that the cause of the change in the window factor has disappeared, this series will be extended to higher and lower temperatures.

The tentative second law heats from these four series are, 188.4, 187.5, 189.8, and 137.4 kcal/mole and the tentative third law heats calculated using the free energy functions given by Stull and Sinke (2) are 187.1, 185.1, 186.4, and 186.1 kcal/mole for series I through IV, respectively. It should be noted that the adoption of any constant window correction factor will not effect the second law heat but will have an effect on the value of the third law heat. Since the window corrections used to calculate the third law heats were those obtained at the conclusion of the series, the third law heats for series I through III represent upper limits to the third law heat.

References

- (1) R. Szwarc and E. R. Plante, NBS Report 8573
- (2) D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements, American Chemical Society, Washington, D. C. (1956).