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VAPORIZATION OF TANTALUM CARBIDE-HAFNIUM CARBIDE

SOLID SOLUTIONS AT 2500° TO 3000° K

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ABSTRACT

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The vaporization rates in vacuum of hot-pressed HfC, TaC, and solid solutions of these two carbides in the temperature range of 2500° to 3000° K were determined by a Langmuir type method. The results show that a composition near 70 mol percent TaC · 30 mol percent HfC exhibits the lowest vaporization rate of any composition within this pseudo-binary system. Variations in initial sample bulk density and vapor-specie condensation on the furnace wall have negligible effects on the measured vaporization rates. Preliminary information concerning the influence of time on the vaporization rate of selected compositions is discussed.

INTRODUCTION

The refractory carbides as a class are the highest melting materials known today. As such, they are of interest as potential materials for applications that require high temperatures of operation. One such application is in the field of thermionic energy conversion. Thermionic parameters, for example, work function and emission flux, have been measured for some carbides^{1,2,3} and suggest that these materials are useful emitters. A major liability of carbides for this application is

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their relatively high rates of vaporization. Excessive vaporization of an emitter material would lead to degradation of the critical cathode-anode spacing and the possibility of short circuiting the cell by condensation on electrical insulators.

The study reported herein was initiated to determine the vaporization characteristics of the binary carbide system TaC-HfC. This system was chosen for study because its components are the highest melting of the refractory carbides and have low vaporization rates.^{4,5,6,7} The component carbides are soluble in all proportions.⁸ A composition within this solid-solution region, 80 TaC · 20 HfC, has been reported⁹ to have a melting temperature higher than either TaC or HfC. This presents the possibility that such a solid-solution composition might exhibit a vaporization rate lower than either component carbide.

In this study, the vaporization rates of TaC, HfC, and intermediate solid-solution compositions were determined in vacuum between 2500° and 3000° K by a Langmuir type method. A composition exhibiting minimal vaporization rate was found. The effect of vapor-specie condensation on vaporization rate was ascertained by making measurements in cold wall (condensable vapor) and hot wall (noncondensable vapor) furnaces. Preliminary experiments to determine the influence of time on the vaporization rate were also made.

EXPERIMENTAL

Materials and Sample Preparation

Table I lists the chemical and X-ray diffraction results for the commercially supplied starting materials. A formula for each is given that

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includes the major metallic impurities. The $(\text{Ta}_{0.988}\text{Nb}_{0.011}\text{W}_{0.001})\text{C}_{0.932}$ composition will hereinafter be referred to as $\text{TaC}_{0.93}$: the $\text{HfC}_{0.982}$ will be referred to as $\text{HfC}_{0.98}$. The

$(\text{Ta}_{0.782}\text{Hf}_{0.202}\text{Nb}_{0.007}\text{Ti}_{0.005}\text{Zr}_{0.004})\text{C}_{0.925}$ will be referred to either as nominally 80 mol percent $\text{TaC}_{0.93}$ · 20 mol percent $\text{HfC}_{0.93}$ or 80 · 20 composition.

The C-metal ratios of the tantalum and hafnium carbides determined from the chemical analysis are 0.93 and 0.98, respectively. The corresponding values obtained through the use of the measured lattice parameters (given in table I) and published a_0 against C-metal ratios are 0.95 to 0.99 for tantalum carbide^{10,11,12} and 0.89 to 0.96 for hafnium carbide.^{12,13,14} These wide ranges found by use of the various published relations of a_0 against C-metal ratio are due to difficulty in carbon analysis, variation in kind and content of impurities, and insensitivity of the lattice parameter to carbon content at high carbon concentration. The C-metal ratios determined from the chemical analyses are, however, of the same order of magnitude as those determined from the lattice parameters. The C-metal ratio arrived at by chemical analysis will be used here because of the insensitivity of lattice parameter to carbon content.

In addition to the three compositions given in table I, compositions of 50 mol percent $\text{TaC}_{0.96}$ · 50 mol percent $\text{HfC}_{0.96}$ and 25 mol percent $\text{TaC}_{0.97}$ · 75 mol percent $\text{HfC}_{0.97}$ were also prepared. This was accomplished by mixing the $\text{TaC}_{0.93}$ and $\text{HfC}_{0.98}$ powders in the proper ratio before forming the test specimens. The initial C-metal ratios given for these compositions after forming were calculated from those of the starting carbides.

Solid cylindrical pieces were formed by hot pressing at temperatures of 2500° to 3000° K at 3500 psi and for times of 10 minutes to 1 hour in a graphite die. Solid cylinders 5/8 inch in diameter by 1/4 inch long were formed. The hot-pressing equipment has been described in Ref. 15. In order to attain homogeneous solid solutions in the 50 · 50 and 25 · 75 specimens, it was necessary to press for 1 hour at 3000° K.

Test specimens 5/8 inch (O.D.) by 3/8 inch (I.D.) by 1/4 inch long were fabricated from the solid hot-pressed cylinders by electric-discharge machining. This hollow-cylinder geometry was used to prevent cracking of the specimen during heating and cooling and for greater uniformity of temperature within those specimens heated directly by induction. An approximate blackbody hole with a depth to diameter ratio of at least 5 to 1 was drilled in the center of the ring parallel to its length. Free carbon was removed from the specimen surface with a wire brush and by grinding by hand on 600 abrasive cloth. The homogeneity of the test specimens was judged from the X-ray diffraction patterns.

X-ray diffraction patterns were obtained with a diffractometer at a scanning speed of $1/2^\circ(2\theta)/\text{min}$ and Ni filtered Cu radiation. The a_0 values were obtained by applying a least-squares extrapolation of $1/\sin^2\theta$ on an IBM 704 computer.

The densities of the hot-pressed specimens were determined by weighing in air and distilled water on an analytical balance. The theoretical density of each composition was calculated from the measured lattice parameter. The results are expressed as percent of theoretical density.

Specimens of 90 to 93 percent of theoretical density were obtained for $TaC_{0.93}$, 86.6 to 98 percent of theoretical density for 80 · 20 composition, 88.8 to 95.5 percent theoretical density for 50 · 50 composition, 91 percent of theoretical density for 25 · 75 composition, and 65.5 to 90 percent of theoretical density for $HfC_{0.98}$.

Vaporization Measurements

The vaporization-rate measurements were carried out in both hot- and cold-wall types of furnaces. This was done to determine the influence of the condensation of the vaporized material on the vaporization rate. The cold wall furnace has been described previously.¹⁶ In brief, it consisted of a 1-inch (I.D.) water-cooled continuously evacuated quartz tube. The specimen was supported on three 0.060-inch tungsten rods. The specimen was directly heated inductively by a 1/2-megacycle power source. By this arrangement, the hot specimen was directly exposed to the water-cooled quartz tube. A few measurements were also made in a hot wall furnace, which has been described.¹⁷ This furnace was also continuously evacuated. The specimen was placed inside a 1-inch-diameter by 1-inch-long tungsten cup, which, in turn, was placed inside a $1\frac{1}{2}$ -inch-diameter by 3-inch-long tungsten susceptor. The susceptor was inductively heated by a low-frequency power source. By this arrangement, the specimen and the walls of the tungsten cup were at approximately the same temperature. There was never any detectable physical adherence of the specimen to the tungsten cup.

The temperature in a sight hole in the specimen was measured with a disappearing-filament optical pyrometer, which had been calibrated against

a standard tungsten filament lamp with all optical elements in the light path.

A typical vaporization-rate determination involved weighing the specimen to the nearest 0.2 milligram, inserting the specimen into the furnace, and evacuating the furnace to 1×10^{-6} torr (cold cathode gauge). The specimen was then heated slowly to 2100° K so that the pressure never exceeded 1×10^{-4} torr. The time required was about 5 minutes. This temperature was maintained until the system pumped down to less than 5×10^{-5} torr, which required 1 to 2 minutes. The specimen was then brought to the desired temperature in 1 to 2 minutes and maintained constant, $\pm 30^{\circ}$ K, for 1/2 to 1 hour at higher temperatures (2800° to 3000° K) and 2 to 4 hours at lower temperatures (2500° to 2800° K). The pressure during this period was between 5×10^{-5} and 5×10^{-6} torr. At the end of the heating period, the power to the furnace was turned off, and the specimen was cooled to less than 1300° K in 2 minutes. After cooling to room temperature, the specimen was reweighed. The first two determinations on each specimen were made at 2400° to 2500° K. The vaporization rate calculated for the first determination was always very large due to outgassing of highly volatile impurities and was therefore discarded. After the first two determinations, each succeeding measurement was made at a higher temperature. The total heating time a specimen received varied depending on the number of measurements made, but was always less than 20 hours. The total weight loss of any specimen, even after many determinations, was never greater than 0.5 weight percent. A few preliminary measurements were made at constant temperature with varying

heating times. The same general procedure as described above was followed for these determinations.

The vaporization rate R was calculated from the equation

$$R = \frac{\Delta W}{(\Sigma A)t} \left[\frac{g}{(\text{cm}^2)(\text{sec})} \right]$$

where ΔW is the weight lost in grams, t is the time of heating in seconds, and ΣA is the total surface area in cm^2 and includes the outer cylindrical surface, end surfaces, and "effective" area of the inside of the hollow cylinder. The effective area of the inside of these hollow cylinders was calculated from an equation given by Speiser, et al.,¹⁸ that is,

$$A_{ID} = \pi l \left[(d^2 + l^2)^{1/2} - l \right]$$

where l is length of the cylinder and d is its inside diameter. This expression was derived from the cosine law of vaporization. It corrects for the material vaporized from the inside of a hollow cylinder but not lost from the cylinder due to recombination on the opposite inner wall. It assumes 100 percent recombination of all material striking the opposite wall. This correction was always less than 10 percent of the total surface area.

RESULTS AND DISCUSSION

The term vaporization is used here in its broadest sense, that is, to mean a gross mass loss of the specimen. The experimental conditions do not fulfill, in the strictest sense, all the requirements of an ideal Langmuir determination (very large vacuum chamber compared to specimen size, specimen geometry, etc.). The approximations are good enough,

however, so that the data may be interpreted as having some kinetic significance. In this discussion, no extensive reference to kinetics will be made. Also, while it is known that TaC vaporizes incongruently⁵ and HfC congruently⁴, the nature of the vaporization mechanism of the solid solutions is not known, and no conclusions concerning this mechanism are to be drawn from the present data.

X-ray diffraction of the surface of all five hot-pressed compositions, prior to vaporization determinations, showed them to be homogeneous and single-phase face-centered-cubic materials. The lattice parameters of the hot-pressed specimens are shown in table II. The larger standard deviations for the 50·50 and 25·75 compositions are due to their broader diffraction peaks and lack of resolution of the α_1 , α_2 lines.

The TaC_{0.93} and 80·20 specimens, in the as-hot-pressed state, were golden yellow in color, while the other three compositions of higher Hf content were a silvery gray. After several vaporization determinations, the surface of all compositions was a metallic silver color. The interior of the TaC_{0.93} and 80·20 specimens, even after large weight losses, remained golden yellow. Santoro¹⁹ observed in the Ta-C system that TaC was golden yellow in color when x was greater than 0.8 and a metallic silver at less than 0.8. He presents evidence that the color transition is related to the electronic structure, which is altered by addition or removal of carbon atoms. In the case of Ta-C system, the number of electrons per unit cell is decreased by reducing the total number of carbon atoms. In the binary TaC-HfC system, the number of electrons

per unit cell is decreased by substituting Hf for Ta atoms. In the latter case, this is due to the fact that the Hf has four electrons in its outer shell, while Ta has five electrons. Thus, the transition of color caused by either the reduction in carbon content or by Hf substitution for Ta can be related to the electron concentration in the unit cell. Therefore, the color change from golden yellow to gray observed in the hot-pressed binary-carbide compositions as the Hf content increases from $TaC_{0.93}$ to the 50·50 composition is attributed to a decrease in electron concentration. Furthermore, the appearance of a gray surface layer on the initially golden yellow $TaC_{0.93}$ and 80·20 compositions after vaporization measurements is related to a decrease in electron concentration caused by loss of carbon.

The vaporization data for each carbide composition studied is presented individually in Figs. 1 to 5. Initially, the experimental data points were plotted in these figures and the limits of the scatter, shown by dashed lines, were drawn to include all the data points. In any figure, for example, Fig. 2, there is no apparent grouping of any one set of data points (i.e., one density and furnace condition). This general dispersion of the data points for various sample densities and furnace conditions suggests that, within the range of densities studied and for the two furnace conditions used here, these variables have no significant effect on the measured vaporization rate. Fries²⁰ observed for NbC that the presence or absence of a hot or cold wall had a negligible effect on the vaporization rate. This observation having been made, a least-squares line was calculated for each material using all

the data points. The least-squares line is shown in Figs. 1 to 5 as a solid line. The least-squares calculation was made on an IBM 704 computer. In every case the determination coefficient was greater than 90 percent. This coefficient is the percent probability that there is a linear correlation between the variables, log rate, and $1/T^0$ K.

The vaporization data for $TaC_{0.93}$ specimens of 90 and 93 percent T.D. are shown in Fig. 1. These values were obtained from measurements made in the cold wall furnace. The vaporization-rate data points given by Coffman et al.⁵ for specimens of $TaC_{0.97}$ with initial densities of 95 percent T.D. and Hoch et al.⁶ for $TaC_{0.96}$ all fall within the scatter band shown in Fig. 1. The slopes of the least-squares lines fitted to their data points are very nearly equal to one another, but approximately 18 percent larger than that obtained from the present measurements. It is suggested that the larger slope for the literature data is due to the difference in the C-metal ratios of the specimens (0.93 for the present material compared with 0.96 and 0.97 for the literature carbides).

Vaporization results for the 80·20 composition given in Fig. 2 also show a scatter band. There is some indication that the scatter is less at the higher temperatures.

The vaporization results for the 50·50 composition are given in Fig. 3. The scatter remains about the same at all temperatures. The vaporization rate of only one specimen of the 25·75 composition was measured, and the results are given in Fig. 4.

The vaporization rate results for $HfC_{0.98}$ are shown in Fig. 5. The vaporization rate data points given by Coffman et al.⁴ obtained from specimens

of $(\text{Hf}_{0.95}\text{Zr}_{0.05})\text{C}_{0.96}$ with an initial density of 70 percent of theoretical density all fall within the scatter band shown in Fig. 5. A least-squares fit of Coffman's data gives a line with a slope 7 percent greater than that obtained from the present data. The vaporization rate data of Bolgar et al.⁷ for HfC_x are approximately two orders of magnitude larger than the present. The slope of Bolgar's data is almost identical to that given by Coffman et al.⁴. Storms²¹ compared Bolgar's vaporization values of other materials with currently accepted values for these materials and found the results of Bolgar to be very much larger in every case.

In Fig. 6, the least-squares-fitted vaporization curves for each carbide composition studied are shown along with data for tungsten. In the case of tungsten, the curve represents the literature data,²² and the points are the present determination. The data for tungsten are included so that direct comparisons of the vaporization of the carbides with this material can be made. Tungsten was chosen for comparison because it has the lowest vaporization rate of any known material in this temperature range (2500° to 3000° K). Of the carbide materials studied, the 80·20 composition possesses the lowest volatility, and $\text{HfC}_{0.98}$ is the most volatile in the temperature range considered. The vaporization of the 80·20 composition approaches that of tungsten at the higher temperatures.

From the slope of the curves for $1/T$ against vaporization rate in Fig. 6, the activation energy ΔE^* of the vaporization process was calculated from the Arrhenius equation. These values are tabulated in Fig. 6. Examination of the activation-energy values shows that increasing the TaC

content in the binary compositions causes only a slight decrease in ΔE^* up to 50 mol percent TaC. When the TaC content exceeds 50 mol percent, ΔE^* decreases sharply. This suggests that the vaporization processes may be different.

Variation of the vaporization rate as a function of composition at 2500°, 2600°, 2700°, and 2900° K is shown in Fig. 7. This figure was constructed from the data given in Figs. 1 to 5. The width of the scatter band and the least-squares vaporization-rate value (shown as a circle) are presented. Straight lines are drawn to pass as near as possible to the least-squares points. It appears that there is a composition near the intersection of these two curves possessing a minimum vaporization rate. This composition lies between the 80 TaC_{0.93} · 20 HfC_{0.93} and 50 TaC_{0.96} · 50 HfC_{0.96} experimental points and is nearer the former.

There are several important points to be made concerning the interpretation of Fig. 7. The C-metal ratio of the experimental materials is not constant, but varies from 0.93 for the TaC and 80 · 20 compositions to 0.96 to 0.98 for the 50 · 50, 25 · 75, and HfC compositions, respectively. Seigle et al.²³ have shown that, in the case of TaC, the vaporization rate decreases with decreasing C-metal ratio. One might therefore similarly argue that the decrease in vaporization rate shown in Fig. 7 is due to a varying C-metal ratio rather than to the TaC to HfC compositional ratio. This is not believed to be true for the following reasons. First, the C-metal ratio of the TaC_{0.93} and 80 · 20 compositions are equal; therefore, the observed lower vaporization rate of the 80 · 20 composition, at a given temperature, must be due to the change in the Ta to Hf ratio. Secondly,

the compositions 50 TaC_{0.96} · 50 HfC_{0.96}, 25 TaC_{0.97} · 75 HfC_{0.97}, and HfC_{0.98} exhibit, for all practical purposes, equal C-metal ratios, therefore the observed decrease in the vaporization rate must also be due to the variation in the Ta to Hf ratio in these compositions. Thirdly, using Seigle's et al.²³ data for TaC, let us estimate the magnitude and direction of shift of the vaporization rate of the TaC_{0.93} composition at 2700° K if the C-metal ratio were raised to a level comparable to the higher carbon content compositions, that is, 0.97. The vaporization rate would be shifted upward from the present 2.5×10^{-7} gram per square centimeter per second to about 6×10^{-7} gram per square centimeter per second. For the assumption that Seigle's data for TaC also holds for the 80 · 20 composition, an increase in the C-metal ratio to 0.97 would shift the vaporization rate of this material upward from 1×10^{-7} gram per square centimeter per second to about 3.5×10^{-7} gram per square centimeter per second. This would shift the composition of the minimum toward higher Hf contents (i.e., from about 30 up to approx. 50 mol percent HfC). This would not, however, negate the basic conclusion that a composition exists in the TaC_x - HfC_x binary system, which possesses a minimum volatility.

Another factor that could influence this conclusion is the effect of heating time on the vaporization-rate values. Preliminary data (from a continuing program) for TaC_{0.93} and the 80 · 20 composition at 2600° K, using the cold wall furnace, shows that the vaporization rate decreases with increased heating time. The vaporization rate of TaC_{0.93} decreases from 1×10^{-7} to 7×10^{-8} gram per square centimeter per second in 13 hours, while the 80 · 20 composition shows a decrease from 4×10^{-8} to 2×10^{-8} gram

per square centimeter per second in 40 hours. In both cases, the new values are within the scatter of the short-time data reported herein. Furthermore, the heating time used for a rate determination at a given temperature for each composition was approximately the same. This then further minimizes the effect of time on the vaporization-rate values and, from the standpoint of the time effect, makes the compositional comparison of Fig. 7 valid at a given temperature.

Kaufman et al.²⁴ applied the Schottky-Wagner model to the ternary Ta-Hf-C system and calculated the vapor pressures of Ta, Hf, and C over (Ta-Hf)C as a function of temperature and composition. From these values, they calculated the vaporization rates through the Langmuir equation. The calculated initial rates of vaporization of Kaufman et al.²⁴ show fair agreement with observed rates at 2600° K. Also the observed minimum in the vaporization rate is predicted from their calculations.

CONCLUDING REMARKS

All evidence indicates that there is a composition in the binary system between TaC_x - HfC_x that possesses a minimum volatility or a maximum stability. This composition appears to be near the 80 $TaC_{0.93}$ • 20 $HfC_{0.93}$ experimental composition. The vaporization rate of this composition approaches that of tungsten at high temperatures. The influence of density variation and vapor-specie condensation on the vaporization rate is less than the precision of measurement of the vaporization rate. With the passage of time, at a constant temperature, the vaporization rate of both $TaC_{0.93}$ and the 80 • 20 specimen decreased. This decrease is not large and is well within the scatter band in each case.

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DIFFRACTION RESULTS OF STARTING MATERIALS^a

80 TaC • 20 HfC		
Theoretical	Actual	Theoretical
6.30	5.85 0.03 5.82 74.23	6.23 75.21
93.70	18.92	18.56
	----- 0.036 <.001 .32 .13 .16 ----- ----- <.003 .18 .021 .012	
HfC _{1.0}	(Ta _{0.782} Hf _{0.202} Nb _{0.007} Ti _{0.005} Zr _{0.004})C _{0.925}	(Ta _{0.8} Hf _{0.2})C _{1.0}
50	47.9	50
1.0	0.925	1.0
	4.483 (±0.001)	

ubic materials.

TABLE I. - CHEMICAL ANALYSIS AND X-RAY

	TaC		HfC
	Actual	Theoretical	Actual
Analysis weight percent:			
Total C	5.98		6.20
Free C	0.11		0.01
Combined C	5.87	6.22	6.19
Ta	----	93.78	----
Hf	----		93.72
W	0.11		----
Fe	----		<0.005
Si	<.01		<.01
Nb	.52		----
Ti	----		----
Zr	<.01		<.01
Co	.057		----
Cr	.051		----
B	Not detected		<.005
O ₂	.19		.007
N ₂	.005		.014
H ₂	----		.0031
Formula	(Ta _{0.988} Nb _{0.011} W _{0.001})C _{0.932}	TaC _{1.0}	HfC _{0.982}
C, a/o	48.2	50	49.6
C/metal	0.932	1.0	0.982
Lattice parameter, A	4.455 (±0.001)		4.6400 (±0.0002)

^aAll three hot-pressed compositions are single-phase face-centered-cu

TABLE II. - LATTICE PARAMETERS OF HOT
PRESSED CARBIDES

Composition	Lattice parameter, $a_0, \text{\AA}$
$\text{TaC}_{0.93}$	4.4559 (± 0.0006)
80 $\text{TaC}_{0.93}$ · 20 $\text{HfC}_{0.93}$	4.4820 (± 0.0002)
50 $\text{TaC}_{0.96}$ · 50 $\text{HfC}_{0.96}$	4.552 (± 0.005)
25 $\text{TaC}_{0.97}$ · 75 $\text{HfC}_{0.97}$	4.590 (± 0.008)
$\text{HfC}_{0.98}$	4.6400 (± 0.0002)

VAPORIZATION RATE OF $TaC_{0.93}$ IN VACUUM IN COLD WALL FURNACE AS FUNCTION OF TEMPERATURE

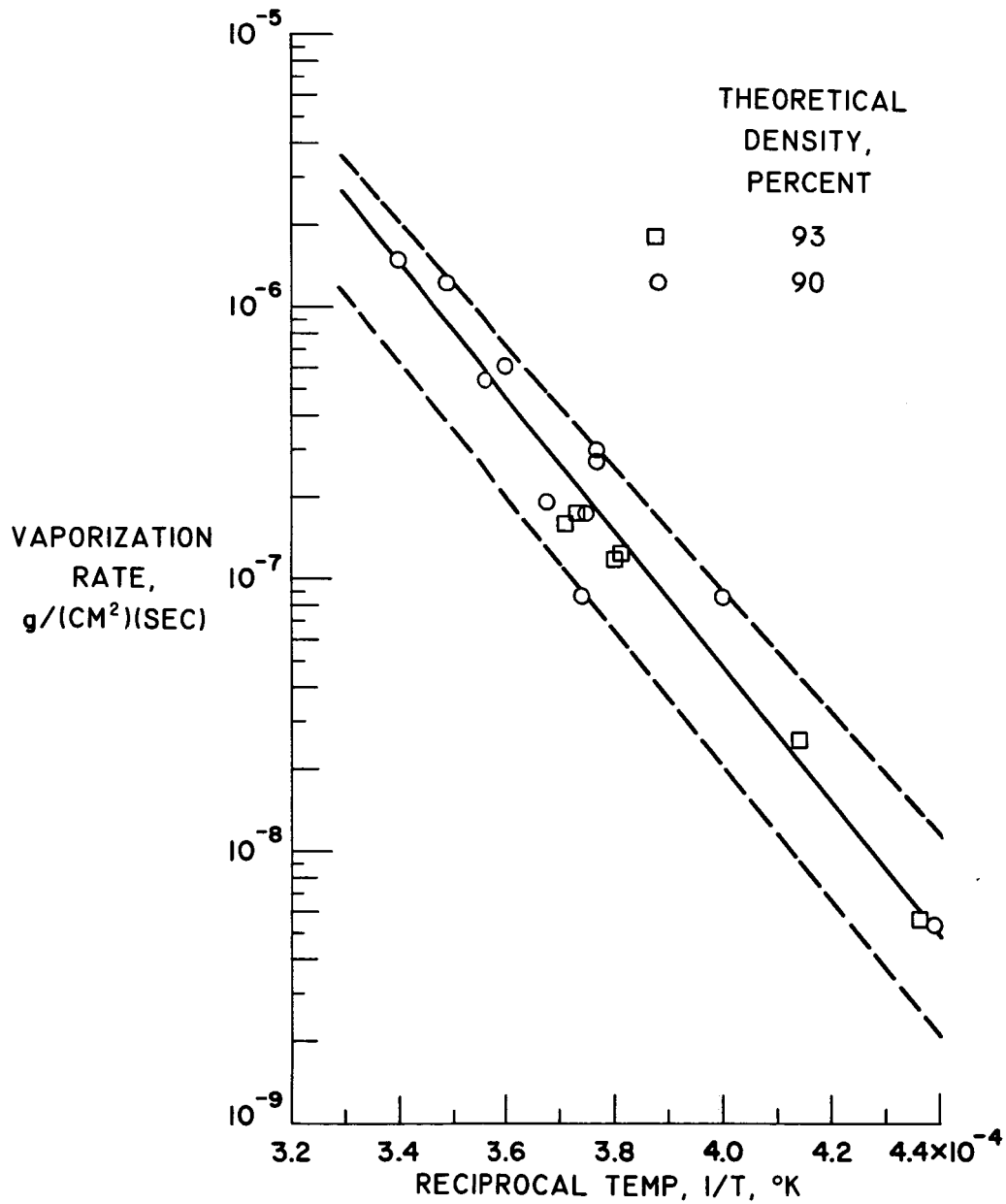


Figure 1

VAPORIZATION RATE OF 80 TaC_{0.93} · 20 HfC_{0.93}
 IN VACUUM IN COLD WALL AND HOT WALL
 FURNACE AS FUNCTION OF TEMPERATURE

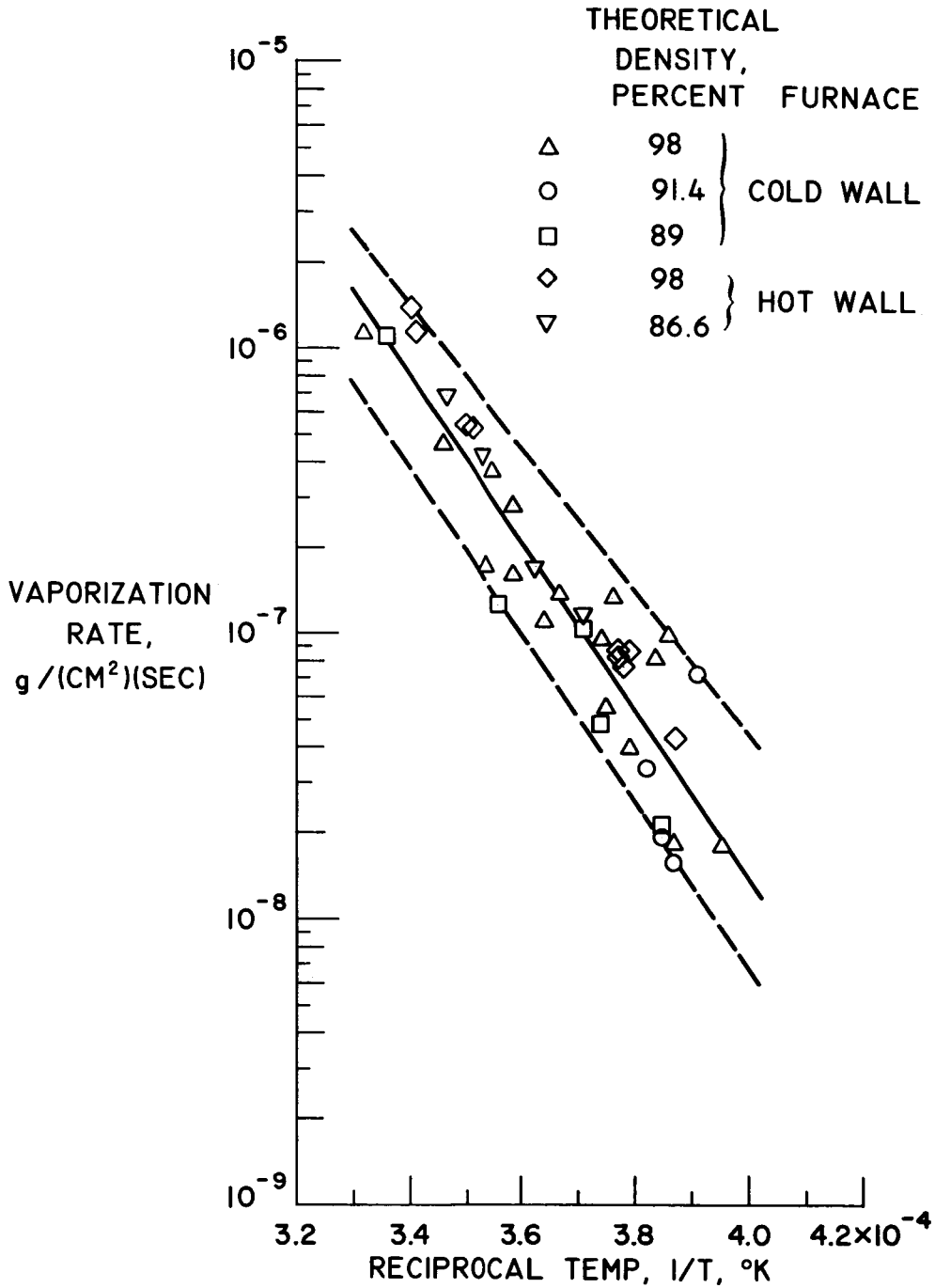


Figure 2

VAPORIZATION RATE OF 50 TaC_{0.96} · 50 HfC_{0.96}
 IN VACUUM IN COLD WALL FURNACE
 AS FUNCTION OF TEMPERATURE

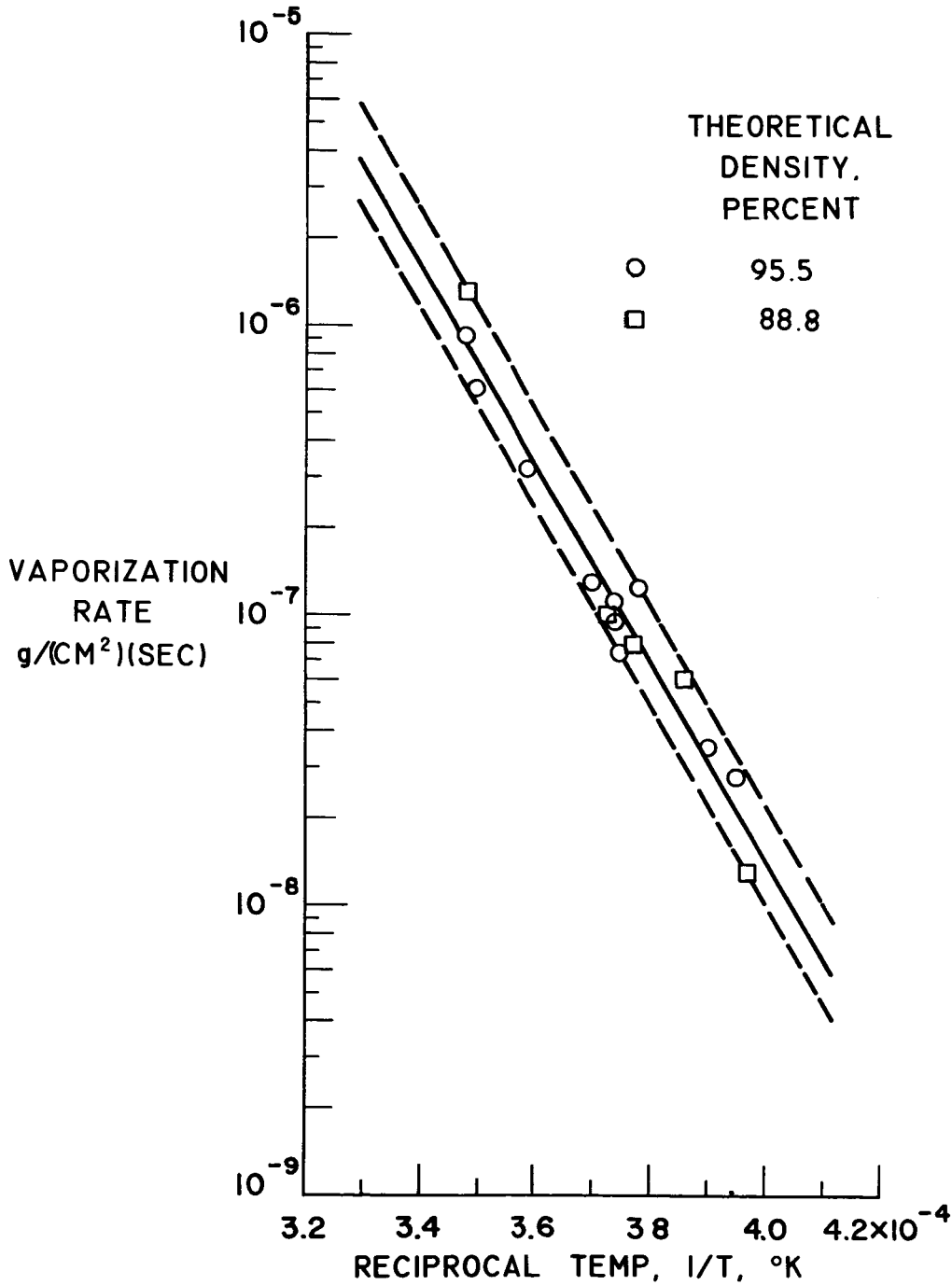


Figure 3

VAPORIZATION RATE OF 25 TaC_{0.97} · 75 HfC_{0.97}
IN VACUUM IN COLD WALL FURNACE AS FUNCTION
OF TEMPERATURE. INITIAL DENSITY OF SPECIMEN,
91 PERCENT OF THEORETICAL DENSITY

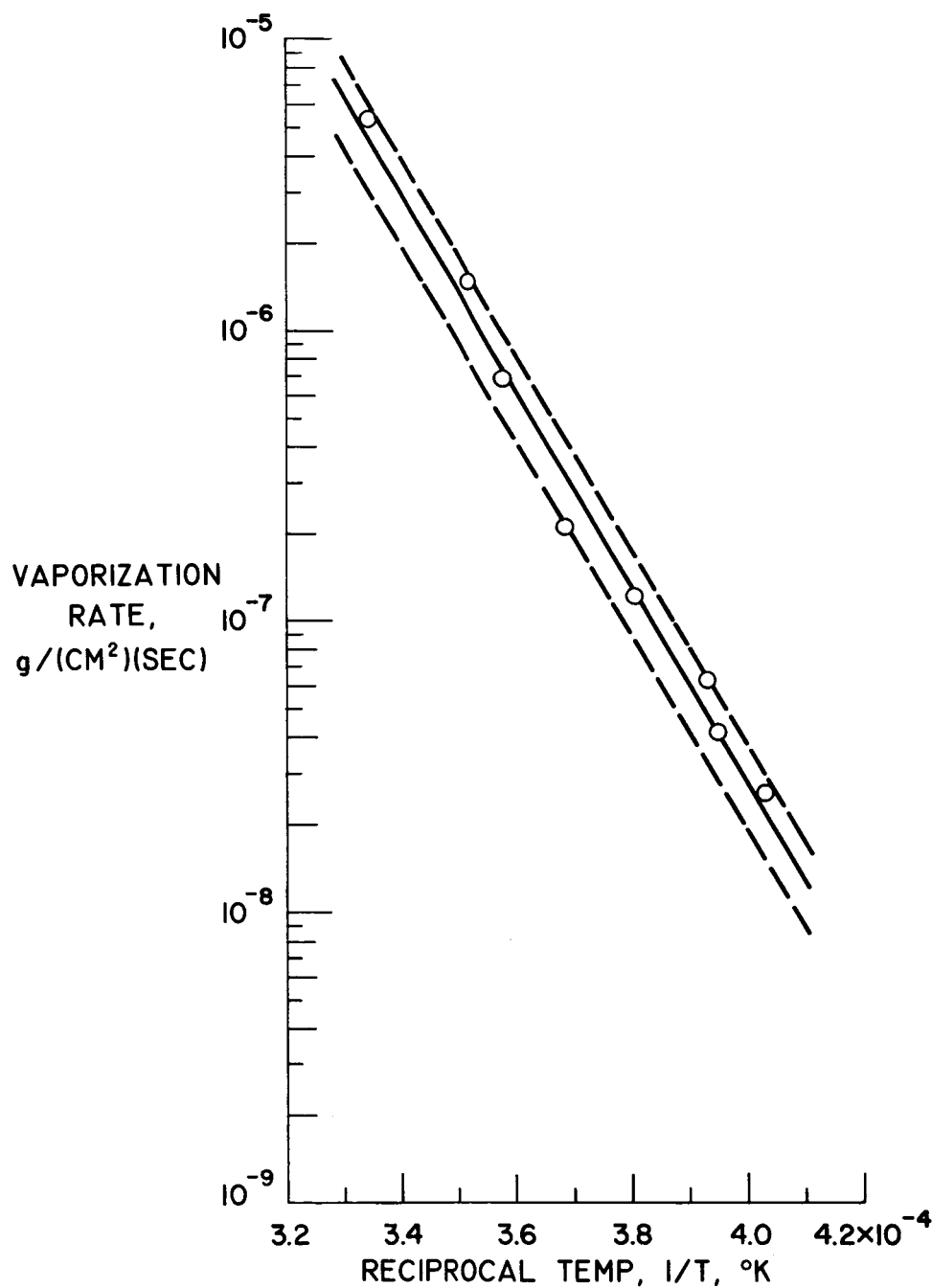


Figure 4

VAPORIZATION RATE OF $HfC_{0.98}$ IN VACUUM IN HOT WALL AND COLD WALL FURNACE AS FUNCTION OF TEMPERATURE

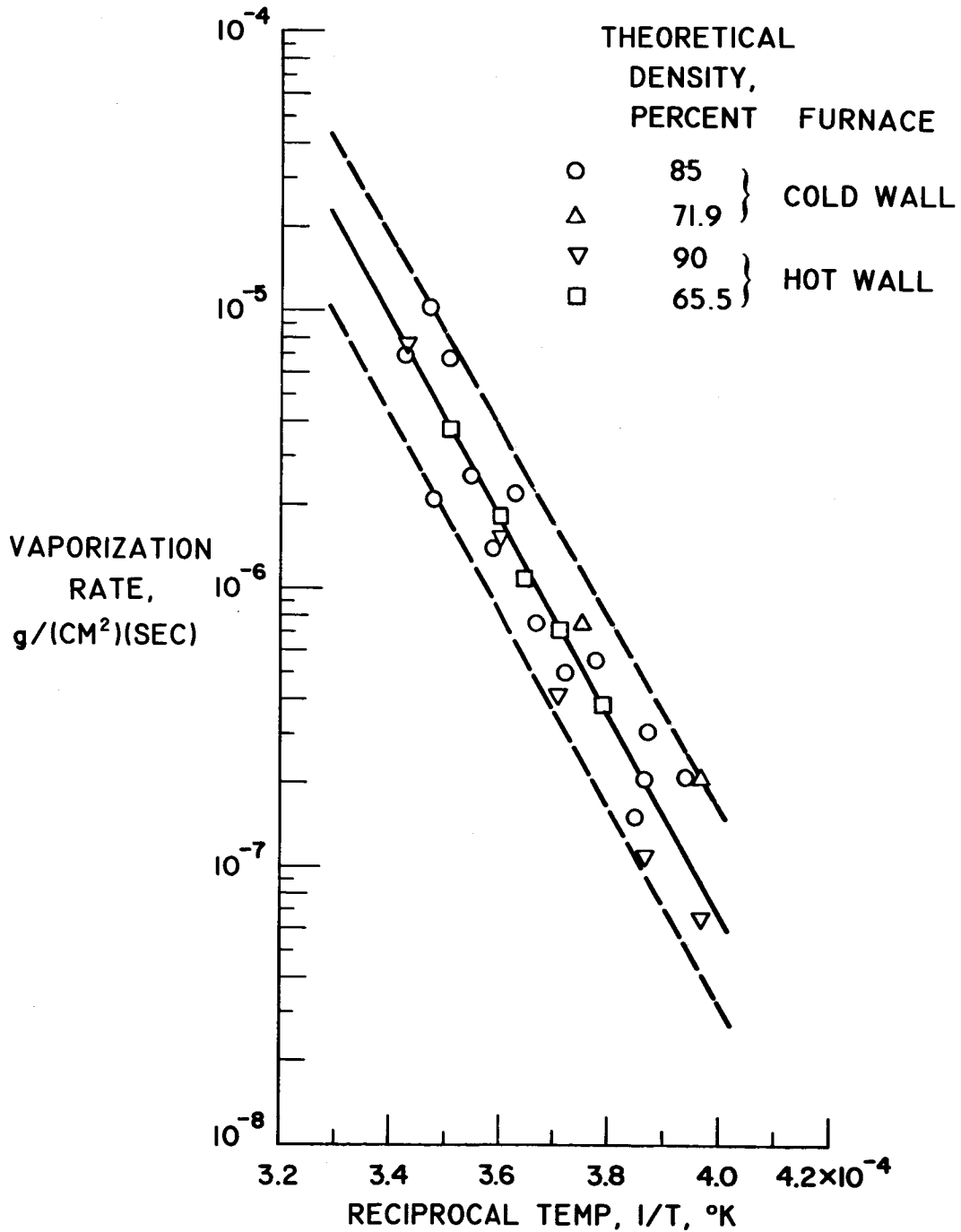


Figure 5

COMPARISON OF CARBIDE AND TUNGSTEN VAPORIZATION RATES IN VACUUM AS FUNCTION OF TEMPERATURE (LEAST-SQUARE LINES)

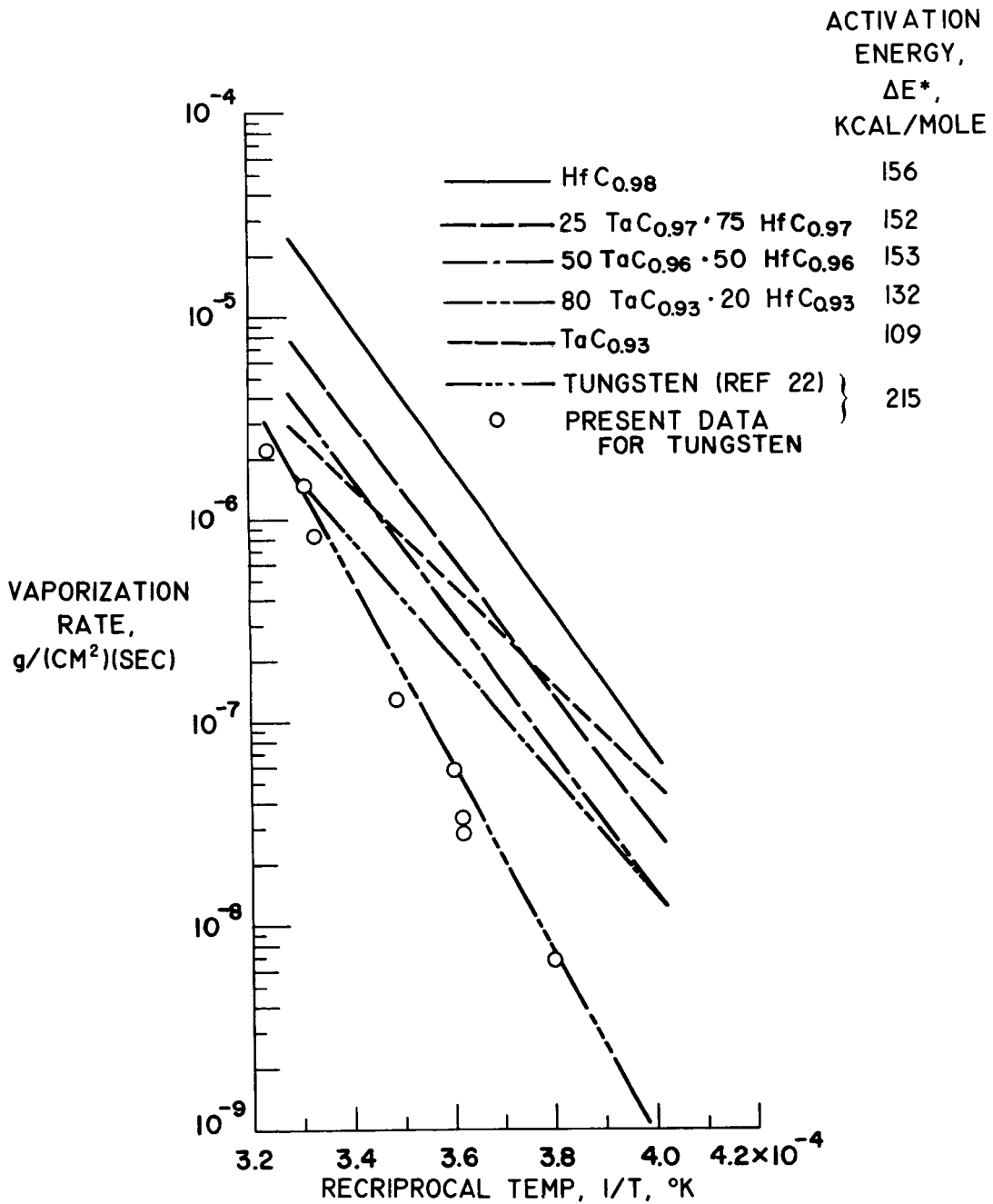


Figure 6

VAPORIZATION RATE IN VACUUM AS FUNCTION OF CARBIDE COMPOSITION AT 2500°, 2600°, 2700°, AND 2900° K

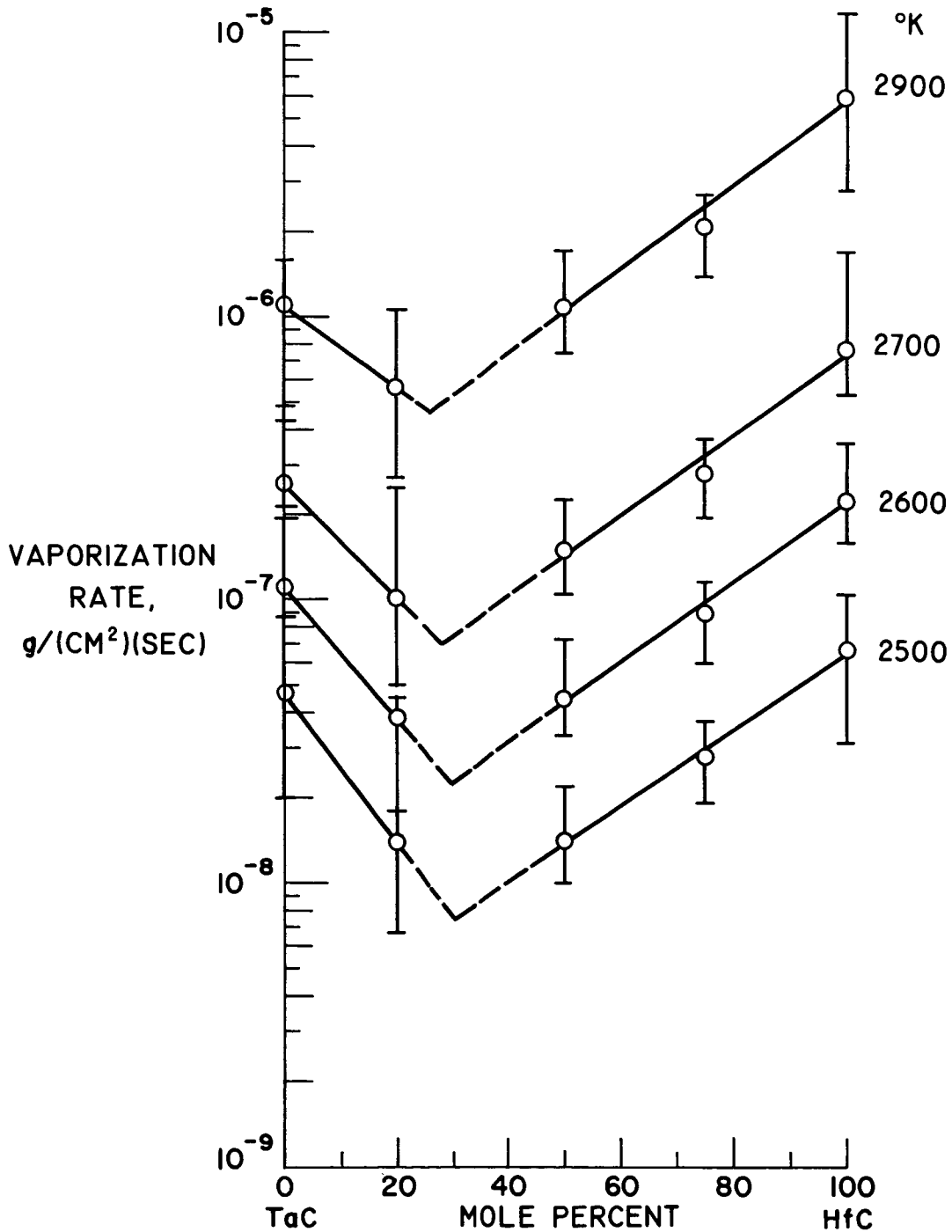


Figure 7