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VAPOR-PRESSURE DATA EXTRAPOLATED
TO 1000 ATMOSPHERES (1.01×108 N/m²)
FOR 13 REFRACTORY MATERIALS WITH
LOW THERMAL ABSORPTION CROSS SECTIONS

by Charles C. Masser Lewis Research Center Cleveland, Ohio

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SUMMARY

With the continual increase of interest in high-temperature technology, knowledge of the vapor pressure of refractory materials is becoming essential. Such is the case in the conceptual studies of nuclear systems such as the liquid-core and gas-core nuclear rockets, where attention must be given to the vapor pressure of the materials used.

Existing vapor-pressure data were collected for 13 materials with atmospheric boiling points over 3000° K and thermal absorption cross sections less than 5 barns $(5.0\times10^{-28}~\text{m}^2)$. All the data were discussed and extrapolated to 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$; with the addition of an error analysis, a temperature range at a given pressure was calculated to indicate the possible error introduced by scatter in the original data. At 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$, the element that has the highest boiling point is tungsten $(9340^{\circ}~\text{K})$, while at the same pressure niobium carbide has the highest boiling point of the compounds $(8400^{\circ}~\text{K})$.

INTRODUCTION

As interest in high-temperature technology increases, the need for predicting the vapor pressure of materials at these high temperatures and pressures becomes more important. One field of particular interest is nuclear engineering, where the systems usually involve high temperatures and pressures. One group of materials that is in frequent use in nuclear engineering concepts has low vapor pressure and low thermal absorption cross section σ . This type of material is used in gas-core (ref. 1) and liquid-core (ref. 2) nuclear-rocket concepts. In these concepts, hydrogen propellant is radi-

antly heated by a nuclear fuel. However, hydrogen gas at temperatures less than $5000^{\rm O}$ K can not absorb radiant heat because of its transparency. However, particles can be suspended in the hydrogen propellant to absorb the radiant heat leaving the reacting fuel and then to conduct the heat to the hydrogen propellant. If it is assumed that only the particle absorbs radiant heat, a low-vapor-pressure material is necessary to keep the vaporization at a minimum. Also the material must have a low thermal absorption cross section in order not to cause an increase in the critical mass of the system.

Two criteria were used in selecting the materials in order to limit the scope of the study. First, the materials must have an atmospheric boiling point over 3000° K. Second, they must have a thermal absorption cross section less than 5 barns $(5.0\times10^{-28}~\text{m}^2)$. References 3 and 4 contain general summaries of vapor-pressure data for the elements with estimated atmospheric boiling points, and reference 5 contains the values of thermal absorption cross sections.

Vapor-pressure data for 11 elements and 2 compounds were selected and analyzed. Table I lists the materials that were chosen, their values of thermal absorption cross section, and the references from which the vapor-pressure data were taken. There are compounds which would qualify in the selection, such as some oxides and carbides of the elements chosen; however, there are insufficient vapor-pressure data available for these compounds to permit extrapolation to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$. Within

TABLE I. - REFRACTORY MATERIALS INVESTIGATED

| Material | l . | nal absorption ss section | Vapor-pressure reference |
|--------------|----------|------------------------------|-----------------------------|
| | b | m ² | |
| Carbon | 0.00373 | 0.00373×10 ⁻²⁸ | 7 |
| Cerium | . 73 | . 73 | 9 |
| Molybdenum | 2. 70 | 2.70 | 6, 10, 11 |
| Niobium | 1. 16 | 1. 16 | 12, 13 |
| Niobium | 1. 16373 | 1. 16373 | 26, 27 |
| carbide | | | |
| Platinum 196 | . 70 | . 70 | 14, 15 |
| Platinum 194 | 1. 2 | 1. 2 | 14, 15 |
| Ruthenium | 2. 56 | 2.56 | 16, 17, 18 |
| Silicon | . 16 | . 16 | 19 |
| Tungsten 184 | 2.0 | 2.0 | 22 |
| Vanadium | 5.0 | 5.0 | 23 |
| Yttrium | 1.31 | 1.31 | 9, 24 |
| Zirconium | . 185 | . 185 | 25 |
| Zirconium | . 18873 | . 18873 | 28, 29 |
| carbide | | _ | |

the group of materials chosen, there are several cases where more than one set of vapor-pressure data is presented, and in these cases the results are compared. This study was performed to collect, evaluate and select the best vapor-pressure data available, and then to extrapolate them to 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$. By taking into account the experimental scatter in the data points and the temperature range over which the experiment was performed, a possible temperature range was calculated for pressures of 1, 10, 100, and 1000 atmospheres $(1.01\times10^5, 1.01\times10^6, 1.01\times10^7, \text{ and } 1.01\times10^8 \text{ N/m}^2)$.

COLLECTION AND EVALUATION OF VAPOR-PRESSURE DATA

Examination of the available data indicate that most experimental data were obtained at temperatures less than 3000° K and that, hence, the vapor pressures were in the range of 10^{-5} to 10^{-10} atmospheres (1.01 to 1.01×10^{-5} N/m²). Therefore, an extrapolation of at least 7 orders of magnitude is required to reach the desired 1000 atmospheres (1.01×10⁸ N/m²).

During the collection and evaluation of vapor-pressure data, it was necessary to judge the reliability of reported vapor-pressure measurements. In the cases where more than one set of vapor-pressure data exists for a given material, each is discussed. If, for any reason, one set is preferred over the other, the reasons are discussed and only the preferred set is retained; otherwise all sets are retained. The following factors were considered:

- (1) The reaction and equilibrium behavior of the system
- (2) The identification of the various gaseous species in the system
- (3) The experimental technique by which the vapor pressure was measured
- (4) The range and scatter of the vapor-pressure data

The investigation of the general behavior of the system should reveal the following information: first, whether there is any reaction between the sample and any other part of the system. If there is a reaction, the resulting phase may vaporize and affect the vapor-pressure measurements, or it may contaminate the sample by changing its composition. The measured vapor pressure thus would not be of the pure sample but of the contaminated one. Second, the equilibrium of the system must be understood. Two factors that affect this are congruence and invariance. For congruence, a phase must vaporize to give a gas of the same composition as the liquid or solid phase. This result is demonstrated by whether the composition of the residue changes after several successive vaporizations. If the residue is always the same, the system is congruent. For invariance, the rate at which vapor leaves the sample must be constant. This condition can be established by noting the pressure in successive experiments at the same temperature.

If the pressure remains constant during the entire course of vaporization, the process is invariant.

The various gaseous species must be identified to complete any vapor-pressure experiment. Several different species may vaporize from a sample, and each must be identified and its share of the vapor pressure calculated or measured. Whenever vapor-pressure data are extrapolated, the vapor pressure of each individual species is extrapolated rather than the sum of the partial pressures of the species.

Vapor-pressure measurements on high-temperature materials are most suitably made by using either the Knudsen or the Langmuir method. Both methods require a high-vacuum system. In the Knudsen method, the sample is contained in an inert crucible that has a small, thin orifice. Equilibrium is established inside the crucible if the orifice is sufficiently small. However, all the vapor striking the orifice inlet does not leave the orifice outlet. The ratio between the rate at which vapor leaves the orifice outlet and that at which vapor strikes the orifice inlet is given by a "Clausing factor." This Clausing factor is governed only by the dimensions of the orifice. The rate of effusion through the orifice is then governed by the Clausing factor, the temperature, the vapor pressure, and the molecular weight of the effusing vapor species. In the Langmuir method, no crucible is used but rather free evaporation occurs from the entire sample surface. The vapor pressure is therefore a function of the rate at which material sublimes from the sample, the surface area and the absolute temperature of the sample, and the molecular weight of the vapor leaving the sample.

METHOD OF EXTRAPOLATION

The curve that was fitted to the data and extrapolated to 1000 atmospheres $(1.01\times10^8~{\rm N/m^2})$ can be derived from the Clapeyron equation under the assumptions that (1) the heat of vaporization is constant, (2) a volume of liquid or solid is negligible compared with that of the vapor, and (3) the vapor conforms to the ideal gas law. The resulting equation is of the form

$$\log P = \frac{A}{T} + D \tag{1}$$

where A and D are constants, P is vapor pressure in atmospheres (N/m^2) , and T is temperature in ${}^{0}K$. The majority of the selected vapor-pressure reports use equation (1) to express their vapor-pressure data mathematically and to estimate the atmospheric boiling point.

The least-squares method was used to fit the selected vapor-pressure data to equation (1). In the majority of cases, the referenced literature already reported the results using this method with equation (1). However, the vapor-pressure data were refitted to equation (1) using the least-squares method to put all the data on a common basis for comparison.

The possible error in predicting a value of vapor pressure from extrapolated data originates from three sources. First, there is the error introduced by the three assumptions used to derive the Clausius-Clapeyron equation (eq. (1)). The importance of this error cannot be assessed until additional experimental data at higher temperatures become available. Second, a systemic error may already be present in the original vapor-pressure data. Assessment of the magnitude of this type of error is also not possible. Third, there is an error caused by the random scatter of the data. This error can be estimated.

Figure 1 shows a schematic drawing of the error analysis used to estimate the third type of error. By using the common logarithmic coordinate of vapor pressure and reciprocal temperature, equations in the form of equation (1) are represented by straight lines. In figure 1, the lines W and X, which are visually drawn, are the boundary lines that encompass at least 90 percent of the data points. As the number of data points increases, these lines usually become parallel and equidistant from the line generated when curve fitting the data to equation (1). The diverging lines, Y and Z, encompass all possible straight lines that can be drawn through the data. These two straight lines are then extended to a pressure of 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$. The maximum error. or as it is called hereinafter, the ''temperature uncertainty'', is the difference at a given vapor pressure between the temperature value given by equation (1) and the values given by the two diverging lines, Y and Z. Figure 2 shows the procedure, using the set of molybdenum vapor-pressure data from reference 6. The calculated temperature uncertainty is for a given set of vapor-pressure data and reflects only the random error caused by the scatter in the data. Figure 1 shows that the magnitude of the temperature uncertainty at a given pressure is also dependent on the amount of extrapolation from the original data. Where two or more sets of data are selected, each is extrapolated to 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$. The results are then combined; the average value of A and D are found and these average values are used in the extrapolation. Also the temperature uncertainty at a given pressure includes the entire range found for all sets of data. The results of the extrapolations and error analysis are shown in table II to IV.

DISCUSSION OF MATERIALS

Carbon

Reference 7 is the most recent work on the vapor pressure of carbon with the influence of large carbon polymer species. Mass spectrographic studies were performed on carbon in the temperature range from $1800^{\rm O}$ to $2700^{\rm O}$ K. The ions observed were C_1^+ , C_2^+ , C_3^+ , C_4^+ and C_5^+ ; the intensities of C_6^+/C_1^+ and C_7^+/C_1^+ were less than 5×10^{-4} at 2500° K, and no results were reported for these two species. To minimize temperature uncertainties reference 7 assumed the vapor pressure of C₁ to be known and its associated value for the heat of vaporization ΔH_0^0 to be equal to 169.58 kilocalories per gram atom (709.52 kJ/g-atom). A least-squares treatment was applied to the relative intensities C_n^+/C_1 to calculate $\Delta H_0^0(C_n)$ where $n \le 5$. The ratios were divide by 2.30, 3.66, 4.96, and 6.30 for C_2 to C_5 , respectively, to convert to relative pressures. A trial and error graphical method was used to calculate the temperature of the total carbon vapor pressure at 1 to 1000 atmospheres $(1.01\times10^5 \text{ to } 1.01\times10^8 \text{ N/m}^2)$. A summation of the partial pressure of C_1 to C_5 is made in table II(a) for total carbon pressures of 1, 10, 100, and 1000 atmospheres $(1.01\times10^5,\ 1.01\times10^6,\ 1.01\times10^7,\ and\ 1.01\times10^8\ N/m^2)$. Figure 3 shows the extrapolation of the carbon species. The errors involved in C2 to C₅ are based on a given value of C₁; therefore, any error in C₁ increases the errors of the larger carbon polymers. In addition, carbon polymers larger than C5 start to influence the total vapor pressure in this pressure range.

In reference 8 is described a mass spectrometric study of the vapor ejected from a graphite sample that was flash heated by a focused laser beam. The relative abundance of the carbon polymer species, C_1 to C_{11} and C_{14} , at approximately 4000° K was obtained. The relative ion intensities of the various carbon species did not vary significantly for different graphite samples; however, a standard deviation of about 50 percent necessitated a large number of measurements on each carbon species. A typical averaged mass spectrum is presented in reference 8, with the extrapolated results of reference 7, and is reproduced in table II(b). The agreement between Drowart, et al. (ref. 7) and Berkowitz, et al. (ref. 8) is good considering the differences in the methods used. It is also interesting that, from the data of reference 8, the carbon species C_7 approaches the magnitude of C_4 and C_5 in importance and that at higher pressures and temperatures it may become dominant.

TABLE II. - EXTRAPOLATED VAPOR-PRESSURE DATA

(a) Data for carbon from reference 7

| | | | | l vapor | pressures o | of carbon | | | | | Total vapor | Extrapo- lated | Temper uncert | |
|------|-----------------------|------|----------------------|---------|---------------------|-----------|----------------------|------|----------------------|------|-----------------------|-------------------------|------------------|------------|
| | ^C 1 | | C ₂ | | C ₃ | | C_4 | | C ₅ | pr | essure | tempera- | °K | |
| atm | N/m ² | atm | N/m ² | atm | N/m ² | atm | N/m^2 | atm | N/m^2 | atm | N/m ² | ture, ^O K | K. | percent |
| 0.11 | 0. 12×10 ⁵ | 0.30 | 0.30×10 ⁵ | 0.49 | 0.5×10 ⁵ | 0.04 | 0.04×10 ⁵ | 0.06 | 0.06×10 ⁵ | 1 | 1. 01×10 ⁵ | 4100 | 3840 to 4380 | -6 to +7 |
| .8 | .81 | 3.1 | 3.1 | 4.6 | 4.7 | .6 | .6 | .9 | .91 | 10 | 1.01×10 ⁶ | 4540 | 4220 to 4890 | -7 to +8 |
| 6 | 6.1 | 31 | 31 | 42 | 43 | 8 | 8.1 | 13 | 13.2 | | 1.01×10 ⁷ | 5070 | 4650 to 5540 | -8 to +9 |
| 42 | 42.5 | 292 | 296 | 361 | 366 | 120 | 122 | 185 | 187 | 1000 | 1.01×10 ⁸ | 5740 | 5150 to 6400 | -10 to +11 |

(b) Relative concentrations of carbon vapor species above graphite at 4000° K

| Reference | | Carbon molecular species | | | | | | | | | | |
|-----------|----------------|--------------------------|----------------|----------------|----------------|----------------|----------------|-------|----------------|-----------------|-----------------|-----------------|
| | C ₁ | С2 | c ₃ | C ₄ | C ₅ | C ₆ | C ₇ | С8 | C ₉ | C ₁₀ | C ₁₁ | C ₁₄ |
| 7 8 | 22. 2 37. 0 | 62. 5 31. 4 | 100.0 100.0 | 7. 8 2. 13 | 11. 1 7. 9 | 0.413 | 1. 11 | 0. 19 | 0. 11 | 0. 32 | 0. 15 | 0. 042 |

Cerium

The vapor-pressure data for liquid cerium were obtained directly from Habermann, et al. (ref. 9) and consist of 19 data points in the temperature range from 1861° to 2252° K. A direct-weight-loss modification of the Knudsen effusion technique was used involving a quartz-fiber microbalance. An analysis showed the cerium to be 99.9 percent pure. The major impurities detected were tantalum, 100 parts per million (ppm); iron, 250 ppm; oxygen, 345 ppm; carbon, 200 ppm; nitrogen, 150 ppm; and traces of calcium, silicon, fluorine, and hydrogen, 95 ppm. Table II(c) indicates the results when the vapor-pressure data were extrapolated to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$.

Molybdenum

Three references were used for the extrapolated vapor pressure of solid molybdenum. Edwards, et al. (ref. 10) used the Langmuir vacuum-evaporation method; nine

TABLE II. - Continued. EXTRAPOLATED VAPOR-PRESSURE DATA

(c) Cerium

(f) Data for molybdenum from reference 11

| 1 | Vapor essure | Extrapo- lated | Tempera uncerta | | ĺĺ | Vapor essure | Extrapo- lated | Tempera uncertai | 1 |
|-----------|---|-------------------------------------|--|---|-----------|----------------------|-------------------------------------|--|---|
| atm | N/m ² | tempera- ture, ^O K | °K | percent | atm | N/m ² | tempera- ture, ^O K | °K | percent |
| 10 100 | $ \begin{array}{c} 1.01 \times 10^{5} \\ 1.01 \times 10^{6} \\ 1.01 \times 10^{7} \\ 1.01 \times 10^{8} \end{array} $ | 4 200 5 160 | 3480 to 3 680 4080 to 4 430 4940 to 5 560 6250 to 7 460 | -2 to +3 -3 to +5 -4 to +8 -6 to +12 | 10 100 | 1.01×10 ⁷ | 5340 6440 | 4500 to 4 830 5180 to 5 690 6110 to 6 910 7430 to 8 810 | -3 to +4 -3 to +6 -5 to +7 -7 to +10 |

(d) Data for molybdenum from reference 10

(g) Data for molybdenum, combined data of references 6, 10, and 11

| | 1.01×10 ⁵ | | 4880 to 5 350 | -4 to +5 | 1 | 1.01×10 ⁵ | 4800 | 4500 to 5 350 | -6 to +11 |
|------|----------------------|--------|----------------|------------|------|----------------------|------|----------------|------------|
| 10 | 1.01×10 ⁶ | 6 100 | 5740 to 6 510 | -6 to +7 | 10 | 1.01×10^6 | 5630 | 5180 to 6 510 | -8 to +15 |
| 100 | 1.01×10 ⁷ | 7 590 | 6980 to 8 320 | -8 to +10 | 100 | 1.01×10^{7} | 6820 | 6110 to 8 320 | -10 to +22 |
| 1000 | 1.01×10 ⁸ | 10 040 | 8900 to 11 530 | -11 to +15 | 1000 | 1.01×10 ⁸ | 8620 | 7430 to 11 530 | -14 to +33 |
| 1 | 1 | ı | 1 | 1 1 | 1 . | i | L. | 1 | ı J |

(e) Data for molybdenum from reference 6

(h) Data for niobium from reference 12

| | 1. 01×10 ⁵ | | 4590 to 5 090 | -2 to +8 | 1 1.01×10 ⁵ | | 4360 to 4 800 | -4 to +6 |
|------|-----------------------|-------|---------------|-----------|-----------------------------|------|---------------|-----------|
| 10 | 1.01×10 ⁶ | 5 480 | 5310 to 6 090 | -3 to +11 | $10 1.01 \times 10^6$ | 5090 | 4870 to 5 500 | -4 to +8 |
| 100 | 1.01×10 ⁷ | 6 570 | 6290 to 7 580 | -4 to +15 | 100 1.01×10 ⁷ | 5830 | 5510 to 6 440 | -5 to +10 |
| 1000 | 1.01×10 ⁸ | | | | $ 1000 1.01 \times 10^8$ | | 6340 to 7 780 | -7 to +14 |

vapor-pressure data points were recorded in the temperature range from 2151° to 2462° K. The molybdenum sample was at least 99.957 percent pure. Spectroscopic analysis showed the presence of 0.023 percent carbon and 0.01 to 0.001 percent each of iron and silicon. In table II(d), extrapolation of the data of reference 10 to 1000 atmospheres $(1.01\times10^{8} \text{ N/m}^{2})$ is presented.

The second study (Vozzella, et al., ref. 6) also used the Langmuir method to measure the vapor pressure of solid molybdenum. An automatic recording semimicro vacuum balance and a calibrated optical pyrometer were used to obtain vapor-pressure measurements in the temperature range from 2141° to 2533° K; 12 data points are presented. An analysis of the sample showed the molybdenum to be 99.89 percent pure. Impurities amounted to 1100 ppm; oxygen, 30 ppm; carbon, 70 ppm; and traces of iron, nickel, chromium, and silicon, totaling 1000 ppm. By taking into account the spread in the data, an extrapolation to 1000 atmospheres (1.01×10⁸ N/m²) yielded the results shown in table II(e).

The third study (Fries, ref. 11) on the vapor pressure of solid molybdenum also used the Langmuir method to measure vapor pressure. The apparatus used by Fries (ref. 11) was essentially the same as that used by Vozzella, et al., (ref. 6). Optical pyrometer readings recorded 12 data points in the temperature range from 2086° to 2489° K. Analysis of the sample indicated maximum impurities amounting to 1085 ppm consisting of oxygen, 45 ppm; nitrogen, 20 ppm; niobium, tungsten, and zinc, each 150 ppm; iron, 75 ppm; tantalum, zirconium, strontium, cobalt, titanium, potassium, and silicon, each 45 ppm; and trace materials amounting to 180 ppm. Fitting the data to equation (1) and extrapolating it to 100 atmospheres (1.01×10⁸ N/m²) yielded the results shown in table II(f).

Since each set of data (refs. 6, 10, and 11) yields different results for the vapor pressure at 1 to 1000 atmospheres (1.01×10 5 to 1.01×10 8 N/m 2) all three sets were combined. Therefore, a vapor-pressure line was computed by averaging the least-squares line calculated in each case. The results of this procedure are listed in table II(g), along with the temperature uncertainty which was also calculated by using all three sets of data.

Niobium

Two sets of data for the vapor pressure of solid niobium are discussed herein. The first set (ref. 12) was presented in 1959. The Langmuir method was employed, and temperatures were measured under blackbody conditions by sighting with an optical pyrometer into a hole drilled into the sample. Seventeen data points were recorded in the temperature range from 2304° to 2596° K. The sample purity was 99.9 percent, but no mention was made of the types of impurities; however, the sample was thoroughly out-

gassed before it was heated inductively and measurements were taken. In table II(h) the data of reference 12 are extrapolated to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$.

In 1962, another experiment on niobium vapor pressures was presented, in reference 13. Again the Langmuir method was used, and temperatures were measured with an optical pyrometer, which was sighted on a blackbody hole drilled in the niobium sample. The experimenter used a high-temperature thermobalance which incorporated a new furnace design that gave stable temperatures up to 3000° K. The niobium sample purity was 99.975 percent. An analysis showed that impurities amounted to 248 parts per million; carbon, 20 ppm; oxygen, 100 ppm; nitrogen, 8 ppm; hydrogen, 5 ppm; tantalum, 100 ppm; iron, 8 ppm; and silicon, 7 ppm. The raw vapor-pressure data used in reference 13 were received from Woerner, et al. (ref. 13) and consisted of 32 data points in the temperature range from 2241° to 2588° K. A least-squares fit to equation (1) was applied, and the data were extrapolated to 1000 atmospheres (1.01×10⁸ N/m²). The results are shown in table II(i).

Each set of data (refs. 12 and 13) is essentially in the same temperature range, and the resulting least-squares vapor-pressure lines are parallel. This result indicates that the experimenters are in agreement on the slope of the vapor-pressure curve but that a systemic error in the temperature or weight measurements caused a shift in the vapor pressure values. The difference in the two curves on the temperature scale is 40° K. When the results are averaged, a vapor-pressure line parallel to and between the

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(i) Data for niobium from reference 13

| | | 1 | | | | |
|------------------------|---|-------------------------------------|--|-----------------------------------|--|--|
| | Vapor | Extrapo- | Temperature | | | |
| pressure | | lated | uncert | ainty | | |
| atm | N/m ² | tempera- ture, ^O K | o _K | percent | | |
| 1 10 100 1000 | $ \begin{array}{c} 1.01 \times 10^{5} \\ 1.01 \times 10^{6} \\ 1.01 \times 10^{7} \\ 1.01 \times 10^{8} \end{array} $ | 4760 5430 6300 7530 | 4520 to 5040 5080 to 5840 5800 to 6950 6750 to 8580 | -5 to +6 -6 to +8 -8 to +10 | | |
| 1000 | 1.01/10 | 1000 | 0130 10 0300 | -10 10 +14 | | |

(j) Data for niobium, combined data of references 12 and 13

| | | | ĺ | 1 | |
|---|------|-----------------------|------|--------------|------------|
| | | 1.01×10 ⁵ | 4660 | 4360 to 5040 | -6 to +8 |
| | 10 | 1.01×10^{6} | 5280 | 4870 to 5840 | -8 to +11 |
| | 100 | 1. 01×10 ⁷ | 6100 | 5510 to 6950 | -10 to +14 |
| | 1000 | 1.01×10 ⁸ | 7220 | 6340 to 8580 | -12 to +19 |
| Į | | | | J | 1 |

two sets of data is formed. Since there is no clear reason to prefer one set of data to the other, the results shown in table II(j) lie between the results calculated from Speiser, et al. (ref. 12) and Woerner, et al. (ref. 13).

Platinum

The first set of platinum vapor-pressure data discussed herein is presented in reference 14. The Langmuir technique was used, and the vapor pressure of solid platinum was measured in the temperature range from 1571° to 1783° K. The platinum sample was at least 99.95 percent pure, but no mention was made of the types of impurities. Only nine data points are presented by Dreger, et al. (ref. 14), and five of these are within 5° K of 1740° K; therefore, it was difficult to estimate an error throughout the temperature range investigated. The vapor-pressure curve calculated from the data of reference 14 resulted in an equation that was of the same form but numerically different from that calculated in reference 14. At 1000 atmospheres (1.01×10⁸ N/m²), equation (1) predicts a temperature of 5430° K, whereas the equation calculated in reference 14 predicts 6490° K. Since Dreger, et al. (ref. 14) may not have used the least-squares method for calculating the vapor-pressure equation, or because other unmentioned factors may have entered his calculations, these data were not used for extrapolation purposes.

A second set of platinum vapor-pressure data is presented in reference 15. A microbalance was used to measure the vapor pressure of solid platinum by the Langmiur technique over the range from 1916° to 2042° K. A plot of the 18 data points shows a good distribution over the temperature range (Hampson, et al. (ref. 15)), but since the temperature range was only 125° K, the temperature uncertainty becomes quite large at 1000 atmospheres $(1.01\times10^{8}~\text{N/m}^{2})$. The platinum sample was approximately 99.7 percent pure. The major impurities were palladium, iridium, and rhodium at percentage levels of 0.01 to 0.1 percent. Copper and iron were estimated at percentage levels of 0.001 to 0.1 and silver at less than 0.001 percent. From an extrapolation to 1000 atmospheres $(1.01\times10^{8}~\text{N/m}^{2})$, vapor-pressure and temperature estimates were computed, as shown in table II(k).

Ruthenium

Survey studies were made of three references containing information on the vapor pressure of solid ruthenium. In reference 16, 24 data points for the vapor pressure of solid ruthenium in the temperature range from 2036° to 2591° K are presented. Data

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(k) Platinum

| 1 | Vapor ressure | Extrapo- lated | Tempera uncerta | |
|------------------------|---|-------------------------------------|---|--------------------------|
| atm | N/m ² | tempera- ture, ^O K | ^o K | percent |
| 1 10 100 1000 | 1.01×10^{5} 1.01×10^{6} 1.01×10^{7} 1.01×10^{8} | 4070 4780 5790 7330 | 3640 to 4 740 4130 to 5 880 4760 to 7 760 5620 to 11 400 | -14 to +23 -18 to +34 |

(1) Data for ruthenium from reference 16

| | 1 | 1.01×10 ⁵ | 4280 | 3960 to | 4 620 | -7 to +8 |
|---|------|-----------------------|------|---------|-------|------------|
| Ì | | 1.01×10 ⁶ | | 4450 to | 5 440 | -9 to +10 |
| | | 1.01×10 ⁷ | | 5070 to | 6 610 | -12 to +14 |
| | 1000 | 1. 01×10 ⁸ | 7040 | 5900 to | 8 430 | -16 to +20 |
| | | 1 | I | 1 | | |

were taken by both the Knudsen method and the Langmuir technique. Sixteen data points were obtained by the Knudsen method, while the other eight points were obtained by the Langmuir technique. The Knudsen method employed ruthenium 103 as a radioactive tracer in the vaporizing ruthenium metal. The radioactivity of the target on which the effusion beam condensed was then compared with a previously calibrated sample.

The Langmuir evaporation studies (Panish, et al. (ref. 16)) were performed on a small cylindrically shaped pellet of ruthenium metal containing a blackbody hole for temperature measurements. The ruthenium samples were analyzed spectroscopically, and trace amounts of impurities were found; however, the types and amounts were not reported. By extrapolating the data to 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$, results for the vapor pressure of ruthenium were calculated and are shown in table II(1).

Reference 17 presents studies of the vapor pressure of solid ruthenium in the temperature range $2011^{\rm O}$ to $2330^{\rm O}$ K. By using the Langmuir technique in conjunction with a microbalance built inside the vacuum system, nine data points were obtained. The sample of ruthenium was between 99.8 and 99.98 percent pure, with the major impurities being platinum and calcium from 0.01 to 0.1 percent. Extrapolation of these nine data points yields the values given in table II(m) showing estimated temperatures for pressures up to 1000 atmospheres (1.01×10⁸ N/m²).

Reference 18, reports the vapor pressure of solid ruthenium in the temperature range from 1918^o to 2377^o K, also using the Langmuir method. A microbalance was used for weight measurements, and a calibrated pyrometer was used for temperature mea-

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(m) Data for ruthenium from reference 17

| | Vapor essure | Extrapo- lated | Temper uncertz | |
|------------------------|---|-------------------------------------|--|---|
| atm | N/m ² | tempera- ture, ^O K | ^o K | percent |
| 1 10 100 1000 | $ \begin{array}{c} 1.01 \times 10^{5} \\ 1.01 \times 10^{6} \\ 1.01 \times 10^{7} \\ 1.01 \times 10^{8} \end{array} $ | 4080 4650 5410 6470 | 3870 to 4230 4340 to 4880 4950 to 5770 5750 to 7050 | -5 to +4 -7 to +5 -8 to +7 -11 to +9 |

(n) Data for ruthenium from reference 18

| 1 - | _ | | | _ |
|------|-----------------------|------|--------------|------------|
| | 1.01×10 ⁵ | | 4010 to 4710 | -8 to +8 |
| 10 | 1. 01×10 ⁶ | 5040 | 4520 to 5570 | -10 to +11 |
| | 1.01×10 ⁷ | 5960 | 5180 to 6800 | -13 to +14 |
| 1000 | 1.01×10 ⁸ | 7280 | 6060 to 8730 | -17 to +20 |
| l . | | l . | | |

(o) Data for ruthenium, combined data of references 16 to 18

| | 1.01×10^{5} 1.01×10^{6} | 4240 4870 | 3870 to 4710 4340 to 5570 | -9 to +11 |
|-----|--|--------------|------------------------------|------------|
| 100 | 1. 01×10 ⁷ 1. 01×10 ⁸ | 5710 6910 | 4950 to 6800 5750 to 8730 | -13 to +19 |

surements. Two ruthenium samples of different purities were used. Sample 1 had a purity greater than 99.97 percent, with the major impurities being less than 0.02 percent osmium and less than 0.007 percent rhodium. Sample 2 had a purity greater than 99.8 percent, with the major impurities being less than 0.1 percent platinum and calcium. In reference 18, 42 data runs are presented using sample 1, and 52 runs are presented using sample 2. Extrapolating the data to 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$, results in the vapor-pressure values presented in table II(n).

Again, all the resulting vapor-pressure equations of references 16 to 18 were averaged and extrapolated to 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$. All three references overlap in the temperature range studied, and the slope of the vapor-pressure curve is approximately the same for each reference. Therefore, the result of extrapolating the combined data is a vapor-pressure curve between the two outer, or most separated, sets of data. These results are presented in table II(o).

Silicon

Silicon vaporizes in the same manner as carbon. The various silicon species each have a certain partial pressure at a given temperature and possess their own value for the heat of vaporization. The partial pressure of each silicon species must be known in order to extrapolate the silicon vapor pressure to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$.

Reference 19 describes sublimation studies of silicon with a mass spectrometer. Molecules Si_1 to Si_7 were found, and their intensities were measured at a temperature of 1660° K. The heats of sublimation were measured (Honig, ref. 19) for the four most abundant species, Si_1 to Si_4 . The measured heats of vaporization and the known relative intensities and total vapor pressures of the silicon species at 1600° K are used to extrapolate the partial pressures of Si_1 to Si_4 to 1000 atmospheres (1.01×10⁸ N/m²). The total pressure measured at 1600° K was revised by Honig (ref. 19), and is reported in reference 20. Table II(p) gives the partial vapor pressures of Si_1 to Si_4 at total pressures of 1, 10, 100, and 1000 atmospheres (1.01×10⁵, 1.01×10⁶, 1.01×10⁷, and 1.01×10⁸ N/m²). Figure 4, in which the silicon pressures are plotted, was used to calculate the total silicon pressure graphically.

TABLE II. - Continued. EXTRAPOLATED VAPOR-PRESSURE DATA

(p) Silicon

| | | Par | rtial vapor p | ressure | of silicon | | | | Total | Extrapo- | Minin | |
|-------|-----------------------|-------|-----------------------|---------|-----------------------|------|-----------------------|------|-----------------------|-------------------------|------------------|------------|
| | Si ₁ | | Si ₂ | | Si ₃ | | Si ₄ | 1 | apor essure | lated tempera- | temper uncert | |
| atm | N/m ² | atm | N/m ² | atm | $_{ m N/m}^2$ | atm | N/m ² | atm | N/m ² | ture, ^O K | °K | percent |
| 0. 24 | 0. 25×10 ⁵ | 0. 16 | 0. 16×10 ⁵ | 0. 19 | 0. 19×10 ⁵ | 0.41 | 0. 42×10 ⁵ | | 1.01×10 ⁵ | 2730 | 2430 to 3140 | -11 to +15 |
| 1.4 | 1.4 | 1.6 | 1.6 | 2.0 | 2 | 5.0 | 5. 1 | 10 | 1.01×10 ⁶ | 3010 | 2600 to 3610 | -14 to +20 |
| 8 | 8. 1 | 15 | 15.3 | 21 | 21.5 | 56 | 57 | | 1. 01×10 ⁷ | 3350 | 2770 to 4220 | -17 to +26 |
| 45 | 46 | 145 | 148 | 210 | 215 | 600 | 613 | 1000 | 1.01×10 ⁸ | 3760 | 3000 to 4990 | -20 to +33 |

Honig (ref. 19) performed 11 runs on Si_1 , 4 on Si_2 , 2 on Si_3 , and 1 on Si_4 . No estimate of error was possible for Si_3 and Si_4 . At 1600^{O} K, the temperature at which the experiment was performed, the combined partial pressures of Si_2 , Si_3 , and Si_4 contribute only 5 percent toward the vapor pressure of silicon.

More recently, reference 21 presented a thermodynamic study of silicon carbide using a mass spectrometer. By measuring the partial pressure of silicon over silicon carbide, reference 21 calculates the total vapor pressure of pure silicon as 10 times lower than that presented by Honig (ref. 19). However, extrapolation to 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$ was not possible since the partial pressure of each molecular species was not calculated. A more extensive study is necessary before reliable silicon

vapor pressures from 1 to 1000 atmospheres $(1.01\times10^5 \text{ to } 1.01\times10^8 \text{ N/m}^2)$ can be calculated.

Tungsten

The vapor pressure of solid tungsten is reported in reference 22, where 10 data points are recorded in the temperature range from 2574° to 3183° K. The Langmuir method was used with the aid of a vacuum microbalance. A calibrated optical pyrometer was used to measure temperatures by sighting on a blackbody hole drilled in the specimen. Results of a spectrochemical analysis indicate a maximum impurity content of 0.02 percent where molybdenum and silicon are the principal impurities. The results obtained by extrapolating these data to 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$ are shown in table II(q).

Vanadium

The vapor pressure of solid vanadium was measured in the temperature range from 1666° to 1882° K in reference 23 by the Langmuir method. The vanadium sample was

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(q) Tungsten

| Vapor pressure | | Extrapo- lated | Temperature uncertainty | | |
|-------------------|----------------------|-------------------------------------|----------------------------|----------|--|
| atm | N/m ² | tempera- ture, ^O K | ^o K | percent | |
| | 1.01×10 ⁵ | 5740 | 5620 to 5 930 | -2 to +3 | |
| | 1.01×10^{6} | 6580 | 6420 to 6 880 | -2 to +5 | |
| | 1.01×10 ⁷ | 7730 | 7470 to 8 180 | -3 to +6 | |
| 1000 | 1.01×10 ⁸ | 9340 | 8930 to 10 110 | -5 to +9 | |

(r) Vanadium

| 10 1.01×10 ⁶ 4060 3920 to 4 260 -3 to + 100 1.01×10 ⁷ 4800 4590 to 5 120 -4 to + 1000 1.01×10 ⁸ 5880 5540 to 6 430 -6 to + | | 1.01×10 ⁵ | 3510 | 3420 to | 3 640 | -3 to +4 |
|---|------|----------------------|------|---------|-------|----------|
| | | | 4060 | 3920 to | 4 260 | ~3 to +5 |
| 1000 1 01×10 ⁸ 5880 5540 to 6 430 -6 to + | | | 4800 | 4590 to | 5 120 | -4 to +7 |
| 2000 21.02.20 0000 0010 00 0 100 0 10 1 | 1000 | 1.01×10 ⁸ | 5880 | 5540 to | 6 430 | -6 to +9 |

heated by radiofrequency induction, and temperature measurements were made with an optical pyrometer that was sighted on a blackbody hole drilled in the sample. An analysis of the sample showed it to be 99.6 percent vanadium. The measured impurities were 0.2 percent carbon, 0.1 percent hydrogen, with traces of iron, silicon, manganese, copper, and calcium comprising the other 0.1 percent. No correction factor was applied to the vapor-pressure measurements resulting from these impurities. However, in several of the initial runs, gas was evolving from the sample (during heating), which would indicate outgassing of some impurities, and these runs were rejected; 12 data points were recorded. The least-squares method was used to calculate the best straight line through the data and to extrapolate it to 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$. The spread of the vapor-pressure data was also used to calculate the temperature uncertainty from 1 to 1000 atmospheres $(1.01\times10^5~\text{to}~1.01\times10^8~\text{N/m}^2)$, and the results are presented in table II(r).

Yttrium

The vapor pressures of liquid yttrium from two references are discussed and compared herein. Reference 24 contains vapor-pressure data on liquid yttrium in the temperature range from 1774° to 2103° K. Rates of vaporization were measured as a function of temperature by an inductively heated, tungsten Knudsen effusion cell. Weight measurements were made with a vacuum balance, while temperatures were recorded by use of an optical pyrometer. Seven vaporization data points were recorded from the sample of yttrium, which contained about 0.4 percent calcium. However, the orifice of the Knudsen cell was not thin, and a Clausing factor of 0.36 was used in the calculations.

Reference 9 presents a vapor-pressure study of liquid yttrium. Again, the Knudsen method was used in conjunction with a quartz-fiber microbalance for weight measurements, and an optical pyrometer was used for temperature measurements. Data for 18 runs were received from Habermann, et al. (ref. 9); the data were in the temperature range from 1861° to 2252° K. The yttrium metal was better than 99.88 percent pure. The impurities were tantalum, 400 ppm; iron, 150 ppm; oxygen, 300 ppm; carbon, 150 ppm; fluorine, 100 ppm; and 65 ppm of additional impurities.

In extrapolating the vapor-pressure data, only the data of reference 9 were used. The advantages of this set of data were the following. First, the orifice in the Knudsen cell was much thinner than that used in reference 24. This led to a Clausing factor of 0.9666 compared with 0.36 in reference 24. Second, 18 data points were received from Habermann, et al. (ref. 9) compared with 7 presented in reference 24. Table II(s)

shows the results of extrapolating the data of reference 9 to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$, along with the calculated temperature uncertainty.

Zirconium

Extrapolated vapor-pressure data for zirconium are based on the experiment described in reference 25. The vapor pressure of solid zirconium was measured between 1949 and 2054 K by a modified method of the Langmuir technique. The zirconium sample was heated inductively by high-frequency current, while temperature measurements were taken from optical pyrometer readings. Weight loses were determined by two methods: first, by collecting and analyzing the evaporated film and, second, by direct measurement of the sample weight loss.

The zirconium sample contained 0.99 atom percent hafnium, 0.05 atom percent tungsten, and 0.37 atom percent of other impurities, which included mostly silicon and

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(s) Yttrium

| | Vapor essure | Extrapo- lated | Temperat uncertair | | |
|------------------------|---|-------------------------------------|--|---|--|
| atm | N/m ² | tempera- ture, ^O K | ° _K | percent | |
| 1 10 100 1000 | 1.01×10^{5} 1.01×10^{6} 1.01×10^{7} 1.01×10^{8} | 4 170 5 210 | 3 410 to 3 590 4 050 to 4 390 5 000 to 5 630 6 530 to 7 850 | -2 to +3 -3 to +5 -4 to +8 -6 to +13 | |

(t) Zirconium

| | 1. 01×10 ⁵ | | 4 440 to 5 240 | -6 to +11 |
|------|-----------------------|-------|-----------------|------------|
| 10 | 1.01×10 ⁶ | 5 580 | 5 170 to 6 450 | -7 to +16 |
| | 1.01×10 ⁷ | | 6 180 to 8 370 | -10 to +22 |
| 1000 | 1.01×10 ⁸ | 8 860 | 7 690 to 11 940 | -13 to +35 |

(u) Niobium carbide (data from ref. 26)

| 1 | 1.01×10 ⁵ | 6 180 | 5 880 to 6 880 | -5 to +11 |
|------|----------------------|--------|------------------|------------|
| 10 | 1.01×10 ⁶ | 7 620 | 7 120 to 8 880 | -7 to +16 |
| | 1.01×10 ⁷ | | 9 020 to 12 500 | -9 to +26 |
| 1000 | 1.01×10 ⁸ | 14 250 | 12 320 to 21 130 | -14 to +48 |

and aluminum. The temperature range of the experiment was only 105^{0} K, and even though a plot of the data shows a good distribution over the temperature range, the extrapolation of the data to 1000 atmospheres (1.01×10⁸ N/m²) predicts a large temperature uncertainty. Table II(t) summarizes the extrapolation of the least-squares curve fit and the possible temperature variation with pressure.

Niobium Carbide

The vaporization behavior of solid niobium carbide was observed experimentally by Fries (ref. 26). The Langmuir method was used to measure the vapor pressure of niobium carbide, and eight data points were recorded over the temperature range from 2260° to 2940° K. The samples were heated inductively, and temperature measurements were made by sighting into a blackbody hole drilled into the sample. Weight measurements were made of the samples before and after each run in order to calculate weight loss.

Analysis of the sample indicated a nearly stoichiometric compound NbC $_{0.924}$, with 0.88 percent free carbon, 0.5 percent oxygen, 0.31 percent nitrogen, and traces of tungsten and tantalum at 500 to 1000 ppm and of zirconium, zinc and molybdenum at 100 to 300 ppm. The nearly stoichiometric niobium carbide was observed to vaporize noncongruently and to lose carbon preferentially, and it was assumed that the carbon vapor leaving the sample was monatomic. A fair amount of scatter occurred in the eight data points which when extrapolated to 1000 atmospheres $(1.01\times10^8~{\rm N/m}^2)$ created a large temperature uncertainty at a given pressure. The extrapolations are listed in table II(u) for pressures from 1 to 1000 atmospheres $(1.01\times10^5~{\rm to}~1.01\times10^8~{\rm N/m}^2)$.

TABLE II. - Continued. EXTRAPOLATED

VAPOR-PRESSURE DATA

(v) Calculated vapor pressures from reference 27

| Partial vap | or press | Tota | al vapor | Calculated | |
|----------------------|--|--|---|--|--|
| Niobium Carbon | | pressure of niobium | | temperature, ^O K | |
| $_{ m N/m}^2$ | atm N/m ² | | carbide | | |
| | | | atm | N/m ² | |
| 0.09×10 ⁵ | 0.91 | 0.92×10 ⁵ | | | |
| 1.01 | 9.0 | 9. 1 | 10 | $[1,01\times10^{6}_{-}]$ | 5620 |
| 14. 2 | 86 | 87 | 100 | 1.01×10^{7} | 6730 |
| 172 | 830 | 842 | 1000 | 1. 01×10 ⁸ | 8400 |
| | obium N/m ² 0.09×10 ⁵ 1.01 14.2 | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ |

The vapor pressure of niobium carbide was also studied analytically in reference 27. Experimentally measured vapor-pressure data of niobium and carbon were used in thermodynamic formulation to calculate the partial pressure of niobium and carbon over niobium carbide. Table II(v) indicates the results of these calculations for total pressures of 1, 10, 100, and 1000 atmospheres $(1.01\times10^5, 1.01\times10^6, 1.01\times10^7, \text{ and } 1.01\times10^8 \text{ N/m}^2)$.

There are several possible reasons why the data of Fries (ref. 26) and the analytical approach of Kaufmann, et al. (ref. 27) differ by $1\frac{1}{2}$ orders of magnitude.

- (1) Fries (ref. 26) assumed that only monatomic carbon vaporized from the niobium carbide sample. Monatomic carbon is the major constituent of the vapor in the temperature range of the experiment performed by Fries (ref. 26) but polyatomic species are always present, and at higher temperatures they are dominant.
- (2) Fries (ref. 26) was unable to measure the partial pressure of niobium. In the temperature range of the experiment, the partial pressure of niobium may not have influenced the total vapor pressure; however, the partial pressure of niobium must be known to extrapolate the data to 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$.
- (3) The data used by Kaufman, et al. (ref. 27) had to be extrapolated to higher pressures. A certain amount of error is always present with experimental data, and this error is enlarged when the data are extrapolated.

The extrapolation of vapor-pressure data must be done very carefully with full knowledge of the type of experiment and the errors involved. As shown in reference 26, the data may be entirely valid for the temperature range in which they were obtained, but meaningful extrapolation to higher pressures may not be possible. It was decided that the analysis of Kaufman, et al. (ref. 27) predicts more accurately the vapor pressure of niobium carbide from 1 to 1000 atmospheres $(1.01\times10^5 \text{ to } 1.01\times10^8 \text{ N/m}^2)$ than does the extrapolation of the data of Fries (ref. 26); therefore, only the analysis of reference 27 is recommended. The partial pressures of niobium and carbon, in addition to the total pressure of niobium carbide calculated from reference 27, are shown in figure 5.

Zirconium Carbide

The vaporization of solid zirconium carbide is discussed in references 28 and 29. The Langmuir method was used, and temperatures were measured with an optical pyrometer, which was sighted on a blackbody hole drilled in each specimen. The specimens were made from hot-pressed zirconium carbide powder containing 2.13 percent impurities. Analysis of the impurities showed 1.1 weight percent free carbon, 0.58 weight percent silicon, 0.30 weight percent niobium, and 0.05 weight percent each of boron, iron, and molybdenum. Most impurities near the surface were evaporated during

TABLE II. - Concluded. EXTRAPOLATED VAPOR-PRESSURE DATA

(w) Zirconium carbide

| | Partial vap | or press | pressure of | | | Extrapo- lated | | |
|------------|-----------------------------|----------|---------------------------|----------------------|----------------------|-------------------|--------------|------------|
| Zii atm | rconium N/m ² | atm C | arbon N/m ² | zirconium carbide | | tempera- ture, | °K | percent |
| | , | | | atm | N/m ² | ^o K | | |
| 0. 73 | 0. 74×10 ⁵ | 0. 27 | 0. 27×10 ⁵ | 1 | 1.01×10 ⁵ | 4940 | 4620 to 5420 | -6 to +10 |
| 7.3 | 7.4 | 2.7 | 2. 74 | 10 | 1.01×10 ⁶ | 5610 | 5150 to 6330 | -8 to +13 |
| 73 | 74 | 27 | 27. 4 | 100 | | 6570 | 5890 to 7670 | -10 to +17 |
| 730 | 740 | 270 | 274 | 1000 | 1.01×10 ⁸ | 7930 | 6870 to 9730 | -13 to +23 |

the early heatings and all the reliable vapor-pressure measurements were obtained thereafter. Observations of the specimen and the sublimate during the course of the experiment indicate that the vaporization of stoichiometric zirconium carbide is congruent; that is, no change of the specimen surface composition occurs as the vaporization process proceeds. For this experiment, 31 runs were performed. Both the partial pressure of zirconium and the partial pressure of carbon are reported in the temperature range from 2246° to 2898° K. Partial pressures of zirconium and carbon were extrapolated separately to 1000 atmospheres (1.01×10 8 N/m 2). These two extrapolated curves were then added to give a total pressure for a given temperature, for pressures up to 1000 atmospheres (1.01×10 8 N/m 2). The results are listed in table II(w) and are shown in figure 6. The partial vapor pressure of carbon that is extrapolated is the sum of all the carbon species. Therefore, since the larger carbon polymers (C $_2$ to C $_5$) become dominant at higher temperatures, the error of the carbon vapor-pressure extrapolation increases with temperature.

In figure 7 are plotted the vapor pressures of all the materials chosen from 1 to 1000 atmospheres $(1.01\times10^5 \text{ to } 1.01\times10^8 \text{ N/m}^2)$.

CONCLUDING REMARKS

Existing vapor-pressure data were collected from the literature for 11 elements and 2 compounds. The materials chosen had a thermal neutron absorption cross section less than 5 barns $(5.0\times10^{-28} \text{ m}^2)$ and an atmospheric boiling point over 3000° K. The data were curve fitted to an equation of the following form:

$$\log P = \frac{A}{T} + D$$

TABLE III. - CALCULATED CONSTANTS OF VAPOR PRESSURE EQUATION (EQ. (1))

| Material | | Constants | 3 |
|----------------------|---------|-------------|------------------|
| | A | D | |
| | | Pressure in | |
| | | atm | N/m ² |
| Carbon ₁ | -37 067 | 8.078 | 13.084 |
| Carbon ₂ | -42 798 | 9. 924 | 14.930 |
| Carbon ₃ | -41 115 | 9. 720 | 14.726 |
| Carbon ₄ | -50 165 | 10.818 | 15.824 |
| Carbon ₅ | -50 820 | 11. 132 | 16. 138 |
| Cerium | -22 816 | 6.419 | 11. 425 |
| Molybdenum | -32 468 | 6. 768 | 11.774 |
| Niobium | -39 308 | 8.444 | 13.450 |
| Platinum | -27 546 | 6.747 | 11. 753 |
| Ruthenium | -32 927 | 7.766 | 12. 772 |
| Silicon ₁ | -22 951 | '''' | 12. 796 |
| Silicon ₂ | -29 509 | 10.009 | 15.015 |
| Silicon ₃ | -30 383 | 10.393 | 15.399 |
| Silicon ₄ | -31 913 | 11. 266 | 16. 272 |
| Tungsten | -44 680 | 7.790 | 12.796 |
| Vanadium | -26 134 | 7.441 | 12.447 |
| Yttrium | -20 821 | 6.001 | 11.007 |
| Zirconium | -30 158 | 6.399 | 11.405 |
| Zirconium over | -38 591 | 7.729 | 12. 735 |
| zirconium carbide | | | |
| Carbon over | -38 591 | 7. 289 | 12. 295 |
| zirconium carbide | | | |
| Niobium over | -37 048 | 6.649 | 11.655 |
| niobium carbide | | | |
| Carbon over | -33 368 | 6.880 | 11.886 |
| niobium carbide | | | |

where A and D are constants, P is vapor pressure, and T is temperature. This equation has the form of a straight line when log P is plotted as a function of reciprocal temperature. The constants A and D were obtained for each of the materials discussed herein and are listed in table III. Selection of the constant D depends on whether pressure is expressed in atmospheres or newtons per square meter.

Equation (1) was used to extrapolate the vapor-pressure data to 1000 atmospheres $(1.01\times10^8~\text{N/m}^2)$. Whatever limitations exist in using the preceding equation for extrapolating vapor-pressure data exist in the extrapolations presented herein. An error anal-

TABLE IV. - RANGE OF VAPOR-PRESSURE DATA AND SUMMARY OF VAPOR-PRESSURE EXTRAPOLATION

| Material | Pressure | Vapor pressure | | | | | |
|----------------------|---|--|---|--|---|--|--|
| | atm | $_{ m N/m}^2$ | 1 atm; 1.01×10 ⁵ N/m ² | 10 atm; 1.01×10 ⁶ N/m ² | 100 atm; 1.01×10 ⁷ N/m ² | 1000 atm; 1.01×10 ⁸ N/m ² | |
| | | | | Extrapolated | l boiling point, ^O K | | |
| Carbon | 1 ×10 ⁻¹² to 2 ×10 ⁻⁵ | | 4100 | 4540 | 5070 | 5740 | |
| Cerium | 1. 6×10^{-6} to 2. 1×10^{-4} | 1.6×10^{-1} to 2. 1×10^{1} | 3560 | 4200 | 5160 | 6670 | |
| Molybdenum | 4. 3×10^{-9} to 1 $\times10^{-6}$ | 4.4×10^{-4} to 1 $\times 10^{-1}$ | 4800 | 5630 | 6820 | 8620 | |
| Niobium | 7. 6×10^{-10} to 2. 4×10^{-7} | 7.7×10^{-5} to 2.4×10 ⁻² | 4660 | 5280 | 6100 | 7220 | |
| Niobium carbide | | (a) | 4810 | 5620 | 6730 | 8400 | |
| Platinum | 1. 7×10^{-8} to 2. 3×10^{-7} | 1. 7×10 ⁻³ to 2. 3×10 ⁻² | 4070 | 4780 | 5790 | 7330 | |
| Ruthenium | 2. 3×10^{-10} to 1. 7×10^{-5} | 2.3×10^{-5} to 1.7 | 4240 | 4870 | 5710 | 6910 | |
| Silicon | 1. 3×10^{-9} to 1. 3×10^{-6} | | 2730 | 3010 | 3350 | 3760 | |
| Tungsten | 2. 5×10^{-10} to 5. 4×10^{-7} | | 5740 | 6580 | 7730 | 9340 | |
| Vanadium | 5.4×10^{-9} to 3.5×10^{-7} | 5. 5×10^{-4} to 3. 6×10^{-2} | 3510 | 4060 | 4800 | 5880 | |
| Yttrium | 6.0×10^{-6} to 2.6×10^{-4} | | 3480 | 4170 | 5210 | 6950 | |
| Zirconium | 8. 5×10^{-10} to 5. 3×10^{-9} | | | 5580 | 6850 | 8860 | |
| Zirconium carbide | 1. 3×10 ⁻¹⁰ to 2. 8×10 ⁻⁶ | 1. 3×10^{-5} to 2. 8×10^{-1} | 4940 | 5610 | 6570 | 7930 | |

^aAnalysis.

TABLE V. - BOILING-POINT TEMPERATURES OF

SELECTED REFRACTORY MATERIALS

(a) At 1000 atmospheres $(1.01 \times 10^8 \text{ N/m}^2)$

| Temperature, | Thermal absorption cross section, σ | | | | |
|----------------|-------------------------------------|-------------------------|-------------------------|--|--|
| K | σ ≤ 1.0 | $1.0 < \sigma \leq 2.0$ | $2.0 < \sigma \leq 5.0$ | | |
| 9000 to 10 000 | | Tungsten 184 | | | |
| 8000 to 9 000 | Zirconium | Niobium carbide | Molybdenum | | |
| 7000 to 8 000 | Zirconium carbide | Yttrium | | | |
| | Platinum 196 | Niobium | | | |
| | | Platinum 194 | | | |
| 6000 to 7 000 | Cerium | | Ruthenium | | |
| 5000 to 6 000 | Carbon | | Vanadium | | |
| < 5000 | Silicon | | | | |

(b) At 100 atmospheres $(1.01\times10^7 \text{ N/m}^2)$

| 7000 to | 8 000 | | Tungsten 184 | |
|---------------|-------|--------------------------------|-----------------|------------|
| 6000 to | 7 000 | Zirconium Zirconium carbide | Niobium carbide | Molybdenum |
| 5000 to | 6 000 | Platinum 196 | Platinum 194 | Ruthenium |
| | | Cerium | Yttrium | |
| 1000 to | E 000 | Carbon | | XI 34 |
| 4000 to <4000 | 5 000 | Silicon | | Vanadium |
| 4000 | | SHICOH | | |

ysis was used to find the temperature uncertainty in the extrapolated vapor pressure due to the scatter of the original data. The vapor-pressure data were generally taken in the range from 10^{-10} to 10^{-5} atmospheres $(1.01\times10^{-5}$ to $1.01~\rm N/m^2)$, and table IV summarizes the results by showing, for each chosen material, the range of the original data and the predicted boiling points at 1, 10, 100, and 1000 atmospheres $(1.01\times10^5, 1.01\times10^6, 1.01\times10^7, and 1.01\times10^8~\rm N/m^2)$.

In tables V(a) and (b), the refractory materials are grouped according to boiling point ranges and thermal absorption cross sections. At 1000 atmospheres $(1.01\times10^8 \text{ N/m}^2)$ the element that has the highest boiling point is tungsten (9340° K), while at the same pressure niobium carbide has the highest boiling point of the compounds (8400° K).

Lewis Research Center,

National Aeronautics and Space Administration, Cleveland, Ohio, April 17, 1967, 122-28-02-16-22.

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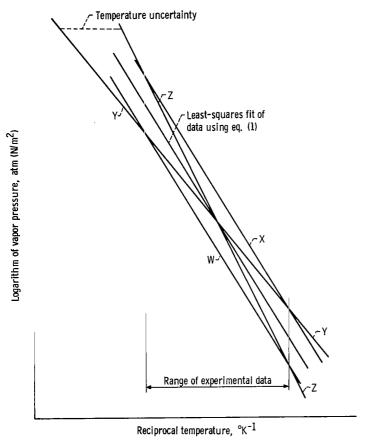


Figure 1. - Schematic drawing of visual error analysis.

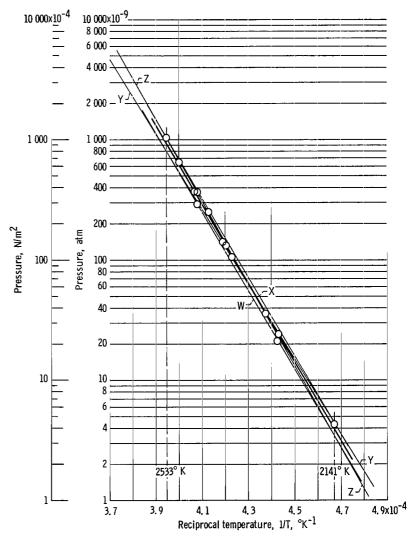


Figure 2. - Method of extrapolation using molybdenum vapor pressure data from reference 6.

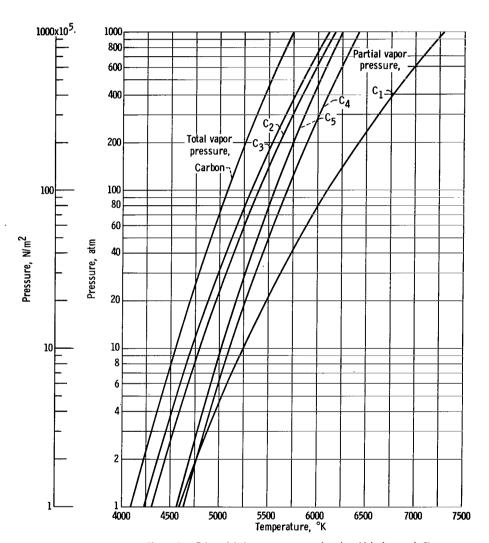


Figure 3. - Extrapolated vapor pressure of carbon (data from ref. 7).

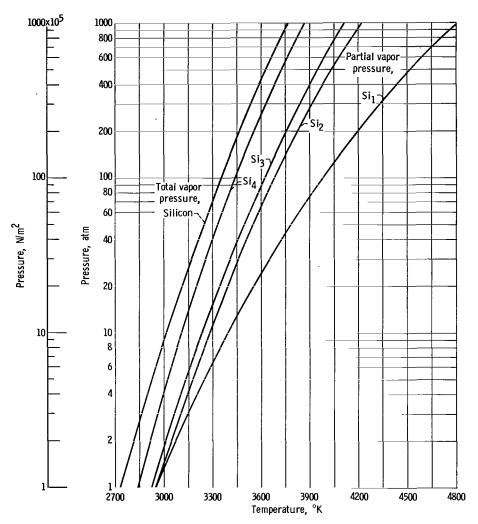


Figure 4. - Extrapolated vapor pressure of silicon (data from ref. 19).

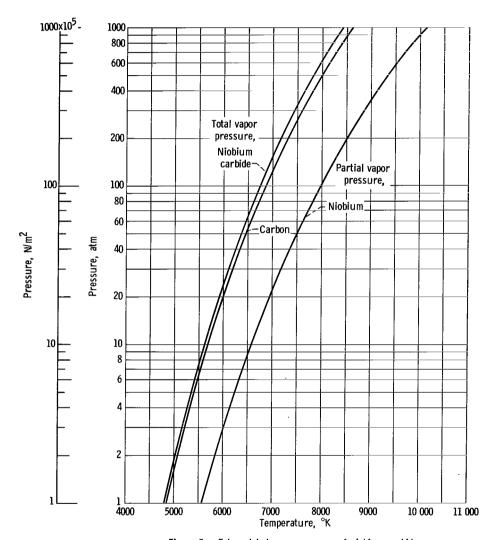


Figure 5. - Extrapolated vapor pressure of niobium carbide.

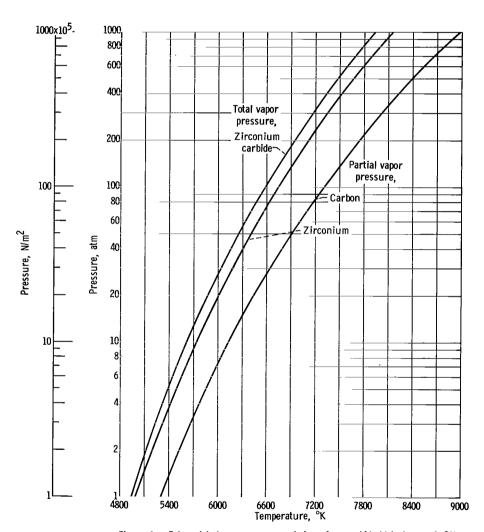


Figure 6. - Extrapolated vapor pressure of zirconium carbide (data from ref. 29).

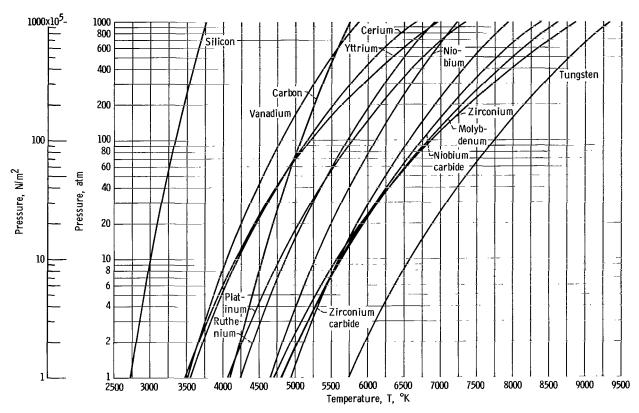


Figure 7. - Extrapolated vapor pressure data of selected refractory materials.

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