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FOREWORD

The ICRPG Working Group on Thermochemistry consists of individuals especially qualified by virtue of competence and experience in the areas of generation, evaluation and application of thermochemical data in rocket motor performance calculations. This Working Group, currently under the chairmanship of Mr. T. O. Dobbins of the Advanced Research Projects Agency, is successor to the JANAF-ARPA-NASA Thermochemical Panel.

The major part of this meeting was devoted to reviews and evaluations of recent advances in thermochemical data of interest and in experimental equipment and procedures. The proceedings are published in two volumes. This document, Volume I, contains the unclassified presentations while Volume II contains the Confidential presentations.

T. L. Reedy

RECENT MICROWAVE SPECTRA STUDIES OF HIGH TEMPERATURE SPECIES

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National Bureau of Standards, Washington 25, D. C.

Microwave spectroscopy is a valuable tool for determining the structure of molecules in the gas phase with high accuracy. However, the use of this method for studying molecular species in high-temperature systems involves a number of difficult experimental problems. The choice of materials with suitable electrical, mechanical, and chemical properties is not easy. Furthermore, the intensity of the spectra usually decreases rapidly with increasing temperature.

A high-temperature spectrometer has been constructed at N.B.S. and used to investigate several molecules. The waveguide is made of stainless steel and is contained in a quartz vacuum jacket. The central part is heated by an external tube furnace, while the ends are at room temperature. The sample is vaporized from a boat in the center and condenses in the cool region. The system has been operated up to 1000°C, and it can be used at frequencies up to at least 60,000 Mc.

The microwave spectra of both AlF and AlCl have been observed in the high-temperature spectrometer. These species were produced by reduction of the trihalides with aluminum metal at a temperature of 600-700°C. In the case of the fluoride, a mixture of AlF_3 and Al was placed in the hot zone. For the chloride, AlCl_3 was maintained in a separate chamber at a temperature of about 75°C, and the AlCl_3 vapor was passed over liquid Al in the hot region. The AlF and AlCl spectra are typical of diatomic molecules; the transitions were identified with complete certainty by measurement of nuclear quadrupole hyperfine structure and Stark effects. The molecular constants are given in Table I.

The spectrum of LiCl has also been measured and analyzed. This is the last of the alkali halides to be studied by microwave methods. The results are given in Table II.

Efforts have been made to observe spectra of polyatomic species, particularly the alkali hydroxides. However, these experiments have so far been unsuccessful.

TABLE I. MOLECULAR CONSTANTS OF ALF AND ALCL

	<u>AlF</u>	<u>AlCl³⁵</u>	<u>AlCl³⁷</u>
B_e	16562.5 Mc	7312.76	7140.70
α_e	148.4 Mc	48.10	46.32
r_e	1.65437 Å	2.13016	2.13016
μ	1.5 D	~ 1-2 D	
eqQ (Al ²⁷)	-37.6 Mc	~ -35 Mc	

TABLE II. CONSTANTS OF LiCl

	<u>LiCl³⁵</u>	<u>LiCl³⁷</u>
B_e	21181.1 Mc	20989.9
α_e	240.2 Mc	236.9
γ_e	1.2 Mc	1.2
r_e	2.02067	2.02067
μ (v=0)	7.12 D	7.12 D

APPLICATION OF THE TECHNIQUE OF MATRIX ISOLATION TO THE STUDY
OF THE INFRARED SPECTRA AND THE STRUCTURES OF INORGANIC
MOLECULES STABLE AT ELEVATED TEMPERATURES*

by

David White

Cryogenic Laboratory, Department of Chemistry
The Ohio State University

ABSTRACT

The analysis of the infrared absorption spectra of several inorganic molecular species trapped in solid rare gas matrices is discussed. It is shown that the interpretation of these spectra, to establish a frequency assignments and the molecular symmetries, depends in large part on the assumption that the vibrational isotopic shifts of trapped species are the same as those of the free molecules. The validity of this assumption is examined by a comparison of the gas phase infrared spectra of some simple molecules with their matrix spectra.

Since the first application by Linevsky¹ of the technique of matrix
(1) M. J. Linevsky, J. Chem. Phys., 34, 587, (1961).
isolation to the study of the spectra of molecular species stable at
elevated temperatures, a number of systems have been investigated. One
of the best examples of the usefulness of this technique to obtain a
frequency assignment and the molecular symmetry, from which thermo-
dynamic calculations using statistical methods can be made, is the study
of the infrared absorption spectrum of B_2O_3 ^{2,3}. Even though the spectrum
(2) W. Weltner and J. R. W. Wam, J. Chem. Phys., 37, 292 (1962).
(3) A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys.,
38, 87 (1963).

of this molecule is quite complex it is nevertheless possible from an
analysis of the $B^{10}-B^{11}$ isotopic shifts to make a complete assignment
of the fundamental frequencies and determine the molecular symmetry, C_{2v} .
It can also be shown that the B-O-B apex angle is considerably greater
than 90° , the expected value from purely valence considerations.

We have recently obtained the infrared absorption spectra of sev-
eral oxides of lithium trapped in solid rare gas matrices. The situation
here is considerably more complex than in B_2O_3 . On vaporization of solid
 Li_2O , a large number of molecular and atomic species are formed and
simultaneously trapped in the rare gas matrix. It is not possible to
find conditions which produce predominately a single lithium oxide vapor
species. In analysing the observed spectrum it is therefore necessary
to properly assign the observed bands to the different molecular species
trapped in the matrix. Figures 1 and 2 show the spectra of the matrix
isolated vapors. From the Li^6-Li^7 isotopic shifts it is possible to
show that the strong triplet at $986.5, 1010$ and 1028.5 cm^{-1} is due to

* This research is supported by the Chemistry Office of the Advanced
Research Projects Agency and monitored by the Office of Naval Research
under contract Nonr-495(12).

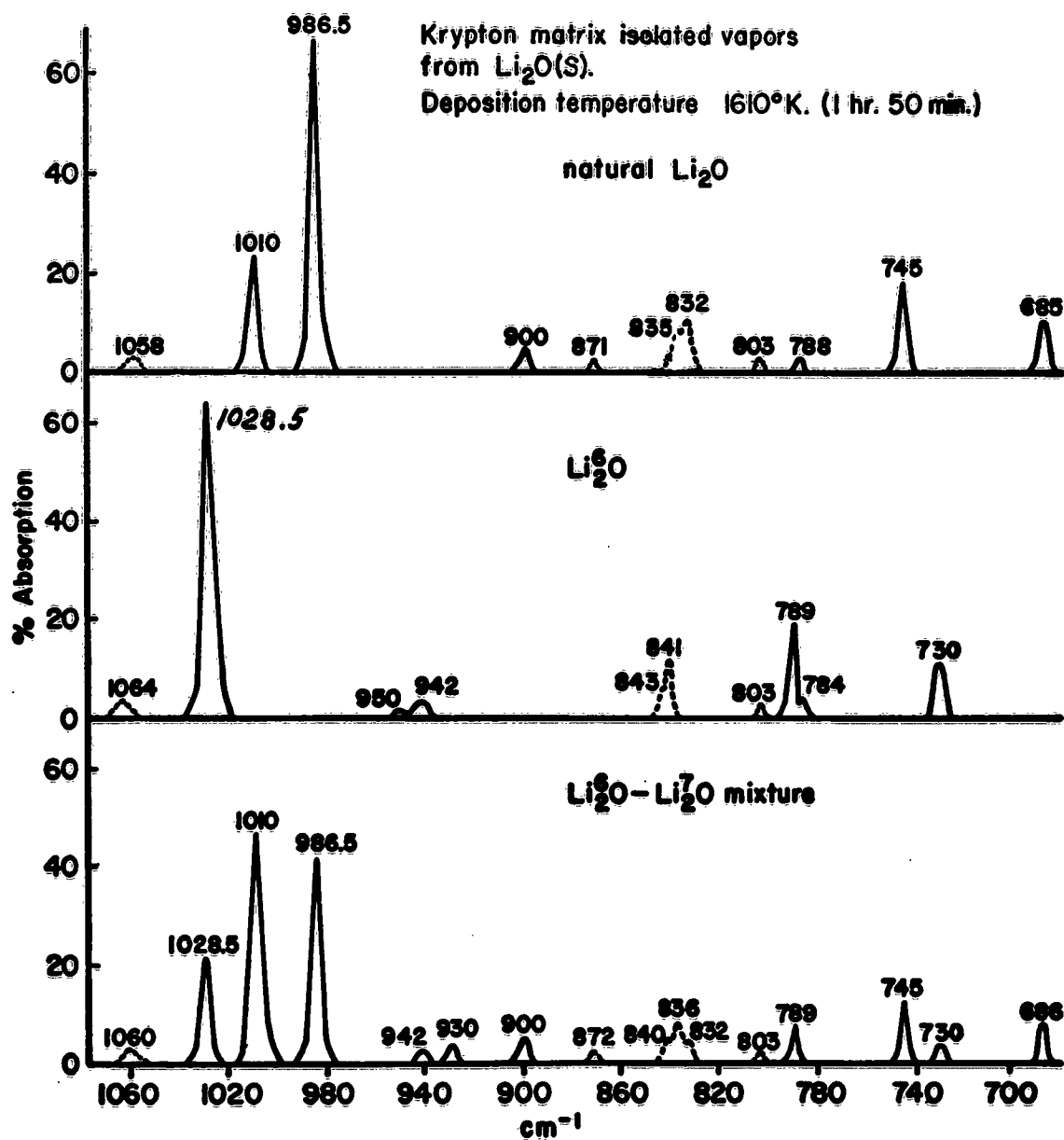


FIGURE 1. SPECTRA OF MATRIX ISOLATED Li_2O AND LiO .

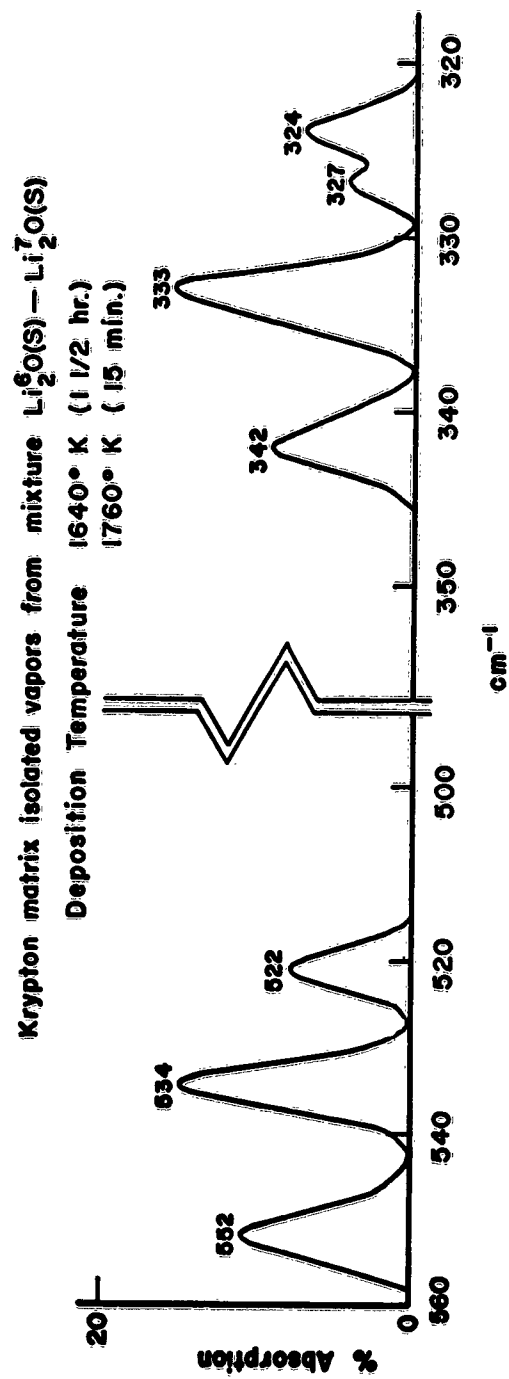


FIGURE 2. SPECTRUM OF MATRIX ISOLATED Li_2O_2 .

LiO and the low frequency triplets as shown in Fig. 2 due to the molecule Li_2O_2 . A detailed discussion of the results has been published very recently⁴. It is also possible to show, on the basis of the isotopic

(4) D. Waite, K. S. Seshadri, M. F. Dever, D. E. Mann and M. J. Linevsky, J. Chem. Phys., **39**, 2463 (1963).

shifts that the molecule Li_2O is linear and that Li_2O_2 is rhombic similar to the alkali metal halide dimers.

The use of isotopic shifts in the interpretation of above spectral data is based on two assumptions:

- (1) The force fields of isotopic molecules are identical. This is the basis of the Teller-Redlich product rule.
- (2) The observed fundamental frequencies of matrix isolated molecules are to a good approximation the zero order frequencies of the free molecule.

The first of these assumptions is practically always fulfilled. This has been demonstrated experimentally in a large number of cases. The second assumption has, however, not been carefully examined. Excepting in the case of hydrogen containing molecules, where the corrections for anharmonicity are large, the observed fundamentals of gaseous molecules are to a good approximation the zero-order frequencies. Thus the Teller-Redlich rule can be used to calculate vibrational isotopic shifts. If it can be assumed that the matrix frequencies are very nearly those observed in the gas phase then the second assumption would also be valid in the analysis of matrix spectra. In order to determine the relation between gas phase frequencies and matrix frequencies, the infrared spectra of some simple molecules trapped in solid matrices has been carefully studied. The results for HCl under conditions of medium and high resolution are described briefly below.

The matrix apparatus used in these experiments was miniaturized in order to permit flexibility in coupling to various types of spectrometers. The cryostat, cold window and radiation shield are shown in Fig. 3. It can be seen that the apparatus is very compact. The refrigeration for the cold window is supplied by a two stage Joule-Thomson liquifier which inserts in the tube supporting the cold window. A complete description of this cryostat has recently been published⁵. This cryostat has another advantage over the conventional designs using liquid refrigerants, namely the temperature of the cold window can be varied continuously in the temperature range 15 to 200°K.

The infrared absorption spectrum of HCl isolated in a solid argon matrix is shown in Fig. 4 at two temperatures, 4°K and 20°K. The isotopic concentration is that of naturally occurring HCl. The spectrum shows several sharp features which can be separated into two types by their temperature dependence. The pair of bands designated as Q, which are due to the isotopic species HCl^{35}Cl , HCl^{37}Cl , show no temperature dependence of the intensity. The intensities of the other features, designated P(1) and R(0), are very strongly temperature dependent. In fact the P(1) feature observed at 20°K disappears completely at 4°K. It reappears, however, on warming to 20°K so that the effect is reversible. It is obvious from these results that two different spectra are obtained for HCl trapped in the rigid matrix. One can be ascribed to HCl molecules in which

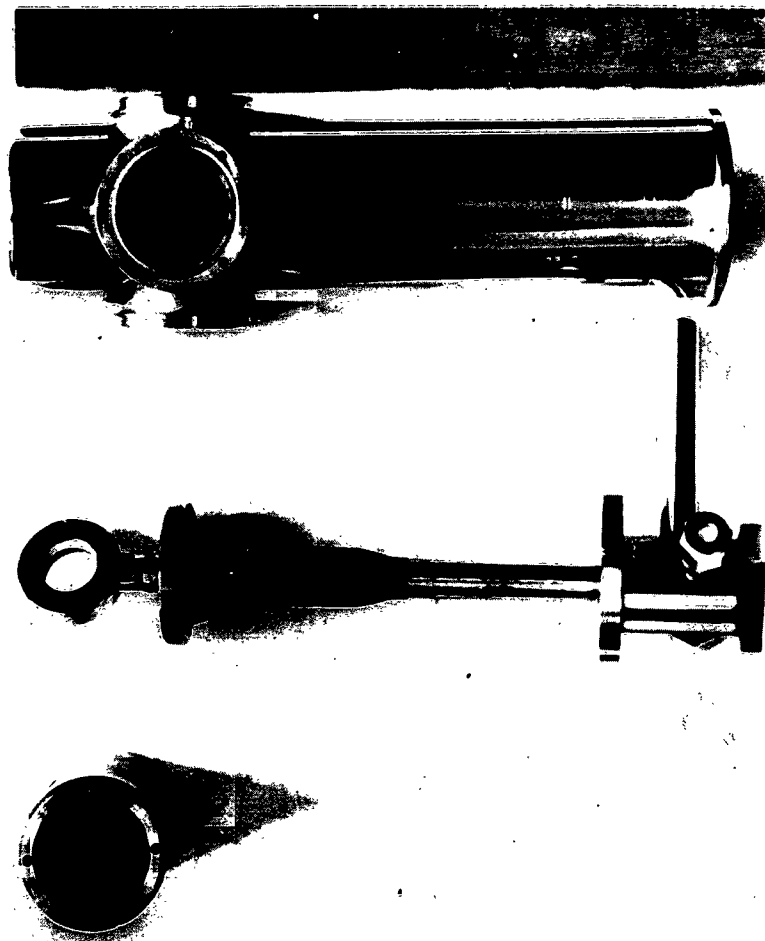


FIGURE 3. MINIATURE MATRIX CRYOSTAT.

H Cl⁺-Ar (1:1000) matrix

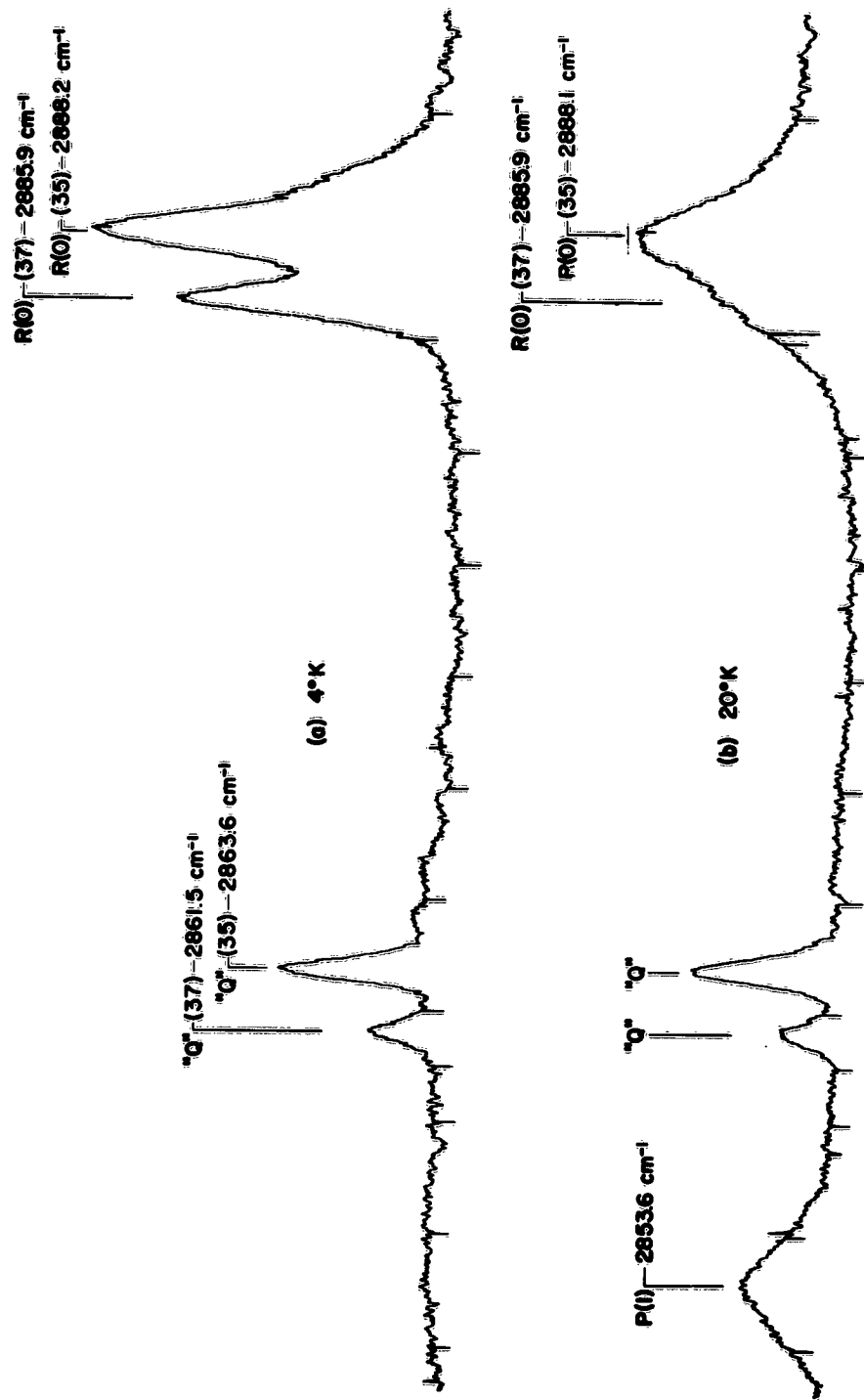


FIGURE 4. SPECTRUM OF MATRIX ISOLATED HCl.

the rotation is hindered, the R(0) and P(1) features. Since the P(1) band arises from transitions in the first excited rotational state, at 4°K this band is absent due to depopulation of this state. The second spectrum, the Q features, arise from HCl molecules whose rotations are completely quenched. This type of behaviour might explain the multiplicity of bands frequently observed in matrix spectra. This can be seen in Fig. 1 where two bands have been assigned to the same vibrational mode of LiO. A similar situation has, been found in matrix isolated LiF¹ and BO₂³. Another possibility for the occurrence of multiple bands is the freezing in of excited electronic states.

The infrared absorption spectrum of HCl has been examined under conditions of much higher resolution than shown in Fig. 4 to obtain more precise information on the isotopic shifts as well as the true band widths. The data shown in Fig. 4 were obtained using a Perkin-Elmer Model 99 monochromator fitted with a small grating. The high resolution data given below were obtained with a large grating instrument having a resolution of approximately 0.03cm⁻¹ in the region of the HCl fundamental. The high resolution data for HCl trapped in solid argon at 20°K are summarized below.

	HCl ³⁷ (cm ⁻¹)	HCl ³⁵ (cm ⁻¹)
Q of matrix spectrum	2861.477	2863.557
P(1) of gas phase spectrum	2863.007	2865.086

It can be seen that the HCl³⁷-HCl³⁵ shift in the matrix spectrum, 2.080cm⁻¹, is nearly identical to the isotope shift of the gas phase P(1) rotational-vibrational band, 2.079cm⁻¹. Thus to a good approximation matrix isotopic shifts are very nearly gas phase isotopic shifts. This has been verified not only in HCl but in a number of other cases. It should, however, the matrix band is shifted considerably from the gas phase band center. The shift in the case of HCl trapped in argon is approximately 22cm⁻¹ to the red or slightly under 1% of the fundamental frequency. The fact that the shift is nearly the same for both isotopic species can be accounted for on theoretical grounds.

The magnitude of the matrix shifts are of considerable importance in the analysis of isotopic shifts of matrix spectra using the Teller-Redlich product rule. Even though we have demonstrated that isotopic shifts in matrices are nearly identical to gas phase shifts in a large number of cases, the quantity of importance in determining molecular symmetry is not the shift but the ratio of frequencies. Thus the magnitude of the matrix shift determines the reliability of conclusions based on the product rule. In cases where the shifts are of the order of one to two percent of the fundamental frequency, or less, which seems to be the rule rather than the exception the product can be used with considerable confidence in the analysis of matrix spectra.

The high resolution spectra of simple molecules trapped in rigid matrices are of considerable importance in understanding the nature of the interactions between a trapped species and the host lattice. A complete discussion of this problem will be deferred to a latter date. It should, however, be pointed out that the half widths of matrix bands are quite small ... of the order of 0.2-0.3cm⁻¹. Thus small vibrational

isotopic shifts can be readily investigated. This is of considerable importance on the analysis of spectra of polyatomic molecules, particularly molecules containing a large number of atoms.

SOME RECENT INFRARED SPECTRA OF THORIA, ZIRCONIA AND HAFNIA
BY MATRIX ISOLATION

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ABSTRACT

The infrared spectra of several high temperature molecules, vaporized from thoria, zirconia and hafnia, have been observed using the technique of matrix isolation. Such molecules as ThO_2 , ThO , ZrO_2 , ZrO and HfO have recently been observed. A linear model for ThO_2 and ZrO_2 is consistent with the observed frequencies and tentative assignments for these molecules have been made. No evidence for HfO_2 molecule was found. The fundamental vibrational frequencies for ThO , ZrO and HfO were established.

INTRODUCTION

With the application of the matrix isolation technique to high temperature vapors¹, a new source of experimental spectroscopic data has become available which heretofore was unattainable. The technique has proved itself particularly well suited to the study of the infrared spectra of high temperature molecular species, and when used with isotopically substituted materials, has provided a powerful means of elucidating molecular structures.^{2,3,4}

As Brewer had recently pointed out⁵, there were no spectroscopic data available for any metal dioxide molecules and to our knowledge, this research represents the first attempt to obtain such information. The matrix isolation technique has been extended to materials that vaporize at temperatures as high as 2700°C and is possibly the only technique capable of obtaining infrared spectra of very refractory materials. Although it is at present impossible to obtain a complete vibrational frequency assignment on the oxides of thoria, zirconia and hafnia from our measurements, nevertheless, it is felt that the asymmetric stretching frequencies for ThO_2 and ZrO_2 can be reliably assigned and various possibilities for the other fundamentals can be inferred. It is anticipated that, by using isotopically substituted oxides (viz. ^{18}O enriched materials), complete assignments can be obtained.

EXPERIMENTAL

The basic experimental techniques have been adequately described elsewhere.¹ It was found necessary to modify the vapor source in order to attain high enough temperatures to effect the vaporization of the materials under investigation. Figure 1 gives a schematic of the new source used in these investigations. Essentially, the induction coils were moved from the outside of the quartz envelope to the inside so that better coupling and hence higher temperatures could be reached.

Vaporization was carried out from either tungsten or iridium cells having an orifice of approximately 2 mm. In the case of the iridium

cell, this was so constructed as to fit inside of a tungsten cell so that the tungsten cell acted as a susceptor. The iridium cells were fabricated by Englehard Industries and were of welded construction with the effusion orifice being the only opening. Loading of these cells was accomplished through the orifice. Temperatures were read on a black body hole located in the base of the tungsten susceptors with a micro-optical pyrometer. All matrix gases were Matheson research grade materials. Prior to isolation, samples were thoroughly degassed in situ at temperatures slightly higher than those at which isolation was carried out. Nevertheless, traces of water were still evident in the resulting matrix isolated spectra and indeed it is well known that both thorium and zirconia tenaciously retain water. The presence of small amounts of both CO and CO₂ were also evident in the various spectra and is presumably due to carbon impurity in the Knudsen cells or to the presence of carbonate in the refractory oxides. All spectra were recorded with a Perkin Elmer Model 112 double pass spectrophotometer in the region 2 μ to 40 μ .

The results for thorium, zirconia and hafnia are given below.

RESULTS AND DISCUSSION

Thorium The infrared spectrum of thorium in solid argon matrices was reported previously.⁶ At that time, those frequencies due to ThO₂ and to ThO were given along with a tentative assignment based on a linear molecular configuration for ThO₂. These spectra are included in Figure 2, (Spectra A and C). During the course of this year's investigation, the spectrum in solid argon was re-examined using an iridium cell and also spectra in solid krypton and xenon were observed. These spectra are given as B, D and E of Figure 2. Unless otherwise noted, the containers used were tungsten. The temperature of vaporization, T_v, and the time of deposition, t_v, are also included in Figure 2. The ratio of matrix to trapped species was estimated to vary between 500:1 to 200:1. It is evident from Figure 2 that the spectrum obtained from the iridium cell shows no signs of the presence of ThO (877 cm⁻¹ - 881 cm⁻¹ in solid argon), this frequency being definitely established by vaporization of a mixture of Th and ThO₂ (Spectrum C). Apparently, the amount of ThO in the vapor is greatly influenced by the tungsten crucible; however, the spectra show no evidence for any tungsten oxides and, indeed, except for the disappearance of ThO, the major bands are identical to the spectra obtained from tungsten cells. These major bands must be presumed to be due to ThO₂. The appearance of a very weak band at around 1030 cm⁻¹ and the disappearance of the very weak band at 1311 cm⁻¹ should be noted. More will be said about these bands when the results for ZrO₂ are given. The spectra obtained in solid krypton and solid xenon (D and E) show typical matrix shifts, the magnitude of which are quite reasonable. It is interesting to note that the weak band at 722 cm⁻¹ in solid argon does not have a counterpart in either solid krypton or solid xenon and for this reason might reasonably be regarded as a so-called matrix effect, peculiar to argon. The spectrum obtained in solid xenon shows peaks which are much broader and indeed in one case split (719 cm⁻¹, 721 cm⁻¹), indicating possible multi-sight matrix effects.

In general, the spectra are quite simple, with only one strong peak

(736 cm^{-1} in A) and one weak peak (approximately 787 cm^{-1} in argon), assignable to the ThO_2 molecule. The frequency around 880 cm^{-1} in argon must be assigned to ThO based on the spectrum obtained from the mixture of Th and ThO_2 . Regardless of whether the molecule is bent or linear, the strong peak (736 cm^{-1} in A) for ThO_2 is undoubtedly due to the asymmetric stretching frequency ν_3 , since in either configuration this mode should give rise to the most intense fundamental. Assuming a linear configuration, point group $D_{\infty h}$, two fundamental frequencies should be active. These are ν_3 and ν_2 (the bending mode), whereas ν_1 , the symmetric stretching frequency, is inactive. Unfortunately, the frequency ν_2 is most likely beyond the spectral range of our measurements ($> 40\mu$) and is, therefore, not observable. Using the equations for the linearly symmetric XY_2 valence force model, as given in Herzberg⁷, the fundamental ν_3 (736 cm^{-1} in A) gives a stretching force constant, $k_1 = 4.49 \times 10^5$ dyne/cm. With this constant and the above mentioned equations, ν_1 is estimated to lie around 680 cm^{-1} . If the frequency at 787 cm^{-1} in solid argon is due to a combination of $\nu_1 + \nu_2$ (active in $D_{\infty h}$), ν_2 must then lie around 110 cm^{-1} . Further credence to this assignment can be added by estimating ν_2 by a comparison with the CO_2 molecule. In CO_2 , the ratio of the bending force constant, $k_d/12$, to the stretching constant, k_1 , is equal to .0336⁷. Using this ratio, a bending constant for ThO_2 of around $.15 \times 10^5$ dyne/cm is obtained which yields a value for the bending frequency, ν_2 , of about 135 cm^{-1} . Considering the nature of this calculation, this is in good agreement with the 110 cm^{-1} value obtained from the combination band. On the other hand, if the molecule is bent (point group C_{2v}), all three fundamentals are active and the band at 787 cm^{-1} can conceivably be due to ν_2 . However, until further spectra on isotopically substituted materials are obtained, this possibility will be deferred. Indeed through the use of O^{18} enriched ThO_2 and the measurement of the resulting isotopic shifts of the observed frequencies, more definite conclusions can be obtained about the configuration and frequency assignment for this molecule.

Zirconia Matrix isolation of the vapors in equilibrium with zirconia was carried out in solid argon and solid krypton. Both tungsten and iridium cells were used as containers for the zirconia. The zirconia powder was obtained from the Zirconium Corporation of America, grade A-H, and had a purity of better than 99.9%. Isolation of the vapors from a mixture of Zr and ZrO_2 was also carried out in solid argon. Typical infrared spectra are given in Figure 3. The use of iridium cells proved to be somewhat marginal as containers for zirconia since it was found that temperatures in excess of the melting point of iridium were necessary to obtain reasonably intense spectra. Therefore, the spectra obtained from iridium are in general much weaker than those from tungsten. Except for two bands at around 1850 cm^{-1} , the infrared spectrum of zirconia (e.g. spectrum A, Figure 3) bears a close resemblance as far as relative distribution and intensity of the peaks are concerned, to that of thorium. This suggests that ZrO_2 is quite similar in structure and bonding to ThO_2 . The spectrum obtained from the mixture of Zr and ZrO_2 is particularly noteworthy. In this case, the most intense peak, 960 cm^{-1} , spectrum C, is undoubtedly due to ZrO since, in the presence of the metal, ZrO should be the major product of vaporization. The suggested ground state configuration for ZrO^8 is $^3\Delta$ with a vibrational frequency of 936 cm^{-1} . It has been our experience that in general matrix shifts are towards longer wave

lengths and our observed frequency of 960 cm^{-1} appears to be inconsistent with the reported value of 936 cm^{-1} for the vibrational frequency of the ground state.⁸ It is, of course, possible in the case of sizable molecules to have matrix shifts towards shorter wave lengths and thus account for this apparent discrepancy. However, an alternate explanation is possible. It has been suggested⁹ that indeed the ground state configuration for ZrO is $^1\Sigma$ with a measured vibrational constant of 978 cm^{-1} and that the $^3\Delta$ state is a very low lying excited state. If this is so, our value of 960 cm^{-1} is entirely consistent. A weak frequency at 925 cm^{-1} in solid argon and a stronger frequency at 913 cm^{-1} (spectrum D) in solid krypton are also observed. It is entirely conceivable that these lower frequencies belong to the $^3\Delta$ configuration (vibrational frequency 936 cm^{-1}) and in reality the $^1\Sigma$ state is the ground state of the molecule since the 960 cm^{-1} band is by far the most intense one. However, this explanation would demand that the population of $^3\Delta$ state is somehow frozen into the matrix even though the matrix temperature is quite low. Similar effects have been observed before in the matrix isolation of BO_2 .² If the above explanation is true, it would indicate that the ground electronic configuration for ZrO is $^1\Sigma$ rather than $^3\Delta$.

Similar to the case of thoria, the spectra obtained using iridium cells (spectra B and E) show no signs of the ZrO vibrational frequency and in this case, apparently there is an enhancement of ZrO when vaporization is carried out from tungsten cells. There is little doubt that the frequency at 818.7 cm^{-1} in argon and its counterpart at 810 cm^{-1} in krypton belong to the ZrO_2 molecule. The weak frequency at 884 cm^{-1} in argon and 878 cm^{-1} in krypton likewise can be assigned to ZrO_2 . This frequency is only evident in the spectra obtained from tungsten and is lacking in the spectra from iridium cells. However, the iridium spectra are quite weak and indeed the matrix may be too dilute so that this weak frequency is observable. A new, rather strong, band appears at around $1035\text{--}1041\text{ cm}^{-1}$ in solid argon (spectrum B) and at 1036 cm^{-1} (spectrum E) using iridium containers. It is very unlikely that this feature is due to ZrO_2 since it is not seen in the other spectra. It is possible that this feature is due to some iridium oxygen compound; however, it is felt that the stability of any iridium oxide would be much too small to make it stable at the temperatures of vaporization. An alternate explanation which appears to be more plausible is that these frequencies are due to the presence of ozone in the matrix. A very intense fundamental for gaseous ozone lies at 1043 cm^{-1} ¹³ and would be expected to shift towards longer frequencies in the matrix. In iridium containers, a great deal of oxygen is presumably evolved when zirconia is vaporized. It is altogether possible that this oxygen, when trapped in the matrix and simultaneously subjected to the rather large radiant flux from the hot Knudsen cell, can undergo a reaction to form a significant amount of ozone. In any case, these frequencies can not be assigned to the ZrO_2 molecule. A similar frequency was reported, although much weaker in intensity, in the spectrum of thoria contained in an iridium crucible. The frequencies in Figure 3 around 1300 cm^{-1} (1311 cm^{-1} in argon spectrum A) do not appear to be due to ZrO_2 since these frequencies, as mentioned previously, are also present in the spectra obtained from the thoria vaporization. It appears then that only the frequencies at 818.7 cm^{-1} and that at 884 cm^{-1} (both in solid argon) and their counterparts in solid krypton are assignable to the ZrO_2 molecule. These are quite

analogous to the ThO₂ frequencies, both in intensity and in relative wave length. Therefore, proceeding similarly to the ThO₂ case, the lower frequency is assigned to the asymmetric stretch, ν_3 . Again using a linear configuration, a stretching force constant, $k_1 = 4.65 \times 10^5$ dyne/cm. is obtained. This leads to a value of about 700 cm⁻¹ for the symmetric stretch, ν_1 . If the frequency at 884 cm⁻¹ is again assumed to be due to $\nu_1 + \nu_2$, a value of ν_2 around 184 cm⁻¹ is obtained. Using the ratio obtained from CO₂ for $k_d/l^2:k_1 = .0336$, the bending constant for ZrO₂ is equal to $.156 \times 10^5$ dyne/cm. and leads to a value of around 150 cm⁻¹ for ν_2 . Again it seems that the agreement is satisfactory. Further proof of the linearity of ZrO₂ is suggested by the structure of the 818 cm⁻¹ fundamental. Under the best resolution attainable in our experimental set-up (approximately 1.5 cm⁻¹), four shoulders are just discernable on the low frequency side of the 818 cm⁻¹ peak. Five naturally abundant isotopes are present in zirconium; these have masses 90, 91, 92, 94 and 96 and relative abundances of 51.5%, 11.2%, 17.1%, 17.4% and 2.8% respectively. It seems plausible to assign the five observed peaks, 818.7 cm⁻¹, 817.7 cm⁻¹, 815.7 cm⁻¹, 814.0 cm⁻¹ and 811.4 cm⁻¹ to ν_3 of each of the isotopic ZrO₂ molecules. Admittedly, because of the rather poor resolution, it is difficult to obtain good peak frequencies for these bands. Nevertheless, some indication of the O ZrO angle can be deduced from these frequencies using the usual equations for the frequency ratio for an isotopically substituted XY₂ molecule. The ratio for any two frequencies is given by:³

$$\frac{\nu_3}{\nu_3'} = \left[\frac{1 + \frac{32}{m_x} \sin \alpha}{1 + \frac{32}{m_x'} \sin \alpha} \right]^{\frac{1}{2}}$$

where m_x and m_x' are the atomic weights of any two zirconium isotopes and α is one-half the apex angle.

Indeed, using the observed frequencies, an apex angle around 180° fits the data satisfactorily. We hope to re-examine these bands under high resolution so that a more precise calculation can be carried out.

The bands around 1850 cm⁻¹ can only be accounted for as being due to some impurity or to low lying electronic transitions in ZrO₂. Their assignment to combinations or overtones in ZrO₂ does not seem to be likely.

Again, more definite conclusions concerning the frequency assignment and structure of ZrO₂ should be possible with the use of O¹⁸ isotopically enriched material.

Hafnia A sample of hafnia of better than 97% HfO₂ was obtained from the Zirconium Corporation of America, the major impurity being ZrO₂. Vaporization was carried out from tungsten cells on hafnia and a mixture of hafnia and hafnium metal. The resulting infrared spectra of the vaporization products in solid argon, krypton and xenon are given in Figure 4. Except for a band at 810 cm⁻¹ in solid krypton, assignable to ZrO₂, only a single feature appears in all the spectra. This feature (960 cm⁻¹ - 952 cm⁻¹) must be assigned to the HfO molecule since it is present in the spectrum obtained under reducing conditions (Hf + HfO₂). It should be noted that

the HfO and ZrO frequencies are very close and indeed are within several wave numbers of each other. This is somewhat unexpected in view of the fact that HfO is heavier and larger than ZrO. Indeed it is conceivable that the matrix shift in HfO is towards shorter wave lengths since this molecule is quite large and thus the observed matrix frequency of HfO lies close to that for ZrO. Again, it is seen (spectrum D Figure 4) that the xenon matrix gives a much broader appearing band.

No evidence for the HfO₂ molecule was found in the matrix spectra even at temperatures up to 2700°C (spectrum A).

In summary, the infrared spectra of ThO₂, ThO, ZrO₂ and ZrO have been observed in rare gas matrices. A linear model for ThO₂ and ZrO₂ is consistent with the observed frequencies and tentative assignments for these molecules have been made. No evidence for the HfO₂ molecule was found. The fundamental vibrational frequencies for ThO, ZrO and HfO were established. More definite assignments in the case of the triatomic molecules await the use of O¹⁸ isotopically enriched material.

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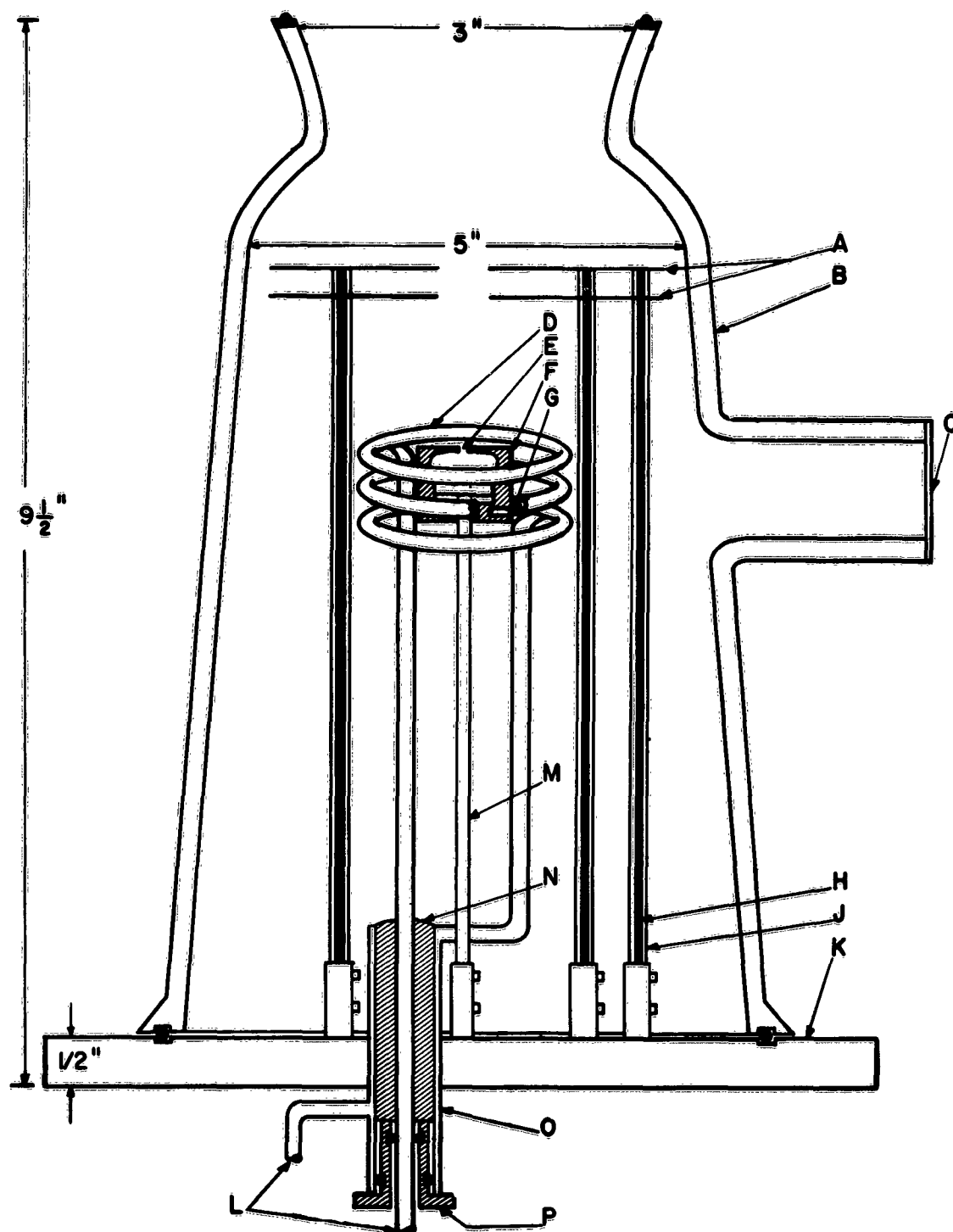


FIGURE 1. HIGH TEMPERATURE VAPOR SOURCE FOR MATRIX ISOLATION

- | | |
|------------------------------|-----------------------------------|
| A TANTALUM RADIATION SHIELDS | H TUNGSTEN SUPPORTS |
| B QUARTZ ENVELOPE | J QUARTZ SLEEVE |
| C QUARTZ WINDOW | K BRASS HEADER |
| D INDUCTION COIL | L WATER INLET AND OUTLET |
| E ORIFICE | M TUNGSTEN ROD |
| F KNUDSEN CELL | N and P TEFLON INSULATOR AND PLUG |
| G BLACK BODY HOLE | O WATER JACKET |

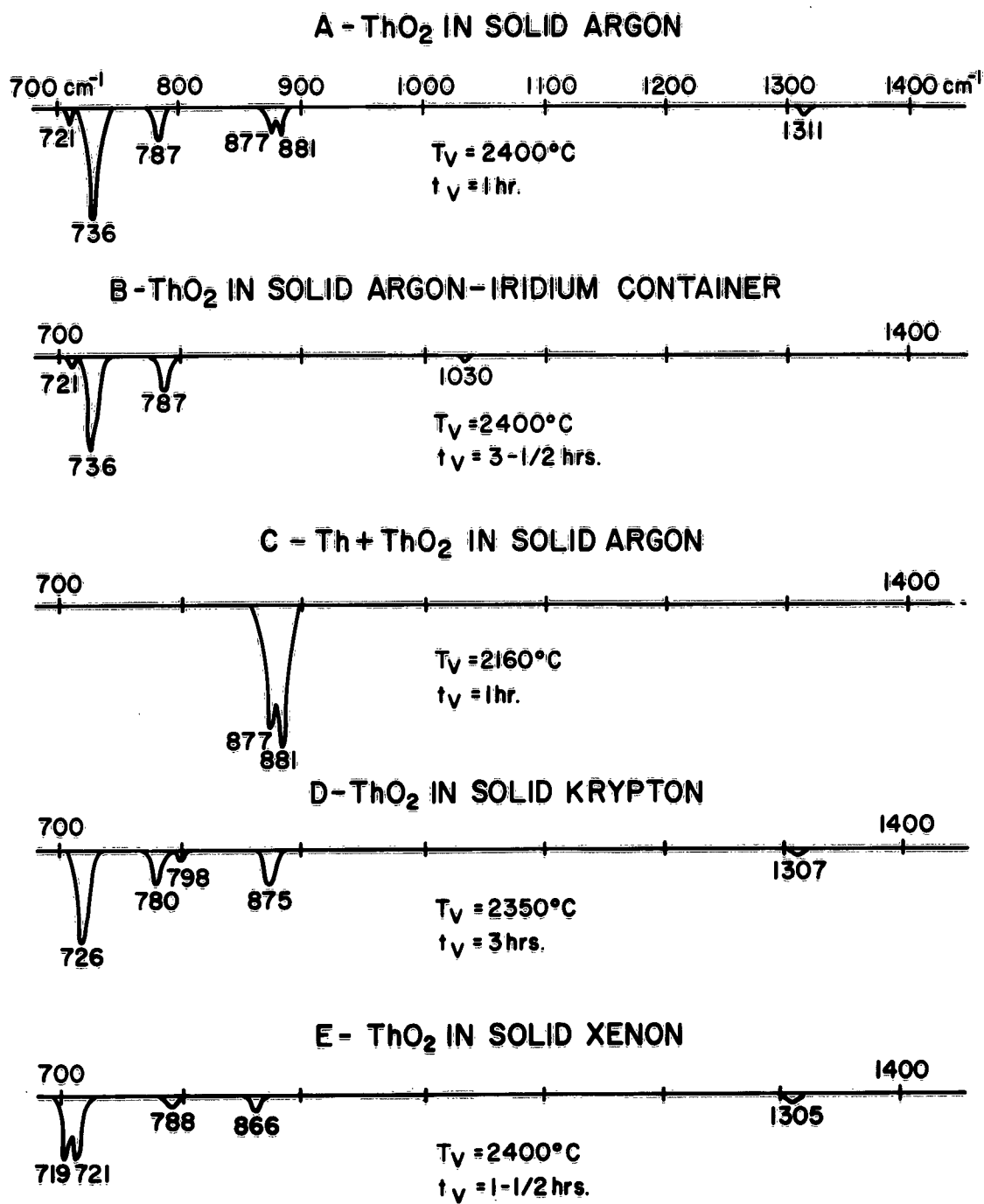


FIGURE 2. INFRARED SPECTRA FROM THORIA IN VARIOUS MATRICES.

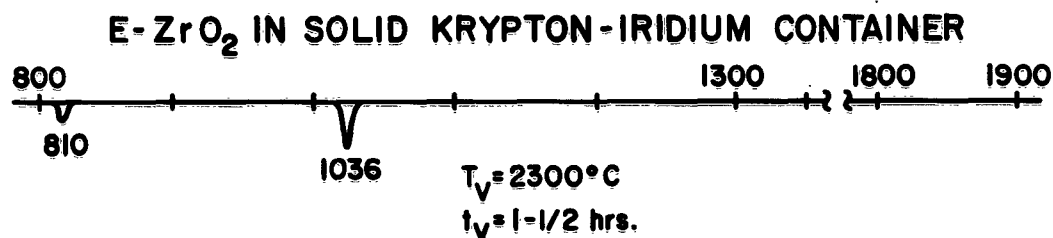
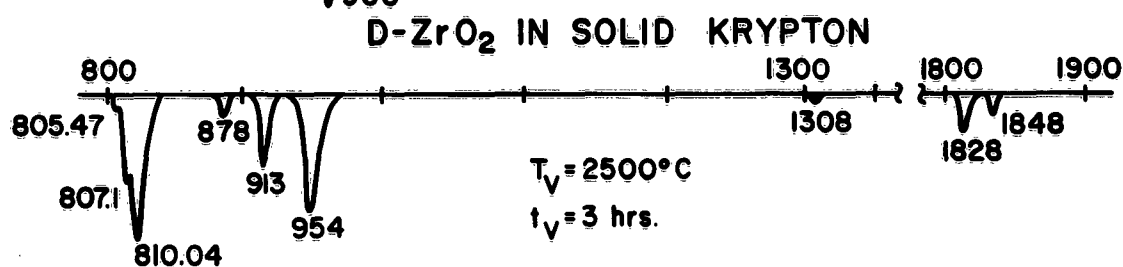
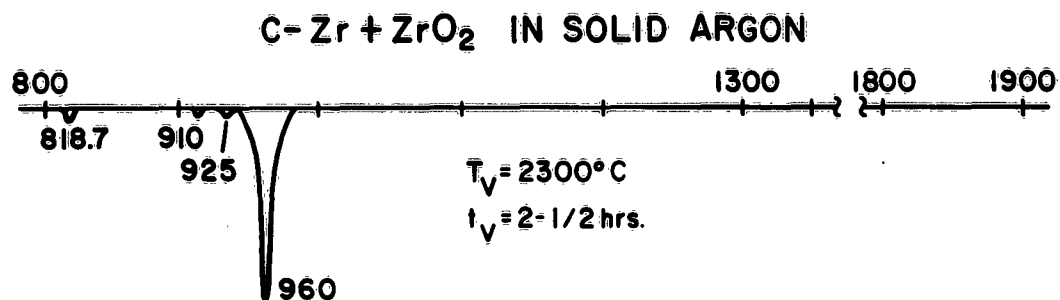
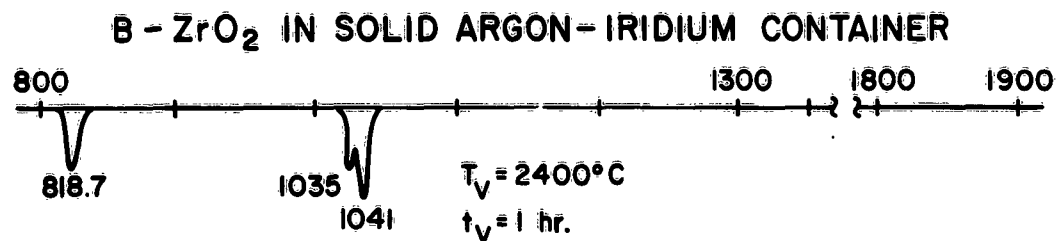
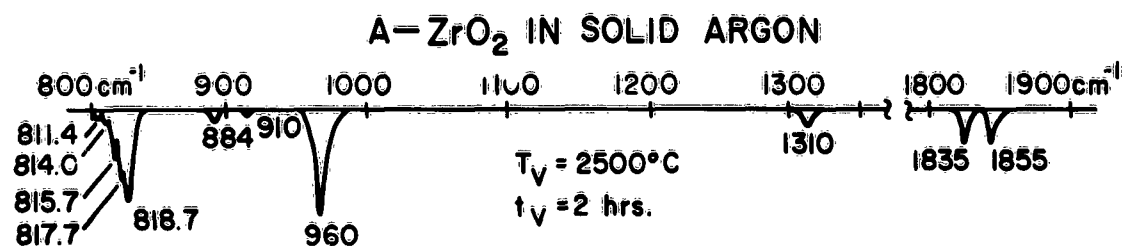


FIGURE 3. INFRARED SPECTRA FROM ZIRCONIA IN VARIOUS MATRICES.

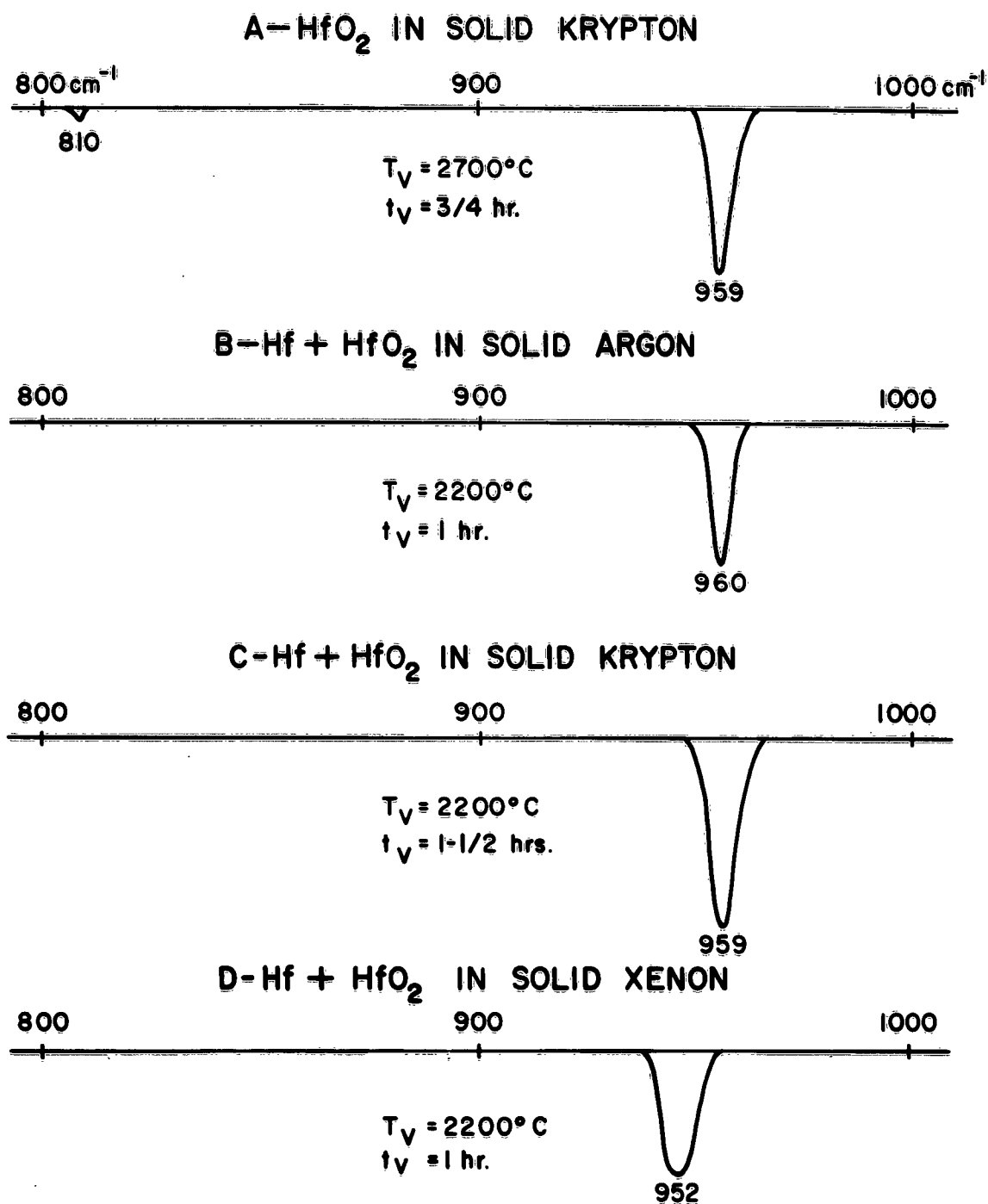


FIGURE 4. INFRARED SPECTRA FROM HAFNIA IN VARIOUS MATRICES.

INFRARED SPECTRA BY MATRIX ISOLATION OF SOME LOW-MOLECULAR-WEIGHT INORGANIC COMPOUNDS

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ABSTRACT

Some preliminary results of the matrix isolation studies on lithium fluoride, aluminum fluoride, and lithium metaborate are presented. It is too early to draw any firm conclusions.

INTRODUCTION

In this study the recently developed matrix isolation technique (ref. 1) is being used to obtain spectral data for the high-temperature vapor species of some low-molecular-weight inorganic compounds. These data will be used to calculate thermodynamic functions.

The equipment used in this work is similar to that of Snelson and Pitzer (ref. 2) and the notation is the same. M is the number of moles of matrix gas deposited on the cooled window and H is the number of moles of optically active species trapped in the matrix.

EXPERIMENTAL WORK

Lithium Fluoride

To establish an experimental technique for the new equipment, lithium fluoride was chosen as the test material. We selected this compound because it has been studied previously by the matrix isolation technique. (ref. 1, 2) In addition, the spectrum will be used for comparison when the two mixed-metal halides, lithium aluminum fluoride and lithium beryllium fluoride, are examined in the near future.

The infrared spectrum of the lithium fluoride which was isolated in an argon matrix is shown in Figure 1. The spectrum is the same as that observed previously except for two new absorption bands at 280 and 254 cm^{-1} . These bands were not observed in the earlier work because of instrumental limitations. It is too early to make an assignment for these new bands, but it is possible they are connected with the B_{1u} out-of-plane bending mode of the lithium fluoride dimer. More work will be done with isotopically enriched lithium fluoride to clarify this problem before work is done on the mixed metal fluorides of lithium, beryllium, and aluminum.

Aluminum Fluoride

Aluminum fluoride is assumed to have a planar configuration belonging to the point group D_{3h} which is analogous to boron trifluoride. Three of the fundamental frequencies are active in the infrared region; using the nomenclature of Herzberg, (ref. 3) they are ν_2 , ν_3 , and ν_4 . ν_3 and ν_4 are doubly degenerate and the totally symmetrical stretching vibration, ν_1 , is inactive in the infrared. Mass-spectrographic and vapor pressure measurements indicate the vapor species over solid aluminum fluoride consists

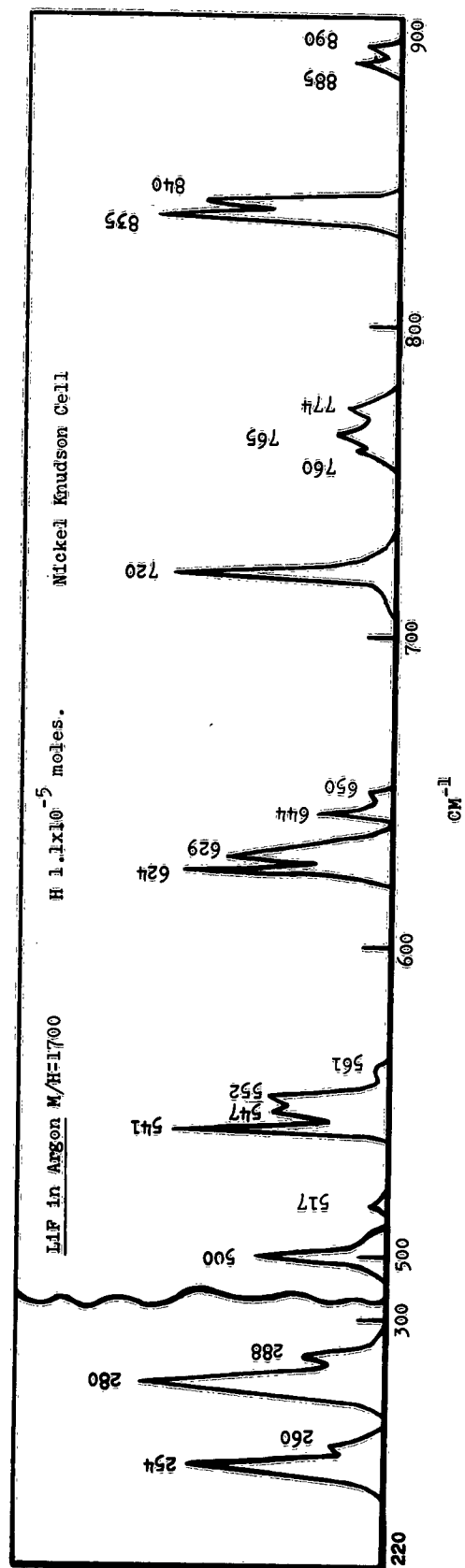


Figure 1
Infrared Spectrum of LiF in Argon

largely of monomer and a small percentage, 5%, of dimer. (ref. 4).

The infrared spectrum of aluminum trifluoride trapped in matrices of neon, argon, and krypton is shown in Figure 2. Effusion cells of graphite and platinum were used with no noticeable alteration in the structure of the spectrum. The purity of the aluminum fluoride was tested spectroscopically and found to be greater than 98%.

Interpretation of the infrared spectrum of aluminum trifluoride (Figure 2) is considerably more difficult than expected. Only one gas-phase infrared vibration frequency, at 945 cm^{-1} , has been observed. This was assigned to ν_4 . (ref. 5) Estimates of ν_2 and ν_3 at 400 and 300 cm^{-1} have been made. (ref. 6) Tentatively the frequencies, A, C, and D, are assigned to ν_4 , ν_2 , and ν_3 , respectively. No attempt has been made to explain the complex structure of these bands. It could be due to poor isolation of the active species; however, more experimental work is required to verify this point.

The presence of an absorption band at B is difficult to explain in terms of the molecule AlF_3 . The band might be due to the diatomic species AlF , which could result from the reduction of aluminum trifluoride. Diatomic AlF is a well-characterized species, and its visible spectrum is fairly well established. (ref. 7) The fundamental vibration frequency lies at 798 cm^{-1} in the ground state. Although the matrix frequency of the band at B is somewhat lower than the reported gas-phase value, a shift to the red is not uncommon in matrix work.

To test this possibility, the spectrum of AlF was observed by heating a mixture of aluminum trifluoride and aluminum. (ref. 7) The results for neon and argon matrices are shown in Figure 3. The strong absorption at A is undoubtedly due to diatomic AlF and establishes that the absorption band at B in Figure 2 cannot be due to AlF , since the frequency is distinctly different. In the argon matrix, the band due to AlF is split. This type of effect has been observed previously in matrix work. (ref. 1, 2) In the isolation experiment, $M/H = 5400$ (Figure 3), only two other weak absorptions occur at B and D. The former is ascribed to AlF_3 and the latter to polymeric material. In the experiments conducted at comparatively low M/H values, the intensity of the absorption band at D is greatly increased. In addition, certain other bands appear; these are also presumably due to polymeric species. There is a possibility that some of the weak absorption peaks which occur at low M/H values are due to AlF_2 . However, formation of this species is not likely on a thermodynamic basis.

More work is required to clarify many points in the spectrum of aluminum trifluoride, and it is hoped that this will be done shortly. In Figure 2 the absorption band at D is incomplete in the argon and krypton matrices; this is due to limitations in the spectroscopic equipment. We hope to extend the spectroscopic range from 245 to 200 cm^{-1} .

Lithium Metaborate

The matrix-isolation spectrum of lithium metaborate was observed in neon and argon matrices. The results obtained so far are complex. Some of this complexity is undoubtedly due to the mixed isotopic species, and before any useful results are obtained from this particular molecule, it will be necessary to use the monoisotopically substituted compound. Professor

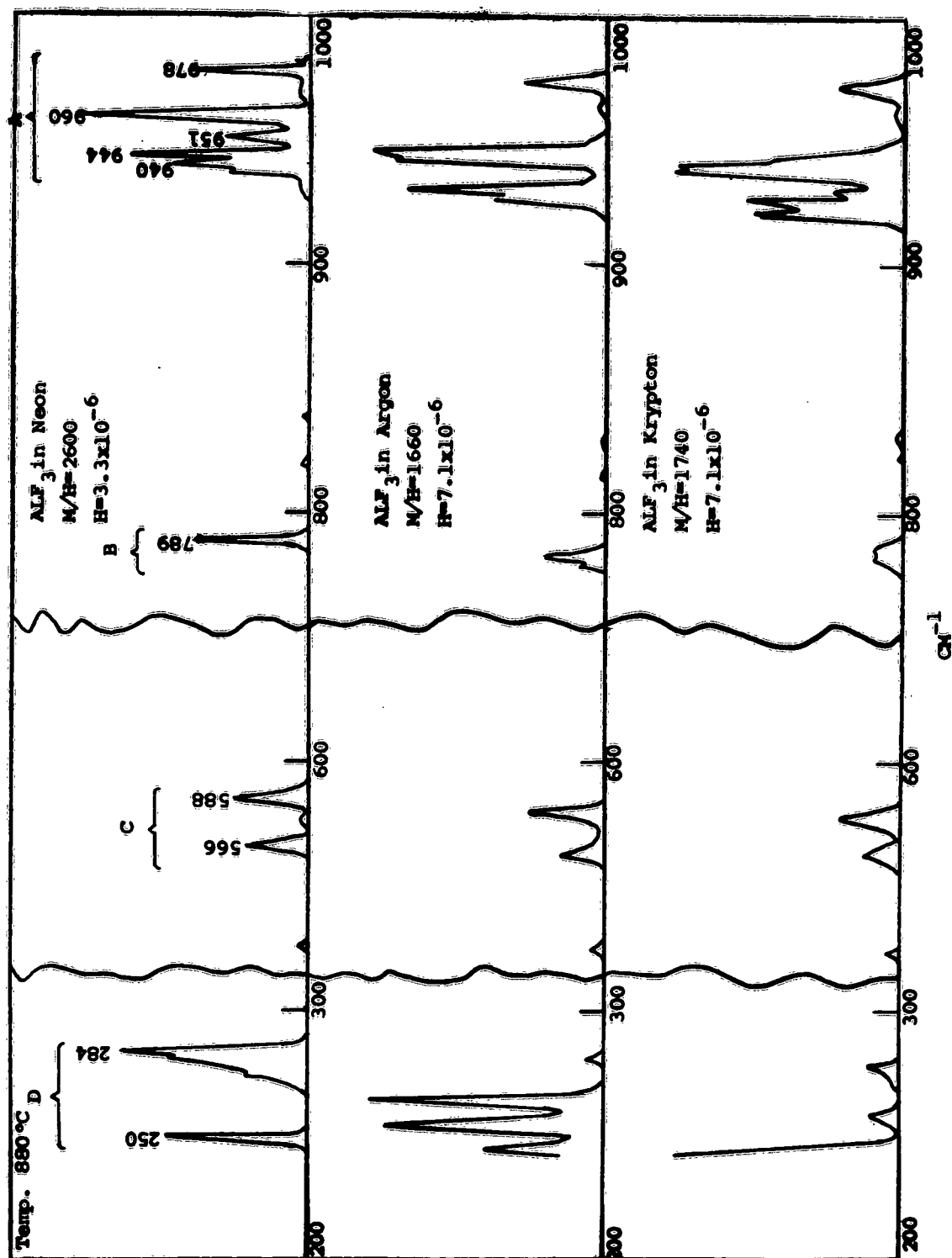


Figure 2
Infrared Spectra Of AlF_3 In Neon, Argon, And Krypton

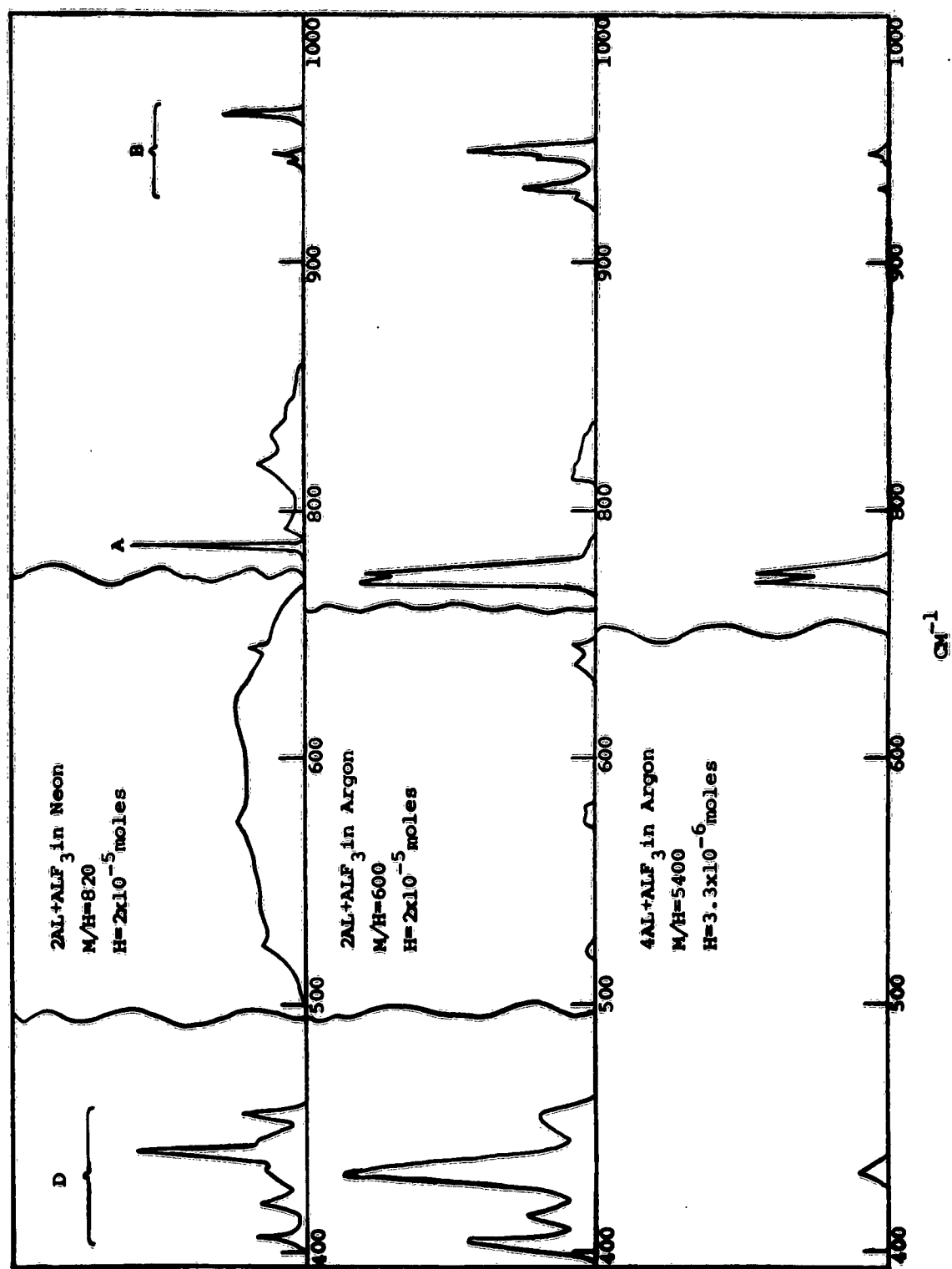


Figure 3
Infrared Spectra Of 2Al + AlF₃ In Neon And Argon

D. White indicates that the lithium metaborate spectrum is complicated by polymeric species. Unless the initial results of the matrix-isolation experiments with the monoisotopically substituted lithium metaborate show considerable simplification over the spectra observed thus far, work on this compound will not be continued.

CONCLUSION

As mentioned previously, these results are preliminary in nature, and it would be premature to draw any conclusions at this stage. It is hoped that the studies on beryllium fluoride, beryllium chloride, lithium-aluminum fluoride, and lithium-beryllium fluoride will be started shortly. In addition, if future studies on aluminum fluoride do not show any simplification at high matrix dilution, the matrix spectrum of boron trifluoride will be observed and used for comparison purposes.

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THERMODYNAMIC PROPERTIES OF VAPORIZING MOLECULES

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ABSTRACT

The thermodynamics of vaporization of some high-temperature materials is considered in the light of recent spectroscopic studies in these laboratories. The spectra of the vaporizing molecules were measured after trapping them in a solid inert gas at 4° or 20°K, i.e. the experiments utilized the matrix-isolation technique. The following materials were studied: boric oxide, carbon, silicon carbide, tantalum oxide, tungsten oxide, lanthanum carbide, and boron carbide.

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This is a brief review of the thermodynamic implications of some spectroscopic studies of vaporizing molecules made in these laboratories. The species investigated were vaporized from high-temperature materials and trapped, i.e. matrix-isolated, in a solid inert gas at 4° or 20°K. Spectroscopy was then applied to study the electronic states and vibrational frequencies of the molecules in this gas-like environment. This information is essential to the application of the third-law to mass spectrometry measurements of vapor pressure and the derivation of correct heats of vaporization. The materials investigated and the vaporizing molecules which have been studied spectroscopically are as follows:

1. boric oxide	→	$B_2O_3, (B_2O_2)$
2. carbon	→	C_3, C_2
3. silicon carbide	→	$SiC_2, Si_2C, Si_2, Si_2C_3$
4. tantalum oxide	→	TaO, TaO_2
5. tungsten oxide	→	$WO, WO_2, \dots$
6. lanthanum carbide	→	LaC_2
7. boron carbide	→	$BC_2, B_2C.$

Each of these systems will be considered briefly here.

1. Boric oxide is more relevant to chemical propellant than to materials research, but it was studied to demonstrate that the matrix isolation technique could be satisfactorily extended to the trapping of

"high-temperature" vapors in inert gas matrices at 4° and 20°K. This was successfully shown, and indeed, infrared studies of the trapped molecules led to large changes in the vibrational assignment of B_2O_3 and consequent changes in the thermodynamic functions. This work was carried out with J. R. W. Warn and has been published.¹ It has been corroborated by the more recent matrix study of Sommer, White, Linevsky, and Mann on B_2O_3 .²

2. Carbon vaporizes predominately to yield C_3 molecules and the properties of C_3 have eluded researchers for many years. Gausset, Herzberg, Lagerqvist, and Rosen³ have only recently made progress in their spectroscopic studies of this molecule. Their work, combined with our rather extensive studies in absorption and emission of C_3 trapped in neon matrices at 4°K, has led to the following ground state ($^1\Sigma_g^+$) vibrational assignment for C_3 : $\nu_1 = 1235$, $\nu_2 = 70$, and $\nu_3 = 2040$ cm^{-1} . The low bending frequency found by Gausset, et al, causes a large alteration in the free energy functions of C_3 and changes the ΔH° of vaporization from 188 to 205 kcal/mole. The former value was obtained by Drowart, Burns, De Maria, and Inghram⁴ from mass spectrometric measurements but utilizing an estimated value of $\nu_2 \cong 500$ cm^{-1} . The agreement between their second-law value (186.7 ± 1.5 kcal/mole) and their third-law determination has now been removed. This is puzzling in view of their careful second-law work involving the determination of C_3 to C signals at each temperature. However, there seems to be little doubt at the present time that the 70 cm^{-1} bending frequency is correct.

The original matrix work on C_3 and C_2 , carried out with P. N. Walsh has been published in a short note.⁵ Two articles with P. N. Walsh, C. L. Angell, and D. McLeod, Jr. are in press.⁶

3. Silicon carbide vaporizes predominately to silicon atoms, but the vapor also contains an appreciable concentration of SiC_2 and Si_2C molecules.⁷ These molecules, and also Si_2 and Si_2C_3 , have been observed spectroscopically in neon and argon matrices at 4° and 20°K when the vapor from silicon carbide (at 2500°C) is trapped. The aspects of these studies which affect the thermodynamics of vaporization of silicon carbide arise from a reassignment of the $Si=C$ stretching frequency in SiC_2 and the appearance of Si_2C_3 in the matrix. The force constant for the $Si=C$ bond in SiC_2 is found to be 7.4×10^5 dynes/cm as opposed to the less likely value of 2.9×10^5 dynes/cm found from Kleman's⁸ assignment by Drowart, et al.⁷ This is because of our revision of ν_1 from 591 cm^{-1} ⁸ up to 852 cm^{-1} . Using this new force constant

and others derived from C_3 ⁶ and Si_2 ,⁷ new sets of vibrational frequencies can be calculated for the vaporizing silicon-carbon molecules. However, the changes are not large enough to appreciably affect the thermodynamic functions.

The spectrum of Si_2C_3 appears strongly in the matrix, and since our vaporization temperatures are higher than those during the mass spectrometric work, it seems probable that Si_2C_3 is as important as SiC_2 in the vapor at these higher temperatures. This supports the extrapolation to higher temperatures of the meager vapor pressure data for Si_2C_3 of Drowart, *et al*, and indicates that Si_2C_3 should be included in their calculation of the total vapor pressure over silicon carbide.

The spectroscopic work on the silicon-carbon system was carried out with D. McLeod, Jr. and is about to be submitted for publication.

4. The vaporization of Ta_2O_5 has been studied in a mass spectrometer by Inghram, Chupka, and Berkowitz.⁹ The spectra of the TaO and TaO_2 molecules have also been observed in neon and argon matrices. Many electronic transitions were observed including the two TaO systems analyzed by Premaswarup and Barrow.¹⁰ Our work is in support of a $^2\Delta$ ground state for TaO . Both fluorescence and infrared absorption spectra and O^{18} substitution have given more information about the ground state, but the research is not complete as yet.

5. WO and WO_2 have been observed in a similar manner to the tantalum oxide case, but work has not progressed as far on this system.

6. An attempt was made to observe the spectrum of the LaC_2 molecule detected mass spectrometrically by Chupka, Berkowitz, Giese, and Inghram¹¹ over solid lanthanum carbide at 2500°K. Although the visible spectrum of neon and argon matrices contained several areas of absorption attributed to LaC_2 , the strength of the lanthanum atom bands masked any structural features. The infrared spectrum of an argon matrix at 20°K indicated that bands at 434, 1307, and 1831 cm^{-1} might be attributed to vibrations of this molecule in the ground state. If correct, these results indicate that the molecule contains a $C\equiv C$ unit.

7. The vaporization of boron carbide yields mostly boron atoms, but there are very small amounts of B_2C and BC_2 molecules in the vapor.¹² These molecules do not then contribute appreciably to the thermodynamics of vaporization of B_4C . Some attempts have been made to trap and measure their

spectra because of interest in their bonding properties. This work has met with some success, but it is incomplete at the present time.

ACKNOWLEDGMENT

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ULTRAVIOLET SPECTROSCOPY

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We begin by emphasizing that the interest of ultraviolet spectroscopists may be more properly described as electronic spectroscopy. The part of our interests appropriate for the present panel is in the electronic (and consequent geometric and vibrational) properties of small, unstable inorganic molecules. These properties have been elucidated, since the early days of quantum mechanics, mainly through high resolution ultraviolet, visible and near infrared spectroscopy of gas phases. For descriptions of excited electronic states, this method has been the exclusive experimental one, even for stable molecules. We shall give here a brief description of the spectrographs common to all such studies, a list of sources of radiation from molecules of interest, and a case history or two to illustrate the power and the limitations of the spectroscopic approach to the identification and detailed characterization of unstable species.

The spectrographs should be light-tight and self-contained units consisting of an entrance slit to accept light from the source under study, a diffraction grating (reflection) to disperse the light and a photographic plate-holder and plate for recording the spectrum. The grating may have a plane or concave surface. The former has the advantage of somewhat superior optical performance which must be balanced against the disadvantage of necessary auxiliary optics and reflections, with consequent light losses. For survey work, for example in searches for new spectra, the spectrograph might be about a meter long. For study of fine details the higher dispersion and practical resolving power of a five to ten meter instrument usually will be necessary. Particularly in the latter case the very fastest photographic surfaces known for each spectral region must be used. With high dispersion, the graininess of such surfaces is not disastrous.

Sources of interest which may be focussed on the slits of such spectrographs include arcs, sparks, flames, discharge tubes and electric furnaces. The latter two types have been by far the most fruitful for detailed study because it is possible to make the exciting conditions milder and the resulting spectra simpler. An example should make the distinctions clear. One of the oldest of known band spectra is the green emission from a boron flame or arc. However, the spectrum observed under these conditions of high temperature and pressure is so complex that interpretable features could not be resolved even under the very highest resolving power. In order to identify the emitter of the bands it was necessary to develop the bands in other

sources. One such source -- the simplest one -- has turned out to be a quartz electrodeless discharge tube through which BF_3 flows slowly at a pressure of a few millimeters of mercury. Rotational fine structure of the bands can then be resolved and its analysis shows beyond doubt that the emitter is the linear and symmetrical BO_2 molecule.

Another, more complete, case history should illustrate the dangers of casual identification of high temperature species. When aluminum metal is heated to about 2000°C in an electric resistance (carbon tube) furnace, an extensive emission spectrum can be observed in the visible and near-infrared spectral regions. This band spectrum was first observed by Zeeman who performed a vibrational analysis and assigned the emission to the AlC molecule. Since Zeeman was unable to obtain sufficient resolution to attempt a rotational analysis, he identified the emitter on less rigorous evidence. The vibrational structure of the spectrum is definitely that of a diatomic molecule, but Zeeman's vibrational frequencies $\omega_e'' = 350.01 \text{ cm}^{-1}$ and $\omega_e' = 278.80 \text{ cm}^{-1}$ seemed too low for AlC by comparison with the known values for the similar molecules AlO and AlF .

Zeeman performed experiments using a zirconia liner to exclude the presence of carbon from the region of the furnace from which spectra were observed, and, on the basis that the spectrum did not seem to occur with only aluminum in this liner, he concluded that the emitter must contain both aluminum and carbon. We have found that above about 1100°C aluminum reacts with zirconia to produce Al_2O_3 and we have not been able to obtain the spectrum in question by heating Al_2O_3 . In addition, we have observed the homonuclear diatomic molecules Ga_2 , In_2 , and Tl_2 under similar conditions and the vibrational frequencies observed for these molecules correlate quite well with those of "AlC". These facts led to extensive investigation of the "AlC" spectrum which resulted, through rotational analyses and the observation of alternation of intensity, in the definite assignment of the emitter as Al_2 . Rotational and vibrational constants were obtained for each electronic state.

It is instructive to compare these results to those of the mass spectrometric analysis of the aluminum-carbon system by Chupka, Berkowitz, Giese and Inghram. There, the only molecule identified definitely was Al_2C_2 , which was present in ten times the amount of any other molecule, including Al_2 . This is a typical result. As yet, few of the polyatomic high temperature molecules observed easily by mass spectroscopy have been identified definitely from their optical spectra. (That is, detailed characterizations such as those mentioned here have

been limited to a few polyatomic and very many diatomic molecules). It is not known whether this is because such spectra lie at wavelengths difficult to study or because they are largely predissociated. However, it does seem obvious that the two approaches, far from being competitive, are largely complementary, and that both are very necessary to further understanding of high temperature molecules.

X-RAY STUDY OF 1-ETHYLDECABORANE

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ABSTRACT

The molecular structure of 1-ethyldecaborane has been established by single crystal X-ray analysis. The compound crystallizes in the orthorhombic system with cell dimensions $a = 10.11$, $b = 14.40$, and $c = 7.28\text{\AA}$. The space group is $P2_1 2_1 2_1$ and the unit cell contains four molecules of $B_{10}H_{13}C_2H_5$. The compound is a simple substitution derivative of decaborane and no significant distortion of the decaborane configuration is induced by the substitution.

INTRODUCTION

In the last few years a great deal of work has gone into elucidating the chemistry and properties of boron hydrides. In most substitution reactions a variety of isomers are possible and the possibility of rearrangements of the boron and hydrogen atoms have to be considered. Even when one specific product has been isolated it, frequently, is difficult to be sure what it is that has been isolated. It was this type of question which led to the present work. A group at the National Bureau of Standards had separated a particular isomer of a substituted decaborane with the probable formula $B_{10}C_2H_{18}$. The problem was to establish whether it was an ethyl or a dimethyl derivative and where substitution had taken place on the decaborane molecule.

Experimental Procedure and Cell Data. The experimental procedures used are quite standard. The compound is a liquid at room temperature (melting point $\approx 10^\circ\text{C}$) and was supplied to us in thin walled capillaries. A low temperature arrangement was devised which enabled a single crystal to be grown and maintained at approximately -20°C on a precession camera. Film data was collected covering about two-thirds of the available reciprocal lattice. The intensities were read on a densitometer and corrected and scaled by standard methods.

The relevant symmetry and cell data are:

Space Group $P2_1 2_1 2_1$

a = 10.11Å

b = 14.40Å

c = 7.28Å

z = 4

$\rho_{\text{calc}} = 0.91 \text{ gm/cc}$

Structure Determination. The structure was established by the application of the Karle and Hauptman¹ phase determining procedures to the hk0 data. Enough phases were established to compute an electron density projection which revealed that the compound was an ethyl derivative and established the general location of the boron framework. Some trial and error procedures were then used to get the best boron arrangement consistent with the projection data. The best arrangement could be interpreted in terms of a decaborane molecule substituted at the B1 position.

The final projection is shown in Figure 1. The crosses mark the final refined positions. It is not necessarily obvious that the boron peaks correspond to a decaborane configuration, but, if the projection is considered in conjunction with a model on the same scale, the fit is excellent.

Having good x and y parameters from the projection and knowing the molecular orientation, the z parameters were readily obtained from an interatomic vector map. The boron and carbon positions were then refined by a least squares technique using all the data. The hydrogen atoms were located by a three dimensional electron density difference map to confirm that there was no rearrangement of hydrogen atoms. This was followed by a final least squares refinement of all the atoms.

RESULTS

The molecular configuration is shown in Figure 2. The ethyl group is attached to the boron 1 of an essentially undistorted decaborane molecule. It is tucked underneath the boron framework and the carbon atoms lie almost in a plane defined by B1, B3, and the midpoint between B6 and B9 so that the molecule almost has mirror symmetry. The C1 atom lies in the plane and the C2 atom is only 0.1Å out of the plane.

From the molecular packing, shown in Figure 3, it can be seen that the small deviation from mirror plane symmetry could be ascribed simply to packing considerations. If this is the case, then the isolated molecule in the liquid or gaseous state would be expected to effectively have mirror plane symmetry.

The bond distances observed in the boron and carbon skeleton are shown in Figure 4. These distances are all quite normal. The B-B distances, with one exception, agree within the limits of error with the values found for decaborane itself.^{2,3} The B2-B6 and B4-B9 distances appear to be significantly shorter than the other B-B distances in both decaborane and ethyldecaborane. However, in decaborane the B1-B3 distance is, also, in 1.71Å range. The longer B1-B3 distance in ethyldecaborane can be explained on simple steric grounds. The ethyl group lies directly underneath the B1 and B3 atoms. When all of the hydrogen atoms in the immediate neighborhood are considered, it is obvious that some crowding occurs which can most easily be alleviated by the stretching of the B1-B3 distance.

Distances involving hydrogens are not sufficiently accurate to warrant more than quoting average figures. The C-H and B-H (terminal) both average 1.1Å and the B-H (bridge) have an average value of 1.27Å.

SUMMARY

The net result of this study has been to confirm the existence of simple substitution derivatives of decaborane. This has been tacitly assumed in the past, but, since the structures of the acetonitrile⁴ and dimethyl sulfur⁵ derivatives of decaborane do have rearrangements of the bridge hydrogens, this is a point worth confirming. Also, substitution at the one position has been suspected but not unambiguously established before.

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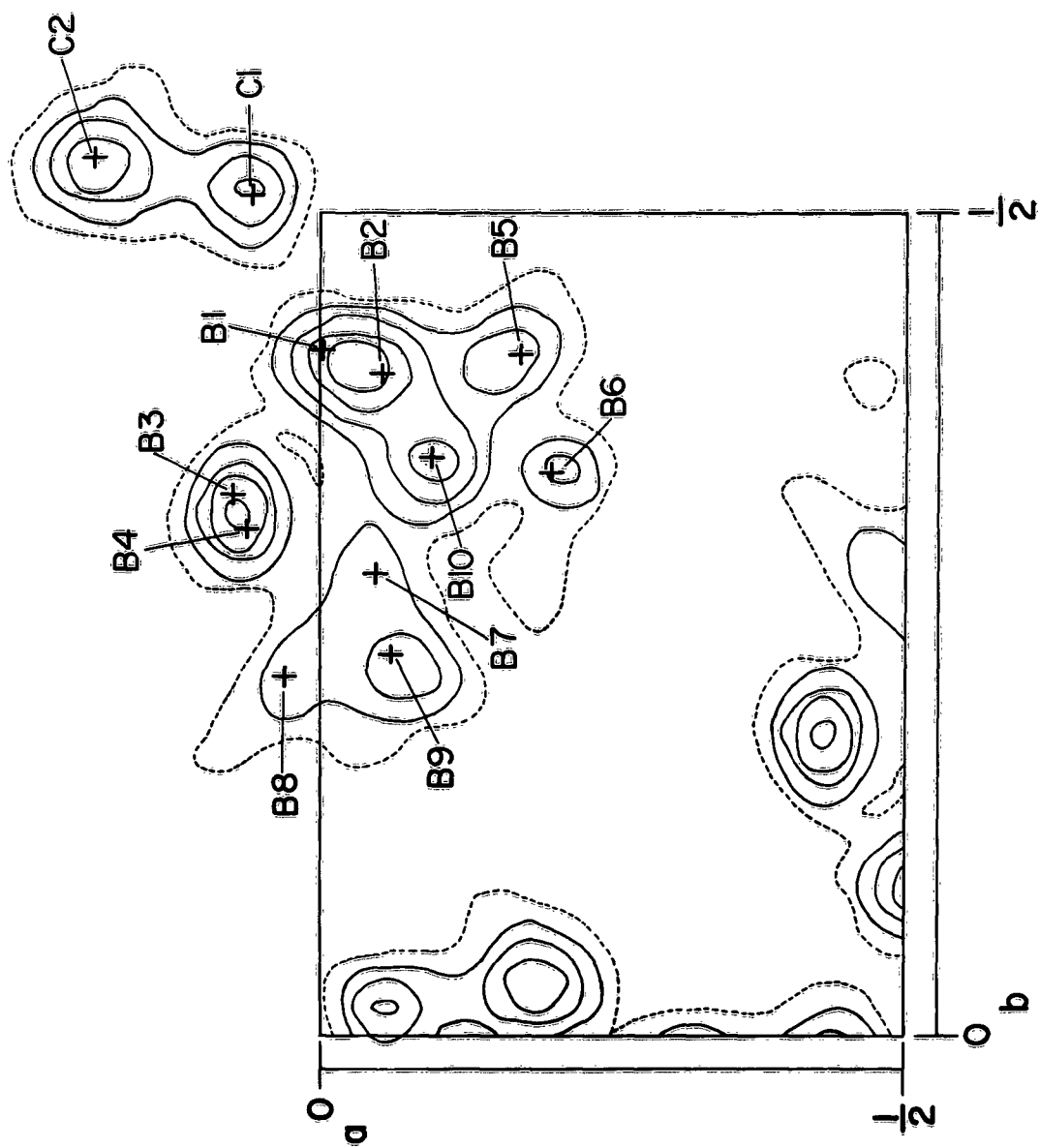


Figure 1. HKO ELECTRON DENSITY PROJECTION

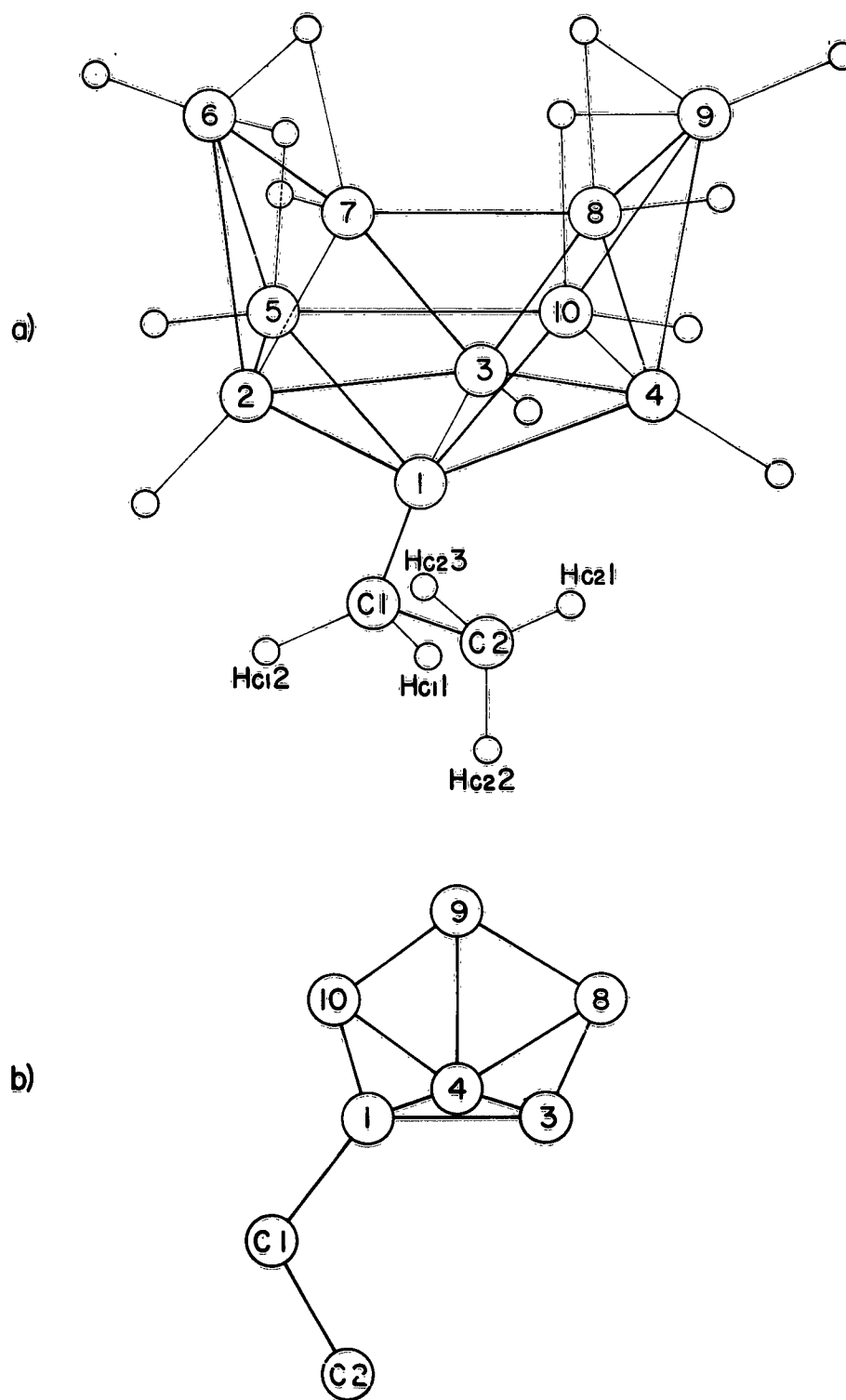


Figure 2. MOLECULAR CONFIGURATION

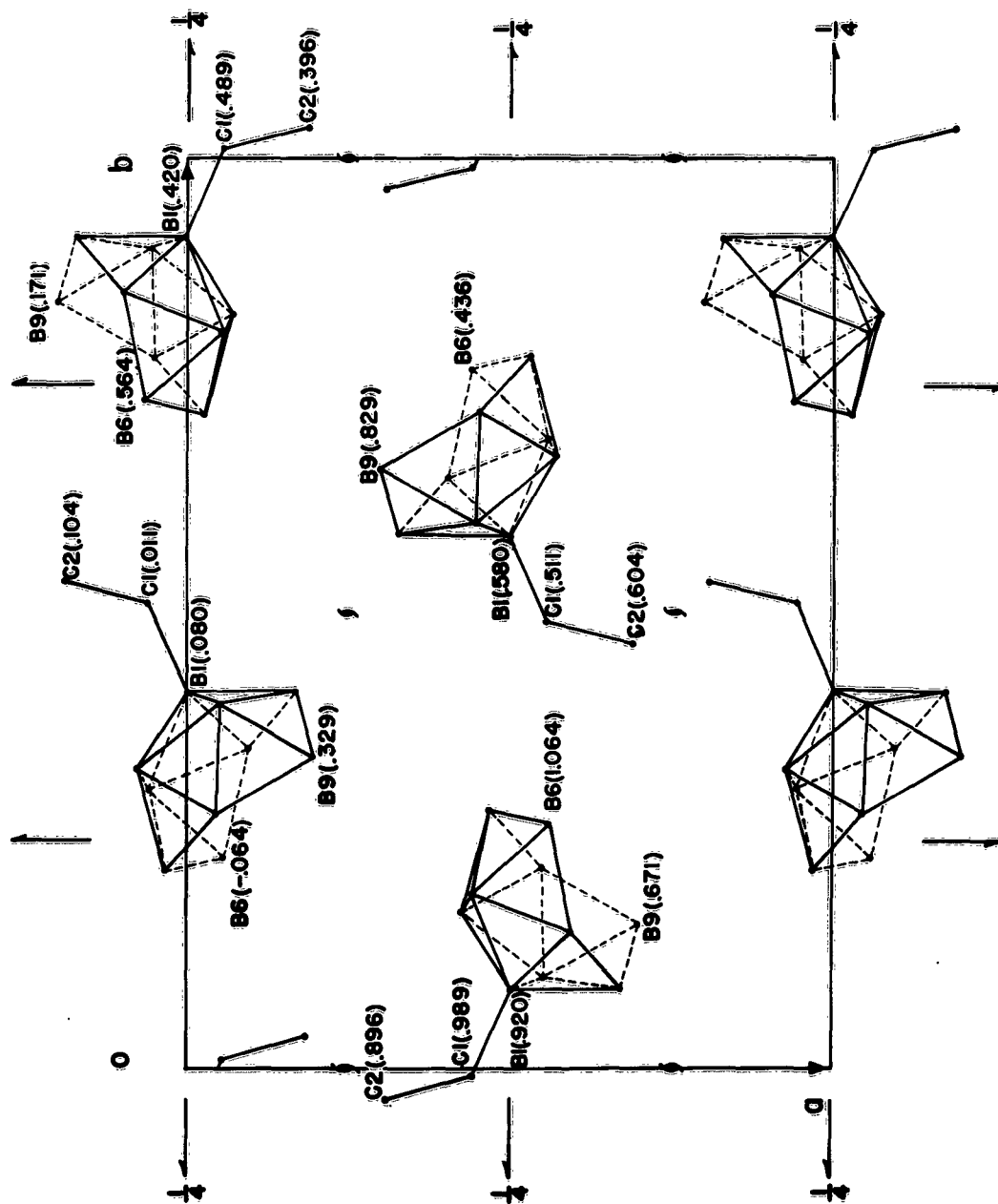


Figure 3. MOLECULAR PACKING.
PARENTHESES CONTAIN Z PARAMETERS OF INDICATED ATOMS.

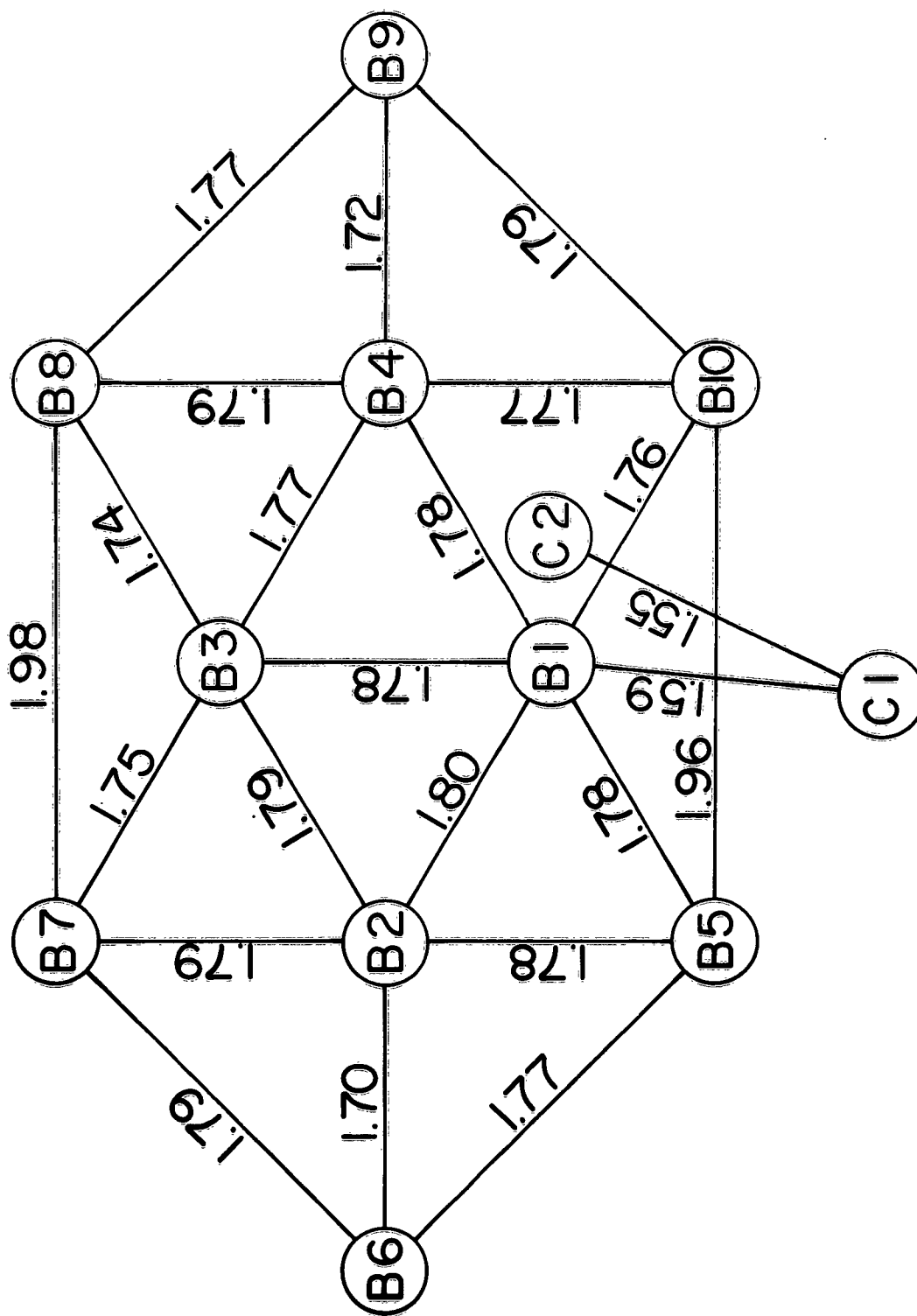


Figure 4. BOND DISTANCES IN ANGSTROM UNITS.

THERMOCHEMISTRY OF THE NOBLE GAS FLUORIDES

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INTRODUCTION

Since the announcement of the first authentic compound of a noble gas by Bartlett¹ a year and a half ago, and then formation of a binary compound containing xenon by Claassen, Selig and Malm² at Argonne National Laboratory, a great amount of theoretical and experimental interest in such compounds has developed among chemists.

Over the past six months several thermochemical studies have been reported. However, the number of existing noble gas compounds has also increased so that the rate of production of compounds continues to exceed the number which have been studied thermochemically.

The noble gas fluorides produced thus far are: XePtF₆, XeF₂, XeF₄, XeF₆, XeOF₄, XeOF₂, KrF₂, KrF₄ and Radon Fluoride. Other compounds that have been made include XeO₃, and Na₄XeO₆ · YH₂O. Heavy metal perxenates of barium, copper, silver, lead and uranium have been prepared from the sodium salts.

Thermochemical data have thus far been obtained only for XeF₂, XeF₄, XeF₆, and XeO₃. In most instances the purity of material has been less than is usually desired for definitive thermochemical data, but nevertheless has been sufficient for determining bond energies, tests of the third law of thermodynamics or of the correctness of some of the theoretical approaches.

THERMOCHEMICAL DATA

Xenon Tetrafluoride

Structure Xenon tetrafluoride has been found by x-ray^{3,4,5} and neutron diffraction⁶ and spectroscopic measurements⁷, to be a square planar molecule with the xenon atom in the center and four fluorine atoms at the four corners approximately 90° apart. The Xe-F distances are 1.95 (± 0.01) Å. The crystal is monoclinic with cell dimensions, a = 5.050 Å, b = 5.922 Å, c = 5.771 Å and β = 99.6° ± 0.1°. The structure may be visualized as a body centered cubic structure with the xenon atoms at the corners and the body center. The melting point is ~ 114° C. The x-ray density is 4.04 gr/cc.

Vapor Pressure The vapor pressure of XeF₄ has not yet been the subject of a separate study, however as a part of preparative studies⁸ it is reported to be 3 mm at 25° C.

Heat of Sublimation Jortner, Wilson and Rice⁹ have determined the heat of sublimation of XeF₄ over the temperature range from -15° C to 22° C in an ultra violet spectrometer by measuring the change in optical density at a constant wave length. A 2nd law plot of the log of the relative intensities vs 1/T°K have a value of ΔH sub (XeF₄) of 15.3 ± .2 Kcal/mole.

Heat of Formation The heat of formation has been determined from heats of reaction with aqueous iodide solution (Gunn and Williamson)¹⁰ and by reaction with HF (Stein and Plurien)¹¹. The values are not in good agreement.

$$\Delta H_f^\circ \text{XeF}_4 (\text{g}) = -45 \text{ Kcal/mole (Gunn and Williamson)}$$

$$\Delta H_f^\circ \text{XeF}_4 (\text{g}) = -55 \text{ Kcal/mole (Stein and Plurien)}$$

The Gunn and Williamson value was obtained for the solid (-60 Kcal/mole) and was converted to the gas phase using the heat of sublimation of Jortner, Wilson and Rice⁹. Gunn and Williamson estimate that XeF₂ impurities could further reduce their value by 10 Kcal. The average energy per bond calculated from these data and the heat of dissociation of F₂ of +37 Kcal, are not seriously different, being 30-32 Kcal.

Specific Heat We have determined the specific heat XeF₄ (containing about 2% impurities) between 30°K and room temperature. A small adiabatic calorimeter was used. The smoothed data are given in Table I. The shape of the heat capacity curve is similar to that of molecular crystals such as benzene or CO₂. There were no apparent abnormalities in the heat capacity data to room temperature. The entropy of XeF₄ at 298.16°K as determined from the heat capacity was 35.0 entropy units ± 1.

Standard Entropy and Free Energy of Formation $\Delta S_f^\circ(\text{s})$ and $\Delta F_f^\circ(\text{s})$ for the solid calculated from the above data and the $\Delta H_f^\circ(\text{s})$ of Gunn and Williamson, were -102.5 cal./mole deg. and -29.4 Kcal/mole respectively.

Third Law Check A check of the existing data by means of the Third Law of Thermodynamics has been made and found to agree to within the experimental error. The spectroscopic vibrational frequencies of Claassen, Chernick and Malm were used. The molecule has D_{4h} symmetry. The value of the ν₄ mode is still uncertain, however the suggested value of 221 cm⁻¹ is used in our calculation. A summary of the third law calculation is found in Table II. Although it is perhaps premature to make this comparison before more complete data are available, the close comparison indicates that no major features such as rotational transformations have been missed.

Xenon Difluoride

Structure Xenon difluoride is a linear molecule with the Xenon atom in the center and a Xe-F distance of 2.00 ± .01 Å^{3,12}. The crystal is body centered tetragonal. The melting point⁸ is reported as 140° C. The x-ray density is 4.3 gr/cc.

Vapor Pressure The vapor pressure has not been the subject of a specific study. Agron¹³ has reported a value of 3.8 mm at 25° C.

Heat of Sublimation The heat of sublimation has been determined by Jortner, Rice and Wilson⁹ to be 12.3 ± 0.2 Kcal/mole.

Heat of Formation A preliminary value for the heat of formation

of XeF_2 has been determined by Bisbee and Johnston, Hamilton and Rushworth¹⁴ by combustion with NH_3 in a standard combustion calorimeter. The XeF_2 sample used was found to contain 25% XeF_4 . The measured data were corrected for the energy released due to the XeF_4 by using Gunn and Williamson's value for the heat of formation of XeF_4 . The uncertainty in the XeF_4 data makes a minor contribution to the correction term. The value obtained is -28.5 Kcal/mole for the solid, with about 1 Kcal uncertainty. The Xe-F bond energy in XeF_2 is calculated to be 27 Kcal. There is no additional reported thermodynamic data on XeF_2 .

Xenon Hexafluoride

Structure The structure of xenon hexafluoride has not yet been established. It is expected that the molecule will be octahedral or a distorted octahedron. The melting point is reported to be 46°C . The material is very reactive and is difficult to prepare and retain in the pure state.

Vapor Pressure The vapor pressure is reported to be 29 mm at 25°C and 3 mm at 0°C .

Heat of Sublimation Values for heat of sublimation between 9 and $14^{10,15,16}$ Kcal/mole have been reported. Contamination with XeOF_4 is suspected to have caused the low results. The most reasonable values appear to be between those for XeF_2 and XeF_4 (13-14 Kcal/mole.)

Heat of Formation Stein and Plurien¹¹ have determined the heat of formation of XeF_6 by combustion in hydrogen at 130°C .

$$\Delta H_f \text{XeF}_6(\text{g}) = -78.7 \text{ Kcal/mole}$$

The average Xe-F bond energy in XeF_6 is calculated to be 31.5 Kcal. This value appears to be somewhat high in relation to that of XeF_2 and XeF_4 , but is sufficiently close for present needs. There is no known additional reported thermodynamic data reported for XeF_6 .

Other Noble Gas Compounds The only other known thermodynamic data in the literature is the $\Delta H_f(\text{s}) = +96 \pm 2 \text{ Kcal/mole}$ for XeO_3 reported by Gunn¹⁷.

SUMMARY

The preparation of stable chemical compounds containing the noble gases constitutes a notable event in the history of chemistry. Once again a tradition has been toppled. With every such break with the past, comes the need to understand just what has happened and to see if it can be applied to similar systems. More detailed information has been obtained about these compounds than exists for any other similar class of inorganic compounds. The interest in obtaining the thermodynamic stability of these compounds is obvious but the results are not limited to them. The preparation of these compounds is already contributing to the preparation of new compounds of analogous structure which do not contain noble gases

and is aiding in the understanding of the structures and bonding of the interhalogen compounds to use but two examples. As is indicated in this contribution, the thermochemical data is still rather limited but has nevertheless indicated the broad outlines of the stability of these compounds.

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This book is a publication of the Conference on Noble Gas Compounds held at Argonne National Laboratory in April 1963, and contains contributions from virtually every scientist who has done work in this field.

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TABLE I HEAT CAPACITY AND SPECIFIC HEAT OF XeF₄

<u>T°K</u>	<u>Specific Heat Cal/gram</u>	<u>C_p sat. Cal/mole</u>
10	.0012	.26
20	.0093	1.93
30	.0217	4.49
40	.0318	6.60
50	.0403	8.36
60	.0474	9.83
70	.0532	11.03
80	.0583	12.09
90	.0631	13.09
100	.0676	14.03
110	.0719	14.90
120	.0760	15.76
130	.0800	16.57
140	.0838	17.36
150	.0874	18.13
160	.0912	18.90
170	.0947	19.64
180	.0982	20.37
190	.1016	21.07
200	.1051	21.78
210	.1082	22.44
220	.1116	23.13
230	.1147	23.78
240	.1181	24.48
250	.1213	25.15
260	.1247	25.86
270	.1279	26.52
280	.1312	27.20
290	.1342	27.83
298.16	.1367	28.33
300	.1373	28.46

TABLE II THIRD LAW CALCULATION -XeF₄
Spectroscopic (XeF₄, gas, 1 atom, 298.16)

S°_{tr}	41.896
S°_{rot}	22.725
S°_{vib}	<u>13.058</u>
S°_{total}	77.67 eu

Calorimetric

XeF ₄ (s, 3 mm, 298.16)	$S = 35.0 \pm 1.0$ eu
XeF ₄ (sublimation = 3 mm, 298.16)	$S = 51.3 \pm .5$
XeF ₄ (g, 3 mm, 298) $\rightarrow$ XeF ₄ (g, 1 atom, 298.16)	$S = -11.0 \pm .7$
	<u>$S_t = 75.3 \pm 2.2$</u>

Difference 2.4 ± 2.2 eu

THERMODYNAMIC STUDIES ON SUBSTANCES OF INTEREST
IN A LIGHT ELEMENT PROGRAM. ^(a) PART 1. INORGANIC COMPOUNDS ^(b)

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A. A SURVEY OF THE THERMODYNAMIC DATA OF FLUORINE COMPOUNDS

Previous Publication

About two years ago we prepared a survey [1] of the heats of formation of inorganic fluorine compounds. In that survey the interval covered was from the time of compilation of NBS Circular 500 to about July 1961. The types of information included were enthalpies of reaction, transition, and change of state, as well as equilibrium data for similar processes. Heat capacity measurements, in general, were not included, though reviews giving tabulated thermal functions were. That survey will be taken as a starting point for our discussion.

The compilation that resulted from the survey was not intended to be a final selection of best values for the heats of formation of the compounds listed, but rather was intended to be a reference guide for the working chemist expecting to do a study of thermodynamic properties of one or more fluorine compounds. Such a person can expect to find in the compilation references to most of the studies of this kind that have been made on a particular fluorine compound, and some indication of the kind of information presented.

The tables were organized into sections as shown in Table I. The relative extent of the information contained in the tables is indicated roughly by the number of pages occupied by each section. The most information is available on the binary fluorine compounds, with decreasing amounts of information on more complex compounds. The format and some indication of the kinds of statements found in the tables are shown in figures 1 and 2.

TABLE I. TABLES OF THERMOCHEMICAL DATA

Table	Pages
1. Fluorine	1
2. Binary Fluorides	18
3. Ternary Fluorides	13
4. Quaternary and Higher Fluorides	10
5. Aqueous Fluoride Ion	1
6. Binary Aqueous Species	6
7. Ternary Aqueous Species	2
8. Quaternary and Higher Aqueous Species	1

(a) Material presented before the Thermochemistry Working Group Meeting, Nov. 5-8, 1963, New York, Sponsored by the JANAF Thermochemical Panel. The work described here was carried out under transferred funds contracts as noted and some of the survey of thermodynamic data on fluorine compounds was carried out using direct NBS support. Unless otherwise noted transferred funds were received under ARPA Order No. 20.

(b) Part II of this presentation is classified and appears in Volume II.

TABLE 1. FLUORINE

Substance	D_0 or ΔH° (kcal/mole)	Remarks
$F(g)$		N.B.S. Circ. 500 [9] gives 18.3 for $\Delta H_f^\circ_{298}$. See $F_2(g)$ for extensive later information.
$F_2(g)$	Experimental measurements leading to D_0 or ΔH° for dissociation have been reported as follows: 66[54], 50 ± 6 [55], < 45 [56], 37.7 at 759 to 1115°K or 38.9 at 1000°K[57], > 45 [58], 40-45[59], 37.7[60], 39.9 ± 0.8 [61], 37.0 ± 2 [62], 31.5 ± 0.9 [63], 37.6 ± 1.6 [64], 37.6 ± 0.8 [65], 31[66,67], 38 ± 0.4 [68, 69], 32 ± 3 [70], 37.5[71], 41.3 ± 0.5 [73], 37.1[92], 31.6 ± 4.3 [606], ≤ 39.0 [606].	Discussions and calculations of the dissociation energy have been reported by [9, 11, 14, 18, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 89, 90, 91, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 508]. [105] meas. v.p. and ΔH vap. [540] meas. ionization and dissociation by electron impact. [580] est. D_0 values from -34 to +180.
$F_2(l)$		[105] meas. ΔH fus.
$F_2(c)$		[105] meas. ΔH trans. (c,I) $\rightarrow$ (c,II).

Data in tables 1 - 8 are citations from the literature and have not been critically reviewed for this paper.

All numerical values are in kcal mole⁻¹ unless otherwise specified.

See [9] for additional references prior to 1949.

Superscript _a on ΔH_f values for Br and I compounds indicates that such values are based on $Br_2(g)$ or $I_2(g)$ as standard states.

FIGURE 1. THE TABLE ON FLUORINE.

Compound	ΔH_{298}° (kcal/mole)	Remarks
$\text{AcF}_3(\text{c})$		[20] est. $\Delta H_{298}^\circ = -395$. [12] est. -420 ± 10 . [106] reports ≈ -477 from consideration of the high temp. reaction: $3\text{Li}(\text{g}) + \text{AcF}_3(\text{c}) = \text{Ac}(\text{c}) + 3\text{LiF}(\text{l})$.
$\text{AgF}(\text{c})$	-48.5 [9]	[107] lists ΔH soln. [108] calc. lattice energy. Other reviews give for ΔH_{298}° : -48.5 ± 1.0 [15], -48.7 [12,20].
$\text{AgF}_2(\text{c})$	-88.5 [9]	Other reviews give for ΔH_{298}° : -83.0 ± 2.5 [15], -83 ± 4 [12].
$\text{Ag}_2\text{F}(\text{c})$	-50.4 [9]	[12] lists -50.3 for ΔH_{298}° .
$\text{AlF}(\text{g})$	-61.3 ± 2.0 [35] -49 [510] -59.2 [115] -61.4 [116] -50.9 [607]	The equilibrium: $2\text{Al} + \text{AlF}_3 = 3\text{AlF}$, was studied by [111, 113, 115, 510, 607]. Spectroscopic measurements of D_0 were reported by [74, 112]. [114] lists many ΔF reac. of $\text{AlF}(\text{g})$. D_0 is also reported or discussed by [11, 12, 14, 18, 37, 109, 110, 111, 115, 116]. [547] calc. binding energy. Other reviews give for ΔH_{298}° : -50 ± 5 [109], -51.4 [9], -55 [12], -60 [25], -60.1 ± 1 [26], -60.5 [21], -60.97 ± 1 [24], -61 ± 5 [17], -61.0 ± 2 [15], -61.3 [27, 37].
$\text{AlF}(\text{c})$ hyp.		[109] est. $\Delta H_{298}^\circ = -103$. [12] lists -102 . [34] lists -102 ± 10 . See also [514].
$\text{AlF}_2(\text{g})$ hyp.		[34] lists $\Delta H_{298}^\circ = -114 \pm 5$. [25, 27] est. -157 . [24] est. -172 ± 15 . [26] est. -172 ± 20 .
$\text{AlF}_2(\text{c})$ hyp.		[109] est. $\Delta H_{298}^\circ = -184$. [33] lists -184 ± 10 .
$\text{AlF}_3(\text{g})$	-284.8 ± 6 [34] -285.3 ± 2 [122]	[111, 120, 122, 123, 510] calc. ΔH sub. [121] calc. ΔH vap. [9] lists and [32] reviews ΔH sub. Other reviews give for ΔH_{298}° : -270 [33], -283.0 ± 2 [24, 26], -283.8 [21], -284.8 ± 6 [25, 37], -285.4 ± 5 [27]. See $\text{Al}_2\text{F}_6(\text{g})$ and $\text{AlF}_4\text{Li}(\text{g})$. [121] meas. v.p. [124] meas. ΔH fus.
$\text{AlF}_3(\text{l})$	-356.2 ± 2 [35]	[115, 117, 119] meas. ΔH for the reaction: $\text{Al} + 3/2 \text{PbF}_2 = \text{AlF}_3 + 3/2 \text{Pb}$. See also [116, 118]. See [45] for ΔH_f . [124] meas. ΔH trans. $\alpha = \text{AlF}_3 \rightarrow \beta = \text{AlF}_3$. [514] gives e.m.f. of $\text{Al} = \text{AlF}_3$ electrode. [111, 120, 121, 122, 123] meas. v.p. [38, 516, 517, 518] est. ΔH_{298}° . Other reviews give for ΔH_{298}° : -311 (est.) [9], -323 ± 5 (est.) [12, 20], -331.5 [2], -355.7 [21, 24, 26, 33], -355.8 ± 2 [15], -356.3 [25], -357.0 ± 2.0 [119], -356.3 ± 1 [17], -356.3 ± 2 [37], -356.3 ± 5 [34]. [517] also reviewed ΔH_{298}° . See also $\text{AlF}(\text{g})$, $\text{AlF}_6\text{Na}_3(\text{l})$.
$\text{AlF}_3(\text{c})$	-355.7 [115] -356.15 [116] -356.3 [116, 117, 118] -357.0 ± 2.0 [119]	

FIGURE 2. A SECTION OF THE TABLES OF BINARY FLUORINE COMPOUNDS.

It is of interest here to note how the amount of information available may fluctuate from one part of the table to another. This is roughly indicated by the extent of the remarks found by the compounds. Thus we see very extensive comments for $F_2(g)$ and $F(g)$ in Fig. 1 and also for most of the compounds and phases listed in the section on binary compounds dealing with the fluorides of aluminum, illustrated in Fig. 2. On the other hand, if we turn to a section of ternary compounds of aluminum, such as that dealing with $AlClF(g)$ and related compounds, Fig. 3, we find a remarkable decline in the amount of information available.

The difference in the available information is seen to be even more pronounced if one remembers the difference in the method of reporting the data in the various tables. Within the group of binary compounds, for which we note generally the greatest number of comments per compound, all compounds are listed so far as these could be discerned from the Chemical Abstracts indices and other sources, even though no thermodynamic data were found for them. On the other hand the ternary and more complex compounds are not listed unless thermodynamic data were found for them; and many were not listed for this reason.

Completeness of Existing Thermodynamic Data

A count was made of the compounds in the binary table. A total of 278 was found, roughly three fluorides per element. Those for which sufficient data have been presented to allow the listing of a heat of formation based on experiment numbered 93 compounds, and those for which some data were presented, but insufficient to calculate the heat of formation, numbered another 32 compounds. This left in the survey 153 binary fluorides for which no thermochemical data were presented.

The count of ternary fluorides was incomplete, and a very rough estimate of the possible number was made on the basis of a study of groups Vb and Vlb, for which a recent general survey by George [2] listed 45 compounds. Our tables presented data for 17 of those compounds. The ratio of these two numbers was applied to the remainder of the elements to obtain an estimate of the total number of ternary inorganic fluorine compounds.

The extent of thermodynamic data coverage of the fluorine compounds at the time of the survey is shown in Fig. 4. These kinds of estimates are extremely qualitative, because as time goes by more compounds are discovered, and in fact it is conceivable that measurements of physical properties could lag behind the rate of discovery of new substances.

During the time intervening since preparation of the survey, we have maintained the literature surveillance. The number of references in our file has increased from 625 to over 1100, an increase of about 500 articles in two years. A scan of the binary compounds indicates that of those having no thermodynamic data before, perhaps 5 to 10 percent have had a study sufficient to assign a heat of formation. This is a very small increment, considering the number of papers. The conclusion must be drawn, and this is easily verified by reference to the papers themselves, that the additional papers deal in large measure with compounds already having previous thermodynamic data listed.

TABLE 3. TERNARY FLUORIDES

Species	$\Delta H_f^\circ_{298}$ (kcal/mole)	Remarks
$\text{AcFO}(c)$		[166] gives $\Delta H_f^\circ_{298} \sim -265$ from consideration of the equilibrium: $\text{AcF}_3(c) + \text{H}_2\text{O}(g) \rightleftharpoons \text{AcOF}(c) + 2\text{HF}(g)$; at 1000° K.
$\text{AgAuF}_4(c)$	-149.4 [131]	[131] meas. ΔH hydr.
$\text{AgF}_2\text{H}(c)$ ($\text{AgF} \cdot \text{HF}$)		For the reaction: $\text{Ag}(c) + \frac{1}{2} \text{F}_2(g) + \text{HF}(l) \rightleftharpoons \text{AgF} \cdot \text{HF}(c)$; [178] est. $\Delta F^\circ_0 = -49.0$ on the basis of electrode potentials.
$\text{AlClF}(g)$		[25] est. $\Delta H_f^\circ_{298} = -121$; [24, 27] est. -123 ± 15 ; [26] est. -124 ± 20 .
$\text{AlClF}_2(g)$		[24, 26, 27] est. $\Delta H_f^\circ_{298} = -235 \pm 15$; [25] est. -235.5 .
$\text{AlCl}_2\text{F}(g)$		[27] est. $\Delta H_f^\circ_{298} = -181.8 \pm 15$; [24, 26] est. -186 ± 15 ; [25] est. -186.3 .
$\text{AlFO}(g)$		[24] est. $\Delta H_f^\circ_{298} = -103 \pm 20$; [25] est. -110 ; [26, 27] est. -121 ± 20 .
$\text{AlF}_4\text{K}(c)$ (KAlF_4)		See $\text{AlF}_5\text{H}_2\text{K}_2\text{O}(c)$.
$\text{AlF}_4\text{Li}(g)$ (LiAlF_4)		For the reaction: $\text{LiF} \cdot \text{AlF}_3(g) \rightleftharpoons \text{LiF}(g) + \text{AlF}_3(g)$; [125] meas. $\Delta H^\circ_{1000} = 73 \pm 4$; [122] calc. ΔH sub: [122] est. $\Delta H_f^\circ_{298} = -447 \pm 7$.
$\text{AlF}_4\text{Li}(c)$		[122] meas. v.p. [122] est. $\Delta H_f^\circ_{298} = -512 \pm 5$.
$\text{AlF}_4\text{Na}(g)$ (NaAlF_4)		[121] meas. ΔH vap. See $\text{AlF}_4\text{Na}(l)$ for v.p. studies.
$\text{AlF}_4\text{Na}(l)$		For the reaction: $\text{Na}_3\text{AlF}_6(l) \rightleftharpoons \text{NaF}(l) + \text{NaAlF}_4(l)$; [344] meas. $\Delta H^\circ_{1000} = 22$; [121, 577] meas. v.p.
$\text{AlF}_4\text{Na}(c)$		[345] discusses stability.
$\text{AlF}_6\text{K}_3(c)$ (K_3AlF_6)	-777.9 [9]	
$\text{AlF}_6\text{Na}_3(g)$ (Na_3AlF_6)		See $\text{AlF}_6\text{Na}_3(l)$ for v.p. meas.

FIGURE 3. A SECTION OF THE TABLES OF TERNARY FLUORINE COMPOUNDS.

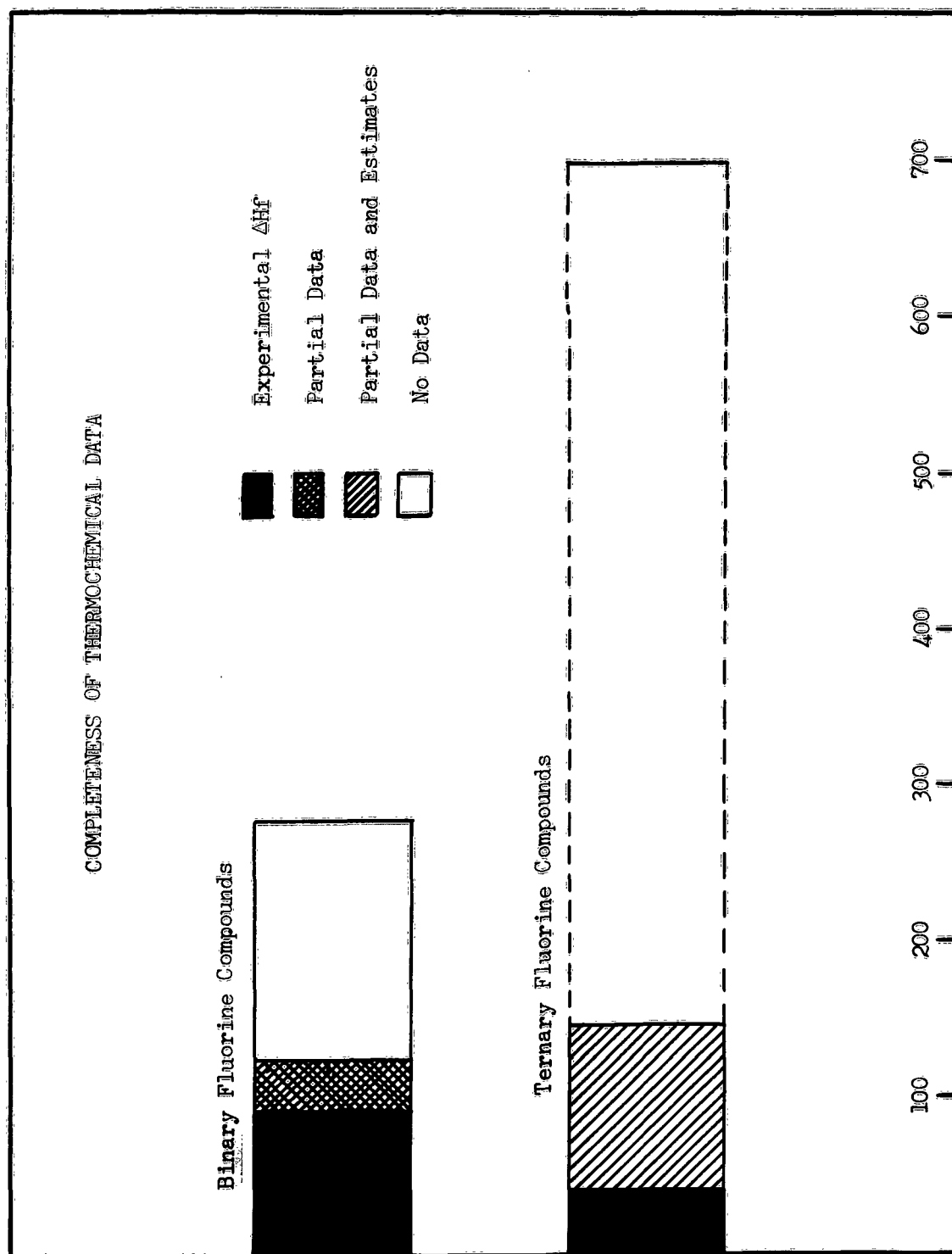


FIGURE 4. COMPLETENESS OF THERMOCHEMICAL DATA ON FLUORINE COMPOUNDS, 1961.

A reflection on the amount of data listed for some of the substances indicates that some scientists will conclude that a new study of a particular compound would be of value, even though there may be very extensive data on that compound. A great deal of work is required in order to settle some of the persistent problems of thermochemistry. For example, despite the great amount of work that has been done in attempts to determine the dissociation energy of fluorine, it is still uncertain by about one kcal mole⁻¹.

Several laboratories are now working very diligently on a systematic study of the thermochemistry of fluorine compounds, in particular. In a program begun about 4 years ago at the Argonne National Laboratory, Hubbard and co-workers have developed methods for direct determination of the heats of formation of binary fluorides by direct reaction of the elements in a calorimeter bomb [3]. They have determined the heats of formation of 14 fluorides, and two compounds not containing fluorine since the initiation of the program. Their results are summarized in Table II. The locations on the periodic chart of the elements involved and of some other elements under study now, or planned for the immediate future, are shown in Fig. 5. The information for Table II and Fig. 5 was kindly supplied by E. Greenberg [4].

TABLE II. HEAT OF FORMATION VALUES OBTAINED AT
ARGONNE NATIONAL LABORATORY BY FLUORINE BOMB CALORIMETRY

<u>Compound</u>	<u>ΔH_f° (kcal. mole⁻¹)</u>
TiF ₄ (s)	-394.2*
ZrF ₄ (c)	-456.8*
HfF ₄ (c)	-461.4*†
MoF ₆ (g)	-372.4*
BF ₃ (g)	-270.1*
SiF ₄ (g)	-386.0*
α SiO ₂ (c)	-217.7*
Vitreous SiO ₂ (c)	-215.9*
UF ₆ (c)	-522.6*
UF ₆ (g)	-510.8
CdF ₂ (c)	-167.4* (in press)
ZnF ₂ (c)	-182.7* (submitted for publication)
MgF ₂ (c)	-264.9
AlF ₃ (c)	-356.5 (believed to be low)
BN (Hex., c)	-59.7** (This is a rough value with probably a couple of kcal. mole ⁻¹ uncertainty at present.)
NbF ₅ (c)	-433.5*
TaF ₅ (c)	-455.1**†
RuF ₅ (c)	-213.4**†

* Final Values

** Tentative Values

† First study of the heat of formation of this compound.

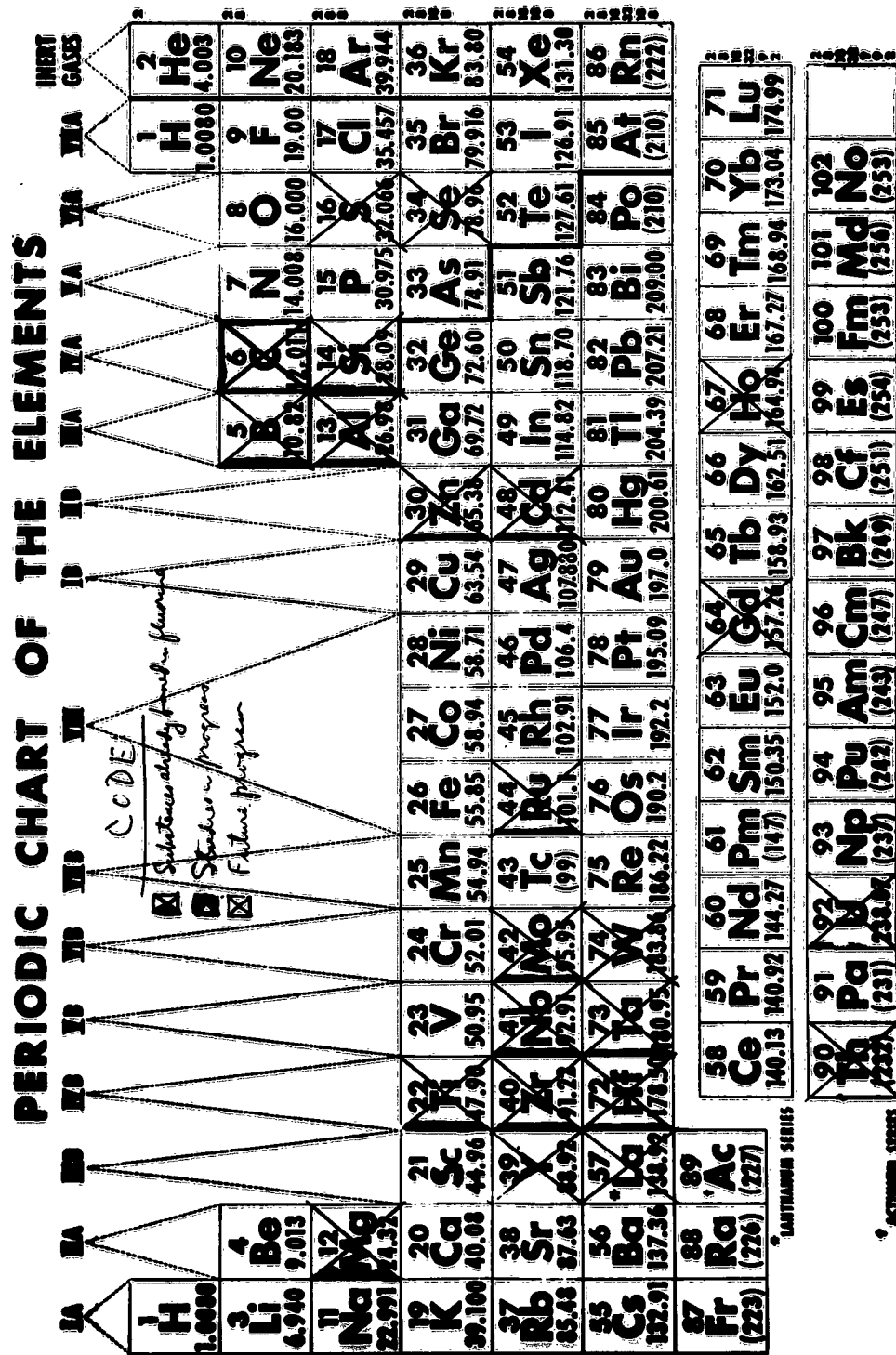


FIGURE 5. POSITIONS OF ELEMENTS BURNED IN FLUORINE AT ARGONNE NATIONAL LABORATORY.

At the Fulmer Research Institute, Gross and co-workers [5] have carried out a systematic study of halides, using either the direct reaction of the elements or metal displacement reactions to obtain heats of formation. Among the compounds for which they have determined the heats of formation are nine fluorides. Their results are summarized in Table III, in which they give a comparison with other reported values. The material in Table III was kindly supplied by Dr. Gross [5].

TABLE III. HEAT OF FORMATION VALUES FOR FLUORINE COMPOUNDS
OBTAINED AT FULMER RESEARCH INSTITUTE

Compound	Circ. 500 Value	Fulmer Value	Later Value	Source
BeF_2	-	-240.5*	-241.2	Skuratov
BF_3	-265.4	-271.2	-269.5	Hubbard
AlF_3	-311	-356.3	-358.3 ⁽¹⁾ -356.6 ⁽²⁾	N.B.S. (1) Hubbard (2)
Na_3AlF_6	-759.6	-784.9 ₅	-784.8	Coughlin
PF_5	-	-381.4	-	-
SF_6	-262	-289.7	-	-
TlF_4	-370	-394.6	-394.2	Hubbard
UF_4	-443	-453.3*	-449.3	Mal'tsev
UF_6	-517	-522.1	-522.6	Hubbard

At the National Bureau of Standards, Armstrong and Jessup [6,7] have developed methods for combustion of gaseous materials in a flame calorimeter, using a fluorine atmosphere. They have also used fluorine as an oxidizer in bomb calorimetry with metals and borides, and have used explosion methods for determining heats of formation of fluorine compounds. The results which they have measured for 9 compounds are listed in Table IV.

TABLE IV. HEATS OF FORMATION DETERMINED IN THE
FLUORINE LABORATORIES AT THE NATIONAL BUREAU OF STANDARDS

Compound	$\Delta H_f^\circ_{298}$
$\text{CF}_4(\text{g})$	-220.4
$\text{HF}(\text{g})$	- 64.63
$\text{NF}_3(\text{g})$	- 29.7
N_2F_4	- 2.0
$\text{N}_2\text{F}_2(\text{cis})$	+ 16.4
$\text{N}_2\text{F}_2(\text{trans})$	+ 19.4
$\text{AlF}_3(\text{c})$	-358.3
$\text{AlB}_2(\text{c})$	- 26.6 (non stoichiometric)
$\text{AlB}_{12}(\text{c})$	- 46.6 (" ")

The work which these three laboratories are carrying out refer principally to compounds stable at room temperature. An examination of the compounds for which heat data are lacking, however, indicates that a large fraction of them are fluorides stable only at high temperatures, or fluorides in which the metallic element is not in its highest state of oxidation. These two classes of compounds are not amenable to study by the devices outlined above. It is obvious that equilibrium studies involving vaporization or gas phase equilibria will be required for many of the compounds for which heats of formation are not now known. While several laboratories are active in this area, we shall not attempt to summarize their work here. Work of this kind will be required on an expanded scale in order to obtain in a relatively few years data on compounds for which none now exists. In studies of this kind, the equilibrium proportions of substances present are generally a very sensitive function of the energy of reaction involved. Yet such studies have, in many cases, led to values for heats of formation which are of relatively low accuracy. It is to be presumed that the reason is principally the difficulty of establishing that parameters being observed are properly associated with a given chemical process, and of establishing an experimental environment in which a true equilibrium exists. These problems are compounded in difficulty by the relative inaccessibility of the temperature and pressure regions in which the equilibria exist in many instances. The careful studies now being made in several laboratories should show the way to handle these problems adequately.

Another area of calorimetry of fluorine compounds which offers an approach to substances not obtainable by reactions involving fluorine directly is HF solution calorimetry. This procedure, probably not being used to an optimum extent at the present, is suitable for study of many substances soluble only with relative difficulty, and may offer an approach to the fluorides of mixed metals. It also offers an avenue to a reproducible standard state for fluorides such as BeF_2 which may tend to form glassy or amorphous solids, and are therefore difficult to

characterize thermodynamically. The aqueous solutions of many fluorides contain complex ions, and the equilibria of these must be properly taken into account if the results of studies by solution calorimetry are to be meaningful.

State of Thermodynamic Data on Selected Compounds

No attempt will be made to give data compound-by-compound for the whole list of compounds of interest to the JANAF Thermochemical Panel, or even for very many of them. Rather a few selected compounds of particular interest will be discussed.

Hydrogen Fluoride

A few years ago [1,6,7] we became aware that data on the heat of formation of CF_4 would be more consistent if the value for the heat of formation of gaseous HF were more negative than the value, -64.2 kcal mole $^{-1}$ listed in NBS Circular 500. In addition, our own measurements on the heat of combustion of NH_3 in HF [6], could readily be interpreted to give a value of -64.63 kcal mole $^{-1}$, and the most accurate of the studies by Von Wartenberg and Schutza [8], led to a value of -64.45 kcal mole $^{-1}$. In the latter study of the direct reaction of H_2 and F_2 , the temperature of the products was kept at 100°C , to eliminate appreciable imperfection of the gas phase of HF.

In addition, spectroscopic evidence from the dissociation energy of HF by Johns and Barrow [9] suggested a value as negative as -65.1 kcal mole $^{-1}$. The use of the data of Johns and Barrow, however, requires the dissociation energy of F_2 , which is inaccessible spectroscopically, and has been the subject of considerable controversy.

Recently Feder et al. [10] have reviewed the foregoing data. They have also added a critical discussion of the equilibrium in the reaction of SiF_4 with H_2O , determined by Lenfesty, Farr and Brosheer [11], and an evaluation of the heat of formation of HF that can be deduced from it and their own data (see Table II) on SiF_4 and SiO_2 . They calculate a value of -64.9 kcal mole $^{-1}$ in this way.

Following a new analysis of the above data and other data relating to aqueous HF, W. H. Evans [12], in the course of preparing material for the revised edition of NBS Circular 500 (still in preparation), has tentatively adopted a value of -64.8 kcal mole $^{-1}$ for $\Delta H_{f298}^\circ [\text{HF}(\text{g})]$. He also adopted a value of -79.50 kcal mole $^{-1}$ for $\Delta H_{f298}^\circ [\text{HF}(\text{aq}, \infty)]$. These values are 0.6 and 0.84 kcal mole $^{-1}$ more negative, respectively, than those in NBS Circular 500 [23]. These changes will affect the accepted values for heats of formation of an undetermined number of fluorides, usually by integral multiples of the suggested changes in HF. An uncertainty of 0.4 kcal mole $^{-1}$ would have to be assigned to this value for the heat of formation of HF in order to include all the principal contributing sources of data.

Beryllium Fluoride

Within the last four years experimental data sufficient to evaluate the heat of formation of BeF_2 unambiguously have been presented. Kolesov, Popov and Skuratov [13] measured the heats of solution of BeO and BeF_2 in aqueous HF , and calculated $-241.2 \text{ kcal mole}^{-1}$ for the heat of formation of $\text{BeF}_2(\text{c})$. Their value is dependent upon the heats of formation of BeO and of $\text{HF}(\text{aq})$. The heat of formation of BeO may be in error by as much as 3 kcal mole^{-1} . The heat of formation of HF they used was that used in NBS Circular 500. When their heat measurements are used with new calculations of auxiliary data, including the heat of formation of HF given in the preceding paragraph, we obtain $\Delta H_{298}^\circ [\text{BeF}_2(\text{c})] = -242.27 \text{ kcal mole}^{-1}$.

Recently Gross [14] has determined the energy of the reaction of PbF_2 with Be , to form BeF_2 and Pb . From his data he calculates $-240.5 \text{ kcal mole}^{-1}$ for the heat of formation of BeF_2 . This value is dependent upon the enthalpy of formation of PbF_2 , which in turn is dependent upon the heat of formation of HF . Without making a new calculation for PbF_2 , the value should be more negative by 1.2 to $1.68 \text{ kcal mole}^{-1}$ if the change in HF is introduced. The heat of reaction of Be with PbF_2 measured by Gross, in this case, should lead to -241.7 to $-242.2 \text{ kcal mole}^{-1}$ for the standard heat of formation of $\text{BeF}_2(\text{c})$. Both of the foregoing values are subject to some uncertainty due to lack of adequate definition of the $\text{BeF}_2(\text{c})$. Kolesov et al. state that their solid was crystalline, but their method of preparation is not known to give a very high degree of crystallinity.

The preliminary work by Simmons [15] and more recent unfinished work by Churney (See Section I B) on the direct combustion of beryllium in fluorine lead to values somewhat more negative, but at present not sufficiently accurate to influence the value accepted for the heat of formation of crystalline BeF_2 . See Section IB for a further discussion of BeF_2 .

Aluminum Fluoride

Gross et al. [16,17,18] carried out reactions of Al with $\text{PbF}_2(\text{c})$ and with $\text{NaF} + \text{PbF}_2$, from which he derived values for the heat of formation of $\text{AlF}_3(\text{c})$ of $-356.3 \text{ kcal mole}^{-1}$ based on the heat of formation of PbF_2 , and $-356.15 \text{ kcal mole}^{-1}$ based on the heats of formation of NaF and Na_3AlF_6 . The reaction of Al with PbF_2 was also carried out by Kolesov, Martynov, and Skuratov [19], and they calculated the heat of formation of $\text{AlF}_3(\text{c})$ to be $-357.0 \text{ kcal mole}^{-1}$. In each case the basis of the calculation involves the heat of formation of HF with a factor of three. Kolesov et al. recalculated the heat of formation of PbF_2 but did not modify the heat of formation of HF used in calculating it. Without completely recalculating the heat of formation of PbF_2 or NaF and Na_3AlF_6 , we can modify the above reported heats of formation of AlF_3 by 1.8 to $2.5 \text{ kcal mole}^{-1}$, making them -358.1 to $-358.8 \text{ kcal mole}^{-1}$ and -357.95 to $-358.65 \text{ kcal mole}^{-1}$ from the measurements of Gross et al.; -358.8 to $-359.5 \text{ kcal mole}^{-1}$ from the measurements of Kolesov, et al.

Direct measurements of the combustion of aluminum in fluorine by Domalski [20], give -358.3 kcal mole⁻¹ for the heat of formation. A study of the same process at Argonne National Laboratory (see Table II) gave a value of -356.5 . However, a note is attached by the authors stating an opinion that this value is too low (presumably not sufficiently negative). The weight of evidence points to a value for the heat of formation of AlF_3 near -358 kcal mole⁻¹.

For comparison with a reaction that is much easier to work with, the reaction of aluminum with oxygen to form the oxide, we show the data in Table V. The recent works from the United States (1945, 1951, 1957) are in excellent agreement. Any large uncertainty remaining in this system is due to the question as to the crystalline state of Al_2O_3 formed (See Section I.C.2). In a relatively short time, a substantial amount of work on AlF_3 has brought the information on this substance to a state comparable to that on Al_2O_3 a few years ago.

TABLE V. COMBUSTION OF ALUMINUM IN OXYGEN

Investigators	Al_2O_3 $-\Delta H_{298}^\circ$ kcal/mole
Mah (1957)	400.4 ± 0.3
Schneider and Gattow (1954)	400.6 ± 2.0 (402 $\pm$ 2)
Holley and Huber (1951)	400.29 ± 0.3
Oketani and Maebashi (1950)	381.02 ± 0.93
Snyder and Seltz (1945)	399.09 ± 0.06
Roth and Muller (1929)	380.1
Moose and Parr (1924)	376.9

Aluminum Fluoride Hydrates

A group of compounds related to $AlF_3(c)$, the hydrates, is much less well understood. We have, in fact, only fragmentary data on these compounds. Table VI lists the compounds and a little about the classes of thermodynamic data that have been presented. A principal difficulty with these compounds is the determination of the true formula, because the water is bound more or less loosely in a gelatinous mass when they are formed in some cases, and it is difficult to establish the stoichiometry. Thus alternate formulas with 3.0 and 3.5 moles of H_2O have been proposed for two hydrates (and also a 3.1 hydrate), but it is not clear whether both a 3 and a 3.5 hydrate exist. Perhaps for related reasons the vapor pressure of water over the hydrates (which as a function of temperature would yield the heat of hydration) is very difficult to obtain on a consistent basis, and so the data are in doubt. Obtaining solubility data is very difficult because of the extreme slowness with which equilibrium is approached. Such direct heat measurements of the heats of solution of the hydrates as have been reported [21,22] are subject to uncertainty because the basis of the mole used is not given, and there is no way to reduce the data to currently accepted formulas and atomic weights. The heat of formation of several hydrates could be related to the heat of formation of $AlF_3(aq)$ if this information

had been given. The heat of solution of anhydrous AlF_3 has not been measured. Knowledge of the heats of formation of the hydrates of aluminum fluoride is so very poor that their study would be of scientific interest. A certain amount of interest is attached to them because, like the hydrates of the chloride the hydrates of aluminum fluoride cannot be directly dehydrated to the anhydrous compound.

TABLE VI. AlF_3 HYDRATES AND ACID HYDRATES

$\text{AlF}_3 \cdot 0.5 \text{ H}_2\text{O}$	Classes of data available
$\text{AlF}_3 \cdot 1 \text{ H}_2\text{O}$	
$\text{AlF}_3 \cdot 2.5 \text{ H}_2\text{O}$	
$\text{AlF}_3 \cdot 3.0$ (or 3.5) H_2O (α)	
$\text{AlF}_3 \cdot 3.0$ (or 3.5) H_2O (β)	
$\text{AlF}_3 \cdot 9 \text{ H}_2\text{O}$	
$\text{AlF}_3 \cdot 3\text{HF} \cdot 3\text{H}_2\text{O}$	
$\text{AlF}_3 \cdot 3\text{HF} \cdot 6\text{H}_2\text{O}$	
	(a) ΔH soln in H_2O and in $\text{HF}(\text{aq})$
	(b) Solubility
	(c) Vapor pressure

In conclusion, it would be well to point out some pitfalls of estimating heats of formation among the fluorine compounds. Because of the difficulties of working with elemental fluorine and HF , there has tended to be a dearth of good experimental thermochemical data on the fluorine compounds. The lack of data has tempted many to estimate heats of formation, either from first principles, or from a correlation with related compounds. The early history of $\text{AlF}_3(\text{c})$ is such a case. For it, values of $-311 \text{ kcal mole}^{-1}$ [23] and $-323 \text{ kcal mole}^{-1}$ [24] were estimated by competent reviewers. The measured value differs from these estimates $25 \text{ kcal mole}^{-1}$ or more. The temptation to view this as an isolated case in which special circumstances render an estimate difficult, is removed if one compares this error with the errors made in other estimates of the heats of formation of fluorine compounds. From our review [1], we have excerpted heats of formation estimated for 14 fluorine compounds for which no experimental measurement existed at the time of the estimate. These are listed in Table VII. For comparison, experimental measurements of the heat of formation made at a later date are listed for these same compounds. The average error is $30 \text{ kcal mole}^{-1}$, and there is a bias of $17 \text{ kcal mole}^{-1}$. The systematic error, which indicates that fluorine compounds tend to be more stable than predicted, may be due to the extreme position of fluorine in the periodic table, which requires extrapolation rather than interpolation among the non-metals.

TABLE VII. ACCURACY OF SOME PUBLISHED ESTIMATES

OF HEATS OF FORMATION OF FLUORIDES

Compound	ΔH_f (kcal. mole ⁻¹)		Error of Estimate
	Estimate	Later Measurement	(kcal. mole ⁻¹)
AcF ₃ (c)	-420 ±10	-477	+57
	-395		+82
AlF ₃ (c)	-311	-357.1	+46 (max.)
	-323	-356.3	+23 (min.)
AsF ₃ (c)	-100 ±40	- 83.3	-17
BeF ₂	-227 ±5 or 10	-241.08	+14 (min.)
	-220	~ -257	+37 (max.)
MoF ₆ (l)	-405	-388.6	-16
NF ₂ (g)	17	8.9, 9.9	+ 8
NbF ₅ (c)	-342	-432	+90
PF ₅ (g)	-315	-381.4	+66
	-420		-39
SF ₄ (g)	-156	-171.7 ±2.5	+16
ThF ₄ (c)	-477 ±10	-482.4	+ 5
TiF ₄ (c)	-370 ±20	-392.5	+22
TiF ₃ (c)	- 65 ±5	- 74.0 ±1.5	+ 9
TiF ₃ (c)	-175 ±10	-136.9	-38
ZrF ₄ (c)	-445 ±30	-456.80 ±0.25	+12

Average Error ±30 kcal. mole⁻¹

Average Bias +17

Estimates and Measured Values are selected from a review by Armstrong and Krieger, Paper No. 2, Progress in International Research on Thermodynamic and Transport Properties, Masi and Tsai, Editors, 1962.

The rather large average error indicates that estimates of heats of formation should be regarded very skeptically.

References to Part I.A.

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B. RECENT STUDIES IN THE THERMODYNAMIC DATA OF BERYLLIUM SPECIES:
THE HEAT OF FORMATION OF BERYLLIUM FLUORIDE

Experimental Combustion of Beryllium in Fluorine

The experimental work described here was performed by Dr. K. L. Churney. A recent study by Kolesov, Popov and Skuratov [1] on the heats of solution of $\text{BeF}_2(\text{c})$ and $\text{BeO}(\text{c})$ in $\text{HF}(\text{aq})$ provided sufficient data to allow calculation of the heat of formation of crystalline BeF_2 . Their work appears to be of good quality. However, two factors have caused us to believe that further work, and a more direct determination of the heat of formation of crystalline BeF_2 are desirable. Recent studies on aluminum fluoride [2,3,4,5] have shown that earlier estimates of the heat of formation of $\text{AlF}_3(\text{c})$ based on solution calorimetry were seriously in error. To be sure, no direct heat of solution of AlF_3 had been possible, and hence one step had previously remained to be estimated. Nevertheless, the recent data on the heat of formation of crystalline AlF_3 are hard to reconcile with older data by Baud [6,7] on the heats of solution of the hydrates of AlF_3 . Hence, some doubt may be cast upon solution calorimetry of light metal fluorides in general. In addition, an incomplete study by Simons [8] gave preliminary values for the direct combination of beryllium with fluorine that were more negative than the heat of formation of BeF_2 derived by Kolesov et al. The study of the direct combustion of beryllium in fluorine was, therefore, undertaken in our laboratories, using the technique developed for the combustion of aluminum in fluorine [2].

The combustion technique involves mixing the beryllium to be burned, with powdered Teflon, and compressing the mixture into a pellet. In order to prevent loss of material on pelleting, the sample preparation procedure was modified to include sealing the powdered materials in a bag of Teflon film. Only very preliminary experiments can be described at this time.

Two combustions of beryllium-Teflon mixtures, one of an aluminum-Teflon mixture and one of Teflon alone, have been carried out. The results of the two combustions involving beryllium are briefly summarized in Table I. In order to prepare the mixtures the powdered metals and Teflon were sealed in Teflon bags, homogenized by movement of an air bubble trapped in the bag, and pelleted after puncturing the bag to allow gas to escape. Weight changes due to sealing bag, mixing contents and pelleting totaled from 0.02 mg to 0.1 mg. Samples were placed on a massive monel or type 304 stainless steel plate resting on the bottom of the bomb. The bomb contained a thin liner made of type 304 stainless steel, for convenience in removing the solid combustion products for weighing. Samples were ignited with a fuse consisting of 5 cm of 0.003 in. dia. tungsten wire. The fuse burns completely.

TABLE I. COMBUSTION OF BERYLLIUM IN FLUORINE

Fluorine pressure	20-21 atm	
State of product:	a) white, fluffy, hygroscopic, amorphous (?) powder b) small amount of BeF_2 glass	
	Experiment 1	Experiment 2
Sample pellet composition:		
Teflon (g)	0.841	2.196
Beryllium (g)	0.422	0.201
Completeness of reaction:	%	%
Not well known:	77-88	> 90
Energy of Be combustion	kcal mole ⁻¹	kcal mole ⁻¹
Not well known:	-244 to -255	—

A slight residue of carbon (0.2 to 0.8 mg) was found after combustion of Teflon and of Teflon-aluminum mixtures. Combustion of Teflon-beryllium mixtures led to a white fluffy powder of BeF_2 , some unreacted beryllium, and a small amount of product of reaction of the pellet support. The latter reaction was substantially reduced when 0.2 g of Be instead of 0.4 g was used. Some BeF_2 appeared to have congealed from the melt in the experiment with 0.4 g Be but no such appearance was observed in the experiment with 0.2 g BeF_2 .

The degree of completeness of the combustions was determined by weighing the liner and its contents. Uncertainties in buoyancy corrections cause the precision of the weighing to be not better than 1 to 2 mg. The products of later experiments will be analyzed by determining the amount of hydrogen evolved on reaction of residual beryllium with acid. This should overcome the more serious difficulty that was encountered in assigning the observed weight change to the amount of material burned. The degree of completeness of the combustion is uncertain principally because two different ways of determining the weight of beryllium fluoride led to different values. The values were 77 or 88% in experiment 1 and >90% in experiment 2. The degree of completeness of combustion is much higher than has been previously reported. In the only previously reported work, that of Simmons, the combustions were 25 to 60% complete in the more favorable cases.

Experimental measurements on the heat of formation are listed in Table II. The data are by no means conclusive, though a strong indication that the value lies near $-242 \text{ kcal mole}^{-1}$ is given by the good agreement of a recent value reported by Gross [9] based on the reaction of Be with PbF_2 , with the measurements of Kolesov, et al [1]. The values in parentheses were calculated using the revised values for $\Delta H_f [\text{HF(aq)}]$ [10], while those not in parentheses were reported by the authors themselves.

TABLE II. EXPERIMENTAL MEASUREMENTS
OF THE HEAT OF FORMATION OF SOLID BeF_2

	ΔH_f kcal mole ⁻¹	Source
BeO + HF(aq) } BeF ₂ (c) + HF(aq) }	-241.2 (-242.27)	[1]
Be + PbF ₂	-240.5 (-242.1)	[9]
Be + F ₂	-256 to -258 a	[8]
Be + F ₂	-244 to -255 a	(this work)

a. Based on incomplete work.

Energy State of $\text{BeF}_2(\text{solid})$

BeF_2 is extremely difficult to prepare in the form of crystals, having a pronounced tendency to form a glass. In the work of Kolesov, et al [1] the sample used is claimed to be crystalline. We have strong doubts that the degree of crystallinity of material was high. The product of combustion of beryllium in fluorine is definitely not crystalline, but amorphous, and very finely divided. It is not clear from the early reports by Gross [9] what form he found for the BeF_2 produced in the reaction of PbF_2 with Be, but it should be suspected to be non-crystalline.

The energy state of non-crystalline may be related to that of crystalline BeF_2 by a study of the heats of solution of the various forms that have been encountered. Such a study of the solution calorimetry of solid beryllium fluoride is proposed in our laboratory. The heats of solution of Li_2BeF_4 , and LiF will also be determined in a related series of experiments to establish the heat of formation of $\text{Li}_2\text{BeF}_4(\text{c})$.

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C. RECENT STUDIES ON REFRACTORY COMPOUNDS.

1. THE HEATS OF FORMATION OF TWO ALUMINUM BORIDES.

The experimental work described in this section was carried out by Dr. E. S. Domalski in our laboratories. ^(a)

The purposes of this work were to provide a review of existing thermodynamic data on the metallic borides, and, by new experimental measurements to augment the existing data on heats of formation of this class of compounds. The data are of immediate application to the combustion of slurries in which solid borides are mixed with a liquid fuel to obtain desirable combustion properties. In addition, the heats of formation are of intrinsic scientific interest, as they are a class of compounds difficult to prepare, and so far, the subject of only a small amount of valid thermodynamic study.

Aluminum Boride Samples

The aluminum borides AlB_2 and $\alpha-AlB_{12}$ were prepared for us by V. I. Matkovich of the Carborundum Company. Boron was mixed with excess aluminum and the mixture was heated to 1200 °C to obtain AlB_2 and to 1700° to obtain $\alpha-AlB_{12}$. A large excess of aluminum was used in each case. The excess aluminum was leached from the AlB_2 by the use of acid, which presumably left a rough surface, as will be noted later. The leaching process did not similarly affect the $\alpha-AlB_{12}$.

The samples were analyzed at the National Bureau of Standards for boron, aluminum, carbon, nitrogen and minor metallic impurities. Oxygen was determined for us by General Atomic, San Diego, California, by neutron activation analysis. The results of the analyses are shown in Table I.

TABLE I

ANALYSES OF ALUMINUM BORIDE SAMPLES

Component	AlB_2		$\alpha-AlB_{12}$ (powder)	
	Obs.	Theor.	Obs.	Theor.
Al	53.00	55.51	17.01	17.22
B	47.04	44.49	81.5	82.78
O	1.0	-	1.3	
N	0.3	-	-	
C	0.08		0.11	
metals	<u>0.17</u>	<u> </u>	<u> </u>	<u>0.22</u>
Total	101.59	100.00	100.14	100.00

(a) This work was carried out for the Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, under Delivery Order (33-616)61-09.

The oxygen content is appreciable in both samples, and the total content of foreign elements is comparable in the two samples. It is not possible to say to what extent the foreign elements are combined differently with boron and aluminum, so the expedient has been adopted of considering C, O and N each individually to be divided between their compounds with aluminum and boron in proportion to the ratio of aluminum to boron in the sample, while the foreign metals were assumed to be uncombined. The aluminum and boron not combined with foreign elements are assumed to be combined in a non stoichiometric ratio, which in the case of AlB_2 is $AlB_{2.215}$ and in the case of $\alpha-AlB_{12}$ is $AlB_{11.96}$. On this basis the aluminum diboride sample was assigned the composition shown in Table II; the α -aluminum dodecaboride was assigned the composition shown in Table III.

TABLE II

COMPOSITION ASSIGNED TO ALUMINUM DIBORIDE SAMPLE

Component	Percent by Weight
$AlB_{2.215}$	97.23
Al_2O_3	0.65
B_2O_3	0.98
AlN	0.27
BN	0.36
Al_4C_3	0.18
B_4C	0.16
Foreign metals	<u>0.17</u>
Total	100.00

TABLE III

COMPOSITION ASSIGNED TO α -ALUMINUM DODECABORIDE

Component	Percent by Weight
$AlB_{11.96}$	97.34
Al_2O_3	0.21
B_2O_3	1.74
Al_4C_3	0.09
B_4C	0.40
Foreign metals	<u>0.22</u>
Total	100.00

These samples are considered to be borides of very high quality according to the present state of the art of making them; and the analytical data reflect the difficulty of preparing very highly pure borides. They also indicate that a limiting factor in the accuracy of the experiments may be the certainty with which the analysis is known. The preparation of the samples and the analyses required a very important fraction of the total effort expended in carrying out the study.

Combustion Measurements and Results

The aluminum boride samples were burned in fluorine in a bomb calorimeter, using the Teflon pelleting technique developed for combustion of aluminum powder in fluorine [1]. Nine experiments were carried out in which the α - AlB_{12} sample was burned, and these and the calculations resulting from them are summarized in Table IV. Samples were ignited by a fuse of tungsten wire weighing about 4.4 mg, which burned completely in the reaction.

TABLE IV

COMBUSTION OF α -ALUMINUM DODECABORIDE (a)

$$\alpha\text{-AlB}_{11.96} + \frac{28.88}{2} \text{F}_2 = \text{AlF}_3(\text{c}) + 11.96 \text{BF}_3(\text{g})$$

kcal mole⁻¹

ΔH° Combustion	3535.4 $\pm$ 4.9 (b)
Correction for incomplete reaction 0.1%	3.5 $\pm$ 1.7
Corrected ΔH°_{298}	3538.9 $\pm$ 5.2
$\Sigma \Delta H^\circ_{298}$ for AlF_3 and BF_3	3585.5 $\pm$ 1.1
$\Delta H^\circ_{f298} [\alpha\text{-AlB}_{12}]$	-46.6 $\pm$ 5.3

^a Preliminary results.

^b The uncertainties are estimates of the standard deviation of a measurement.

Combustion was estimated to be about 0.1% incomplete, on the basis of the unburnt residue in the combustion area. The heat of formation of AlB_{12} is calculated to be -46.6 ± 5.3 kcal mole⁻¹. In calculating this the heat of formation of AlF_3 was taken to be -358.3 kcal mole⁻¹ [1], and the heat of formation of BF_3 was taken to be -269.88 kcal mole⁻¹ [2]. The numbers listed have been corrected for combustion of the impurities.

Five experiments were carried out in which the aluminum diboride sample was burned. The observations are summarized in Table V. In these experiments an abnormally large drift rate of the calorimeter in the fore-period was noted. Observation of a gain in weight of a pelleted sample of AlB_2 which was exposed to fluorine in the bomb, but not ignited,

indicated that the increase over the normal drift rate was due to a slow reaction of the pellet material with fluorine. No such weight change or anomalous fore-period drift rate was observed with AlB_{12} samples. The reaction was therefore attributed to slow reaction of fluorine with AlB_2 . We suspect, though we have not demonstrated, that the acid

TABLE V
COMBUSTION OF ALUMINUM DIBORIDE^(a)

$\text{AlB}_{2.215} + \frac{9.645}{2} \text{F}_2 = \text{AlF}_3(c) + 2.215 \text{BF}_3$	
	kcal mole ⁻¹
ΔH° Combustion	-912.9 $\pm$ 2.0 ^(b)
Estimate of fore-period reaction	- 7.3 $\pm$ 3.6
Correction for incomplete reaction (1%)	- 9.3 $\pm$ 4.6
	-929.5 $\pm$ 6.2
$\Sigma \Delta H^\circ_{298}$ for AlF_3 and BF_3	-956.1 $\pm$ 0.7
$\Delta H^\circ_{298} \text{AlB}_2$	- 26.6 $\pm$ 6.2

^a Preliminary results.

^b The uncertainties are estimates of the standard deviation of a measurement.

treatment of the AlB_2 , used to remove excess aluminum, produced a rough or porous surface due to leaching of aluminum from the boron. This would account not only for an increased reactivity of the AlB_2 , but also for the deficiency of aluminum found by analysis in this sample.

The energy dissipated in this way during the period before ignition was not measured by the ΔR_c and tended to make the measured heat of the reaction too low. The rate of heat evolution was estimated on the basis of the change of the drift rate from its normal behavior, and a correction of about 0.8% of the total heat observed was applied, assuming that the heat evolution occurred at a uniform rate from the time the bomb was loaded until ignition occurred.

The results presented here are preliminary and are subject to revision on the basis of recalculation of the data. However, the general behavior of the heats of formation of the aluminum borides seems to be clear. The heat of formation per B atom is 13.3 kcal mole⁻¹ in AlB_2 and 3.9 kcal mole⁻¹ in AlB_{12} .

References to Part I, C. 1

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C. RECENT STUDIES ON REFRACTORY COMPOUNDS:

2. THE HEAT OF COMBUSTION OF ALUMINUM CARBIDE

An experimental study of the heat of combustion of Al_4C_3 in oxygen has been carried out in order to establish more definitely the heat of formation. The experimental work was done by Dr. R. C. King of our laboratories.

The sample studied had previously been used at the National Bureau of Standards to determine the heat capacity at high temperatures [1] and at low temperatures [2]. In the course of this earlier work, the sample had been exhaustively analyzed, and this fact together with the existence of thermodynamic data on the sample made its study seem well worth while, even though the purity was not extremely high. The sample had been prepared by heating a stoichiometric mixture of aluminum and lampblack in an argon atmosphere at 1800 °C, by the Aluminum Company of America Research Laboratories.

The sample had been spectroscopically and chemically analyzed, and X-ray crystal patterns for it had been obtained. The chemical analysis showed in percent: Al_4C_3 , 94.8; Al, 1.0; C, 1.0; AlN, 1.3; Al_2O_3 , 2.2; Fe, 0.06. This was in reasonably good accord with the spectroscopic analysis, which, in addition to Al, showed significant amounts of Fe, and traces of Ag, Ca, Cr, Cu, Mg, Mn, Ni, Si, Ti, V, Zr. Because the completeness of reaction was to be determined by analysis of the product gases for CO_2 , a determination of total C in the sample was made by the Dumas method. This yielded a total of 24.57 %C. The total carbon found in this way is slightly less than the total carbon from the previous analysis. Whether this is due to inhomogeneity of the sample or to errors in one of the analyses is not known.

A preliminary test of the behavior of the Al_4C_3 sample on exposure to air showed that a gain in weight occurred, which was very gradual at first, and then became increasingly rapid. On the other hand, a sample kept in a desiccator showed no weight change in the same interval of time. This test which extended over an interval of two months showed that, if after opening the sealed vial it was stored in a desiccator, the Al_4C_3 could be handled in air for the short time necessary to weigh the combustion sample and prepare the bomb for a heat measurement, without detriment to the sample.

The experiments were carried out using oxygen bomb calorimetric procedures customary in our laboratory [3]. The unit of energy used here is the joule and is converted to calories using the factor

4.1840 j = 1 calorie. The atomic weight scale used is the 1961 table of atomic weights based on carbon isotope 12.

The completeness of reaction was determined by analysis of the bomb gases for CO₂, which showed that the reaction was very nearly complete in every experiment. (See the column headed CO₂ in Table I.) The observed-to-calculated CO₂ ratio varied from 0.9973 to 1.0027. Values greater than one are possibly due to inhomogeneity of the sample. The heat of combustion per gram of Al₄C₃ burned was calculated using the CO₂ formed as a measure of the amount of reaction. In determining ΔH_{298}° (to α -Al₂O₃), (j g⁻¹) and ΔH_{298}° (kcal mole⁻¹) shown in Table I, corrections were applied for combustion of the combustible impurities. Because no water could be used in the bomb to dissolve oxides of nitrogen, these oxides were absorbed in MnO₂ [4] in the gas absorption train, prior to absorption of CO₂. The oxides of nitrogen were weighed and a correction was applied on the basis that they were solely NO₂.

Experimental Arrangement to Obtain Complete Combustion

Complete combustion was achieved only after several attempts. The solution to the problem of obtaining complete combustion was found in the adjustment of the massiveness of the sample holder. This problem is of general interest in bomb calorimetry and so the approach used will be briefly described.

First attempts to burn Al₄C₃ in a platinum crucible of 10 g, which was satisfactory for benzoic acid, led to melting of the platinum. More massive supports were then tried, and ultimately led to nearly complete combustion. Under these conditions, however, the benzoic acid used for calibrating was found not to burn completely.

The results of these two experiments indicate some limiting factors operating in the selection of sample supports. We presume that to achieve complete combustion it is desirable to have the reaction zone and unburned sample attain as high a temperature as feasible without melting or reaction of the support. Too low a temperature results in incomplete combustion. The conditions for attaining an optimum temperature may not be the same for all substances even though they liberate the same total heat. For example, the products of combustion of an organic compound such as benzoic acid are all gases, and carry a large fraction of the heat rapidly away from the reaction zone. This can easily be seen from the fact that to melt a 10 g platinum crucible requires about 0.9 kcal. The energy involved in a typical combustion is about 10 kcal, an amount greater by a factor of more 10 than that needed to melt the entire crucible. Yet with organic compounds rarely does any part of the crucible melt.

In the combustion of a substance leading to a massive solid product, however, a larger fraction of the total heat is retained in contact with the crucible by that solid product and leads to a higher crucible temperature. This accounts qualitatively for the fact that a solid product may cause melting of a crucible that would have survived combustion of an organic substance.

In this case the problem of the massiveness of the sample support was solved by using one support for the benzoic acid for calibration experiments, and a separate support for the aluminum carbide, each of a suitable size for its reaction, and both remaining in the bomb during all experiments. The support for the benzoic acid was a 10 g platinum crucible, and for the aluminum carbide the support was a thin platinum foil resting on a disc of alumina.

Crystal Form of Aluminum Oxide Combustion Product

A most interesting and important result of the study was the finding that a major fraction of the solid combustion product was delta-phase Al_2O_3 [5,6]. The remainder of the product was alpha- Al_2O_3 . The two phases were quite distinctly segregated in the bomb. The massive boule of combustion product remaining in the reaction zone was $\alpha-Al_2O_3$. The very finely divided solid product condensed on the walls of the bomb was $\delta-Al_2O_3$. The $\delta-Al_2O_3$ formed 45 to 75% of the total reaction product as determined by weighing. This form of Al_2O_3 has been reported to be formed readily in the presence of carbon and nitrogen [6,7], by rapid condensation and cooling from the gas phase [6]. These conditions prevail in the bomb. A different phase was reported by Schneider and Gattow [8] when they determined the heat of combustion of aluminum in oxygen. They described the deposit as $\chi-Al_2O_3$. The reason for the difference between the deposit obtained by Schneider and Gattow and that found by us is not clear, but it is known that the conditions of their experiments contained a similar feature, the presence of carbon, which they introduced in an organic substance used for a combustion promoter. They had the added feature, different from our experiments, the presence of water, formed by combustion of the organic substance. We avoided the use of water in the bomb, because it appeared to react with the aluminum oxide formed. In a test in which a combustion was carried out with one ml of water, in such a position as to be vaporized by the combustion in order to make it an effective absorber of oxides of nitrogen, the bomb was dry at the conclusion of the experiment and the X-ray pattern of the δ -alumina was diffuse, indicating that interaction had occurred between the δ -alumina and the water.

The large fraction of the little known δ -phase in the product raised the question of how much energy difference there is between the two phases. We have not yet measured the enthalpy difference directly. However, the observed energy of combustion was plotted against the fraction of $\delta-Al_2O_3$ (Figure 1) with the expectation that a linear relation between the two would allow extrapolation to 100% $\alpha-Al_2O_3$. The figure shows a relationship, to be sure, but not one that renders extrapolation very easy. The best line, through the data, determined by least squares, is:

$$\Delta U_{obs} (j \text{ g}^{-1}) = -30170.2 + 511.5 (\text{fraction } \delta) \quad (1)$$

From the slope we calculate for the transition, $\alpha-Al_2O_3$ to $\delta-Al_2O_3$, $\Delta H_{298} = 8.8 \text{ kcal mole}^{-1}$. This value is not very certain and could easily be in error by a factor of two.

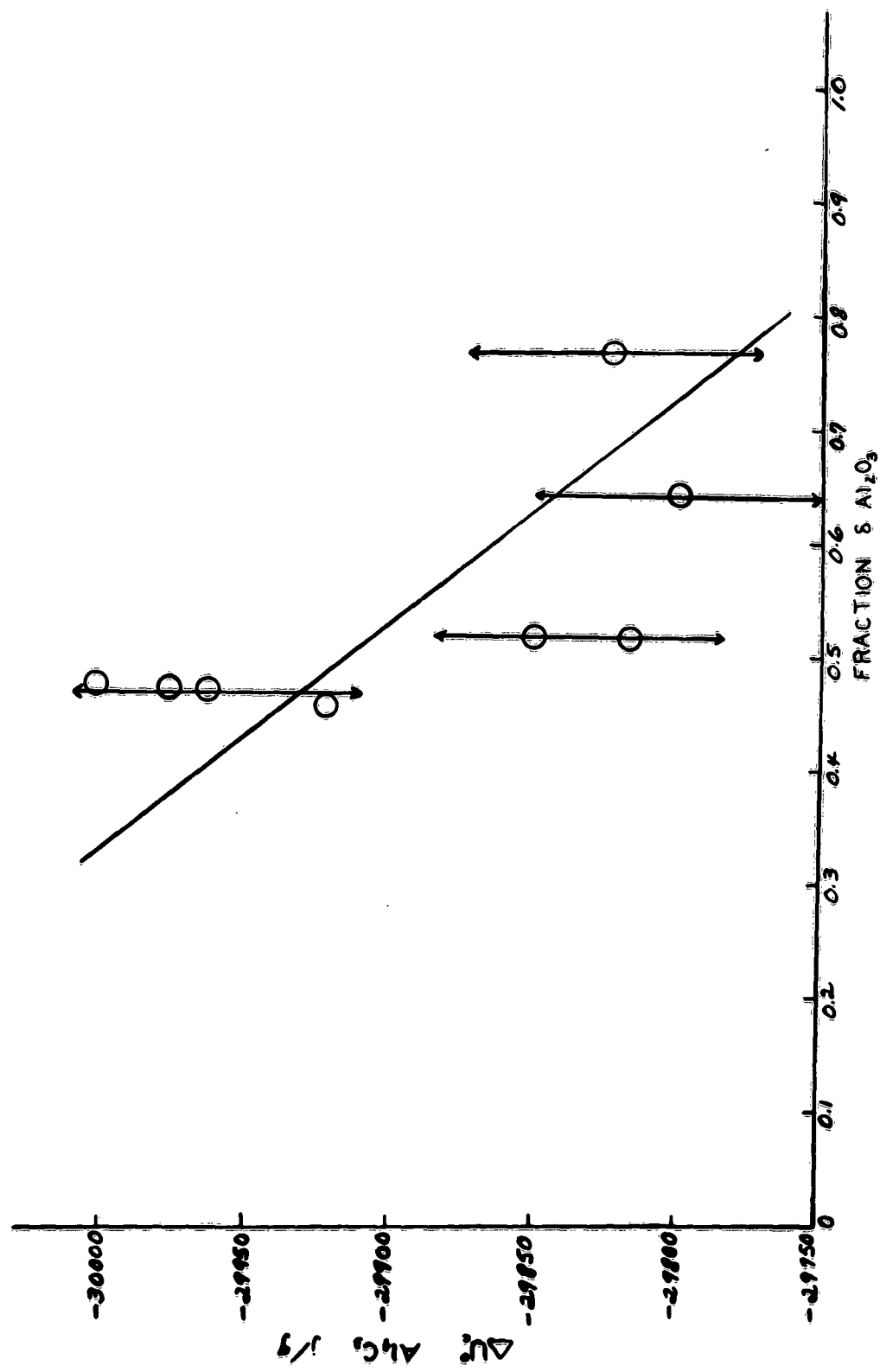


FIGURE 1. VARIATION OF ENERGY OF COMBUSTION OF Al_4C_3 WITH FRACTION $\delta\text{-Al}_2\text{O}_3$ IN THE PRODUCT

The appearance of $\delta\text{-Al}_2\text{O}_3$ in combustion experiments, and its apparently significant energy difference from $\alpha\text{-Al}_2\text{O}_3$ is of considerable interest in the use of aluminum in rocket motors because of the similarity of the chemical environment in rocket output to that in which the δ -phase is readily formed.

Heat Measurements and the Heat of Formation of Al_4C_3

The results of eight combustion experiments are given in Table I.

TABLE I

HEAT OF COMBUSTION OF Al_4C_3

Al_4C_3 , 94.8; Al, 1.0; C, 1.0; AlN, 1.3; Al_2O_3 , 2.2; Fe, 0.06.

Expt. No.	$\Delta U_{\text{B obs}}$ j	Σ corrections j	CO_2 obs/calc	Al_2O_3 $\delta/(\alpha+\delta)$	m_{g}^i g	Δh_{298}° (to $\alpha\text{-Al}_2\text{O}_3$) j/g
10	24763	706	1.0018	0.768	0.80667	30216
11	24733	706	1.0027	.641	0.80629	30128
12	24644	701	.9956	.456	.80018	30155
13	24744	703	.9985	.475	.80128	30245
16	24729	703	.9973	.471	.80186	30205
18	24583	702	.9992	.517	.80094	30081
19	24794	706	1.0000	.517	.80698	30114
20	24779	703	1.0001	.472	.80318	<u>30218</u>

Mean 30170

Standard Deviation of the Mean 21

$$\Delta H_{298}^\circ = 1038.1 \pm 0.7 \text{ kcal mole}^{-1} \text{ (corrected for impurities)}$$

In the table in columns from left to right are listed: experiment number, observed energy of the bomb process, corrections including those for reactions of impurities, fuse energy, and deviations from the standard states, the ratio of the mass of CO_2 observed to that calculated from the analysis of the sample, the fraction of Al_2O_3 in the δ phase, the mass of Al_4C_3 calculated from the observed CO_2 , and the enthalpy of combustion of Al_4C_3 , corrected to provide complete conversion of the product to $\alpha\text{-Al}_2\text{O}_3$. The molar enthalpy of combustion of Al_4C_3 at 298 °K is 1038.1 kcal mole⁻¹ with a standard deviation of the mean of 0.7 kcal mole⁻¹.

In making the corrections for reactions of impurities, it was assumed that AlN burned to form Al_2O_3 and NO_2 to the extent that NO_2 was observed in the products, and that the remainder burned to Al_2O_3 and N_2 . Al, C, and Fe were assumed to burn to the highest oxide in each case.

From our data we calculate the heat of formation of Al_4C_3 to be: $\Delta H_{f298}^\circ [\text{Al}_4\text{C}_3(\text{s})] = -43.0 \text{ kcal mole}^{-1}$. The following auxiliary data were used in the calculation: $\Delta H_{f298}^\circ [\alpha\text{-Al}_2\text{O}_3] = -400.4 \text{ kcal mole}^{-1}$ [9],

$$\Delta H_{f298}^{\circ} [\text{CO}_2(\text{g})] = -94.05 \text{ kcal mole}^{-1} [10].$$

This and other values for the heat of formation of Al_4C_3 are listed in Table II, for comparison. Among the combustion measurements listed

TABLE II

HEAT OF FORMATION OF Al_4C_3

A. Combustion calorimetry		ΔH_{f298}°
Berthelot [11]		-258.9
Wöhler and Hofer [12]		-257.8
Meichsner and Roth [13]		- 48.6 a
This work		- 43.0
B. Equilibrium studies		
Kelley [14] review of Brunner [15]		-117.1
Cox and Pidgeon [16]		- 35.9
Campbell [17]		- 51.2 b
Meschi and Searcy [18]		- 51.0
Efimenko, et al [19] review		
of Prescott and Hincke [20]		- 42.8
Sato [21]		- 63.2

a Recalculated using $\Delta H_{f298}^{\circ} (\text{Al}_2\text{O}_3) = -400.4 \text{ kcal mole}^{-1}$.

b Recalculated using free energy functions for Al_4C_3 from [1,2].

there the work of Berthelot [11] and of Wöhler and Hofer [12] can be disregarded because they were probably made with very impure samples. The measurement by Meichsner and Roth has been recalculated using $-400.4 \text{ kcal mole}^{-1}$ for the heat of formation of the product Al_2O_3 . If it is assumed that they also were getting a phase of Al_2O_3 that is not so stable, then their value might be less negative; and more nearly in agreement with our value.

The values resulting from equilibrium studies at high temperatures in general may be regarded as less accurate than a direct combustion measurement, but as listed in Table II such values cluster around the recent results of combustion measurements.

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SURVEY OF THERMODYNAMIC DATA FOR BERYLLIUM SPECIES*

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In this paper an attempt is made to summarize the available thermodynamic data for beryllium species which are of interest in advanced propellant applications. This is not a critical review, nor is it exhaustive, but it does summarize most of the pertinent data of which the author is aware.

I. Be-O and Be-O-H Species

In Table I are summarized the heats of formation and derived Be-O bond energies for various Be-O and Be-O-H vapor species. Data for the BeO polymers were obtained from a second-law analysis of mass spectrometric data; bond energies for these species were calculated assuming ring structures. Saturated BeO vapor is exceedingly complex, and it is not clear that all of the pertinent species, particularly the sub-oxides, have been identified. Also, no information is available on higher oxides, which may be important under oxidizing conditions.

In treating the hydroxide data, an O-H bond energy of 110 kcal was used. The hydroxide values listed are limiting values obtained from mass spectrometric studies of the reaction of water vapor with beryllia. The data for $\text{Be}(\text{OH})_2(\text{g})$ are in agreement with the results of transport measurements carried out near atmospheric pressure, if in the latter the dihydroxide is assumed to be the principal product. More definitive data are needed on the hydroxides; mass spectrometric studies of the BeO-H_2 reaction are being made in this regard.

Thermal data for crystalline and liquid BeO appear to be fairly well established.³

It can be seen that there is not a great deal of variation among the derived Be-O bond energies. An average $E(\text{Be-O})$ value of 110 kcal can be used to estimate the heats of formation of other species containing Be-O bonds, so that appropriate experimental conditions for thermochemical studies can be chosen.

Except for diatomic BeO, the molecular constants of the vapor species are based entirely upon estimates. Because of the great complexity of the saturated vapor and the low volatility, it is difficult to see how much headway can be made in this area by optical spectroscopic or other structural techniques. It has been suggested^{3a} that the effective ground state of BeO for high-temperature thermodynamic calculations is 3π rather than $^1\Sigma$.

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II. Be-F and Be-Cl Species

Before discussing the individual halide species, a word about the molecular constants of the gaseous dihalides is in order, since these quantities affect the interpretation of the data for the other species. In Table II, the entropies of a number of gaseous Group II metal dihalides evaluated from a second-law treatment of vapor pressure data and condensed phase entropies $[S^0(\text{exp})]$ are compared with corresponding values calculated from available molecular constant-spectroscopic data $[S^0(\text{calc})]$. Polymerization of the vapor was taken into account where necessary. In all cases, the molecular constants of the gaseous dihalides are those given by Brewer et al.,⁴ and are those used in the JANAF Tables. The vapor pressure data are in most cases extensive and in reasonable accord, as are the condensed phase entropies, so that the experimental entropies $[S^0(\text{exp})]$ should be reliable to within 2 e.u. These are the only Group II dihalides for which such extensive data are available.

It can be seen that the experimental entropies of the Be, Mg and Zn halides (the only cases in which bending frequencies have been assigned from observed spectra) are higher than the calculated values by 5 ± 1 e.u. For the Ca and Cd dihalides, Brewer et al.⁴ used the bending frequency as an adjustable parameter which was chosen to give the best agreement between second- and third law heats of sublimation. Since the translational, rotational and electronic partition functions of all the dihalides are reasonably well known, it would appear that the vibrational partition functions of the Be, Mg and Zn dihalides might be in error. A comparison of the entropy discrepancies with the ratio of bending force constant to stretching force constant $[(k\delta/l^2)/k]$ indicates that the difference may arise from the use of bending frequencies for the Be, Mg and Zn dihalides which are too high (the stretching constants are all well known). If a bending to stretching constant ratio of 0.01 is arbitrarily used for all the dihalides, a valence force treatment yields bending frequencies which give agreement between calculated and experimental entropies in each case to well within the estimated errors. In the latter case, the calculated bending frequencies all lie in the range 50 to 200 cm^{-1} , a region in which these substances have not been studied as yet. The above evidence is indirect and, therefore, not conclusive, but it does indicate that the available thermodynamic functions of the gaseous beryllium dihalides are probably in error by significant amounts, and that third-law calculations for these substances should be made with caution. Perhaps the matter can be resolved by new measurements in the far infrared region.

a. Be-F Species

Low-temperature heat-capacity and high-temperature enthalpy data have recently become available for condensed BeF_2 .¹⁴ The entropy of $\text{BeF}_2(\text{c})$ at 298°K is 4.5 e.u. higher than the estimated value used earlier in the JANAF tables. The heat of formation of the crystalline solid appears to be well established, although there is some evidence of polymorphism.

A second-law analysis^{2,7} of extensive vapor pressure data leads to a value of 59 ± 2 kcal/mole for the heat of sublimation of BeF_2 at 298°K. This and data for the crystal lead to $\Delta H_f^{\circ}{}_{298} = -182 \pm 3$ kcal/mole for the $\text{BeF}_2(\text{g})$. Various equilibrium measurements on the BeF_2 -Al system are in agreement with the above.² From transport measurement on the HF-BeO system, Greenbaum et al.⁸ obtained $\Delta H_f^{\circ}{}_{298} = -191$ kcal/mole for $\text{BeF}_2(\text{g})$. The reason for the divergence

between these values is not immediately apparent, although the latter value may be too large negatively because of errors in the free-energy functions of $\text{BeF}_2(\text{g})$.

The values for $\text{BeF}(\text{g})$ in Table III are based on thermochemical data. The BeF dissociation energy of 145 kcal seems a little high when compared to half the heat of atomization of BeF_2 , 148 kcal. Mann¹⁵ interprets the electronic spectrum to yield a dissociation energy of 138 kcal for BeF , while Herzberg¹⁶ and Gaydon¹⁷ estimated values of 125 and 92 kcal, respectively, from less extensive data. Further work is in progress on the sub-fluoride.

b. Be-Cl Species

Crystalline BeCl_2 exists in several modifications, some of which persist as metastable forms, depending on the thermal history.¹⁸ This introduces uncertainties into derived thermal data for the solid, since the crystal form is usually not specified. The latter is true of the heat of formation data for the crystal given in Table III. The entropy of the α' form¹⁸ was recently determined¹⁹ and the value at 298°K is 3.8 e.u. higher than the estimated value used in the JANAF tables; high-temperature enthalpy data were also obtained.¹⁹

There is still some uncertainty about the composition of saturated BeCl_2 vapor. Mass spectrometric studies^{2,13} on saturated and unsaturated vapors indicate that the saturated vapor at about 500°K might contain as much as 30 mole % dimer, in line with earlier vapor density measurements.²⁰ Further work is needed to resolve the situation. The heat of sublimation of $\text{BeCl}_2(\text{g})$ at 298°K has been obtained from a second-law treatment of mass spectrometric data on vapors over material originally identified as α' BeCl_2 . Intensity-temperature data on BeCl^+ , which is believed to be formed solely from dissociative ionization of BeCl_2 monomer at 460 to 540°K, yielded $\Delta H_{298}^{\circ}(\text{sub}) = 33.0 \pm 2$ kcal/mole for $\text{BeCl}_2(\text{g})$.¹³ Total vapor pressure data are also available,^{13,21} but the crystal form is not certain.

The dissociation energy of $\text{BeCl}(\text{g})$ has been determined from mass spectrometric studies of equilibria in the Be-Cl system.¹³ The derived value, 97 kcal, appears reasonable when compared to half the heat of atomization of BeCl_2 , 110 kcal. Margrave and co-workers²² found $D(\text{MX})/D(\text{MX}_2) = 0.46$ for a number of alkaline-earth fluorides. Herzberg¹⁶ and Gaydon¹⁷ estimated $D(\text{BeCl})$ values of 99 and 69 kcal, respectively, from analysis of electronic band spectra. It is interesting to note that for both BeF and BeCl , Herzberg's estimates are closer to the thermochemical values than are those of Gaydon.

The derived Be-Cl bond energies are roughly equivalent to the Be-O bond energies found for the hydroxides and the oxides. This correlation, particularly as to the equivalence of M-Cl and M-OH bond energies, appears to hold for a number of other metals.

III. Miscellaneous Species

Gross and co-workers⁵ have determined the heat of formation of $\text{Be}_3\text{N}_2(\text{c})$ from calorimetric measurements of the reaction of the nitride with chlorine ($\Delta H_{298}^{\circ} = -140.0 \pm 1.8$ kcal/mole) and from the reaction of beryllium with ammonia ($\Delta H_{298}^{\circ} = -140.4 \pm 0.4$ kcal/mole).

Mass spectrometric evidence for the existence of a gaseous oxyfluoride (Be_2OF_2) has been obtained.²³ Other oxyfluorides may also be important.

TABLE I
HEATS OF FORMATION AND BOND ENERGIES OF
Be-O AND Be-O-H VAPOR SPECIES

	ΔH_f° 298 kcal/mole	E(Be-O) kcal	Ref.
BeO	30 ± 3	106	1
(BeO) ₂	-102 ± 10	(93)	1
(BeO) ₃	-260 ± 10	109	1
(BeO) ₄	-377 ± 10	114	1
(BeO) ₅	-495 ± 20	117	1
(BeO) ₆	-631 ± 20	120	1
Be ₂ O	-6 ± 10	111	2
BeOH	$> -25 \pm 10$	< 105	2
Be(OH) ₂	$> -156 \pm 10$	< 118	2

TABLE II
ENTROPY DATA FOR GASEOUS DIHALIDES

MX_2	$T^\circ K$	$S^\circ(\text{exp})$ e.u.	$S^\circ(\text{calc})$ e.u.	ΔS e.u.	$(k\delta^2/l^2)/k$
BeF_2	1100	72.4	67.7	4.7	0.15
$BeCl_2$	500	70.1	64.2	5.9	.09
MgF_2	1800	84.1	80.1	4.0	.16
$MgCl_2$	1200	85.9	81.3	4.6	.12
CaF_2	1950	90.6	89.8	.8	.01
$CaCl_2$	1200	89.6	89.2	.4	.01
$ZnCl_2$	780	80.1	75.6	4.5	.16
$ZnBr_2$	770	86.1	81.2	4.9	.15
$CdCl_2$	1060	88.2	86.5	1.7	.025
$CdBr_2$	900	90.4	89.8	.6	.025

TABLE III
HEATS OF FORMATION AND BOND ENERGIES OF
BERYLLIUM HALIDES

	$\Delta H_f^\circ_{298}$ kcal/mole	$E(\text{Be-X})$ kcal	Ref.
$BeF_2(c)$	-240.5	---	5
	-241.2 $\pm$ 0.8	---	6
$BeF_2(g)$	-182 $\pm$ 3	148	2,7
	-191	154	8
$BeF(g)$	-48	145	9
	> -58	< 155	2,10
$BeCl_2(c)$	-118.2 $\pm$ 0.5	---	11
	-118.0 $\pm$ 0.6	---	12
$BeCl_2(g)$	-85 $\pm$ 3	110	13
$BeCl(g)$	10 $\pm$ 5	97	13

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RECENT STUDIES OF THERMODYNAMIC PROPERTIES OF BERYLLIUM SPECIES

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This is an informal report on recent results of several research groups at the Tuscaloosa Metallurgical Research Center, U. S. Bureau of Mines, and the National Bureau of Standards. In all cases some stages of the work are still in progress and hence subject to future refinement and revision. The results and conclusions stated below are therefore preliminary and tentative, and should not be cited except with these limitations clearly acknowledged, as well as with due credit to the original sources of the results.

RECENT BUREAU-OF-MINES EXPERIMENTAL DATA ON THE ENTHALPY AND HEAT CAPACITY OF CRYSTALLINE AND LIQUID BeF_2

The Bureau of Mines, Tuscaloosa Metallurgy Research Center, University, Alabama, has measured by adiabatic calorimetry the heat capacity of a crystalline sample of BeF_2 from 7° to 300 °K, and by drop calorimetry its relative enthalpy from 273° to approximately 1200 °K. These results, as yet unpublished, were made available to us for this meeting through the courtesy of Carl Rampacek [1], the work having been done by D. F. Smith and A. R. Taylor, Jr. The results are of particular interest at present because they furnish experimental Third-Law entropies for comparison with those arrived at through the available data for the vapor. In Fig. 1 are plotted their low-temperature heat-capacity values (open circles), and in Fig. 2, their high-temperature relative-enthalpy values. X-ray examination indicated that the sample was mostly crystalline but contained a minor amount of the glassy form; and the elemental chemical analysis supplied with the sample by the Oak Ridge National Laboratory is consistent with the tentative assumption that the sample may contain by weight approximately 97.5% of BeF_2 and 2.5% of BeO . (The thermal data have not been corrected yet for impurities in the sample.)

Anticipating a sizeable entropy discrepancy between these results and the available vaporization data on BeF_2 , discussed later, we are interested in examining these data for evidences of their reliability. We took the liberty of computing mean heat capacities from their enthalpy values of Fig. 2 up to 478 °K (well below the melting point) and of plotting these as the four black circles in Fig. 1, where the two branches of the heat-capacity curve so obtained are seen to meet with excellent smoothness. This smooth-joining is strong evidence, I believe, for the probable correctness of the sample masses and calorimetric energy equivalents in the adiabatic and drop calorimetry. Such consistency is of course highly elementary in good calorimetry, but its lack would not necessarily have been revealed by examining either the adiabatic or the drop-calorimetry results alone.

It is of interest that the curve of Fig. 1, which obviously shows quite high precision, nearly coincides with that for alpha-quartz [2] over a range of more than 200 deg (when compared at temperatures in a constant ratio of about 1.3). The crystalline forms of BeF_2 are apparently analogous to those of SiO_2 [3].

There are three breaks in the (main) curve of Fig. 2. (Suggestions have been made that the two minor ones near 500° and 1000 °K may be related to phenomena observed for BeF_2 in the neighborhood of these temperatures [3].) The large hump near 816 °K, the approximate melting point according to several recent workers [4], deserves some comment. The negative slope of part of the hump would mean a negative specific heat and so cannot correspond to complete equilibrium in the drop calorimeter. One explanation [1], rather generally accepted at least in part, is that the BeF_2 , once melted, thereafter failed to crystallize when cooled in the drop calorimeter. The height of the hump in the enthalpy curve may thus represent a lower limit (approximately 1 kcal/mole) to the true heat of fusion of BeF_2 . Future work is planned both at the Bureau of Mines [1] and the National Bureau of Standards to measure the heats of solution of the glassy and crystalline forms of BeF_2 so that the results of drop calorimetry can be corrected to give the presently unknown heat of fusion. The National Bureau of Standards also has active plans to measure the heat capacities of crystalline and liquid BeF_2 — if and when present attempts to obtain pure samples, described later in this paper, are successful.

THERMODYNAMIC CONSISTENCY OF THE AVAILABLE DATA FOR BeF_2

The heat capacities of Fig. 1 have been reported [1] to give a Third-Law entropy of $\text{BeF}_2(\text{c})$ of $S_{298}^\circ = 12.8$ e.u. (cal deg⁻¹) per mole, and from this value and the enthalpy data of Fig. 2 we calculated for $\text{BeF}_2(\text{c})$ $S_{816}^\circ = 28.7$ e.u./mole, assuming the melting point to be 816 °K. (These two values were approximately checked by an independent calculation [5].) Thermodynamic functions for $\text{BeF}_2(\text{c})$ estimated earlier at the National Bureau of Standards [6] are considerably different and must be discarded. The Dow Chemical Company, Thermal Laboratory, has recently revised the JANAF tables for BeF_2 [7], thereby arriving at $S_{298}^\circ = 12.0$ for the crystal by assuming an entropy of fusion of $\Delta S_{815}^\circ = 2.5$ e.u./mole. Incidentally, this tentative entropy of fusion is quite close on a gram-atom basis to experimental values for the supposedly analogous substances quartz and BF_3 [8].

An entropy cycle for BeF_2 is shown in Table I.

TABLE I. ENTROPY CYCLE FOR BeF₂

<u>T(°K)</u>	<u>State</u>	<u>S(e.u./mole)</u>	<u>Source</u>
		(a)	
0	c	0	3rd law
298	c	12.8	Cp (Bur. Mines) [1]
816	c	28.7	H (Bur. Mines) [1]
		(b)	
1150	g, 1 atm	68.2	Mol. consts.; equilibria [9]
1150	g, satd	77.1	Vapor pressure (mean) [6]
1150	l	31.2	" " (2nd law)
816	l	24.3	H (Bur. Mines) [1]

Whence $\Delta S_f = -4.4$

The Third-Law calculation of part (a) is described above. Part (b) starts with an entropy of the ideal gas based on measured and assumed molecular constants, and a Second-Law entropy of vaporization which has been increased by 4.5 e.u./mole over that used earlier [6] in order to correspond closely to that found independently by several observers.

Table I requires a negative entropy of fusion (-4.4 e.u./mole) for thermodynamic consistency, and thus shows a discrepancy which is probably at least 6 e.u./mole. This discrepancy has been discussed by D. L. Hildenbrand and others at this meeting, but there seems to be no consensus as to where the source of the discrepancy lies. In view of the Bureau of Mines data [1], it seems difficult to believe that the Third-Law entropy values derived therefrom can be too high by several entropy units. The entropy of the ideal gas and the Second-Law entropy of vaporization are perhaps most in doubt. Those inclined to attribute the major part of the discrepancy to the use of an unexpectedly high bending frequency (845 cm^{-1}) in calculating the ideal-gas entropy value given in Table I should give due consideration to the fact that a recent paper from Rocket Power, Inc. [10] gives the same ideal-gas entropy within about 0.1 e.u./mole. The latter value was independently arrived at by an experimental study of an equilibrium forming BeF₂(g) from BeO(c) and HF(g) in the neighborhood of 1000 °K.

Clearly, more experimental work is needed to resolve the present discrepancy.

RECENT NBS MASS-SPECTROMETRIC RESULTS

ON BERYLLIUM SYSTEMS

A high-temperature mass spectrometer of the design used by Inghram and Chupka is being employed at the National Bureau of Standards by John Efimenko. During the period of testing and improving the apparatus, a number of qualitative and a few quantitative studies have been carried out on BeF₂ and on the BeO-BeF₂ and BeO-Al₂O₃ systems. The work involving BeF₂ has thus far been hampered by the lack of a pure sample, particularly one free of water. The results described below are

preliminary, and subject to refinement in a continuation of these studies under more favorable conditions.

Figure 3 represents the vapor pressure of BeF_2 in a region below the melting point. The BeF_2 , which had been prepared by decomposing $(\text{NH}_4)_2\text{BeF}_6$, showed on X-ray examination 30 to 70% amorphous content, the crystalline content being hexagonal. The slope corresponds to a Second-Law heat of vaporization (or sublimation) $\Delta H_{755} = 55.35 \pm 0.53$ kcal/mole. However, considering the ill-defined nature of the condensed state of the sample, this value probably has little meaning.

In another study, a mixture of BeO and Al_2O_3 in a tantalum crucible inside a tungsten effusion cell at 2100 °K was scanned. Table II shows the tentative identification of the observed mass numbers (ratio of mass to charge). The formation of many of the species in Table II may be due to the strong reducing action of the tantalum container on the oxides. Heating a 1:1 mole ratio of BeO and Al_2O_3 in a tungsten cell directly gave predominantly the mass numbers 9 (Be^+), 16 (O^+), 27 (Al^+), and 75 ($(\text{BeO})_3^+$).

TABLE II. MASS-SPECTROMETRIC STUDY OF THE
SYSTEM $\text{BeO} + \text{Al}_2\text{O}_3$ at 2100°K (NBS)

<u>Mass No.</u>	<u>Species (?)</u>	<u>Mass No.</u>	<u>Species (?)</u>
9	Be^+	60	
25	BeO^+	70	Al_2O^+
27	Al^+	79(?)	BeAl_2O^+
43	AlO^+	95	$\text{BeAl}_2\text{O}_2^+$
52	BeAlO^+	197	$\text{Ta}^{181}\text{O}^+$
54	Al_2^+	211	
58			

In a third study, whose tentative species identifications are shown in Table III, the system $\text{BeO}-\text{BeF}_2$ was investigated. Owing to the widely different volatilities of BeO and BeF_2 , a "temperature-gradient" cell was used in which BeF_2 vapor, generated by evaporation at 550 (or 650) °K was passed through a considerable thickness of finely crushed BeO , the latter being in an effusion cell at 1475 (or 1675) °K. Several species arising from the water impurity appeared, but disappeared at the highest temperatures.

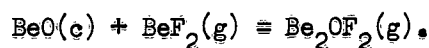
TABLE III. MASS-SPECTROMETRIC STUDY OF THE SYSTEM

BeO + BeF₂ (+H₂O) (NBS)

Mass No.	Species(?)	T(°K)	Mass No.	Species(?)	T(°K)
18	H ₂ O ⁺		38	F ₂ ⁺	
20	HF ⁺		44	BeOF ⁺	(Low)
23	Na ⁺		47	BeF ₂ ⁺	
26	BeOH ⁺	<1700°	64	BeOHF ₂ ⁺	<1800°
27	BeOH ₂ ⁺	Low	72	Be ₂ OF ₂ ⁺	>1600°
36	HO ⁺	<1700°	75	(BeO) ₃ ⁺	

All the mass numbers listed in Tables II and III give shutter responses indicating that they originated in the effusion cell. In addition, in each table no mass number attributed to a species arising from both components was found when the separate components were individually examined. However, in some cases alternative species assignments, such as in place of Ta¹⁸¹⁰⁺ in Table II, have not yet been ruled out.

Dr. Efimenko thinks, however, that there is good reason to believe that the assignment of mass number 72 to the heretofore unreported species Be₂OF₂ is correct. This molecule is easy to formulate on the basis of conventional valences. (Incidentally, its existence had been previously predicted by C. W. Beckett.) The ratio of the intensity for Be₂OF₂ to that for BeF₂, as determined from these NBS studies, are plotted (as the ordinate A) in Fig. 4 over the approximate temperature range 1550° to 1850 °K, and in Fig. 5 over the range 1850° to 2150 °K (a total temperature range of 600 degrees). A is thus assumed to be proportional to the equilibrium constant for the reaction



The slopes of the straight lines in the two graphs give, for the heat of this reaction, Second-Law values of

$$\Delta H_{1700} = 39.25 \pm 3.5 \quad \text{and} \quad \Delta H_{2000} = 40.65 \pm 0.9 \text{ kcal.}$$

(Unfortunately, attempts to correct the two ΔH values to a common temperature in this range, by making use of an equipartitional Cp for Be₂OF₂(g), increased their difference slightly, but not outside the indicated precision.)

APPROACHES AT NBS TO PREPARING PURE

BeF₂ IN DEFINITE POLYMORPHIC FORMS

Since BeF₂ has been shown to exist in at least three different crystalline forms which are difficult to obtain pure, an intensive effort is being made at the National Bureau of Standards to prepare these for subsequent use in accurate measurements of their physical properties — particularly their heat capacities and, to determine their heats of transition and fusion, their heats of solution.

Six different methods, identified in Table IV, are being tried or are under consideration. It is not anticipated that methods 4 and 5 will be put in operation during fiscal year 1964.

TABLE IV. NBS METHODS BEING DEVELOPED TO PREPARE PURE

POLYMORPHIC FORMS OF BeF₂

-
1. Slow crystallization of degassed BeF₂(l).
 2. Steady-state transport via NH₄F (10%, in HF). (*)
 3. Temperature-controlled decomposition of (NH₄)₂ BeF₄. (†)
 4. Vacuum distillation.
 5. Crystallization from solution of BeF₂ in LiF.
 6. Annealing of BeF₂(glassy) at 400°C.
-

(*) Quartz form favored. (†) Crystoballite form favored.

Augustus R. Glasgow, Jr., is pursuing the first five, and George T. Furukawa has explored the sixth method. These methods are discussed in order below.

By the first method, the purest commercially available BeF₂ would be melted and then thoroughly degassed by pumping, with a separation and analyses to identify the trapped solid, liquid, and gaseous by-products so evolved. The liquid BeF₂ is then to be cooled slowly under its own vapor pressure to a controlled temperature in the hope of inducing crystallization of a single polymorph. In order to obtain a definite polymorphic form (one analogous to alpha-quartz, beta-quartz, or crystoballite), it may be necessary to resort to seeding using seed crystals obtained by one of the other methods. Owing to the relatively large heat capacity of the crystallization vessel (a bomb constructed for method 2) and the expected low heat of fusion of BeF₂, the ability to follow the progress of crystallization by a decrease in the rate of cooling is limited. Dr. Glasgow has assembled and constructed apparatus for this method, with the plan of trying its operation in the near future. (In a recent preliminary trial of this method, tests indicated that the BeF₂ product was about 25% crystalline (hexagonal, beta quartz-like form) and 75% glassy.)

The second method being developed involves steady-state transport of the BeF_2 through a suitable solution to a somewhat cooler site of crystallization, and may be called the "hydrofluorothermal" method. This is based on a successful analogous method whereby amorphous quartz is transported by a 10% aqueous solution of NaOH , and crystallizes at another site. In the case of BeF_2 the plan is to substitute a 10% solution of $(\text{NH}_4)_2 \text{BeF}_4$ in anhydrous HF , and the crystallization of a quartz form of BeF_2 is believed to be favored. It is anticipated that the greatest experimental difficulty will be in introducing the HF in liquid anhydrous form, and to this end it is planned to seal the HF in a platinum capsule which is subsequently burst by an internal pressure of 10-30 atm, at temperatures of 100° to 150 °C.

In the third method, $(\text{NH}_4)_2 \text{BeF}_4$ would be decomposed in a small temperature range, and the by-product NH_4F would volatilize. This method apparently favors the formation of the cristoballite form of BeF_2 . If successful, it is presently considered the most promising for producing large quantities of crystalline BeF_2 .

The fourth method is vacuum distillation.

The fifth method involves the crystallization of BeF_2 from a binary liquid solution with another fluoride such as LiF . (The temperature-composition phase diagram of the BeF_2 - LiF system is already known with fair accuracy.) The original solution must of course be sufficiently rich in BeF_2 that this is the equilibrium solid phase. The starting composition would of course determine the temperature at which, upon cooling, crystallization can begin, and hence what crystalline polymorph would result under equilibrium conditions. It may be possible to purify the crystals by extracting the mother liquor with a volatile solvent such as anhydrous HF .

The sixth method consists of annealing pure glassy BeF_2 at about 400 °C. Dr. Furukawa found that after 24 hours of such annealing there was a marked increase in crystallinity as revealed by X-ray examination. The plan is to conduct the annealing in a platinum vessel with intermittent precise measurements of heat capacity to monitor the progress of crystallization more accurately. While this method is straightforward and apparently successful, it is not known with certainty whether a single polymorph of BeF_2 results.

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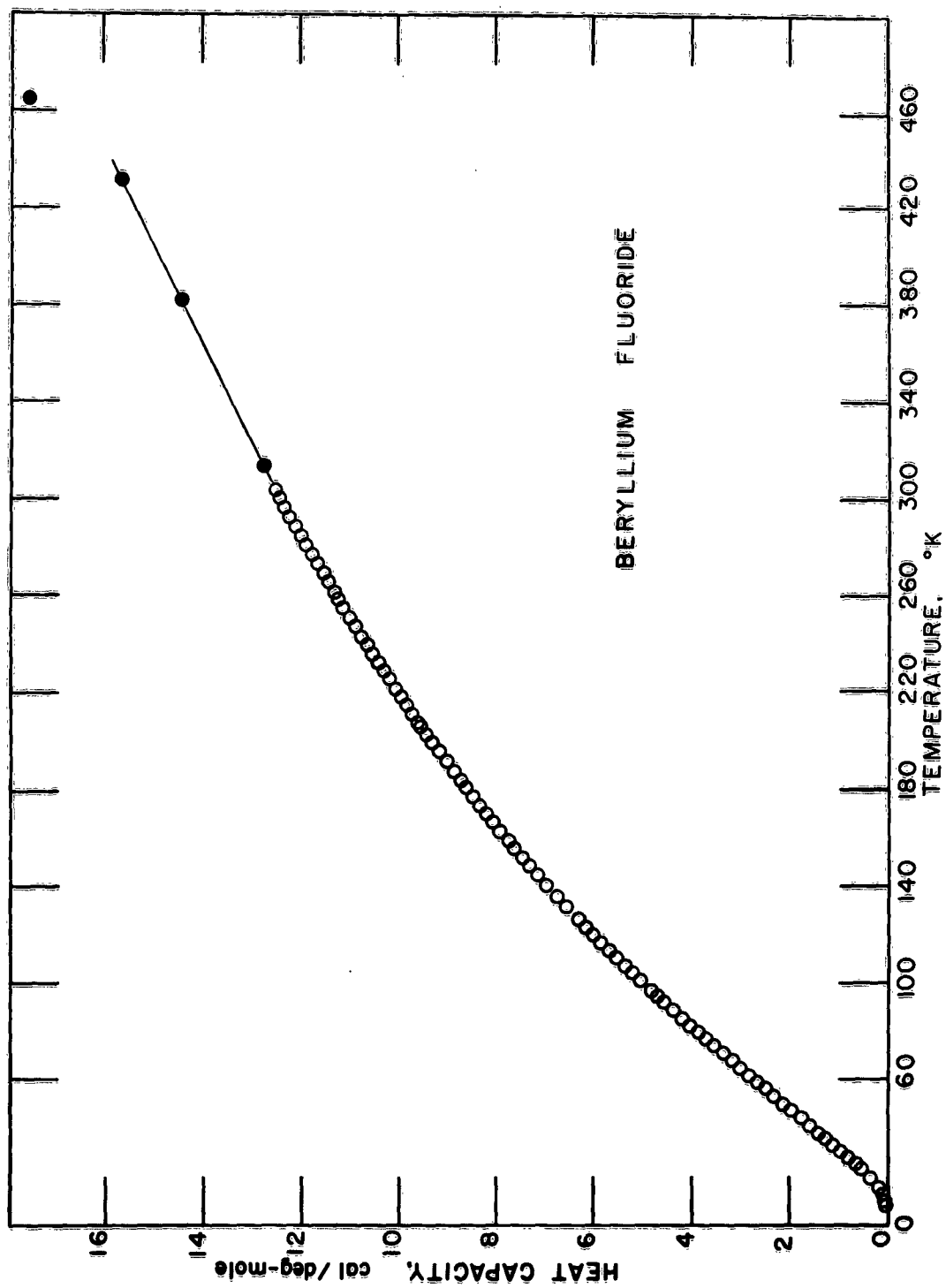


FIGURE 1. C_p OF BeF_2 (c) (BUREAU OF MINES)

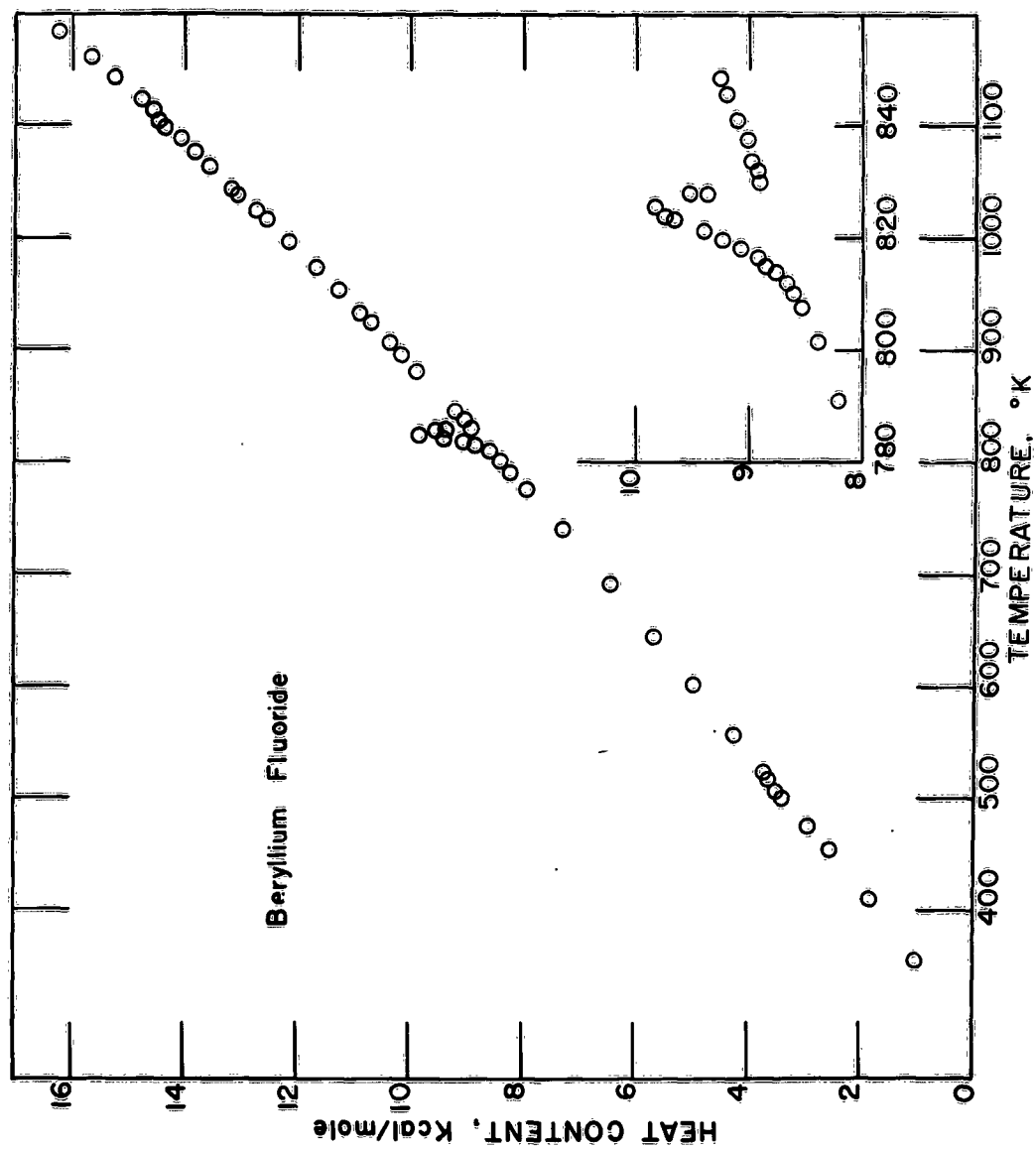


FIGURE 2. $H_T - H_{273.15}$ OF BeF_2 (BUREAU OF MINES)

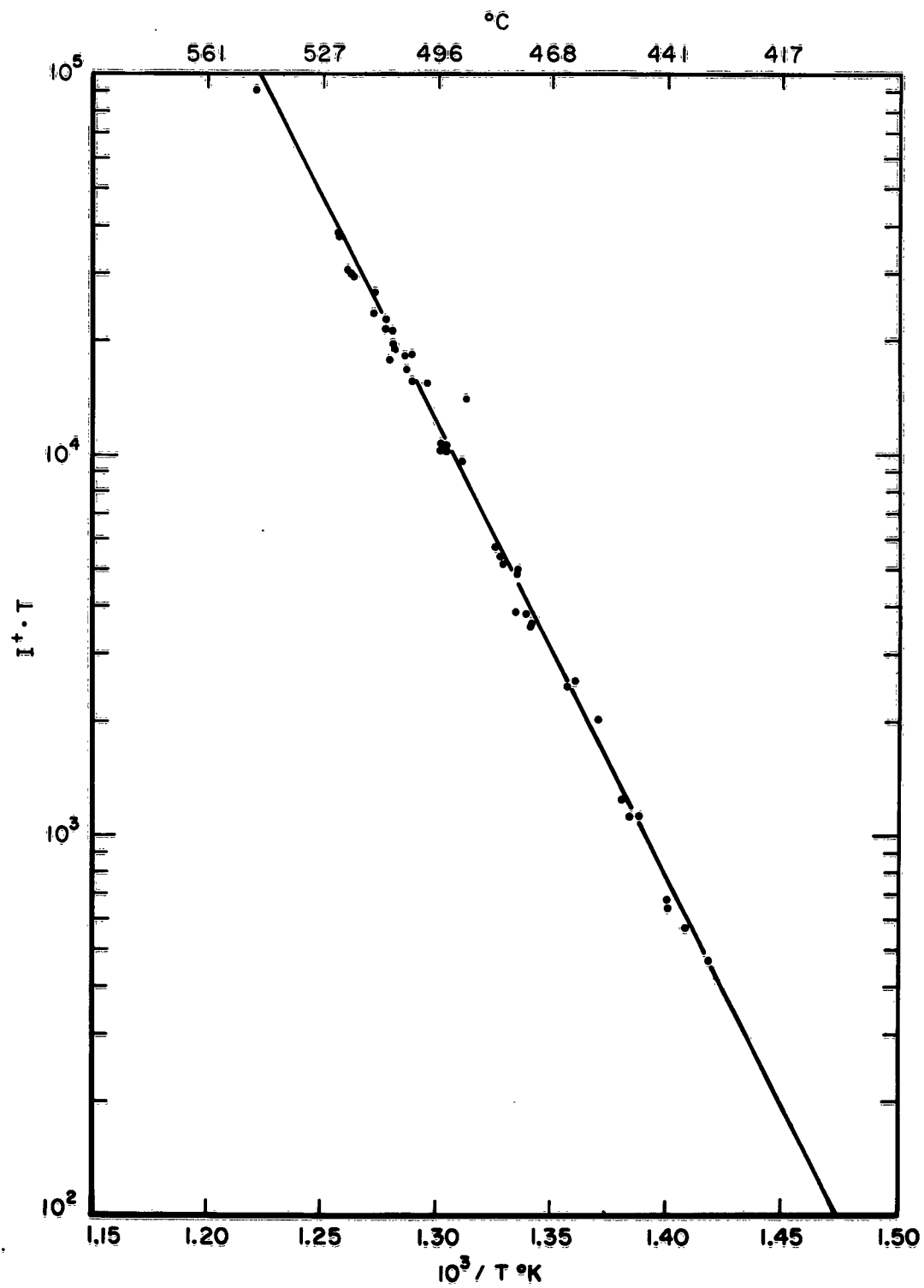


FIGURE 3. BeF₂ VAPORIZATION (NBS)

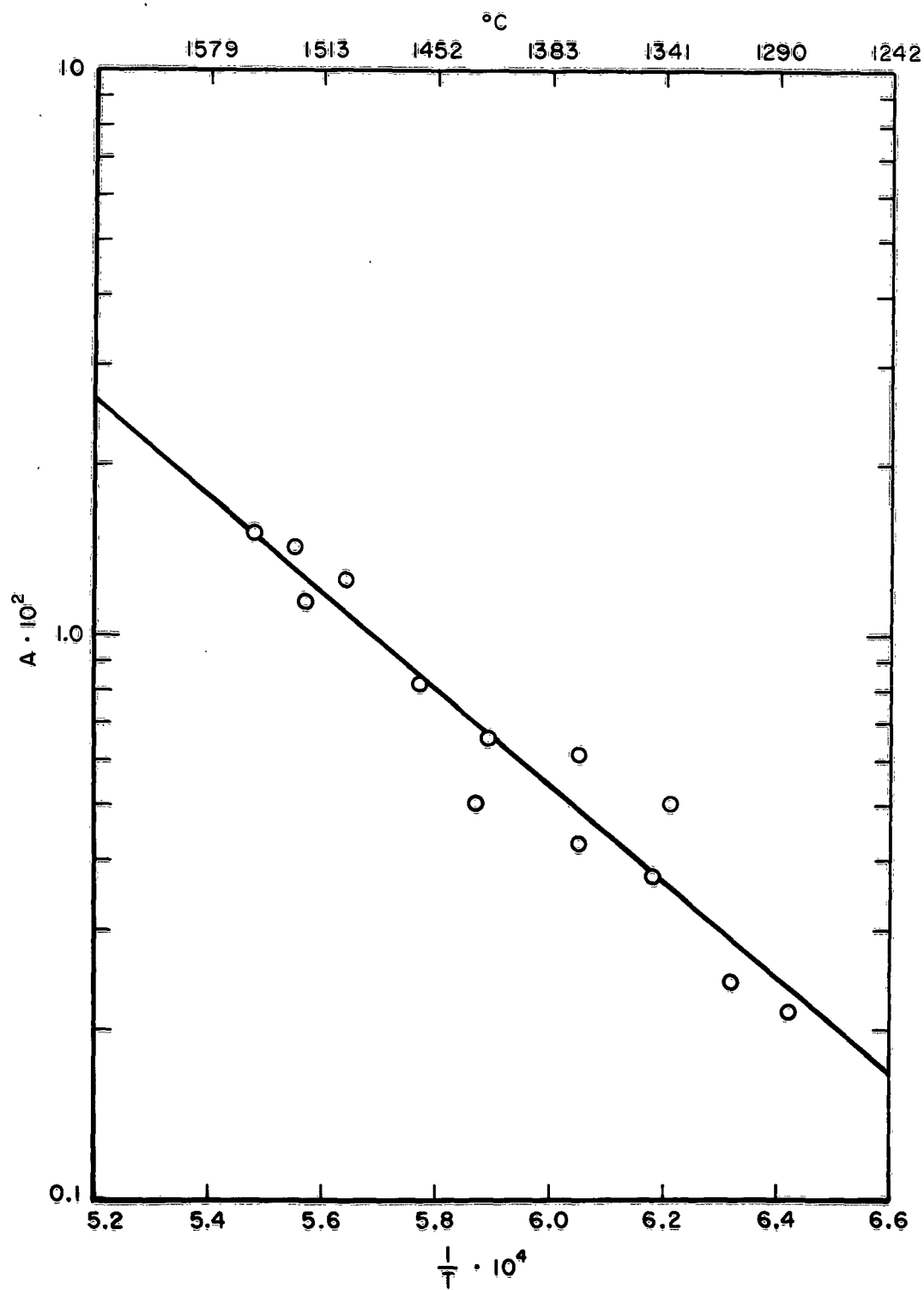


FIGURE 4. $\text{Be}_2\text{OF}_2(\text{g})$ FORMATION, 1550°-1850°K (NBS)

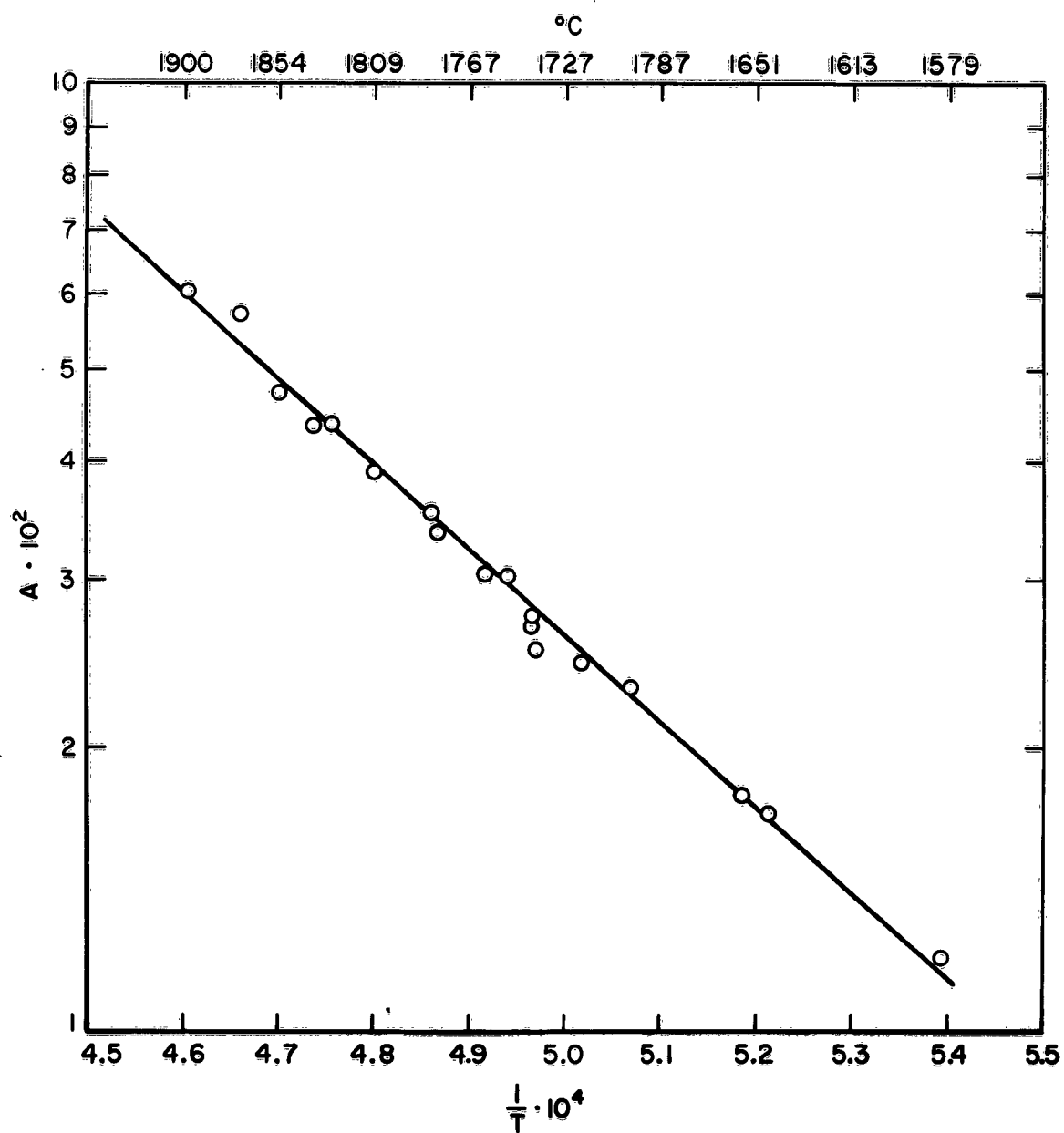


FIGURE 5. $\text{Be}_2\text{OF}_2(\text{g})$ FORMATION, 1850-2150°K (NBS)

THE THERMODYNAMIC PROPERTIES OF SOME BERYLLIUM COMPOUNDS

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INTRODUCTION

During the past three years a program sponsored by Edwards Air Force Base to obtain experimental thermodynamic data on various beryllium compounds has been under way at these Research and Development Laboratories. As a result of this program a considerable amount of experimental thermodynamic data has been made available for aid in computation of performance of propellants containing beryllium compounds. These data have been incorporated in the revised JANAF Tables.

It is the experience of our Research Laboratories that in order to obtain highly precise thermodynamic data that will permit the calculation of heats of formation and standard entropies of gaseous species at high temperatures it is necessary to design a special experiment for nearly every compounds. It has also been found that standard research tools such as time of flight mass spectrometers will not yield precise data for equilibrium conditions due to fragmentation of some of the species by the high electron energies necessary for ionization. Therefore, the requisite thermodynamic data was obtained for the compounds described in this paper by means of transpiration studies, torsion and gravimetric effusion, and the molecular flow reaction study method developed at these Laboratories. Temperature ranges varied between 500 and 3000°K at pressures ranging from atmospheric to 10^{-7} mm Hg. The very high temperatures used in some of these studies were generated either by electron bombardment heating or by vacuum resistance heating. In both cases specially designed furnaces were employed.

The thermodynamic data for compounds discussed in the following sections have been completed and have been published or are in the process of publication at the present time. Other beryllium compounds under study and on which the results have not been published include BeOH , $\text{Be}(\text{OH})_2$ and the heat of sublimation of BeF_2 and the beryllium oxide vapor species. Continuing work on this contract is concerned with the thermodynamic properties of the light metal halides. To date the heat of sublimation of MgF_2 has been completed and the data is reported at the end of this paper.

EXPERIMENTAL RESULTS

BeO Using a specially designed electron bombardment furnace-Southard drop calorimeter combination, the heat capacity between 2273-2573°K and heat of fusion of beryllium oxide were determined. It was found after extensive investigation that rhenium was completely unattacked by solid or liquid beryllium oxide at temperatures as high as 2850°K. Special cells and capsules of this material were used to contain all samples of beryllium oxide. In this manner it was found possible to eliminate all complicating factors of reaction between beryllium oxide and container

material which had previously been encountered.

Based on a large number of individual measurements of the heat capacity between 2273-2573°K, the sensible enthalpy of BeO(s) in this range can be given by the following equation:

$$H_T - H_{298} = 13,937/T - 11,579 \text{ cal/mole} \quad (1)$$

The $\Delta H_{\text{fus}}^{2853^\circ\text{K}}$ for BeO was found to be 16.8 ± 0.8 kcal/mole based on six individual determinations. (Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 18-23, 1963)

BeCl₂ The vapor pressure curve of solid beryllium chloride was determined over the temperature range 440-600°K using torsion and gravimetric effusion procedures. Based on an analysis of the data (plotted in the form of log P vs. 1/T) the following thermodynamic values were obtained:

$$\Delta H_{\text{sub}}^{298^\circ\text{K}} \text{ (2nd law)} = 33.1 \pm 0.5 \text{ kcal/mole}$$

$$\Delta S_{\text{sub}}^{298^\circ\text{K}} = 43.2 \pm 1.5 \text{ cal/deg/mole}$$

A third law value for the $\Delta H_{\text{sub}}^{298^\circ\text{K}}$ of BeCl₂, using the thermodynamic data and thermal functions of the JANAF Tables, yielded a value of 32.1 ± 0.3 kcal/mole. (J. Phys. Chem. 67, 1802 [1963])

From a comparison of the vapor pressure data obtained for BeCl₂(s) by the torsion and gravimetric effusion procedures, coupled with the available thermodynamic data for the dimer of BeCl₂(g), it was concluded that, within the experimental error, only BeCl₂ monomer was formed in the gas phase. It should be pointed out that the extreme hygroscopicity of BeCl₂, coupled with the fact that on heating, the water reacts with the BeCl₂ to yield BeO(s) and HCl(g), makes it mandatory that all moisture be eliminated from the BeCl₂ samples. Even with the greatest precautions some moisture is absorbed by the samples and consequently the precision of the BeCl₂(s) vapor pressure data and, to an even larger extent, the precision of the BeCl(g) data reported below, is not as good as that obtained when dealing with the non-hygroscopic BeF₂(s).

BeCl The reaction



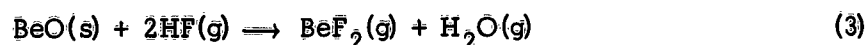
was studied over the temperature range 1573-1723°K using the molecular flow effusion procedure to obtain thermodynamic data for beryllium subchloride, BeCl(g). Over the temperature range studied the ΔH_f was found to be 89.1 ± 7.6 kcal/mole while the ΔS_f was determined to be 39.4 ± 4.6 cal/deg/mole. Employing the $\Delta H_f^{1673^\circ\text{K}}$ obtained from the plot of log K vs. 1/T and the thermodynamic data and thermal functions in the JANAF Tables for BeCl₂(g) and Be(l) the second law value for $\Delta H_f^{298^\circ\text{K}}$ of BeCl(g) was found to be 3.7 ± 3.8 kcal/mole. The $S_{298^\circ\text{K}}$ was found to be

53.0 ± 2.3 cal/deg/mole from a plot of ΔF vs. T . The third law calculation for ΔH_f^{2980K} of $\text{BeCl}(g)$ yields a value of 2.0 ± 0.8 kcal/mole, in excellent agreement with the second law value. (J. Phys. Chem. 68, in press.)

BeF₂ The vapor pressure curve for liquid beryllium fluoride was established over the 823-1223°K temperature range by means of the gravimetric effusion, torsion effusion and transpiration techniques. More than 50 individual pressure measurements were made over the 400° temperature range. A plot of $\log P$ vs. $1/T$ yielded a value (2nd law) for ΔH_f^{2980K} of 53.22 ± 0.18 kcal/mole. A plot of ΔF vs. T led to a value of 38.7 ± 0.6 cal/deg/mole for the $\Delta S_{\text{vap}}^{298}$. (J. Phys. Chem. 67, 36 [1963].)

Calculation of the molecular weight of the vapor species by analysis of the torsion and gravimetric effusion data yielded a value of 44.7 ± 2.4 , compared to the value of 47.0 for the molecular weight of pure BeF_2 . The melting point of crystalline BeF_2 was established as $542 \pm 3^\circ\text{C}$.

A detailed study of the reaction



was carried out between 943 and 1243°K by means of the molecular flow effusion technique to obtain thermodynamic values for $\text{BeF}_2(g)$. At 1093°K the ΔH_r for reaction (3) was found to be 20.5 ± 1.7 kcal/mole and the ΔS_r 6.0 ± 0.3 cal/deg/mole. These values combined with data in the JANAF Tables lead to the following values for $\text{BeF}_2(g)$:

$$\Delta H_f^{2980K} \text{ (2nd law) } = -191.3 \pm 2.0 \text{ kcal/mole}$$

$$S_{2980K}^0 = 52.4 \pm 0.3 \text{ cal/deg/mole}$$

A third law calculation leads to -191.2 ± 0.4 kcal/mole for the ΔH_f^{2980K} of $\text{BeCl}_2(g)$. (J. Phys. Chem. 67, 1191 [1963].)

BeF The reaction



was studied over the temperature range 1425-1675°K using the molecular flow effusion technique. The reaction was carried out in a graphite-beryllium oxide three part cell in which no extraneous reactions were found to occur. In several runs the graphite reactions of the cell were replaced with nickel. This substitution produced no change in the data obtained, thus further confirming the absence of side reactions involving container materials.

A plot of K vs. $1/T$ yielded ΔH^{1550K} of 91.5 ± 3.8 kcal/mole. The ΔS^{1550K} was found to be 44.3 ± 2.4 cal/deg/mole. These values led to a ΔH_f^{2980K} of -48.3 ± 1.9 kcal/mole and an S_{2980K}^0 of 51.1 ± 1.2 cal/deg/mole for $\text{BeF}(g)$. A third law calculation for ΔH_f^{2980K} produced the

value -50.6 ± 0.6 kcal/mole in good agreement with the second law value. (J. Phys. Chem. 67, 703 [1963].)

Be₃N₂ The decomposition pressure of solid beryllium nitride according to equation (5) was measured between 1400 and 1700°K using the torsion effusion technique.



Because of the severe limitations in the measurement of the very small angular displacements, coupled by the fourth power dependency on the pressure, it was only possible to obtain a reliable third law heat of formation for solid beryllium nitride. The value obtained for $\Delta H_f^{298^\circ\text{K}}$ was 140.3 ± 1.5 kcal/mole. (J. Phys. Chem. 68, in press.)

MgF₂ In the course of another investigation where MgF₂(g) was to be passed over another condensed phase, it became necessary to obtain some reliable vapor pressure data for MgF₂(s) at lower temperatures than had been reported. Thus, the vapor pressure of MgF₂(s) was measured by torsion and gravimetric effusion between 1273 and 1513°K. The vapor pressure curve in this region is defined by

$$\log P_{\text{atm.}} = -17,096/T + 7.6845 \quad (6)$$

From analysis of the vapor pressure data the following thermodynamic values were determined for MgF₂.

$$\Delta H_{\text{sub}}^{298^\circ\text{K}} \text{ (2nd law)} = 83.21 \pm 1.03 \text{ kcal/mole}$$

$$\Delta H_{\text{sub}}^{298^\circ\text{K}} \text{ (3rd law)} = 83.95 \pm 0.65 \text{ kcal/mole}$$

$$\Delta S_{\text{sub}}^{298^\circ\text{K}} = 41.78 \pm 0.75 \text{ cal/deg/mole}$$

(J. Phys. Chem. 68, in press.)

RECENT WORK AT ARTHUR D. LITTLE

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INTRODUCTION

The topics discussed are some aspects of the lithium fluoride problem, recent work on the lithium fluoride-beryllium fluoride system, and, in some detail, electric quadrupole deflection experiments.

1. Lithium Fluoride

The lithium problem was re-examined in connection with work on the mixed lithium fluoride-beryllium fluoride system. In spite of rather extensive work in several laboratories, a number of problems still remain, in particular with regard to the precise composition of the vapor. The results of two extended heat-of-sublimation runs in our laboratory are presented in Table I.

TABLE I. Mass-spectrometric heats of sublimation
kcal/mole

	<u>Set 1</u>	<u>Set 2</u>
$\Delta H_{1000}(\text{LiF})$	65.9 ± 0.6 (927°-1013°K)	63.7 ± 0.5 (860°-1060°K)
$\Delta H_{1000}(\text{Li}_2\text{F}_2)$	68.7 ± 0.6 (927°-1013°K)	67.9 ± 0.5 (860°-1060°K)
$\Delta H_{1000}(\text{Li}_3\text{F}_3)$	72.1 ± 0.6 (927°-1013°K)	75.7 ± 1.2 (897°-1060°K)

In deriving these data we have followed the conclusions of Berkowitz, Tasman and Chupka (BTC)¹ concerning the fragmentation pattern of the various species* and have identified the slopes of the $\log I^+T$ vs $1/T$ plots for LiF^+ , Li_2F^+ and Li_3F_2^+ with the heats of sublimation of monomer, dimer and trimer respectively. Results for one of the runs are plotted in Figure 1. For the most abundant species, Li_2F^+ , the results of the two experiments agree within the standard deviation of the slopes; for the other species, the difference between the results of the two runs is slightly greater. In Table II, the

TABLE II. Heats of sublimation of gaseous lithium fluoride, kcal/mole

	<u>This Work</u>	<u>Hildenbrand et al.²</u>	<u>JANAF</u>
$\Delta H_{1000}(\text{LiF})$	64.8 ± 2	63.1 ± 1	65.5 ± 2
$\Delta H_{1000}(\text{Li}_2\text{F}_2)$	68.3 ± 1	66.8 ± 2	73.0 ± 2
$\Delta H_{1000}(\text{Li}_3\text{F}_3)$	73.9 ± 3	-	80.9 ± 2

*The work of Akishin³ on the fragmentation of lithium fluoride is open to serious criticisms, which were discussed at this meeting by J. Berkowitz.

averages of the two sets of data are compared with the data of Hildenbrand et al.², obtained from torsion-effusion vapor pressure measurements and the heat of dimerization of BTC; and the JANAF Table values,⁴ based on vapor pressure measurements from several sources and calculated dimer entropies. Our data give a dimerization energy of 61.3 kcal/mole, in very good agreement with the BTC value of 61.4 kcal/mole. As an example of the problems that remain, it may be noted that while Hildenbrand et al. accepted the BTC dimerization energy value in analyzing their data, they used a dimer-monomer ratio of 1.5 rather than the value of 0.67 obtained by BTC. However, we believe that the averages of the experimental heat of sublimation values obtained in this work and that of Hildenbrand et al., as given in Table III

TABLE III. Recommended heat of sublimation values

$\Delta H_{1000}(\text{LiF})$	64.4 kcal/mole
$\Delta H_{1000}(\text{Li}_2\text{F}_2)$	67.6 kcal/mole
$\Delta H_{1000}(\text{Li}_3\text{F}_3)$	73.9 kcal/mole

represent the best estimates available at this time and are to be preferred to the current JANAF Table values.

2. Lithium Fluoride-Beryllium Fluoride

In relation to this system, we discuss two points: first, some problems connected with the mass spectrometric analysis of mixed systems; and secondly, electrochemical experiments as a very useful and so far unexplored source of thermodynamic data for systems of interest to the Panel.

a. Mass Spectrometer Experiments

We have studied mass spectrometrically lithium fluoride-beryllium fluoride solutions saturated with lithium fluoride and containing about 25% BeF_2 . The mass spectrum of this system is compared to that of lithium fluoride in Table IV. In both cases the ion intensities have been normalized

TABLE IV. Mass spectra of LiF and LiF- BeF_2 solution*

	<u>LiF(c) + LiF-BeF_2 (soln) 990°K</u>	<u>LiF(c) 987°K</u>
BeF_2^+	883	-
BeF^+	332	-
Li^+	229	51
Li_2F^+	100	100
LiBeF_2^+	65	-
LiF^+	37	34
Li_3F_2^+	7	9

*Ion intensities normalized to $\text{Li}_2\text{F}^+ = 100$; uncorrected for isotope distribution.

to $\text{Li}_2\text{F}^+ = 100$. The relative intensities of LiF^+ , Li_2F^+ and Li_3F_2^+ in the two spectra are essentially identical and confirm the existence of saturated LiF vapor over the mixed system. Comparison of the mass spectra then shows that most of the Li^+ ion intensity in the mixed system must be due to the mixed dimer LiBeF_3 , which fragments to give Li^+ and LiBeF_2^+ in the ratio 3:1. $\log I^+T$ vs $1/T$ plots for the various ionic species are in accord with this conclusion. In the only other mass spectrometric work on this system⁵ a high $\text{Li}^+/\text{Li}_2\text{F}^+$ intensity had been taken as evidence of a sharply reduced LiF activity in a 50:50 $\text{LiF}-\text{BeF}_2$ melt. It would now appear that this conclusion was incorrect and that the activity coefficient of LiF in that mixture may be close to unity.

b. Electrochemical Experiments (emf measurement)

From mass spectrometric experiments it was deduced that the activity coefficient of BeF_2 in a solution containing about 75% LiF and 25% BeF_2 was approximately 0.1. To check this conclusion by an independent method electrochemical experiments were carried out in our laboratory by Dr. James D. Birkett. For this purpose a concentration cell containing pure BeF_2 in one compartment and a mixture of 75% LiF and 25% BeF_2 in the other was used. The emf of this cell is given by

$$E = - \frac{RT}{2F} \ln \frac{a_1}{a_0}$$

where a_0 and a_1 are the activity of BeF_2 in the pure liquid and in solution respectively and F is the faraday.

The experiments were carried out in a cell sketched in Figure 2. The two compartments of the cell were separated by a sheet of 1/4 inch graphite containing near its bottom a 1/4 inch diameter plug of porous carbon which served as a junction between the two half cells. The liquid junction potential of fused salt systems of this type is expected to be only of the order of a few mv and will be neglected here. The cell was held in a clay-graphite crucible containing molten lead, the latter serving a thermal reservoir and heat transfer medium. The entire assembly was placed in an open-top muffle furnace, the top of which was sealed with appropriately shaped pieces of alumina and fibrefax. Two sets of data were obtained and are summarized in Table V. The potentials reported are the average of a number of values taken over a period of at least 25 minutes during which the emf stayed within 8 mv of the average value.

TABLE V. Lithium Fluoride-Beryllium Fluoride Concentration Cell Data (Pure BeF_2 vs 25% BeF_2 -75% LiF Soln.)

	<u>E.M.F.</u>	<u>BeF_2 Activity in Solution</u>	<u>Activity Coefficient</u>
906°K	154 mv	0.027	0.11
965°K	148 mv	0.039	0.16
Activity coefficient estimated from mass-spectrometric data			0.1

Within the accuracy of the two types of experiments the electrochemical results confirm the low activity of beryllium fluoride deduced from the mass spectrometric data. It should be stressed that electrochemical experiments on fused salt systems of the type of lithium-beryllium fluoride system provide a very valuable supplement for obtaining thermodynamic data for light metal systems. In particular it should be noted that a large part of the complexity of fused salt electrochemistry is due to the efforts which are made to interpret the observed data in terms of the structure of the ionic species formed. In the present instance, however, we are only interested in the direct results of the emf measurements. The activity ratios obtained in this way give immediately the ratios of the partial pressures of monomer over the solution and over the pure compound. If activities are measured over a range of concentrations, mass spectrometric results may then be used to calculate the partial pressures of dimers and mixed species corresponding to a given activity.

3. Electric Quadrupole Deflection Experiments

We have used an electric quadrupole field in conjunction with the Nuclide high-temperature mass spectrometer to determine whether high temperature species effusing from a molecular beam oven are polar or not and thus to obtain structural information concerning these species. We first describe the experimental arrangement now in use and then review the results obtained so far.

a. Experimental

A distinction should immediately be made between the experiments to be described here and the so-called quadrupole mass spectrometer. In the latter (Figure 3a) a quadrupole field serves to mass-analyze ions produced in a conventional mass spectrometer ion source, the mass filter being placed between the ion source and detector. In our experiments (Figure 3b) a quadrupole field is used to deflect neutral molecules which only then enter the ion source of the mass spectrometer. The experimental arrangement currently in use is shown in Figure 4. The molecular beam is produced in an oven consisting of a pinched-off metal tube provided with an effusion orifice and heated by passing a large electric current through it. The oven is contained in a separately pumped chamber which is separated from the quadrupole chamber and the remainder of the mass spectrometer by means of ball valve. Thus samples can be changed and degassed while the remainder of the mass spectrometer is kept under vacuum. The quadrupole lens is placed in what is ordinarily the Knudsen cell chamber of the mass spectrometer. The lens consists of 4 polished steel rods, one pair of which is grounded while the other pair is connected to a variable high voltage supply capable of supplying up to 60 kv. In practice, potentials up to 35 kv have been reached before electric breakdown occurred. A small slotted rod near the midpoint of the quadrupole lens serves as a beam stop.

The operation of the system is shown schematically in Figures 4a and 5b. With the stop in the position shown in Figure 5a, and with the quadrupole field turned off, molecules effusing from the oven can pass directly into the mass spectrometer, producing what will be referred to as the "straight through beam" signal. By rotating the stop 90° about its axis (Figure 5b)

about 99% of the straight through beam is eliminated. (Geometrically the stop completely shadows the entrance slit, but about 1% of the signal still remains as a result of the scattering of the molecular beam by molecular gas.) If the quadrupole field is now turned on, polar molecules in appropriate rotational quantum states which leave the oven at small angles to the beam axis will be deflected in such a way as to reach the ion source (Figure 5b) and will produce what will be referred to as the "focussed beam" signal.

An example of the type of mass spectrometer trace obtained is shown in Figure 6, which shows the refocussed beam signal for LiBr as a function of voltage. This run was made with an earlier version of the apparatus, in which oven and quadrupole lens were both contained in the Knudsen cell chamber. The direction of the trace is from right to left, the refocussing voltage being alternately turned on and off. In this case the increase in signal obtained by refocussing at high voltages was large enough so that it could be seen superimposed on the direct beam (right-hand part of the trace, 3 v full scale). With the beam stop in (left-hand part of the trace, 100 mv full scale) the refocussed signal at 30 kv is seen to be equivalent to about 2% of the direct beam. It must be stressed that the amount of refocussing is a function of the apparatus geometry, and with the new arrangement described earlier in the section the sensitivity has been increased by approximately a factor of 6.

Of the experiments described below, those on the lithium halides and on lithium oxide were carried out with the first version of the apparatus.⁶ The remainder were carried out with more sensitive equipment described here.

b. Results

(1) Lithium Fluoride and Lithium Chloride. Typical data for these systems are summarized below:

TABLE VI. Electric deflection experiments: lithium halides

<u>Ion</u>	<u>Mass</u>	<u>Ion Current, Arbitrary Units</u>		<u>% Refocussed</u>
		<u>Straight-Through Signal</u>	<u>Refocussed Signal (25 kv)</u>	
Li^+	7	25	0.12	0.5
LiF^+	26	13	0.3 (32 kv)	2.3 (32 kv)
Li_2F^+	33	19	0	0
Li^+	7	4.7	0.024	0.5
LiCl^+	42	8.5	0.18	2.1
Li_2Cl^+	49	10.5	0	0

The refocussed signal observed in the case of the Li^+ and LiX^+ ions is due to the polar monomers LiF and LiCl. The Li-X bond in the dimers Li_2X_2 are expected to be of the same order as the dipole moments of the monomers. Thus a non-planar dimer configuration should have a significant dipole moment. The absence of polarity indicated by a lack of refocussed signal for the dimer ions Li_2X^+ therefore indicates a planar dimer structure.

(2) Lithium Oxide. An account of this work has been published recently.⁶ Data are summarized in Table VII. A non-linear structure for

TABLE VII. Relative ion intensities

	Li^+	Li_2O^+	LiO^+
<u>Straight-through beam</u>	700	650	43
<u>Refocussed beam (stop wire in):</u>			
Increase in signal due to applied potential	No refocussing	No refocussing	
10 kv			1 ± 0.5
15			2
25			3.5
30			4.2
35			5.5

$\text{Li}_2\text{O}(\text{g})$ would be polar and hence would be expected to refocus. Thus the data of Table VII indicate a linear structure for this molecule. On the other hand, refocussing at the LiO peak shows unequivocally the presence of $\text{LiO}(\text{g})$ in the vapor above lithium oxide. The thermodynamic significance of the structure of Li_2O is indicated by the fact that there is a difference of 5 cal/mole/deg in the entropies calculated for a linear and bent structure of this molecule.⁷

In a Knudsen effusion experiment, $\text{Li}_2\text{MoO}_4(\text{g})$ was found to be the principal vapor species at temperatures above 1150°C when lithium oxide was heated in a molybdenum crucible. This result suggests that the electron diffraction pattern for lithium oxide reported by Akishin and Rambidi⁸ (who used a molybdenum crucible) was in fact that of lithium molybdate; the 1.82Å spacing reported by them and assigned to the Li-O distance may be compared to the 1.83Å Mo-O distance in silver molybdate, Ag_2MoO_4 .⁹ Comparison of bond distances makes likely that the Li-O distance in Li_2O is close to the LiF bond distance, i.e. near 1.55Å.

(3) Group II Halides, AlF and BeO . Data for a number of Group II-A and II-B halides are summarized in Table VIII. For molecules which show no refocussing the amount of refocussing which could have been detected is shown under the column headed "Sensitivity." Refocussing of the alkaline earth halides was first reported by Wharton, Berg, and Klemperer.¹⁰ The molecules BaF_2 and CaF_2 span the range from the highest to the lowest polarities found in their experiments. Refocussing was observed for BaF^+ and CaF^+ , thus showing the sensitivity of the mass spectrometric experiments to be comparable to the molecular beam¹⁰ experiments, and confirming the bent structure of these molecules. (Neither of the two molecules produces a parent ion, MF_2^+ , in amounts detectable in our experiments.) For the beryllium halides no refocussing was observed, implying that these molecules are linear. The same holds true of the Group II-B halides. Here the defocussing observed in the case of HgCl_2^+ is a characteristic of linear

molecules. The latter result is particularly gratifying since it has been suggested that refocussing might be observed for linear molecules with very low bending frequencies and peculiar potential functions. At least in the case of HgCl_2 , which has a bending frequency of 70 cm^{-1} and is known to be linear through spectroscopic evidence, this is not the case. The result lends further support to the conclusion that the refocussing in the alkaline earth halides does indeed indicate a non-linear structure.

TABLE VIII. Electric deflection experiments:
Group II Halides, AlF and B_2O_3

<u>Molecule</u>	<u>Ion Observed</u>	<u>% Refocussed</u>	<u>Sensitivity</u>
BeF_2	BeF_2^+	0	0.2% at 30 kv
BeCl_2	BeCl_2^+ BeCl^+	0	0.6% at 36 kv
CaF_2	CaF^+	0.45 at 22 kv	
BaF_2	BaF^+ Ba^+	6.7 at 29 kv 6.0 at 27 kv	
ZnF_2	ZnF_2^+ ZnF^+		0.2% at 25 kv 0.15% at 28 kv
ZnCl_2	ZnCl_2^+		0.25% at 27 kv
HgCl_2	HgCl_2^+	-4.8 at 34 kv (defocussed)	
AlF	AlF^+	0.6 at 27 kv	
B_2O_3	B_2O_3^+		0.13% at 25 kv

For AlF (prepared by the reaction of AlF_3 and Al) a dipole moment of 1.4 debye has been reported by Lide.¹¹ The molecule was run as a check on the sensitivity of the method and was in fact observed to refocus. No refocussing was observed from B_2O_3 , showing it to have a very small dipole moment.

(4) Transition Metal Halides. No refocussing was observed for any transition metal halides, implying that these compounds are linear. In the case of cupric fluoride, no refocussing was observed for CuF_2^+ , showing $\text{CuF}_2(\text{g})$ to be linear. However, the CuF^+ ion showed refocussing, showing that the vapor above $\text{CuF}_2(\text{c})$ contains the diatomic molecule CuF .

TABLE IX. Electric deflection experiments:
Transition metal halides

<u>Molecule</u>	<u>Ion Observed</u>	<u>% Refocussed</u>	<u>Sensitivity</u>
MnF_2	MnF_2^+	0	0.12% at 30 kv
	MnF^+	0	0.3% at 30 kv
MnCl_2	MnCl_2^+	0	0.2% at 23 kv
	MnCl^+	0	0.7% at 20 kv
CoF_2	CoF_2^+	0	2% at 27 kv
	CoF^+	0	0.2% at 30 kv
NiF_2	NiF_2^+	0	0.5% at 30 kv
	NiF^+	0	0.5% at 28 kv
CuF_2	CuF_2^+	0	0.8% at 30 kv
CuF	CuF^+	3 at 30 kv	

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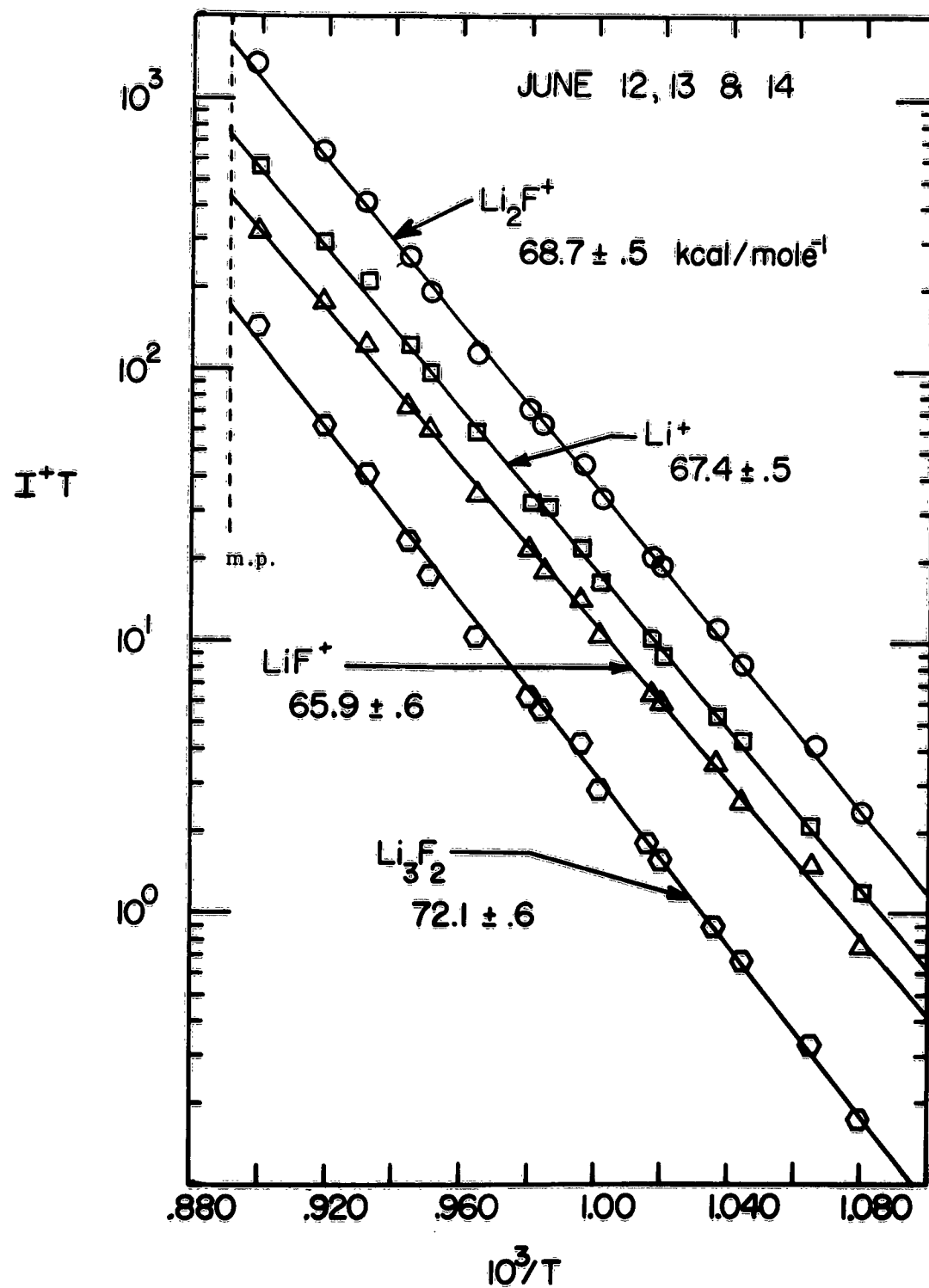


FIGURE 1 LITHIUM FLUORIDE VAPORIZATION

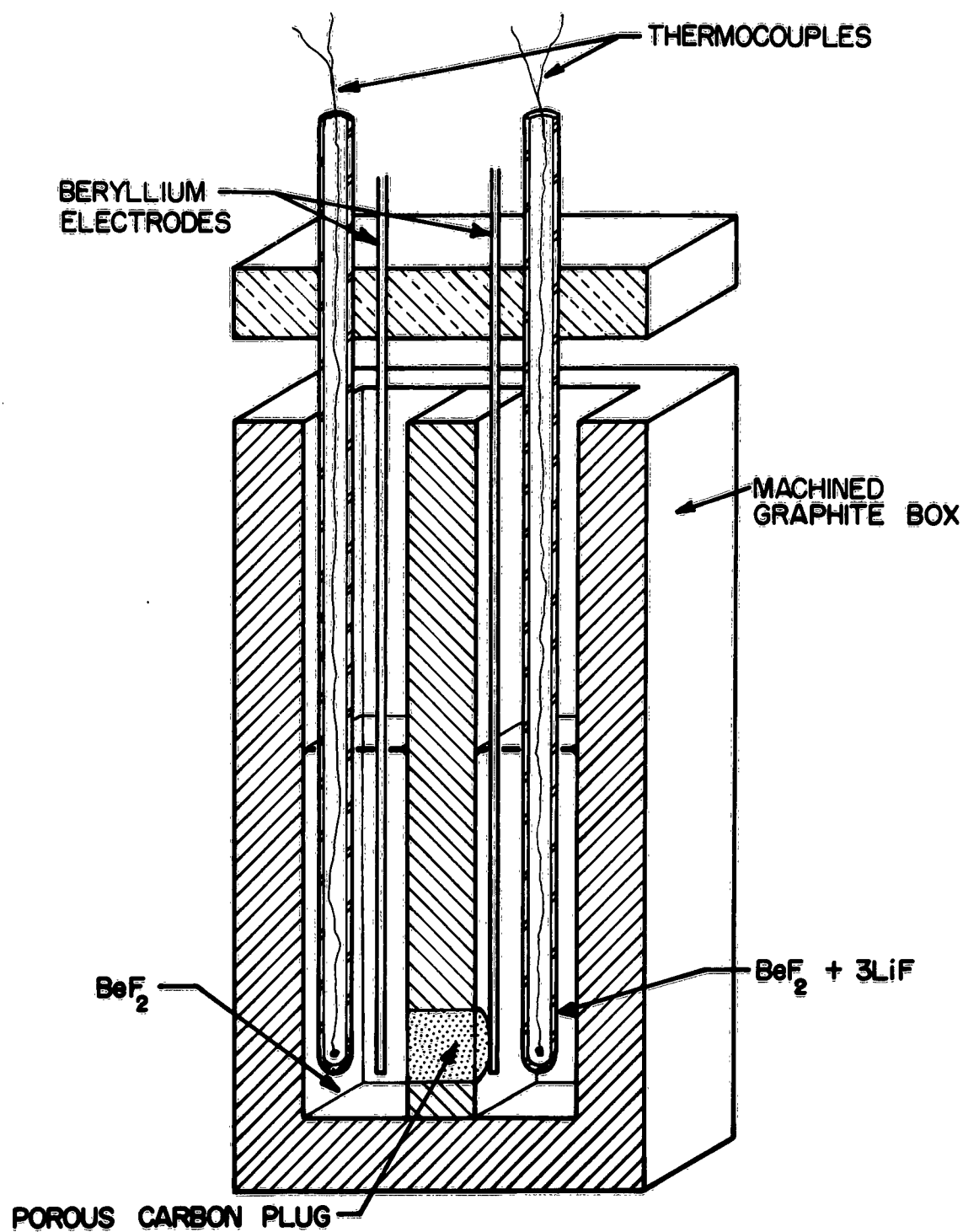


FIGURE 2 EMF CELL

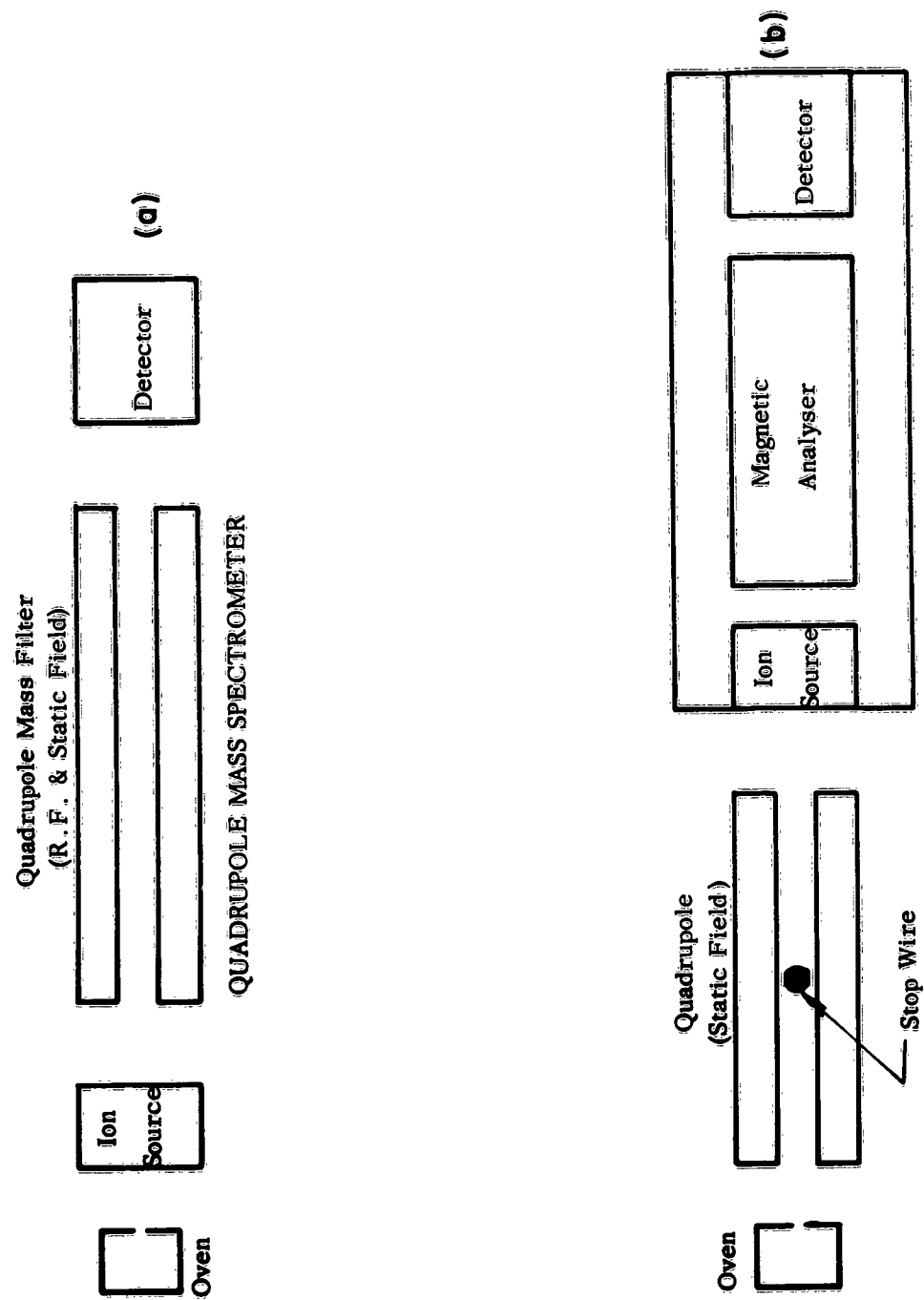


FIGURE 3 ELECTRIC DEFLECTION EXPERIMENT USING QUADRUPOLE FIELD AND HIGH TEMPERATURE MASS SPECTROMETER.

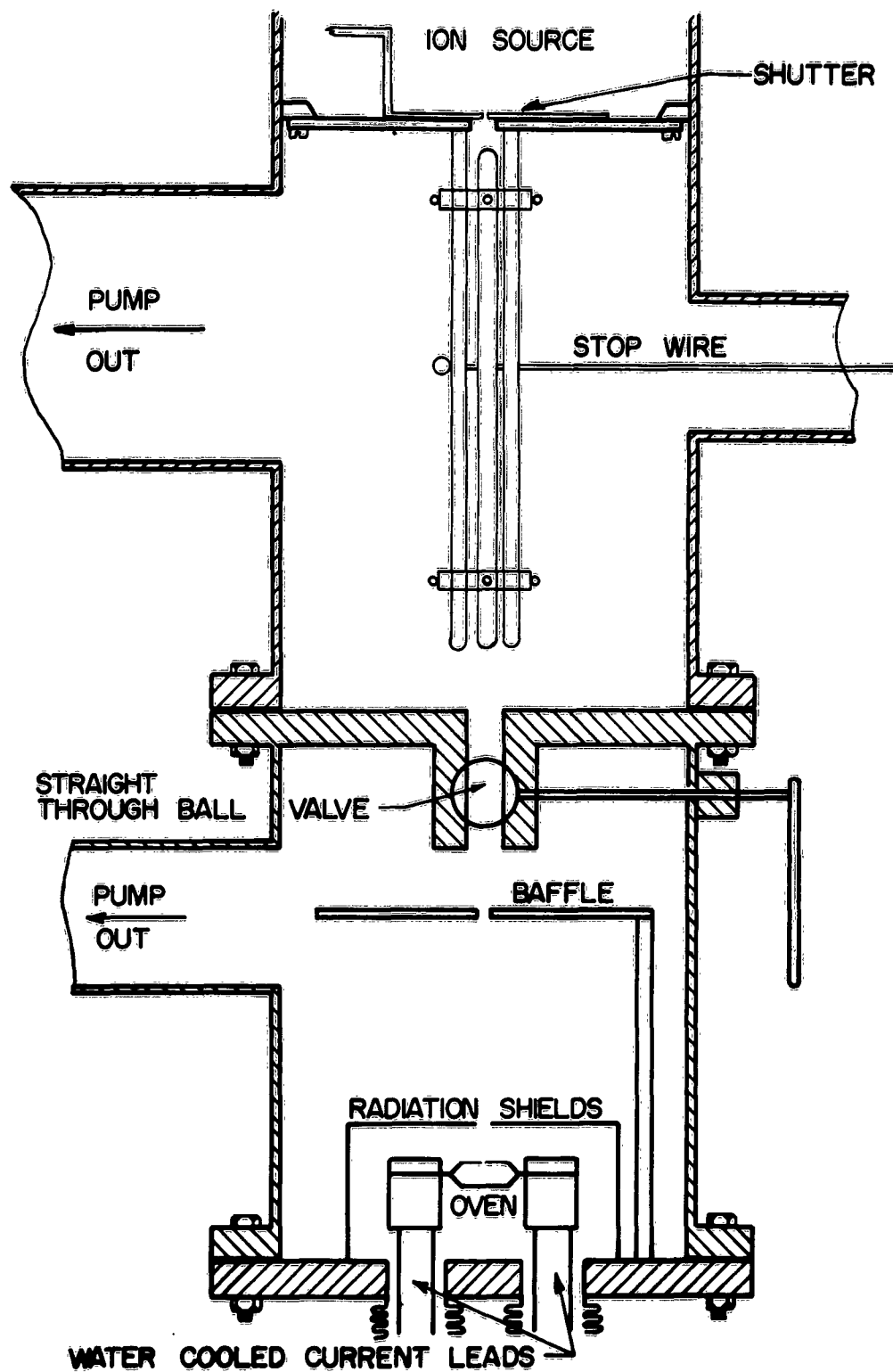


FIGURE 4 ELECTRIC DEFLECTION EXPERIMENT

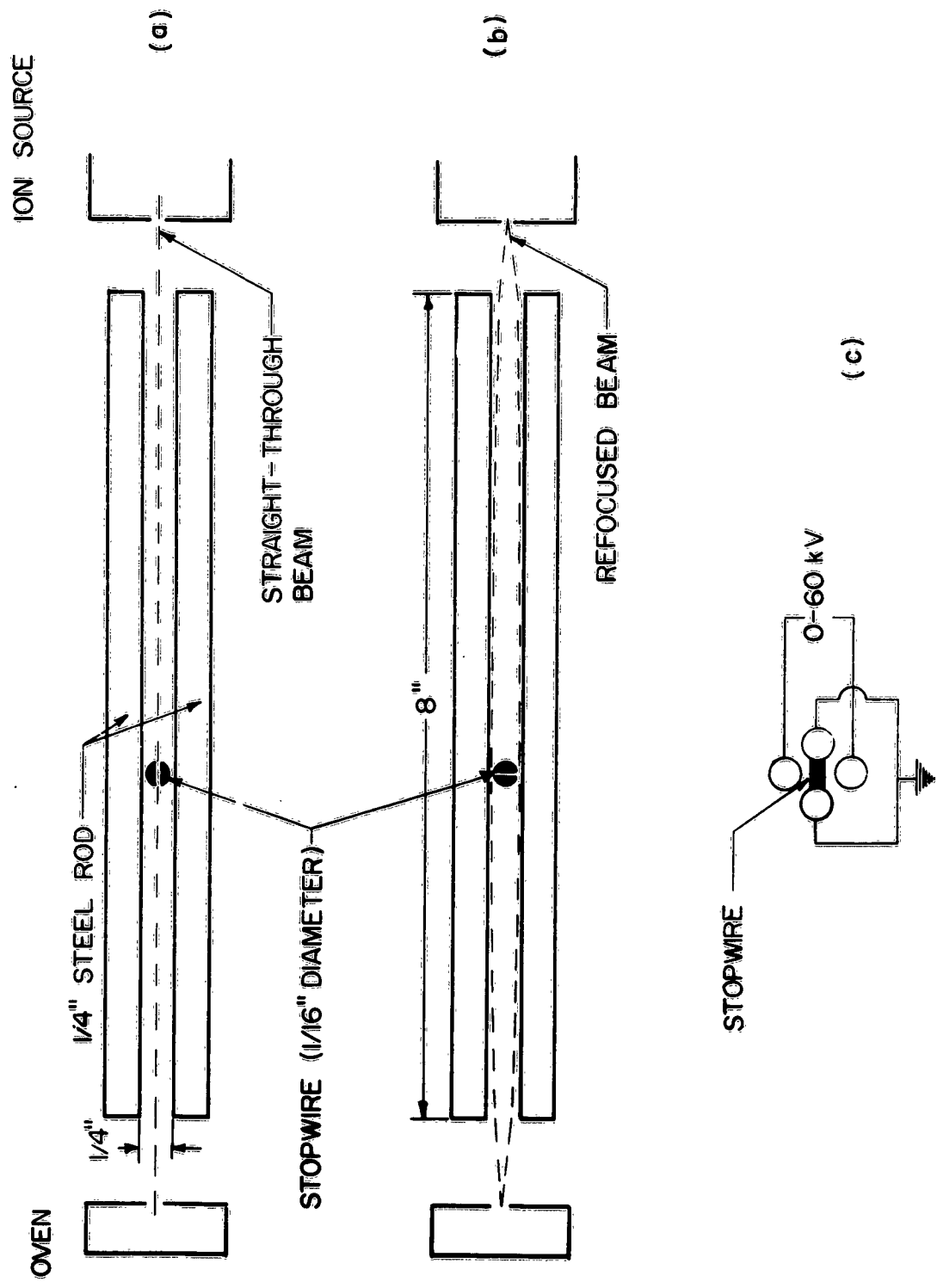


FIGURE 5 ELECTRIC DEFLECTION EXPERIMENT

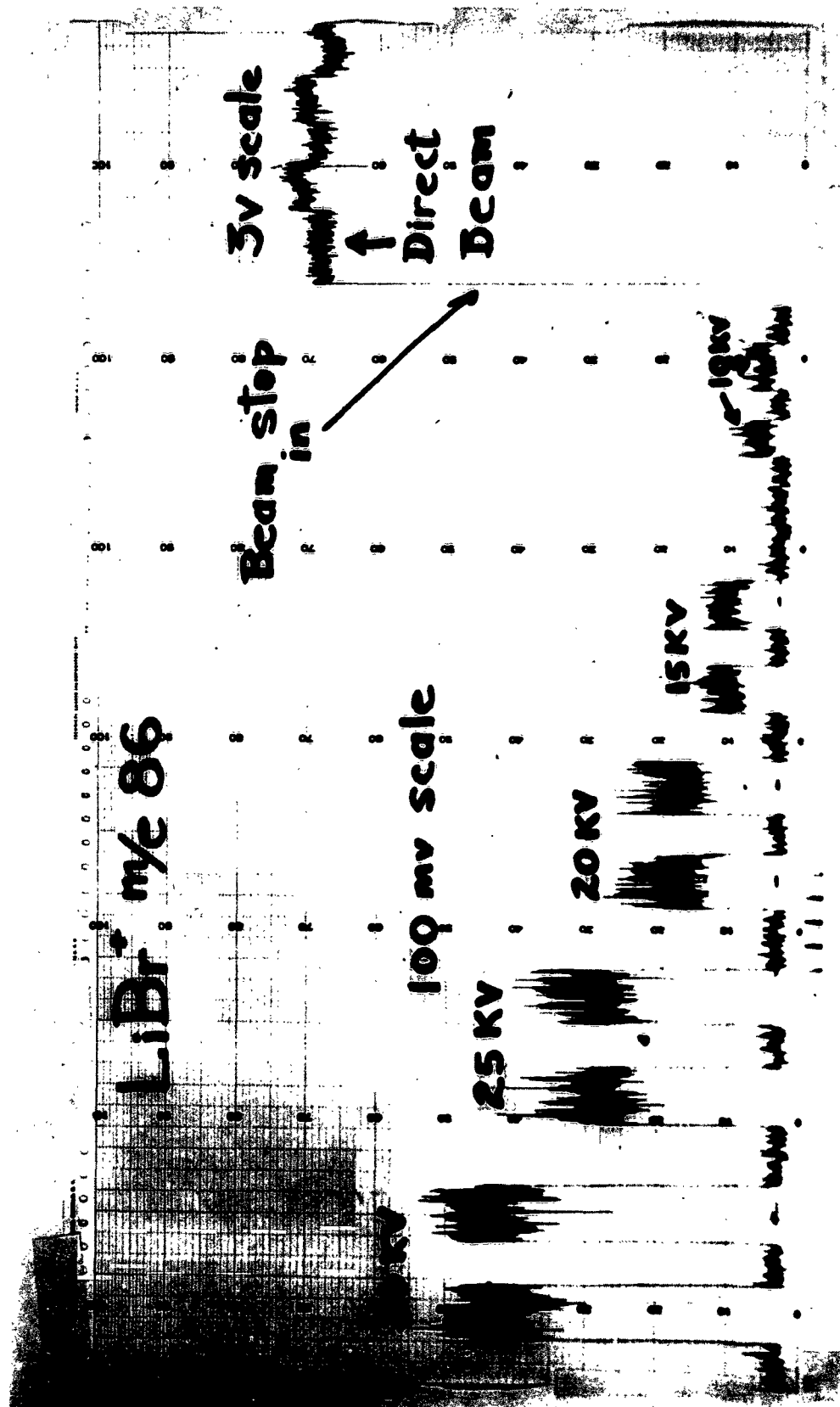


FIGURE 6 LiBr REFOCUSING EXPERIMENT

A NOTE ON THE FRAGMENTATION PATTERN OF LiF*

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Double oven experiments aimed at deducing the mass spectral fragmentation pattern of the various $(\text{LiF})_n$ molecular species have been carried out by Akishin, Gorokhov, and Sidorov¹ and by Berkowitz, Tasman, and Chupka.² The results reported are not in good agreement. It is the purpose of this note to clarify the nature of the disagreement and to present arguments in support of the BTC² results.

It should be stated at the outset that fragmentation patterns as measured with one mass spectrometer need not be reproduced by another mass spectrometer. If there is any difference in kinetic energy between parent ion and fragment ion(s), their focussing characteristics will be different. It is also possible that fragmentation may not be isotropic, and hence will result in collection efficiencies which differ from one instrument to another. If there exists any other mass discrimination in one mass spectrometer with respect to another, this too will affect a comparison of fragmentation patterns. It is likely, however, that the current discrepancy transcends the above considerations.

Using the AGS¹ terminology, we define

$$a_{02} = \frac{I_{02}}{I_{22}}, \quad a_{23} = \frac{I_{23}}{I_{33}}$$

where I_{02} is the Li^+ ion intensity due to dimer, I_{22} is the Li_2F^+ ion intensity due to dimer, I_{23} is the Li_2F^+ ion intensity due to trimer, and I_{33} is the Li_3F_2^+ ion intensity due to trimer. AGS report

$a_{02} = 0.46 \pm 0.13$ and $a_{23} = 3.9 \pm 0.8$. Our contention, based on previous experiments with LiF ^{3,4} is that the ratio of parent trimer peak (Li_3F_2^+) to the total intensity at the Li_2F^+ position in the saturated vapor is only ca. 0.1. Double oven experiments of the type discussed here involve measuring a difference of ion intensities. In order to deduce a fragmentation pattern for the trimer, it is necessary for the fragmented trimer to significantly affect other peaks. Since the Li_3F_2^+ ion intensity is only ~10% of the Li_2F^+ in the saturated vapor, its impact on the Li_2F^+ is too difficult to extract, taking into account the experimental uncertainty. Our contention regarding the ratio of trimer to dimer is further verified by experiments which do not involve fragmentation patterns, and which yield a trimer:dimer ratio of 0.17.⁵

*Work performed under the auspices of the U.S. Atomic Energy Commission.

AGS have not described their double oven experiment, nor have they provided raw data to indicate the magnitude of their experimental uncertainty. Hence we question the validity of their measurement of a_{23} . This in turn has its impact on a_{02} , which is the only coefficient we both report.

We may equivalently define a_{02} in the following way:

$$a_{02} = \frac{I_{02}}{I_2 - a_{23} I_{33}}$$

where I_2 is the total Li_2F^+ ion intensity due to contributions from dimer and trimer, and the other symbols have their previous meaning. Our contention is that $a_{23} I_{33}$ makes too small a contribution to I_2 to be measurable within the experimental uncertainty, largely because the partial pressure of trimer is too small to be significant for this experiment. Hence, our conclusion is that $I_2 \approx I_{22} > a_{23} I_{33}$, and $a_{02} = 0.14 \pm 0.02$. The AGS work concludes that the trimer:dimer ratio is 0.44, in contradiction to all other experimental observations on this system. It is this disagreement with regard to the relative importance of trimer to dimer which is responsible for the ensuing discrepancy in a_{02} .

We are also puzzled by the omission of results for the coefficients a_{01} and a_{12} in the AGS work, which are reported in the BTC paper.

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MASS SPECTROMETRIC SAMPLING OF FLAMES

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ABSTRACT

The pertinence of the Kantrowitz and Grey theory of aerodynamic molecular beams to the problem of sampling high pressure systems with a mass spectrometer is discussed. A simple differentially pumped molecular beam system is described, which gives molecular beams of intensities of about 10^{17} molecules/cc/sec from one atmosphere sources. The behavior of this sampling system with pure gases, mixtures and reactive systems is presented. In beams from gaseous mixtures the mass spectrometer gives a response which depends on the first power of the component molecular weight: $I_x \propto P_x m_x$. Under many sampling conditions a series of polymers or clusters of even the rare gases are formed during the initial expansion process.

INTRODUCTION

The goal of this program is the study of chemical equilibrium involving metals in the burnt gas region of flames where unusual environmental conditions can be readily achieved. In particular, we are interested in studying reactions at temperatures of 2000-3000°K or higher in high partial pressures of water and oxygen. A Bendix time-of-flight mass spectrometer is being used to sample condensible and unstable gaseous species directly from the flame at one atmosphere.

It was recognized in the beginning that the mass spectrometric sampling of flames would be one of the most difficult problems encountered in this study. Consequently, we have devoted much of the effort so far to determining the conditions under which good sampling can occur; i.e., the conversion of the flame gases at one atmosphere to an intense molecular beam with the least possible disturbance of the chemical species originally present.

The use of the mass spectrometer in studying high temperature and reactive species has greatly increased in recent years. In much of the work the gas is introduced into the spectrometer ion source as a molecular beam formed by molecular effusion through a sampling orifice. In such cases the composition of the beam reaching the ion source can be safely related to the composition of the system being studied. However, if the pressure is increased until the mean free path of gas in the system approaches or becomes less than the orifice diameter, the process of beam formation becomes uncertain. In this region it has been variously reported that a maximum in beam intensity will occur with increasing pressure,¹ that a "cloud" forms above the orifice limiting the beam,² and that the intensity

will continue to rise with pressure but with a different slope, predictable from a simple model based on adiabatic expansion.^{3/}

The nature of the flow through an orifice into a vacuum when the flow is continuous, that is, when the upstream mean free path is much less than the orifice diameter, is currently being studied by aerodynamicists and workers desirous of obtaining very intense molecular^{4-6/} beams.

Qualitatively, as a high pressure gas expands adiabatically through an orifice or nozzle into a vacuum, much of the translational and internal energy of the molecules will be converted into directed flow of the gas as a supersonic jet. The gas is thus cooled rapidly as it expands (a much larger effect than Joule-Thomson cooling) with the possibility of shifting composition as long as molecular collisions occur. In addition, the supersonic nature of the flow downstream from the first orifice gives rise to the possibility of shock wave formation in the gas before its density drops to the molecular flow regime.

Theory of Beam Formation Over 10 years ago, Kantrowitz and Grey^{7/} suggested that a more intense molecular beam could be obtained by placing the first slit of a conventional molecular beam system in the flow from a miniature supersonic nozzle. In this way the gas coming through the slit would already be highly oriented and a much stronger beam could be expected. Consider a sampling system consisting of several orifices separating differentially-pumped chambers as shown in Fig. 1. As the pressure behind the first orifice is increased, the flow from the first orifice will undergo a transition from molecular to continuum, and at the higher pressures the second orifice will automatically find itself in a highly directed supersonic flow. This is the situation of interest either in mass spectrometric sampling from high pressure systems or in extending Knudsen beam measurements to higher pressures.

Kantrowitz and Grey developed quantitative expressions to describe the molecular beam obtained from a nozzle source. Later, Parker et al.,^{8/} refined the treatment and obtained expressions for beam intensities and velocities. The assumptions made in the theory were that (1) the flow between the first two slits obeys ordinary continuum flow theory, (2) the expansion of the gas through the first orifice is isentropic, (3) the ratio of specific heats, γ , is constant during expansion, (4) the flow into the second slit is supersonic and undisturbed by the presence of the second slit, and (5) downstream of the second slit no molecular collisions occur.

Of the various expressions derived^{8/} to describe the supersonic molecular beam for a pure gas we will write down only the equation for the intensity in terms of the source conditions:

$$I = \frac{ka_2 a_3 P_0}{(mT)^{1/2} d_{23}^2} \gamma^{1/2} (3 + \gamma M^2) M \left[1 + \frac{1}{2} (\gamma - 1) M^2 \right]^{\frac{1+\gamma}{2(1-\gamma)}} \quad (1)$$

Here I is the total beam intensity in molecules/second at the third slit, a_3 is the area of the third slit, a_2 is the area of the second slit, P_0 and T_0 are the pressure and temperature of the gas upstream of the first orifice, m is the molecular weight of the gas, γ is the specific heat ratio, M is the Mach number of the gas at the entrance to the second orifice and d_{23} is the distance between the second and third orifice.

For comparison, the beam intensity from a conventional molecular effusion source is given by

$$I = k' \frac{P_0 a_1}{(mT)^{1/2}} \frac{a_3}{d_{13}^2}$$

where a_1 is the area of the first slit, and d_{13} is the distance between the first and third slits. In both limiting cases the theory predicts a direct dependence of I on source pressure at constant temperature. However, in the supersonic case, I depends on M and γ in a complex manner and on a_2 , the second slit area, whereas in the molecular effusion case I depends on a_1 , the first slit area. These different dependencies on slit areas lead to interesting consequences which are discussed below.

The Mach number of the gas at the second slit, in the ideal case and for a given γ , depends on the distance in orifice diameters between the first and second slits, and is independent of P_0 , P_1 , T , m or orifice diameter. Such Mach numbers have been calculated for a diatomic gas ($\gamma = 1.4$) by Owen and Thornhill,⁹ and have been verified experimentally with miniature nozzles by Fenn and Reis¹² for Mach numbers up to about 8, corresponding to a ratio of distance to orifice diameter of about 9. At larger distances the observed Mach numbers fall below the calculated values and tend to reach a limiting value.

Experimental In the design of a sampling system for high pressure sources, various departures from ideal behavior must be considered. Two classes of effects can be noted: (1) Those occurring upstream of the second slit or skimmer in the continuum flow and transition regime, and (2) those downstream of the skimmer in the molecular flow regime.

A high pressure gas expanding into an imperfect vacuum will be bounded by a shock bottle. The calculations of Owen and Thornhill apply only to the gas inside this shock bottle, that is, to gas which is as yet unaffected by the ambient gas. The skimmer slit should therefore be situated inside this shock bottle for the gas entering the skimmer to approximate the calculated conditions. Above the shock bottle, reduced intensity and possibly other effects might be expected, particularly with mixtures. Since the skimmer faces the supersonic flow from the first orifice, it should be designed to minimize the formation of a detached shock across the skimmer opening. According to present theory, the skimmer should be conical with a certain maximum apex angle for a given Mach number^{7/} and should have an opening as large as possible and edges as thin as possible. Theoretically, the orifice to skimmer distance determines the Mach number at the skimmer and, hence, the beam intensity, but in practice it influences beam intensity in a more complex way.^{4,5/}

Downstream of the skimmer, molecular flow occurs and pressures and dimensions must be such that scattering is minimized. In addition, with a mass spectrometer as a detector, sufficient differential pumping must be provided to minimize the entry of random or scattered gas into the ion source relative to the beam gas. Finally, one needs sufficient pumping speed in the ion source so that the signal from the beam gas after it is scattered in the ion source will be small compared to the signal from the beam in its first pass through. This is important in comparing signals from stable and unstable or condensible species.

We have constructed a molecular beam sampling system to meet the requirements of sampling one atmosphere flames. A Bendix time-of-flight mass spectrometer is used as a detector. The system is shown schematically in Fig. 1. Because of the problems involved in attaching the sampling system below the mass spectrometer ion source and in using an exposed flame as a source, it seems impractical to use the large diffusion pumps which have been employed by other workers for differential pumping. Fortunately, we were able to get good beam formation with small pumps and several stages of differential pumping.

The pumps used are listed in Table I. A small mechanical shutter was operated in stage 3 where molecular flow prevailed. This permitted the separation of beam and background signals. The thin-edged skimmer orifice was constructed by wrapping 0.009 mm. nickel foil in the form of a 60° apex angle cone with the desired hole diameter remaining open at the end. This fragile but easily constructed cone was supported by a 0.25 mm. thick spun copper cone. The third and fourth slits were formed from thin sheet and were of a size such that the beam completely filled the mass spectrometer ion source slits. The first orifice was either a flat disk soldered to a movable tube, for room temperature work, or a spun, 0.005 in. thick, Pt-Rh cone for flame sampling. Table I also lists typical slit dimensions, spacings and pressures for a one atmosphere source.

Results with Pure Gases The sampling system just described has given an intense, well collimated molecular beam at one atmosphere with orifices as large as 0.25 mm. in diameter with room temperature gases, and as large as 0.40 mm. diameter for flames. The mechanical shutter, which interrupts the beam without interfering appreciably with background gas flow, allows one to distinguish between the beam and the random gas effusing into the ion source from the third stage. In a typical case 20-30 per cent of the total signal is from random gas and is not shutter-dependent. The remaining 70-80 per cent is the shutter-dependent signal due to gas entering the ion source as a beam. With a fast response Sanborn Model No. 150 recorder and rapid closing of the shutter, it was established that about 70 per cent of the shutter-dependent signal is due to the beam on its first pass through the mass spectrometer and 30 per cent due to the scattered beam. With condensible or unstable species, this 30 per cent contribution will be absent.

The beam intensity is critically dependent on the alignment of the first orifice with the rest of the slits, indicating ordered motion of gas from the first orifice to the detector. The scattering of the beam in the second and third stages is that expected for molecular flow and does not seriously limit beam intensities under the normal operating conditions listed in Table I. The small pumps used in these stages do, however, require the use of rather small diameter skimmers to avoid excessive scattering.

The behavior of beam intensity for a pure gas as a function of orifice to skimmer distance is shown in Fig. 2. Changing other distances simply changes the beam scattering in a predictable way, but the orifice-skimmer distance dependence is complicated and not fully understood. Our results are consistent with those reported by Fenn and Scott, except that our limited pumping prevents us from operating at very small orifice-skimmer distances, where it has been observed that the beam intensity again rises. Others have speculated about the shape of these curves.^{4,5} In our studies, we operate near the peak intensity shown in Fig. 2. There is some reason to believe that a detached shock may be presented in front of the skimmer at this point, but it may have little effect on the gases due to the low densities present so many orifice-diameters downstream from the orifice. No direct observation of shock waves in such a system has been reported.

The behavior of the beam intensity with pressure at a fixed orifice-skimmer distance is shown in Fig. 3 for CO₂ and in Fig. 4 for argon. With other parameters held constant, the intensity dependence on first orifice size is greater at low pressures as shown in Fig. 4. The high pressure behavior is complicated by scattering a choice of orifice-skimmer distance, and almost any shape curve can be obtained including, over limited ranges, the first power dependence on pressure predicted by theory.

The actual magnitude of typical beam intensities expressed as molecules/cm²/second at slit No. 3 (where a true molecular beam exists), was determined from calibrations of the mass spectrometer sensitivity with Knudsen experiments using gases at known pressures and with known system geometry. Such a calibration gave a beam intensity from argon at one atmosphere of 10^{17} molecules/cm²/second at the third orifice, 56 mm. away from the first orifice. These intensities are comparable to those reported by Fenn⁴ and Scott⁵ with their much larger systems. With such intensities, beam signals in the mass spectrometer of about 100 have been obtained, with minimum detectable signals of 10^{-4} possible in favorable cases. A shutter-dependent signal from argon 36 in air was readily measured, representing one part in 30,000.

The effect of changing various geometrical parameters of the sampler can be reasonably well predicted. In the second and third stage simple scattering considerations apply and differential pumping of scattered or random gas is necessary. The shape of the first orifice appears not to be critical. Much larger orifices can be used with increased first stage pumping. The variation of skimmer shape and bluntness has not been systematically studied. However, in experiments with a really blunt skimmer consisting of a 4.8 mm. diameter disk with a 0.25 mm. hole, no significant difference in beam intensity was observed at pressures of one atmosphere or lower except that the maximum intensity was shifted to larger orifice to skimmer distances. At 5 atmospheres maximum intensities were reduced about a factor of 5. The mass separation effect, discussed below, was enhanced about a factor of 4 for a H₂-Ar mixture at one atmosphere. The extent of polymerization, also discussed below, was decreased slightly at one atmosphere and markedly at 5 atmospheres. This behavior may be consistent with the interpretation that, at low densities of gas at the skimmer, shocks are too diffuse to be of importance. Because of the fragility of the 0.0088 mm. thick skimmer, one was constructed in the same fashion from 0.05 mm. thick stainless steel sheet. This skimmer gave virtually identical results to those reported here and is being used in future work.

Results with Mixtures When mixtures of gases or reactive systems are sampled, there are several complications which may occur. In a reactive system the composition may change either during the initial expansion or on passing through shock waves, and the net effect will depend on both the nature of the expansion and the kinetics of the reactions involved.

Even in the simple case of sampling unreactive mixtures of different molecular weight gases, there is a question as to the composition in the final beam relative to the initial composition of the mixture. Expression (1) applies only to a pure component and, unlike expression (2), cannot be used directly to treat components of a mixture. It has been known for several years that in a supersonic molecular beam the heavier components will be enriched relative to the lighter along the axis of the beam.¹⁰

This phenomenon has been studied under a variety of conditions and several explanations have been offered for the results obtained.^{10,11,12} The theoretical and experimental situation was sufficiently unclear that we felt it necessary to determine for our beam system the magnitude and behavior of this so-called "mass separation" effect.

The experimental measurement of "mass separation" as a function of various parameters was accomplished simply by preparing known mixtures of gases, calibrating the mass spectrometer for each gas, and then determining the intensities of the various mixture components in the supersonic molecular beam. Initially, a series of 50-50 mixtures of gases with varying ratios of molecular weights were studied. These results showed that in all cases there was an enrichment of the heavier component which increased with the ratio of molecular weights. The effect was large. In the H_2 -Ar mixture the intensity of argon was some 25 times that of H_2 after corrections for mass spectrometer sensitivity.

To try to determine the quantitative relationship between this enrichment effect and molecular weight, a series of experiments was performed in which four or five solute gases at about 1 per cent each were mixed into one of several solvent gases. The solvent would presumably determine the basic course of the expansion and the enrichment of the solutes as a function of their molecular weights could then be studied. This situation also closely approximates that which will occur in the study of equilibria in flames containing small amounts of additives. A variety of solvents and solutes was chosen to give some indication as to the dependence on the solvent as well as on the chemical structure and molecular weight of the solute. The mixtures studied are listed in Table II.

In much of the past work, the total flow of gases through the skimmer was collected, analyzed, and the results compared with the analysis of the initial mixture. In beam sampling applications one is interested in the actual response at the detector caused by the various components in the beam. In the case in which a mass spectrometer is used as a detector this response depends on the density of molecules passing through the ion source, i.e., on the velocity of the species of interest as well as their flux. The response of the mass spectrometer to various densities of the different gases was determined by performing Knudsen runs with each gas at a series of pressures low enough so that scatter-free molecular flow occurred from the first orifice. The same geometry was maintained in these comparisons. In general, plots of ion intensity versus pressure were linear from $1,000\mu$ down to 100μ or less and the slopes were computed for each species. Duplicate runs established the reliability of the slopes to be ± 10 per cent for the rare gases.

Following these calibrations a number of mixtures of gases were made up in a stainless steel tank of about 8 liters volume to a pressure of

about one atmosphere. The gases were allowed to mix for several hours and beam experiments were carried out in which relative intensities were measured for each component. Repeat runs over the pressure range of 700-400 Torr gave agreement to ± 10 per cent.

The data on mass separation were treated in the following manner. A calculated intensity for each species was obtained by multiplying the partial pressure of the species in the tank by the slope obtained from the low pressure calibration runs. Next, the observed intensities were divided into the calculated intensities to give a (calc/obs) ratio for each species. If there were no mass separation, these ratios should all be the same and, if we choose one species, say the solvent, and normalize it to unity, then every (calc/obs) ratio should be unity. Actually, the ratio (calc/obs) decreased with molecular weight in almost every case, indicating an enrichment of the heavier species in the beam. The ratios,

$$\alpha = \frac{(\text{calc/obs}) \text{ solute}}{(\text{calc/obs}) \text{ solvent}}$$

were then plotted versus the ratio of molecular weight, $\frac{m_{\text{solvent}}}{m_{\text{solute}}}$. The results are shown on log-log plots in Figs. 5, 6, 7, and 8. The line indicates the slope the plot would have for a first power molecular weight dependence of the mass separation effect.

Several features can be discerned in these plots. First, and most important, the data fall along a line whose slope is most nearly that for a first power dependence on the molecular weight. Second, within the rather bad scatter of points, the dependence of α on M seems to be reasonably independent of the chemical nature of the species, although the rare gases fall slightly below the solvent and other solutes and there are indications of a dependence on solvent as well. To a first approximation then, one can write $p_x = kI_x^+ / m_x$, at constant temperature. This is to be contrasted with ordinary molecular flow sampling from a Knudsen cell for which $p_x = kI_x^+$ at constant temperature.

The dependence of "mass separation" on other parameters was investigated briefly. In the experiments above, the effect was the same at orifice-skimmer distances of 3 mm. to 13 mm. and over the pressure range 700-400 Torr. At 5 Torr the mass separation effect is greatly diminished as shown in Fig. 5. Results for an equimolar H_2 -Ar mixture are shown in Figs. 9 and 10 as a function of source pressure and orifice-skimmer distance. In other work with the argon isotopes the mass separation seems to remain fairly constant down to 10-20 Torr. The rare gases He, Ne and Ar were added as solutes in a CH_4 -air mixture and the relative intensities measured in the beam from the unignited gases (300°K) and from the burnt

gases (2000°K). The same relative concentrations of the rare gases were obtained at the two temperatures, again showing a first power molecular weight dependence reasonably independent of temperature.

Much study remains to fully understand the behavior of mass separation and its dependence on the many variables in the aerodynamic molecular beam system. For instance, we have implicitly assumed above that in the supersonic beam all species have the same velocity when they enter the mass spectrometer ion source. To the extent that the heavier molecules are actually moving more slowly, their ionization probability will be higher and an apparent mass separation will result.

Results with Reactive Systems With reactive systems, there are two additional effects of importance in high pressure sampling: (1) polymerization or partial condensation, and (2) shifts in chemical composition during expansion. The former effect occurs even in simple gases such as H_2 or Ar but is discussed here since it is related to the ability of the sampler to give a representative analysis of the source gas.

There have been several reports of the formation of polymers in generating molecular beams from high pressure gas.^{13,14,15} We have confirmed the formation of such species and studied their behavior in some detail. The initial results, including observation of Ar polymers to $(Ar)_{20}$ and higher, have been reported. The evidence is very strong that these species are formed from supercooled gas in the process of condensing, and are quenched out by the continued expansion to free-molecule flow. These effects, while very interesting from the standpoint of the nature and kinetics of the molecules formed, can be troublesome in sampling since some of the systems of thermochemical interest at high pressure involve polymers (e.g., sulfur vapor, volatile metals, salts, H_2O and HF).

Of even more concern in our flame sampling work are shifts in chemical equilibria. In complex mixtures it may be difficult even to predict the direction that shifts are likely to take during expansion. What happens in passing through shock waves is even harder to predict. As a consequence, we are experimentally testing the ability of our sampling system to quench known equilibria at high temperature. Although our results thus far with unstable and condensible species have been qualitative only, they are sufficiently encouraging to warrant mention.

Upon adding various materials to flames we have been able to see condensible and reactive species in approximately the proportions expected. Thus, with BCl_3 added to a stoichiometric H_2-O_2 flame (with a theoretical flame temperature of $3078^\circ K$ ¹⁷) the species Cl , HCl and HBO_2 were observed. The Cl^+/HCl^+ ratio, after correction for fragmentation of HCl , was very close to the computed ratio Cl/HCl . Likewise HBO_2 , the major boron-containing species under these conditions, was observed with about the right

intensity. In another experiment Cl_2 was added to a stoichiometric CO-O_2 flame (with a theoretical flame temperature of 2977°K ¹⁷). Only Cl^+ was observed with no observable recombination, during sampling, to Cl_2 . Quantitative tests are in progress to determine actual flame temperatures and the effects of burner, flame and sampling system parameters on the ability to sample highly reactive species.

The authors are indebted to Mr. Thomas O. Dobbins for providing us with theoretical flame calculations and to Drs. Scott, Fristrom and Westenberg for discussions during visits to their laboratories. We also wish to thank Mr. Gordon Cross for his interest in the problem, Mr. George Vowels for carrying out many of the experiments and Mr. George Vaughn for help in the design and construction of the beam system.

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TABLE I

TYPICAL DIMENSIONS AND OPERATING PRESSURES IN SAMPLING
ONE ATMOSPHERE SOURCES

	<u>Dimensions</u>	<u>Distance from Ion Source Electron Beam (mm.)</u>
Orifice No. 1	0.25 mm. dia.	400
Orifice No. 2	0.25 mm. dia.	394
Slit No. 3	0.50 mm. x 9 mm.	344
Slit No. 4	0.75 mm. x 12 mm.	113
Ion Source Slit	0.75 mm. x 15 mm.	25

	<u>Pressure</u>	<u>Pump Used</u>
Source	7×10^2 Torr	
Stage 1	1×10^{-2} Torr	CVC 6" oil diffusion pump, PMC-1440, backed by a CVC DK90 mechanical pump
Stage 2	3×10^{-5} Torr	CVC 2" oil diffusion pump, PMC-115
Stage 3	3×10^{-6} Torr	Edwards 1" Hg diffusion pump, 1 M2
Ion Source	1×10^{-6} Torr	CVC 4" Hg diffusion pump, MHG-180

TABLE II

MIXTURES USED IN MASS SEPARATION EXPERIMENTS

	<u>Solvent</u>	<u>Solutes (about 1% each)</u>
Mixture A, Fig. 5	H ₂	He, Ne, Ar, Kr
Mixture B, Fig. 6	N ₂	He, Ne, Ar, Kr
Mixture C, Fig. 7	CO ₂	He, Ne, Ar, Kr
Mixture D, Fig. 8	N ₂	H ₂ , He, CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , O ₂ , Ar, CO ₂ , CF ₃ Cl, CCl ₄

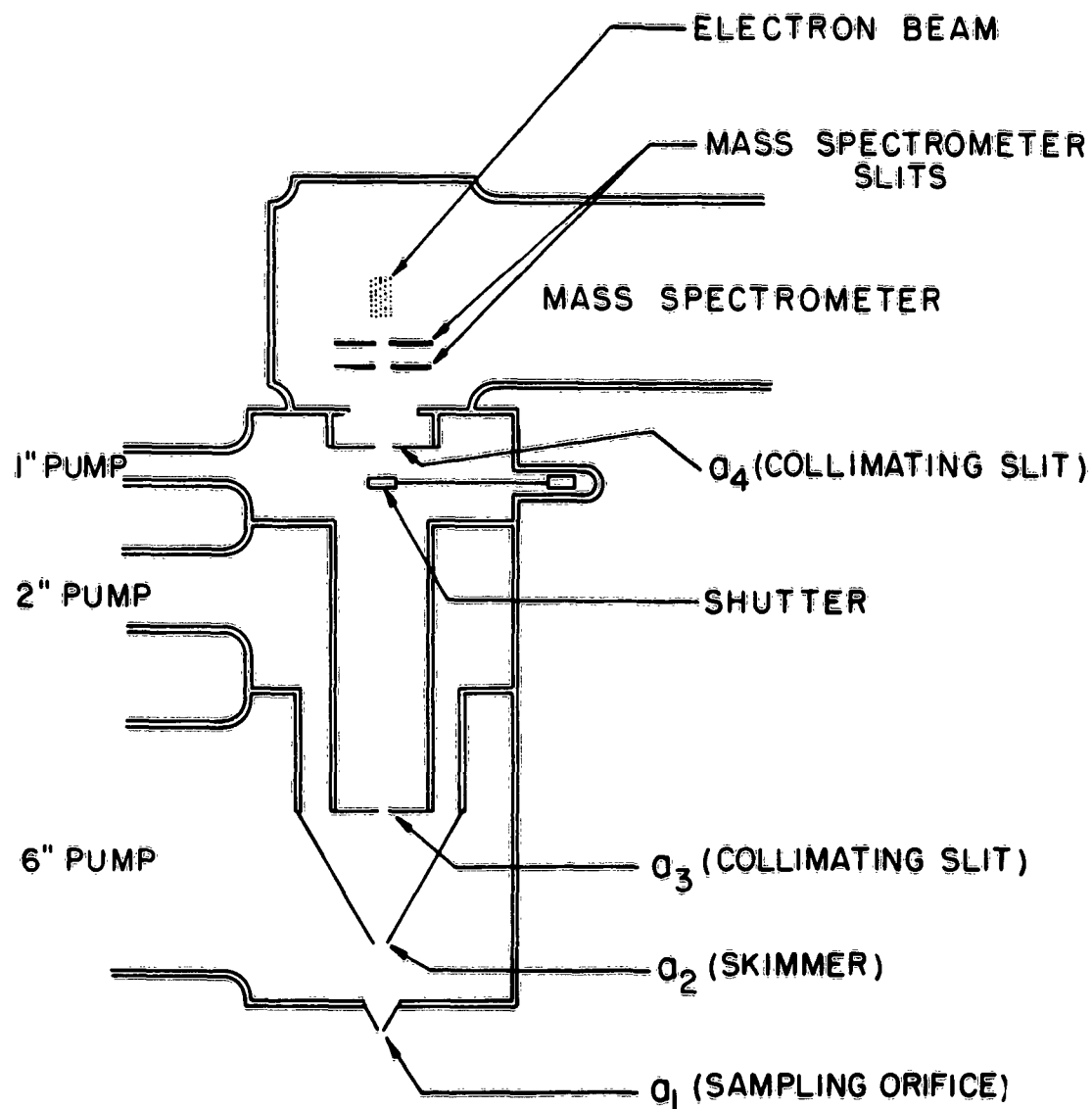


Fig. 1 - Apparatus for the Mass Spectrometric Sampling
of High Pressure Sources

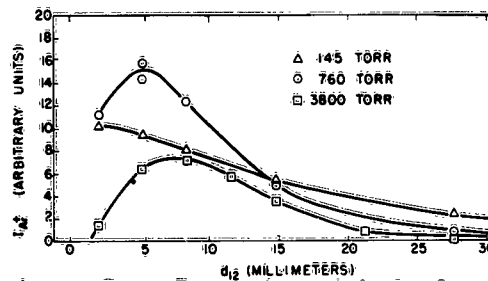


Fig. 2 - Variation of Argon Beam Intensity with Orifice to Skimmer Distance for Several Source Pressures with a 0.05 mm. Diameter Orifice

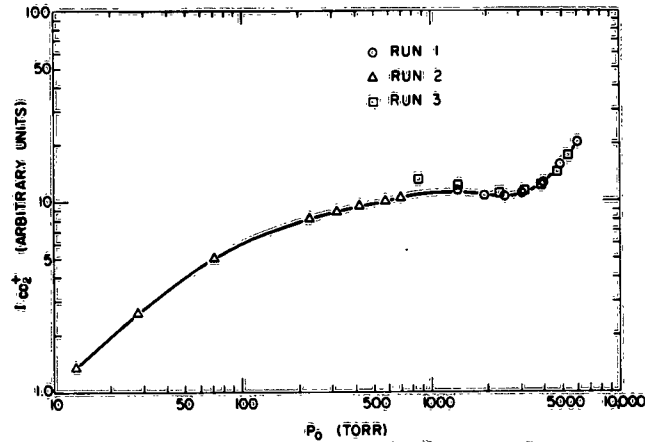


Fig. 3 - Variation of CO_2 Beam Intensity with Source Pressure at Orifice to Skimmer Distance of 6 mm. and with 0.05 mm. Diameter Orifice

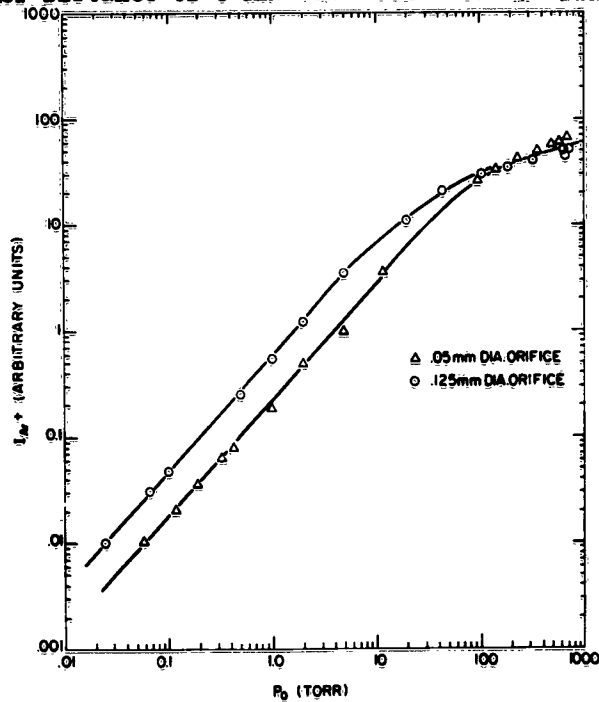


Fig. 4 - Variation of Argon Beam Intensity with Source Pressure at Two Different Orifice Diameters. Orifice to Skimmer Distance Equals 3 mm.

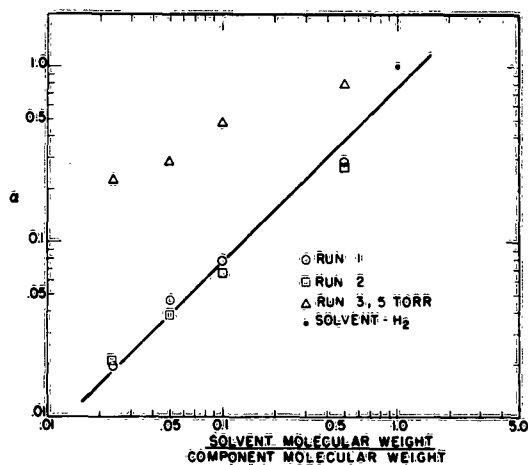


Fig. 5 - Mass Separation Parameter versus Ratio of Molecular Weights for Rare Gas Solutes in H_2 Solvent at One Atmosphere. The Straight Line Represents a First Power of the Molecular Weight Dependence.

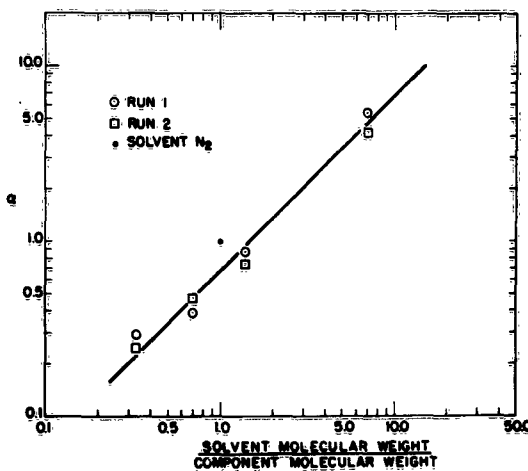


Fig. 6 - Mass Separation Parameter versus Ratio of Molecular Weights for Rare Gas Solutes in N_2 Solvent at One Atmosphere. The Straight Line Represents a First Power of the Molecular Weight Dependence.

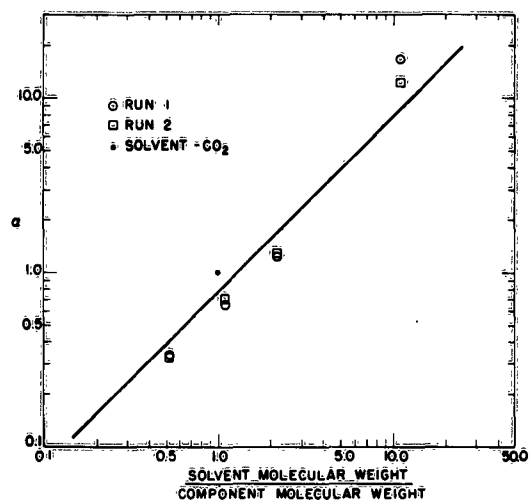


Fig. 7 - Mass Separation Parameter versus Ratio of Molecular Weights for Rare Gas Solutes in CO₂ Solvent at One Atmosphere. The Straight Line Represents a First Power of the Molecular Weight Dependence.

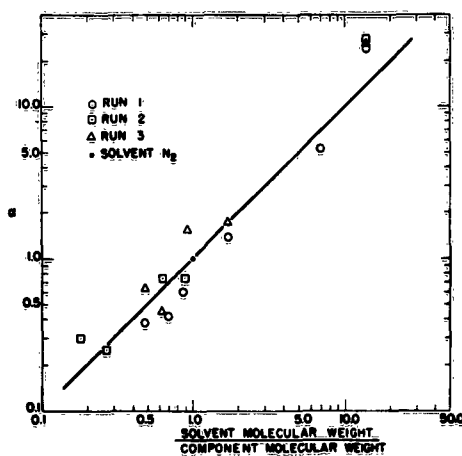


Fig. 8 - Mass Separation Parameter versus Ratio of Molecular Weights for Various Solutes in N₂ Solvent at One Atmosphere. The Straight Line Represents a First Power of the Molecular Weight Dependence.

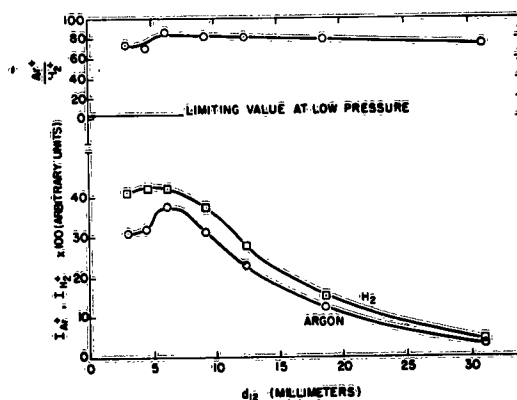


Fig. 9 - Variation of Component Beam Intensities with Orifice to Skimmer Distance for an Equimolar Mixture of H_2 and Ar at One Atmosphere Source Pressure. Orifice Diameter 0.05 mm.

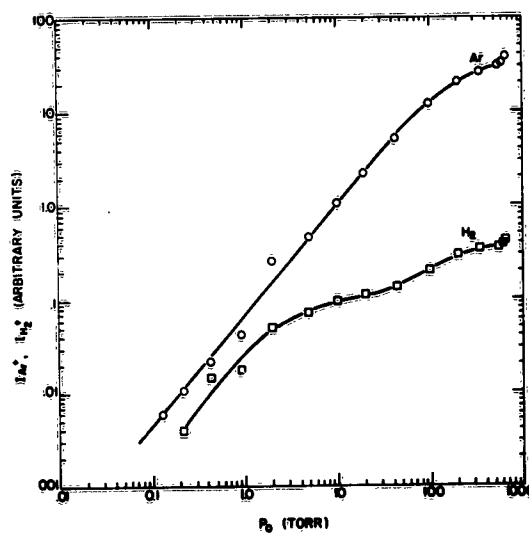


Fig. 10 - Variation of Component Beam Intensities with Source Pressure for an Equimolar Mixture of H_2 and Ar at 6 mm. Orifice-Skimmer Distance. Orifice Diameter 0.05 mm.

THERMOCHEMISTRY OF BORON AND SOME OF ITS COMPOUNDS.
THE HEATS OF FORMATION OF TRIMETHYLAMINEBORANE AND
ORTHOBORIC ACID*

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ABSTRACT

A rotating-bomb calorimetric technique was developed to solve the problem of determining the heats of combustion of organic boron compounds. The heats of combustion of crystalline boron and trimethylamineborane, $(\text{CH}_3)_3\text{NBH}_3$, were determined. The combustion product was a solution of fluoboric acid in excess aqueous HF. The standard heat of formation, $\Delta H_f^\circ_{298,15}$, of trimethylamineborane (c, III) is -34.04 ± 0.55 kcal mole⁻¹. The heat of solution of orthoboric acid in an HF solution chosen to yield the same fluoboric acid solution was determined. The heat of formation of orthoboric acid was calculated; $\Delta H_f^\circ_{298,15}(\text{H}_3\text{BO}_3, \text{c}) = -261.47 \pm 0.20$ kcal mole⁻¹. Combination of these results with data from the literature permitted calculation of the heats of formation of B_2O_3 and B_2H_6 referred directly to crystalline boron.

TEXT

The lack of a method for accurate determination of the heats of combustion and formation of organic boron compounds has been an important gap in the methods of modern thermochemistry. Organic boron compounds, burned alone or admixed with other ordinary combustion promoters, burn incompletely to a poorly defined oxide that occludes carbon and other decomposition products of indeterminate composition. In recent research of this laboratory, a method developed previously for the determination of accurate values of the heats of combustion of crystalline silicon and organic silicon compounds was extended to allow accurate determination of the heats of combustion of elemental boron and organic boron compounds. This method involves combustion of crystalline boron and organic boron compounds mixed with a fluorine-containing combustion promoter, vinylidene fluoride polymer, and with aqueous HF in the bomb so that the boron appears in the products as fluoboric acid in homogeneous solution, approximately $\text{HBF}_4 \cdot 14.5\text{HF} \cdot 58.5\text{H}_2\text{O}$. The

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method was used to determine the heats of combustion of pure samples of crystalline boron and trimethylamineborane.

Measurements were made of the heat of solution of orthoboric acid in an HF solution chosen to produce the same aqueous fluoboric acid solution. These measurements, coupled with the heat of reaction of crystalline boron to give this solution, allowed calculation of the heat of formation of orthoboric acid. By combination of these results with other available thermochemical data, it was possible to derive values of the heats of formation of B_2O_3 and B_2H_6 .

EXPERIMENTAL

The basic procedures used in this research for combustion calorimetric measurements have been described (1). Only modifications made in this research and procedures peculiar to it will be described here.

Combustion Calorimetry

Preparation of Sample Mixtures

Bags of polyester film (1) were used to prepare sample mixtures of crystalline boron or trimethylamineborane and vinylidene fluoride polymer, $(CH_2CF_2)_n$.

Crystalline boron powder, 325 mesh particle size and finer, and vinylidene fluoride polymer, 100 mesh particle size and finer, were weighed into a previously weighed polyester bag. A "bubble" of air was intentionally sealed inside the bag. Manipulation of the bag in such a manner that the air "bubble" was pushed from end to end produced an intimate mixture of the two powders. The polyester bag with its contents was pressed flat in a vise; subsequently, the bag was pricked with the point of a needle to allow escape of the air. The bag was rolled, with the opening made by the needle inside and compacted with a pellet press. The pellet could be prepared without loss of mass detectable by a microbalance.

Pelleted mixtures of trimethylamineborane and vinylidene fluoride polymer in polyester bags were prepared in the same way except that the slightly hygroscopic trimethylamineborane was handled inside a dry box. Trimethylamineborane is a waxy solid, and the mixtures obtained were not as intimate as in the case of boron and polymer. Because trimethylamineborane is slightly volatile, the pellet was sealed inside a polyester envelope.

The polyester bag technique is an invaluable aid in combustion calorimetry of fluorine-containing materials. Recognition of the problems of the hygroscopicity of the polyester and of its tendency to become statically charged must be emphasized. Recent experiments have shown that several compounds, including water, permeate the polyester film very slowly, and appropriate precautions in its use must be taken.

The Chemistry of the Bomb Process

The pellets described in the previous section were burned under 30 atm of oxygen in the presence of excess aqueous HF. In several non-calorimetric experiments, the bomb was discharged and opened as quickly as possible after ignition of the sample. Solid oxidation products never were found. The boron oxide and/or fluoride dissolve rapidly in the HF solution to form aqueous HBF_4 . The chemical reaction was selected with cognizance that oxygen-containing acids such as HBF_3OH exist and might possibly affect the results. The authors wish to acknowledge the helpful advice of Dr. C. A. Wamser who has shown that in the presence of large excesses of HF, the only important boron-containing ion in solution is BF_4^- (2). Some small equilibrium concentration of BF_3OH^- ion does exist, and in order to minimize its effect, however small, the combustion experiments and the comparison experiments (1) were designed to produce the same final solution. The mass of pure boron or of trimethylamineborane was used as a measure of the amount of reaction.

Nitric acid was determined quantitatively by the method previously described (1). The gas produced in selected experiments was checked qualitatively for CO , and none was detected. Mass spectrometer analysis of the HF-free gas from selected experiments failed to show the presence of any gaseous combustion products other than CO_2 and H_2O . There was no evidence for chemical attack on the platinum crucible.

Comparison Experiments

Comparison experiments were used to minimize errors from inexact reduction to standard states caused by lack of data necessary to correct for such effects as the solubility and heat of solution of CO_2 in a rather concentrated solution of HF and HBF_4 . The sample consisted of benzoic acid and hydrocarbon oil (or for the trimethylamineborane experiments, only hydrocarbon oil). The amounts of these materials were so selected that the energy evolved and the CO_2 produced in the comparison experiment were as nearly as possible the same as in the companion combustion experiment. The bomb initially contained an aqueous solution of HF and HBF_4 , which, upon dilution with the water produced by the combustion of the sample, gave a solution of nearly the same amount and concentration as the combustion experiment.

Calorimeter and Bomb

The rotating-bomb calorimeter (3), laboratory designation BMR III, and the platinum-lined bomb (3), laboratory designation Pt-5, have been described.

Solution Calorimetry

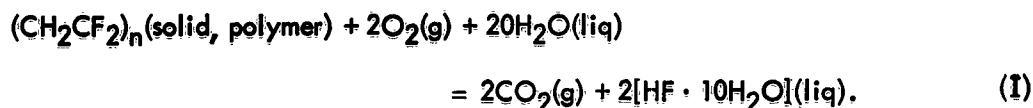
Four heat-of-solution experiments were performed in which crystalline orthoboric acid was dissolved in an HF solution chosen to produce the same final solution as obtained in the combustion experiments. The boric acid was contained in a methylmethacrylate vessel with a flat, smooth-surfaced lid. This vessel, with its contents, was floated in the HF solution inside the bomb. The bomb was placed inside the calorimeter

without the usual inversion. The calorimeter was heated to an initial temperature about 0.5° below the temperature of the isothermal jacket (25°). Time-temperature measurements were made for an initial period, and rotation of the bomb was begun. When the bomb turned, the contents were mixed. The accompanying heat effect was rapid and was observed by time-temperature measurements that were continued until a steady rate of temperature change was obtained again. About 0.15 moles of H_3BO_3 was dissolved in the HF solution with an energy evolution of approximately 2,000 calories. The heat of solution was calculated from the known heat equivalent of the system, $\mathcal{E}(\text{Calor.}) = 4032.3 \text{ cal deg}^{-1}$, and heat capacities of the contents.

Materials

The crystalline boron was supplied by the Eagle-Picher Company. This material had been prepared by hydrogen reduction of purified boron tribromide with deposition on boron filaments and was subsequently float-zoned. The crystalline form of the material was beta-rhombohedral. The boron had been crushed with a so-called 'diamond' mortar. It was necessary to sieve the powder to obtain material of 325 mesh particle size and smaller in order to obtain complete combustion. The sieving was done with stainless steel sieves used as gently as possible. The sieved material was leached with concentrated hydrochloric and hydrofluoric acids, water-washed and vacuum dried. Carbon content was less than 50 parts per million. Emission spectrographic analysis of the powder showed 0.02 percent iron and 0.01 percent silicon as the only detectable impurities.

A vinylidene fluoride polymer (a different sample from the one used in earlier work with silicon compounds) was supplied by the Pennsalt Chemicals Corporation. The value of $\Delta \overline{\text{Ec}}^\circ / \text{M}$ for this material was $-3527.79 \pm 0.64 \text{ cal g}^{-1}$ for combustion according to the reaction



As nearly as could be ascertained from the HF recovery, the composition of the polymer was exactly $(\text{CH}_2\text{CF}_2)_n$. Mass spectrometer examination of the HF-free gas resulting from combustion of the polymer did not reveal the presence of CF_4 or other fluorine-containing molecules.

Fisher "certified reagent" grade boric acid was recrystallized three times from distilled water and air dried at room temperature. The material was stored in sealed containers. Titration with standard alkali in the presence of mannitol indicated 100.0 percent H_3BO_3 .

The benzoic acid was National Bureau of Standards sample 39h. The hydrocarbon oil (3) and polyester film (1) have been described.

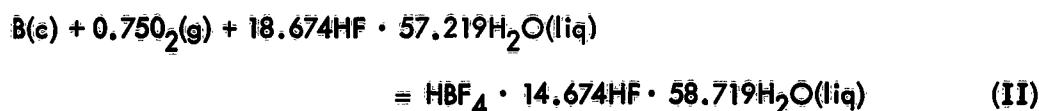
Units of Measurement and Auxiliary Quantities

The results reported are based on a molecular weight of 72.947 for trimethylamineborane and an atomic weight of 10.811 for boron (4) and the relations $0^{\circ}\text{C} = 273.15^{\circ}\text{K}$ and $1 \text{ cal} = 4.184 \text{ joules}$ (exactly). Thermochemical data from the literature were adjusted to the 1961 atomic weight scale when necessary. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

Calorimetric Results

Boron Combustion Results

Ten pairs of satisfactory combustion and comparison experiments were obtained. Eleven experiments were attempted in which 21 percent of the total energy came from boron, and nine were successful with no evidence of incomplete combustion. Three experiments were attempted in which 30 percent of the energy came from boron, and only one experiment was successful. The energy of the reaction



was found to be

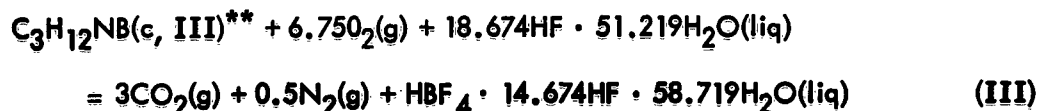
$$\Delta \underline{\text{Ec}}^{\circ}/\underline{\text{M}} = -15998.7 \pm 6.7 \text{ cal g}^{-1} \quad (\text{mean and standard deviation})$$

$$\Delta \underline{\text{Ec}}^{\circ} = -172.9_6 \pm 0.2_0 \text{ kcal mole}^{-1} \quad (\text{mean and uncertainty interval})$$

$$\Delta \underline{\text{Hc}}^{\circ} = -173.4_1 \pm 0.2_0 \text{ kcal mole}^{-1} \quad (\text{mean and uncertainty interval})$$

Trimethylamineborane Combustion Results

Eight pairs of satisfactory combustion and comparison experiments were obtained in nine attempts. About 50 percent of the energy came from trimethylamineborane. The energy of the reaction



was found to be

$$\Delta \underline{\text{Ec}}^{\circ}/\underline{\text{M}} = -11383.3 \pm 1.5 \text{ cal g}^{-1} \quad (\text{mean and standard deviation})$$

** Unpublished work of this laboratory has shown that trimethylamineborane exists in three crystalline forms. Crystal (III) is the form stable at 25° and lower temperatures.

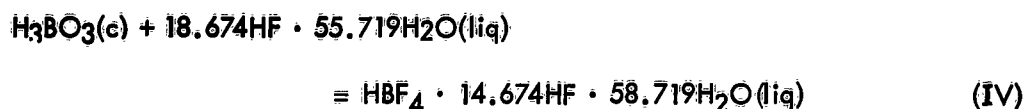
$$\Delta \underline{E}c^{\circ} = -830.38 \pm 0.46 \text{ kcal mole}^{-1} \text{ (mean and uncertainty interval)}$$

$$\Delta \underline{H}c^{\circ} = -832.30 \pm 0.46 \text{ kcal mole}^{-1} \text{ (mean and uncertainty interval)}$$

From combination of the heats of equations II and III with data (5) for the heats of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{liq})$ and heat of dilution data for HF, the heat of formation of trimethylamineborane (c, III) was found to be $-34.04 \pm 0.55 \text{ kcal mole}^{-1}$ (mean and uncertainty interval).

Heat of Solution of H_3BO_3 in Aqueous HF

Four experiments were performed in which orthoboric acid was dissolved in aqueous HF according to the reaction

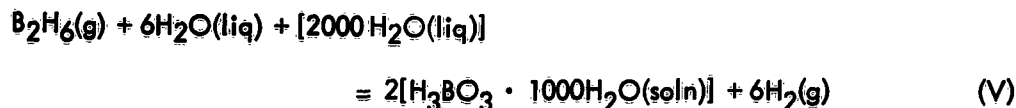


$$\Delta \underline{H}_{298.15}^{\circ} = 14.60 \pm 0.01 \text{ kcal mole}^{-1} \text{ (mean and standard deviation)}$$

From combination of the results of equations II and IV with data (5) for the heat of formation of $\text{H}_2\text{O}(\text{liq})$ and heat of dilution data for HF, the heat of formation of crystalline H_3BO_3 is found to be $-261.47 \pm 0.20 \text{ kcal mole}^{-1}$ (mean and uncertainty interval).

Derived Results

Two modern measurements of the heat of hydrolysis of diborane exist.



$$\Delta \underline{H}_{298.15}^{\circ} = -111.46 \pm 0.46 \text{ kcal mole}^{-1} \text{ [Prosen, et al. (6)]}$$

$$\Delta \underline{H}_{298.15}^{\circ} = -112.22 \pm 0.10 \text{ kcal mole}^{-1} \text{ [Gunn and Green (7)]}$$

These values were combined with the heat of formation of orthoboric acid from this research, the heat of solution of boric acid (6), and the heat of formation of $\text{H}_2\text{O}(\text{liq})$ (5) to derive two values of the heat of formation of diborane (g).

$$\Delta \underline{H}_{298.15}^{\circ} = 8.77 \pm 0.68 \text{ kcal mole}^{-1} \text{ (using value of Prosen, et al.)}$$

$$\Delta \underline{H}_{298.15}^{\circ} = 9.53 \pm 0.42 \text{ kcal mole}^{-1} \text{ (using value of Gunn and Green)}$$

These may be compared with the values 7.53 ± 0.56 (8) kcal mole^{-1} and 7.53 (9) kcal mole^{-1} , both derived from decomposition reactions in which diborane was decomposed into amorphous boron and $\text{H}_2(\text{g})$. It should be noted that although these two values

(references 8 and 9) are in exact agreement, the agreement was forced by use of two quite different values of the heat of formation of amorphous boron, 0.4 ± 0.1 (8) and 1.255 (9) kcal atom⁻¹.

Another approach to the heat of formation of diborane is through the heat of the reaction



$$\Delta H_{-273}^\circ = -31.27 \pm 0.15 \text{ kcal mole}^{-1} \text{ [McCoy and Bauer (10)]}$$

By use of appropriate heat capacity data, the heat of this reaction at 25° was calculated to be -31.40 kcal. By use of $\Delta H_{298.15}^\circ$ of trimethylamineborane from this research and an unpublished value of the National Bureau of Standards for the heat of formation of gaseous trimethylamine, the heat of formation of diborane is calculated to be 5.90 ± 0.64 kcal mole⁻¹.

The value of the heat of formation of crystalline H_3BO_3 was combined with values of the heat of solution of H_3BO_3 , the heat of solution of amorphous B_2O_3 and the heat of transition of amorphous B_2O_3 to crystalline B_2O_3 from reference 6 and the heat of formation of liquid water (5) to calculate the heats of formation of B_2O_3 (amorphous) and $\text{B}_2\text{O}_3(\text{c})$.

$$\Delta H_{298.15}^\circ (\text{B}_2\text{O}_3, \text{amorph}) = -299.74 \pm 0.40 \text{ kcal mole}^{-1}$$

$$\Delta H_{298.15}^\circ (\text{B}_2\text{O}_3, \text{c}) = -304.10 \pm 0.41 \text{ kcal mole}^{-1}$$

The uncertainties expressed are the uncertainty interval.

A comparison of the results of this research with previous values is presented in Table I. It should be emphasized that the derived values from this research are not related to amorphous boron and the uncertainties in its heat of formation.

TABLE I. STANDARD HEAT OF FORMATION AT 298.15°K

	<u>This research</u>	<u>Other recent values</u>	<u>Circular 500 (a)</u>
$H_3BO_3(e)$	-261.47 ± 0.20	-262.16 ± 0.32 (b)	-260.2
$B_2O_3(c)$	-304.10 ± 0.41	-305.34 ± 0.75 (c)	-302.0
$B_2O_3(amorph)$	-299.74 ± 0.40	-300.98 ± 0.75 (c)	-297.6
$B_2H_6(g)$	8.77 ± 0.68	7.53 ± 0.56 (d)	7.5
	9.53 ± 0.42	7.53 (e)	
	5.90 ± 0.64		
$(CH_3)_3NBH_3(c, III)$	-34.04 ± 0.55		

-
- (a) Work cited in reference 5.
 (b) Natl. Bur. Standards Rpt. 7093, Jan. 1, 1961.
 (c) Work cited in reference 6.
 (d) Work cited in reference 8.
 (e) Work cited in reference 9.

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EXPERIMENTAL EVALUATION OF THE HEATS OF FORMATION OF BORON-CONTAINING COMPOUNDS

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INTRODUCTION

In order to calculate accurate values of the performance parameters for rocket propellant formulations, accurate values for the heats of formation of the propellant constituents are required. For many compounds used in older propellant formulations, these data are available from measurements reported in the literature; for other compounds, correlations based on bond energies or molecular structure can be made. However, these latter calculations are generally less reliable than values obtained by accurate thermochemical measurements.

During the past several years, increased emphasis by the Advanced Research Projects Agency and other Government agencies on the development of new classes of solid propellant materials has resulted in the synthesis of many new compounds. One group of compounds which has received considerable attention comprises the amine-boron hydrides. For many of these compounds, the measured values have not been firmly established because of sample impurities or lack of precision in thermochemical measurements which were primarily intended for screening purposes.

In view of the evident need for accurate values of the heats of formation of the amine-boron hydrides in particular, and B-H-C-N compounds (i.e., those containing boron, hydrogen, carbon, and nitrogen) in general, the Research Laboratories of United Aircraft Corporation have undertaken to measure such values for selected B-H-C-N compounds as part of Contract NOW 63-0750-d with the Bureau of Naval Weapons. This report contains a description of the experimental apparatus in the Calorimetry Laboratory in which the measurements are being carried out, a discussion of experimental techniques for determining reliable values of heats of formation of B-H-C-N compounds, and a preliminary value for the heat of formation of hydrazine monoborane (HMB).

EXPERIMENTAL APPARATUS

The apparatus which is being used in this program comprises both calorimetric and analytical equipment. The apparatus in use for the determination of the heat evolved in a reaction consists of an oxygen combustion bomb made of a suitably strong and corrosion resistant material (stainless steel lined with platinum), a calorimeter, and a thermometric system.

The calorimeter, which is quite similar to one described by Hubbard

Katz, and Waddington (Ref. 1) and modified for continual rotation as described by Good, Scott, and Waddington (Ref. 2), is a type in which the bomb is rotated within its water jacket in the calorimeter to mix the products of reaction with a solution placed in the bomb. This type of calorimeter is essential for thermochemical measurements of heats of reaction for those reactions in which a non-homogenous mixture of reaction products is formed within the bomb.

The oxygen combustion bomb is a commercially available adaptation of an Argonne National Laboratories design and has an internal volume of 331.8 ml (Parr Instrument Co., Catalogue No. 1004). This bomb has a teflon head gasket and valve packing, and a Kel-F valve seat. All internal parts of the bomb are 10% iridium-platinum and the bomb cylinder is lined with platinum. The valve needles are standard Parr No. 339 needles which are made to accommodate 1/8 in. Swagelok connections. Adaptors have been made to fit Parr No. 233A snap couplings to these needles so that the valves of the bomb can be easily opened or closed while the bomb is connected to an analytical system. For experiments in which hydrofluoric acid solutions are used in the bomb, the ceramic electrode insulator is replaced with a teflon disc. The bomb solution covers the sides of this disc and a platinum washer protects the top so that when the bomb is fired in an inverted position, the danger of ignition of the teflon is slight. A platinum crucible containing the sample is mounted in an offset gimbal so that the bomb can be set at a 45 deg angle for filling. Amounts of solution as large as 25 ml have been accommodated. Ignition of samples is achieved by means of an iron fuse wire. The temperature in the water jacket of the calorimeter is maintained within a few thousandths of a degree of 28.6317 ohms (30.008 C) by means of a Sargent thermistor controller which has been modified to give greater sensitivity. The calorimeter can contains approximately 2930 ml of water and is maintained within 0.005 g of a constant weight for each experiment by weighing against a brass tare on a 5 Kg capacity Seko 140 series balance. The calorimeter can also contains a stirrer, the rotating mechanism, platinum resistance thermometer and heater. The stirrer is operated at 450 rpm using a belt drive from a synchronous motor. The rotation mechanism operates from a synchronous motor through a gear drive. Revolutions of the drive shaft are counted by means of a cam and switch arrangement and are displayed on an electrical counter which may be set to stop rotation after a given number of revolutions. The rotational speed is 10 rpm.

The thermometric system includes a platinum resistance thermometer of the flat calorimetric type (Leeds and Northrup type 8160B), a G-2 Mueller bridge (Leeds and Northrup type 8069B), and a high sensitivity galvanometer (Leeds and Northrup type HS 2284d). The galvanometer is mounted on a Julius suspension and the light beam is projected vertically over a path of two meters. The sensitivity of this apparatus has been shown to be $1.36 \cdot 10^{-4}$ ohm/cm at 5 ma thermometer current and $3.33 \cdot 10^{-4}$ ohm/cm at 2 ma. The difference between resistance measurements taken at 5 ma and at

2 ma is 0.000806 ohm at a temperature of 28.5854 ohms. The constants for the thermometer, Serial No. 1595911, are $R_0 = 28.5853$ ohms, $C = 0.0039260$, $\delta = 1.49$ with 2 ma current. The calibration of the thermometer was checked using a triple point cell, and the Mueller Bridge calibration was checked using a certificated standard resistor.

In order to measure accurately the heat evolved in the reaction, measurements are taken of the calorimeter temperature as a function of time. In this way, the experiment can be corrected for time-dependent heat leaks. During the fast reaction period, a Gaertner B370A tape chronograph is used to supplement a synchronous electric clock which is used during the slow temperature-rise periods of the experiment. Measurements with these instruments can be made with accuracies greater than 1/1000 and 1/100 minute, respectively.

The analytical apparatus consists of an oxygen filling system, an analytical system for the determination of carbon monoxide and carbon dioxide, and suitable balances and wet chemical apparatus. An analytical balance (Ainsworth Type TC) is used to measure the masses of the sample and the reaction products. With class M weights, this balance gives an accuracy of 1/40 milligram at maximum load. The class M weights in use are of rhodium-plated brass and have been calibrated against a one gram mass which was certified at the National Bureau of Standards. All weights are corrected to vacuum conditions, and apparatus has been installed in the laboratory to keep a daily record of humidity, temperature, and barometric pressure.

The chemical train for purifying the oxygen and filling the bomb is quite similar to the one used by Prosen and Rossini (Ref. 3). It consists of a copper-oxide-filled furnace maintained near 450 C and a purifying tube filled with ascarite, magnesium perchlorate, and phosphorus pentoxide. This system removes all combustible impurities from the oxygen. Pressure is measured by means of a Bourdon-type pressure gage.

An analytical train is available for CO-CO₂ analysis to determine the completeness of combustion of carbon present in the system. This train consists of a furnace packed with copper oxide and an absorption tube packed with ascarite, magnesium perchlorate, and phosphorus pentoxide for the purification of oxygen used in flushing the bomb; an absorption tube packed with sodium fluoride, magnesium perchlorate and phosphorus pentoxide for removal of hydrogen fluoride and water from the gases vented from the bomb; and an absorption tube packed with ascarite, magnesium perchlorate, and phosphorus pentoxide for the removal of carbon dioxide. A second furnace packed with copper oxide and a second set of absorption tubes identical to the first set are used for quantitative conversion of carbon monoxide to carbon dioxide and subsequent absorption of this carbon dioxide. The absorption tubes are filled with helium before weighing. Additional standard chemical apparatus are used for deter-

mination of free boron, carbon, and nitric acid which may be present if combustion is incomplete.

EXPERIMENTAL TECHNIQUES

Calorimetric Techniques. The procedures developed for making calorimetric measurements are essentially the same as those used in most experiments in bomb calorimetry. Experiments in the rotating bomb calorimeter are divided into four time periods of the following duration:

Fore period	20 minutes
Reaction period	20 minutes
Mid period	14 minutes
After period	20 minutes

The relationship of these time periods to a representative temperature-rise curve is shown in Fig. 1.

The starting temperature for all experiments is 28.350000 ohms (27.222 C) and the jacket temperature is maintained constant within ± 0.0003 ohm (~ 0.003 C) at a temperature near 28.6280 ohms (29.971 C) for the course of the experiment. Ignition is achieved by the use of a standard iron fuse wire 5 cm in length. Rotation starts at the twenty-seventh minute and continues until the fifty-fourth minute. During this time, the bomb is rotating at a rate of approximately 10 rpm. This appears to be an ample time period for mixing the contents of the bomb and for determining the energy contribution due to rotation. Starting the rotation at the twenty-seventh minute permits several accurate temperature measurements to be made before rotation starts so that the temperature at the beginning of the rotational period, R_R , will be known.

During the experiment, measurements of resistance are made at two-minute intervals during the fore, mid, and after periods. A 5 ma bridge current is used to give maximum sensitivity. Since the thermometer is certificated using a current of 2 ma, all readings are subsequently corrected to the 2 ma scale. During the first three minutes of the reaction period, the bridge current is reduced to 2 ma and readings of time at set values of resistance are recorded using a tape chronograph. During the remainder of the reaction period, readings are taken at prescribed time intervals ranging from one-half to two minutes depending on the steepness of the temperature-rise curve during successive intervals.

Chemical Techniques. Chemical techniques studied were primarily concerned with the development of optimum methods of handling the highly reactive amine-boron hydrides and development of reaction schemes which minimize the problems associated with the chemical analysis of the products of reaction. The methods in use at the UAC Research Laboratories are a modification and development of those developed at the Bureau of Mine Laboratory, Bartlesville, Oklahoma (Ref. 4). This method makes use of vinylidene fluoride, $(CH_2CF_2)_n$, as an auxiliary substance. The

combustion reaction then becomes:



Using this method, the volume of solution required in the bomb is 10 ml of 20% HF solution. Formation of free boron was found to be the chief problem. A complete quantitative analysis was made of the reaction products to determine the identity of the products of reaction. The bomb solution was filtered to remove boron, which was retained in a filter crucible and oxidized to boric oxide and titrated. Fluoroboric acid is determined by the method of Wamser (Refs. 5 and 6). Carbon dioxide and carbon monoxide were determined by the methods first used by Prosen and Rossini (Ref. 3) as indicated previously. Nitrate was found by Devarda's method. In addition, gas samples were analyzed in the mass spectrograph. The chief difficulty in applying this method is that for complete combustion a maximum of only 20% of the reaction energy may come from the boron. For samples containing high percentages of boron, sample sizes become so small as to limit the accuracy of the derived data. In addition, sample preparation is somewhat more difficult when using an auxiliary substance. However, at present these problems do not appear to be prohibitive.

The techniques which were developed for handling the reactive test samples consist largely of methods for manipulating samples in a dry box and methods for encapsulating samples. The dry box in which the samples are prepared is filled with argon which is continuously purified by passage over barium metal maintained at 450 C and by passage over magnesium perchlorate and phosphorus pentoxide (Ref. 7). In this way, any oxygen, nitrogen, or water which leak into the system are removed. Samples are weighed approximately in the dry box and then sealed in mylar bags. These bags, prepared from mylar sheets of 1 mil thickness, are approximately 3 x 5 centimeters in size and weigh of the order of 0.16 gm. The sample materials are removed from the dry box in the mylar bags, weighed precisely on the balance, returned to the box and pressed into pellets. The finished pellet thus consists of an accurately weighed mixture of vinylidene fluoride and the particular B-H-C-N compound being studied, encapsulated in a mylar shell. The number of moles of each material present is found using the atomic weight values recommended in 1962 (Ref. 8). The finished pellets are sealed in saran bags and stored in the dry box. When the pellets are to be used, they are removed from storage, the saran bag is discarded, and the pellet is reweighed prior to insertion into the bomb.

Data Reduction. The general principles involved in reduction of data from a bomb calorimeter to obtain a value for the energy equivalent (i.e., the energy required to raise the temperature one unit) for the standard initial calorimetric system are described in Ref. 9. The

reduction of data for a calorimetric experiment requires a detailed energy balance which includes consideration of energy increments due not only to combustion but also to stirring, rotation, and thermal conduction in the calorimeter system. The equation derived during the report period for the temperature rise (in ohms) due to these effects is

$$\Delta R = a_f(t_R - t_1) + a_M(t_M - t_R) + k(R_f - R_{mp1})(t_R - t_1) + k(R_M - R_{mp2})(t_M - t_R) \quad (1)$$

where R is the temperature in ohms, t is the time in minutes, a_M and a_f are the slopes of the temperature-rise curve during the mid period and after period, respectively, and k , the cooling constant, is defined by the expression:

$$k = \frac{(a_1 - a_f)}{(R_f - R_1)} \quad (2)$$

In Eq. (2), a_1 represents the slope of the temperature-rise curve during the fore period. The subscripts on the time and temperature terms in Eqs. (1) and (2) refer to the points bearing the same designations in Fig. 1.

The temperatures at the mid points of the reaction period, R_{mp1} , and R_{mp2} , and at the time at which rotation starts, R_1 , are found by fitting parabolas to the data for the four points immediately adjacent to the respective times, i.e., t_{mp1} , t_{mp2} , t_R , by the method of least squares and then solving for the values of the functions at the respective times. The values of the respective mid point times are found as follows:

$$t_{mp1} = t_R - \frac{\sum_{n=1}^{n=R} R_n \Delta t - R_1 (t_R - t_1)}{(R_R - R_1)} \quad (3)$$

and

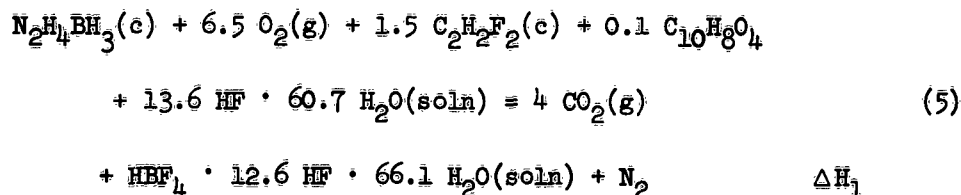
$$t_{mp2} = t_M - \frac{\sum_{n=R}^{n=M} R_n \Delta t - R_R (t_M - t_R)}{(R_M - R_R)} \quad (4)$$

Using the values given above, the corrected temperature rise is given by

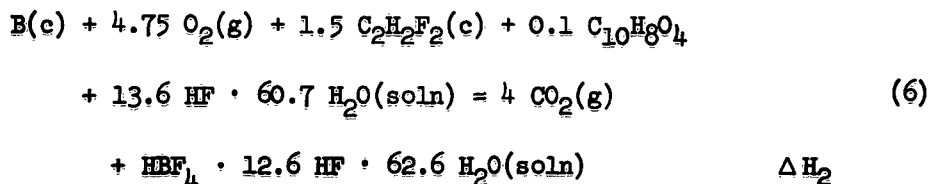
$$\Delta R_c = R_M - R_1 - \Delta R$$

The corrected temperature rise is used to calculate E_1 , the energy equivalent of the initial calorimeter system or may be used to calculate the heat of combustion of a boron-containing compound by methods similar to those outlined in Chapter 2 of Ref. 10.

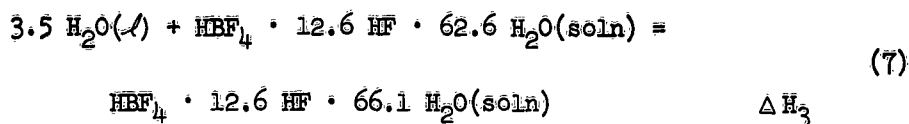
For experiments of B-H-C-N compounds, particularly when using a hydrofluoric acid in the combustion bomb, it is desirable to use a method of substitution in making the heat of combustion measurements. The use of this method is recommended primarily because of uncertainties in the heat of solution of carbon dioxide, but it also has the advantage that the derived heat of formation is referred directly to the elements. The method of substitution consists, in this case, of making two parallel series of combustion experiments on boron and the sample compound using the same experimental conditions and arranging the quantities of sample and auxiliary materials to give nearly the same carbon dioxide, hydrogen fluoride, and fluoroboric acid concentrations in the final solution. The approximate equation for the combustion of hydrazine monoborane is given as follows:



A small amount of nitric acid is also formed. (This conception of the bomb process is supported by mass spectrographic inspection of the gases in the bomb after a combustion experiment and by the analytical work done in developing experimental techniques. Similar results were obtained by Good as described in Ref. 3.) A comparison experiment will take the following course:



The $\text{C}_{10}\text{H}_8\text{O}_4$ is the one mil polyester film (mylar) used to encapsulate the sample. It may be noticed that the major problem in reducing the data derived from measuring the heat evolved in the two sets of reactions described in Eqs. (5) and (6) is that a heat of dilution of the hydrogen fluoride-fluoroboric acid solution in the bomb must be evaluated:



If the heat of formation of 3.5 moles of water is designated as ΔH_4 , the heat of formation of $\text{N}_2\text{H}_4\text{BH}_3$ may be calculated as:

$$\Delta H_f = \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1$$

CALORIMETRIC DATA

Calibration Experiments. The standard calorimetric system has been calibrated using benzoic acid. The defined calorimetric system includes the combustion bomb filled with oxygen and a fuse wire but does not include water, sample, or auxiliary material that may be placed in the bomb. The energy equivalent of this system was determined for the temperature interval between 28 and 30 C by combustion of NBS standard sample benzoic acid 391. For all calibration experiments, the amount of reaction was defined by the amount of reactant. No traces of incomplete combustion were observed. A correction was made for the formation of nitric acid by titrating the bomb liquid with 0.1 N NaOH using phenolphthalein as the indicator and using the value of 59 kJ/mole for the heat of formation of nitric acid. The data was corrected for deviations from standard conditions using the corrections described in the preceding section. The value of the calorie is taken to be exactly 4.1840 joules. This set of calibration experiments (five in all) was conducted without rotation.

A second series of benzoic acid combustion experiments was conducted, this time with the bomb rotating. With suitable correction for rotation and for a small change in the energy equivalent caused by a necessary modification of the calorimeter can, the energy equivalents derived for the two systems agree well. The derived value is 3611.88 ± 0.73 cal/deg.

In addition to the determination of the energy equivalent for the standard calorimetric system described above, the energy introduced by ignition and combustion of the fuse wire was also determined. The objective of this work was to provide an approximate value for the electrical energy input to the system for use in correcting results of subsequent experiments. The electrical energy input to the system is obtained by subtracting the assumed energy of combustion of the fuse wire from the total energy release in the experiment. A value of 7.5 kilojoules/gm (Ref. 10) was used as the heat of combustion for iron in this calculation. The value of electrical energy input resulting from these

experiments is 3.52 calories.

Hydrazine Monoborane. Preliminary work has been done to determine the heat of formation of hydrazine monoborane. A very preliminary value for the heat of formation of this compound is -8 ± 2 kcal/mole based on the results of two calorimetric runs. This value has not as yet had the Washburn corrections applied, nor has a correction for the heat of dilution been applied to compensate for the difference between the end conditions in HMB experiments as compared with those of the comparison experiments with boron. This value may be compared with that of Goubeau and Ricker (Ref. 11), -6.0 ± 2.4 kcal/mole, as derived from a series of heat of combustion measurements in a static bomb.

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TIME-TEMPERATURE PLOT FOR A TYPICAL CALORIMETRIC EXPERIMENT WITH ROTATION

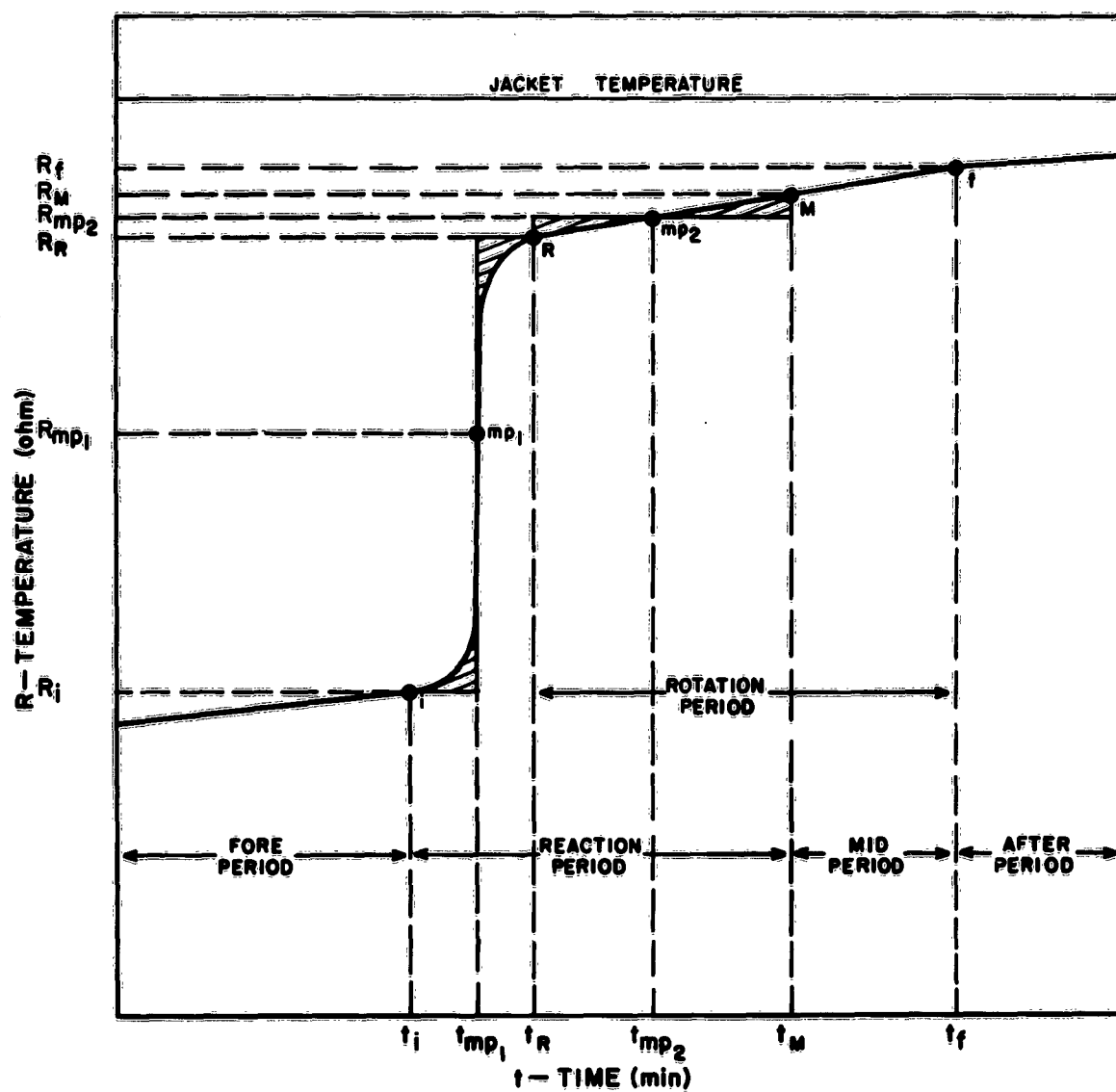


FIG. 1

THERMODYNAMIC STUDIES OF MIXED-METAL COMPOUNDS*

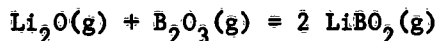
D. L. Hildenbrand, W. F. Hall, N. D. Potter and L. P. Theard

Research Laboratories
Philco Corporation
Newport Beach, California

The following is a brief summary of some thermodynamic studies on mixed-metal systems carried out at Aeronutronic.

I. The $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ System

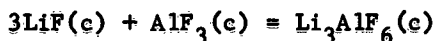
The vapor pressure of liquid LiBO_2 was measured over the temperature range 1120 to 1280°K by the torsion-effusion method.¹ A third-law analysis gave $\Delta H_{298}(\text{sub}) = 86.3 \pm 3$ kcal/mole for $\text{LiBO}_2(\text{g})$. When combined with data for the condensed phase, the data lead to $\Delta H_{298}^\circ = -157.9 \pm 3$ kcal/mole for $\text{LiBO}_2(\text{g})$ and give for the reaction



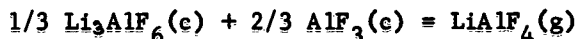
the value $\Delta H_{298}^\circ = -75$ kcal. Better structural and spectroscopic data are needed for $\text{LiBO}_2(\text{g})$.

II. The $\text{LiF}-\text{AlF}_3$ System

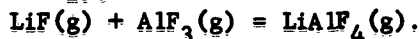
The torsion-effusion method was used to study the sublimation behavior of the $\text{LiF}-\text{AlF}_3$ system at compositions ranging from 25 to 67 mole % AlF_3 .² Univariant behavior was observed at all compositions and, in addition, congruent sublimation was observed at the 50 mole % composition. Vapor pressure was found to be independent of composition over the range 33 to 67 mole % AlF_3 , and higher than that of the 25 mole % AlF_3 composition by a factor of 30. The results are interpreted in terms of one condensed compound, $\text{Li}_3\text{AlF}_6(\text{c})$, and one gaseous compound, $\text{LiAlF}_4(\text{g})$. From the ratio of LiAlF_4 pressures at the 25 and 50 mole % compositions, one calculates $\Delta F_{980}^\circ = -10$ kcal for the reaction



and estimates $\Delta H_{298}^\circ = -806 \pm 5$ kcal/mole for $\text{Li}_3\text{AlF}_6(\text{c})$. From a second-law analysis of vapor pressure data for the 50 mole % composition, one obtains for the process



$\Delta H_{900}^\circ = 65.5 \pm 3$ kcal and, from estimated enthalpies, $\Delta H_{298}^\circ = 69.8 \pm 3$ kcal. A value of -437 ± 7 kcal/mole is derived for the heat of formation of $\text{LiAlF}_4(\text{g})$, which leads to the result $\Delta H_{298}^\circ = -70$ kcal for the reaction

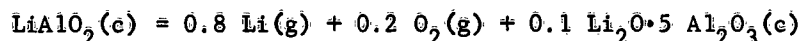


There are essentially no structural or spectroscopic data available for $\text{LiAlF}_4(\text{g})$. For $\text{Li}_3\text{AlF}_6(\text{c})$, entropy and heat-content data are needed.

* This work was supported by the Advanced Research Projects Agency through the Bureau of Naval Weapons.

III. The $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ System

The vaporization behavior of $\text{LiAlO}_2(\text{c})$ was studied in the range 1610 to 1840°K by mass spectrometric and torsion-effusion techniques.² The vaporization process was shown to be



for which a third-law treatment of the torsion data yields $\Delta H_{298} = 94.7 \pm 2$ kcal, and a second-law analysis of the mass spectrometric data yields

$\Delta H_{298} = 99.2 \pm 3$ kcal. A not-very-accurate value of -2180 ± 40 kcal/mole was derived for the heat of formation of $\text{Li}_2\text{O} \cdot 5 \text{ Al}_2\text{O}_3(\text{c})$ at 298°K. No Li-Al-O vapor species were detected.

IV. The $\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ System

Vaporization studies on various compositions on the $\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ system were made by the torsion-effusion method.^{3,4} The system contains two crystalline compounds, with $\text{B}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratios of 1:2 and 2:9. However, both compounds were found to undergo decomposition to B_2O_3 and the next-higher phase before measurable effusion pressures were reached, so that no thermal data for these substances can be obtained in this way. It is estimated that the heats of formation of the compounds from the component oxides at 298°K will be only a few kcals. Gaseous aluminum borates are not of importance.

V. The $\text{LiF}-\text{BF}_3$ System

Some preliminary mass spectrometric studies of vapors in the $\text{LiF}-\text{BF}_3$ system have been made.⁵ Gaseous BF_3 was passed into an effusion cell containing condensed LiF , and the vapors were ionized and mass analyzed. The total concentration of lithium-containing species (as evidenced by the Li^+ signal) was found to increase markedly when BF_3 was admitted to the system. No ions containing both lithium and boron were detected. However, the presence of a number of intense impurity peaks prevented detailed studies. There is other evidence that mixed-metal halide vapors undergo extensive fragmentation on electron impact, so that the large enhancement of the Li^+ signal when BF_3 is admitted to the cell may well indicate the formation of a stable Li-B-F vapor species.

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RESEARCH ON THE THERMODYNAMICS
OF THE Al-B-O, Be-B-O AND Li-B-O SYSTEMS

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INTRODUCTION

In this study vapor pressures over mixed oxide systems are measured isothermally as a function of composition. These measurements provide thermodynamic values for the vapor species and the condensed phases. From the pressure-composition curves and literature data it will be possible to compute activities of the various species in the condensed phases and portions of phase diagrams for these systems.

APPARATUS

The equipment for this research is shown diagrammatically in Figure 1. It consists of a stainless steel high vacuum system which may be baked to 400°C. The vacuum level with the sample at temperature is in the 10^{-7} and 10^{-8} torr range. The furnace is a one-inch diameter, ten-inch long resistance heated platinum-40% rhodium tube surrounded by platinum radiation shields. The furnace temperature is recorded and controlled to $\pm 1/2^\circ\text{C}$. A 1/4-inch diameter, 1/4-inch high platinum Kundsen cell is suspended in the furnace from an automatic recording vacuum microbalance. The quartz beam balance is supported at the fulcrum on steel pivots resting in sapphire cups. Counterweights consist of two parts: a magnet rod surrounded by a solenoid which keeps the balance at its null position, and a steel rod hanging inside a variable permeance transducer which is used as a null detector. Changes in the current flowing in the solenoid are directly proportional to the weight change of the sample. The electronics are essentially the same as those used by Cochran.¹ This current is recorded and provides a plot of sample weight versus time.

Using Langmuir's² equation differentials of the weight-time curve, dw/dt are employed to compute the pressure. Total change in weight, initial composition and vapor constitution are used to calculate the corresponding composition of the condensed phases.

RESULTS AND DISCUSSION

B₂O₃ Studies

In order to calibrate the equipment, the vapor pressure of B₂O₃ was measured. Since B₂O₃ was the principal vapor species expected in the systems to be studied these experiments should yield B₂O₃ vapor pressures which are more consistent with the measurements over the mixed oxide systems than are the literature values.

The vapor pressure of B_2O_3 measured here is compared with previous measurements in Figure 2. Using the free energy functions of Evans³ for the liquid and Sommer *et al.*⁴ for the gas, third-law heats were calculated for this and previous data. These values are given in Table I.

TABLE I

Third-Law Heats of Vaporization for Boric Oxide

<u>Author</u>	ΔH_v° <u>kcal/mole of B_2O_3</u>
This research	100.8
Speiser, Naiditch and Johnston ⁵	99.0
Scheer ⁶	102.9
Nesmeyanov and Firsova ⁷	101.0
White, Walsh, Goldstein and Dever ⁸	100.7
Hildenbrand, Hall and Potter ⁹	<u>101.2</u>

Average 100.9 $\pm$ 0.9

In the course of the B_2O_3 measurements, the sample to orifice area ratio was varied by an order of magnitude. This variation yielded a corresponding apparent vapor pressure difference of a factor of three. A simplified Motzfeldt equation¹⁰

$$\frac{P_{eq}}{P_m} = 1 + \frac{a}{A\alpha} \quad (1)$$

was used to calculate the evaporation coefficient, where P_{eq} and P_m are the equilibrium and measured pressures, a the orifice area, A the sample area and α the evaporation coefficient. The computed value for α was 0.16.

Hildenbrand⁹ was unable to detect a difference in the measured vapor of B_2O_3 by changing his orifice areas by a factor of two. However, he indicated that the sample area to orifice area was considerably larger than is the case in the present work. The orifice area change he used and an evaporation coefficient of 0.16 would have resulted in only a 2% change in the measured pressure. This is better than the precision of his results.

Be-B-O System

Two isothermal experiments have been carried out on the Be-B-O system, starting with an initial composition of $3B_2O_3$ -BeO. Figure 3 shows the results obtained at 1459°K, with the logarithm of the B_2O_3 activity plotted versus the condensed phase composition. A broad two-phase region characterized by a constant pressure with changing composition was found extending to about 50 mole % BeO. This was followed by a decrease in activity to about 80 mole % BeO when the measurement was terminated.

A second measurement at 1350°K (see Figure 4) produced a wider two-phase region, extending to 70 mole % BeO. Here a sharp decrease in activity to 75 mole % BeO was found. At this point the activity continues to decrease, but at a slower rate.

Figure 5 presents a hypothetical phase diagram for the Be-B-O system, modeled after the Mg-B-O system of Davis and Knight.¹¹ The temperature dividing the two immiscible liquids from the liquid-solid region was selected to correspond to that in the Mg-B-O system. Only the 3BeO-B₂O₃ compound has been reported in the literature.^{12,13} For the purposes of this study, it has been given a range of homogeneity and an arbitrary melting point.

If one now analyzes the two isothermal curves using this diagram, one finds that at 1459°K there is a two-phase region extending to 50 mole % BeO. Beyond this, B₂O₃(l) plus liquid region there is a single liquid region. Here the activity of B₂O₃ decreases with composition. The hypothetical phase diagram predicts that this should be followed by a two-phase region, BeO plus liquid. We plan to make further measurements to establish the precise location of the boundary between the single and two-phase regions, and to ascertain whether there are two-phase regions hidden in the scatter of the data.

At 1350°K there is a wider two-phase area consisting of B₂O₃(l) + 3BeO·B₂O₃(s) extending to 70 mole % BeO. The 3 to 1 compound appears to have a homogeneity range which should be followed by a two-phase region 3BeO·B₂O₃(s) + BeO(s). Instead, a break in the curve is found at 75 mole % BeO, followed by an apparently continuing decrease in activity of B₂O₃. The latter portion of the curve may result from diffusion controlled evaporation, particularly since this lower temperature measurement was made with a large orifice. This aspect of the curve will be checked using a smaller orifice. The melting point of 3BeO·B₂O₃ will also be determined to complete the phase diagram.

Mass spectrometric measurements by Büchler¹⁴ on the beryllium rich mixed oxide system indicate that besides B₂O₃ vapor about 1% of the vapor consists of BeB₂O₄. When the activities and compositions of the condensed phases have been established, thermal properties will be calculated for this system.

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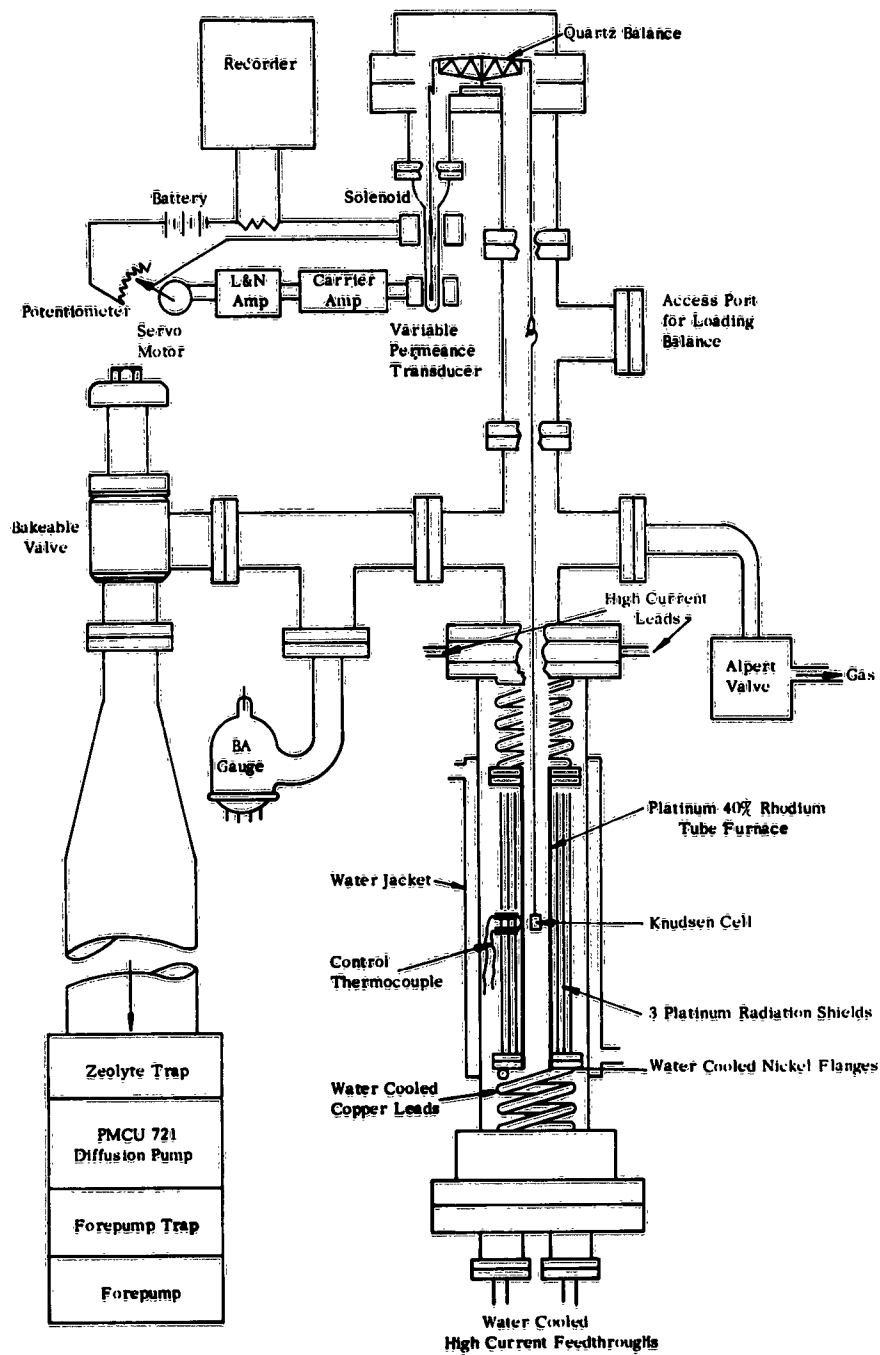


FIGURE 1 HIGH VACUUM MICROBALANCE SYSTEM

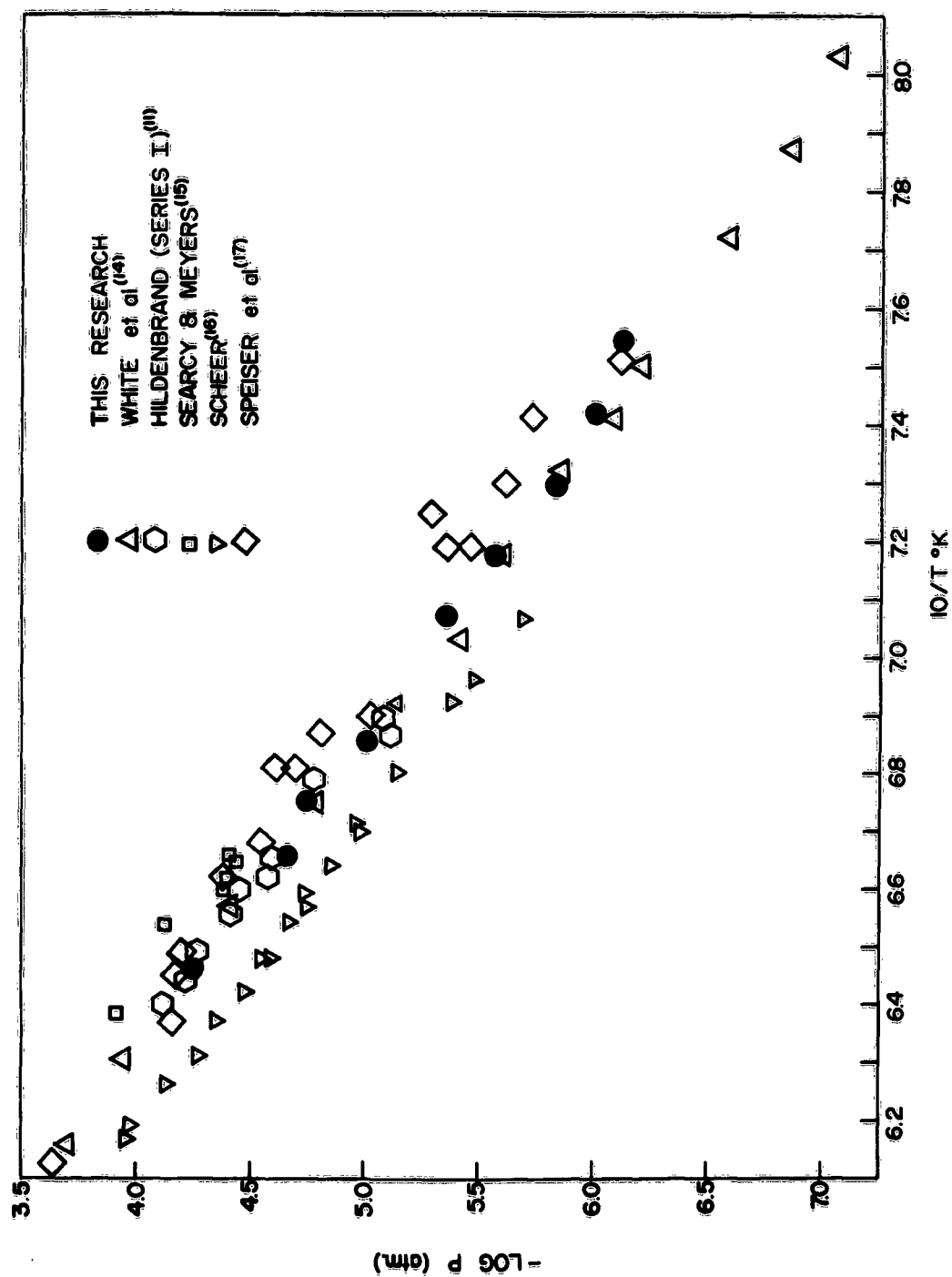


FIGURE 2 B_2O_3 VAPOR PRESSURE OVER BORIC OXIDE

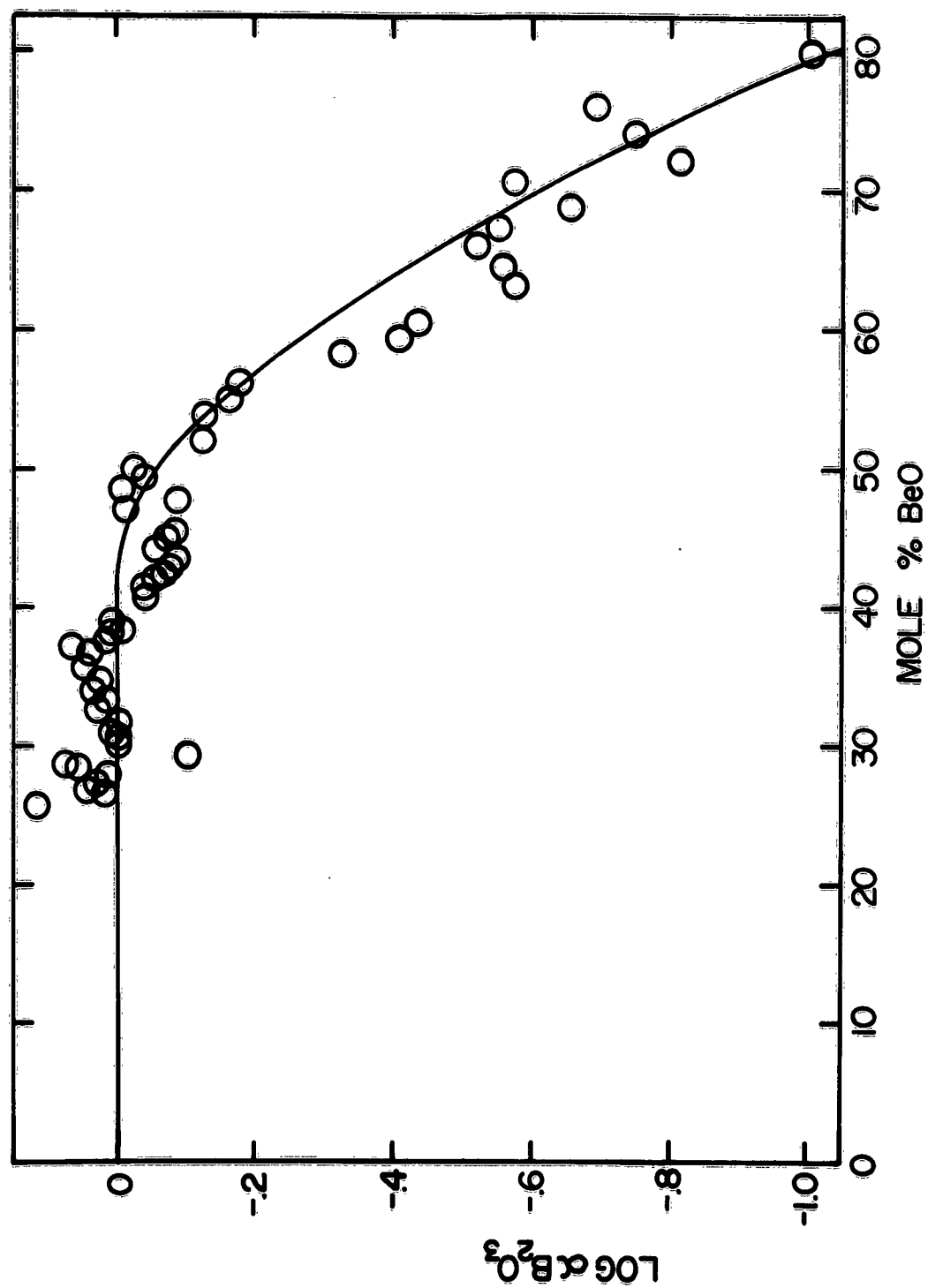


FIGURE 3 ACTIVITY OF B_2O_3 OVER $BeO-B_2O_3$ SYSTEM AT 1459 °K

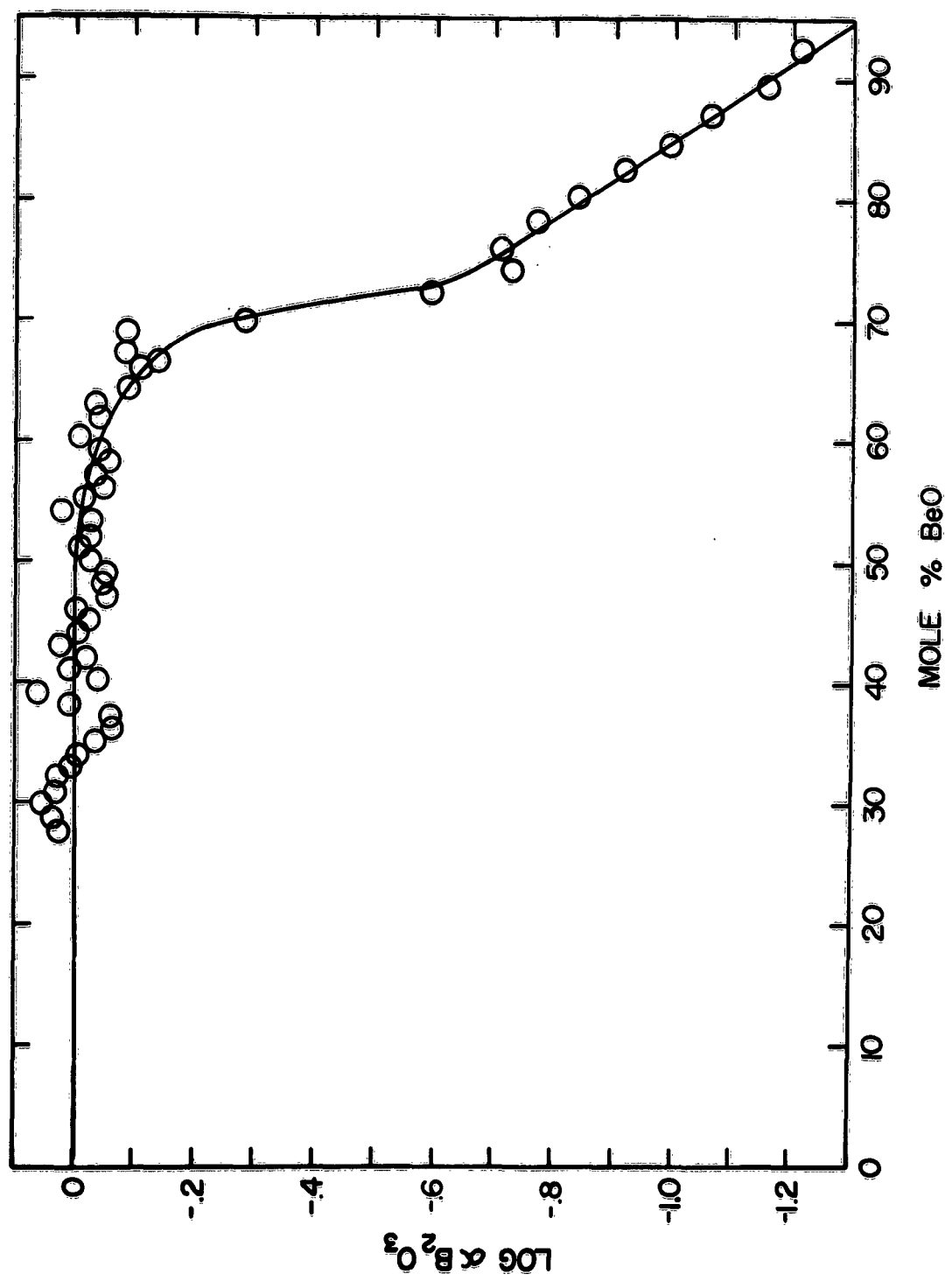


FIGURE 4 ACTIVITY OF B_2O_3 OVER $BeO-B_2O_3$ SYSTEM AT $1350\text{ }^{\circ}K$

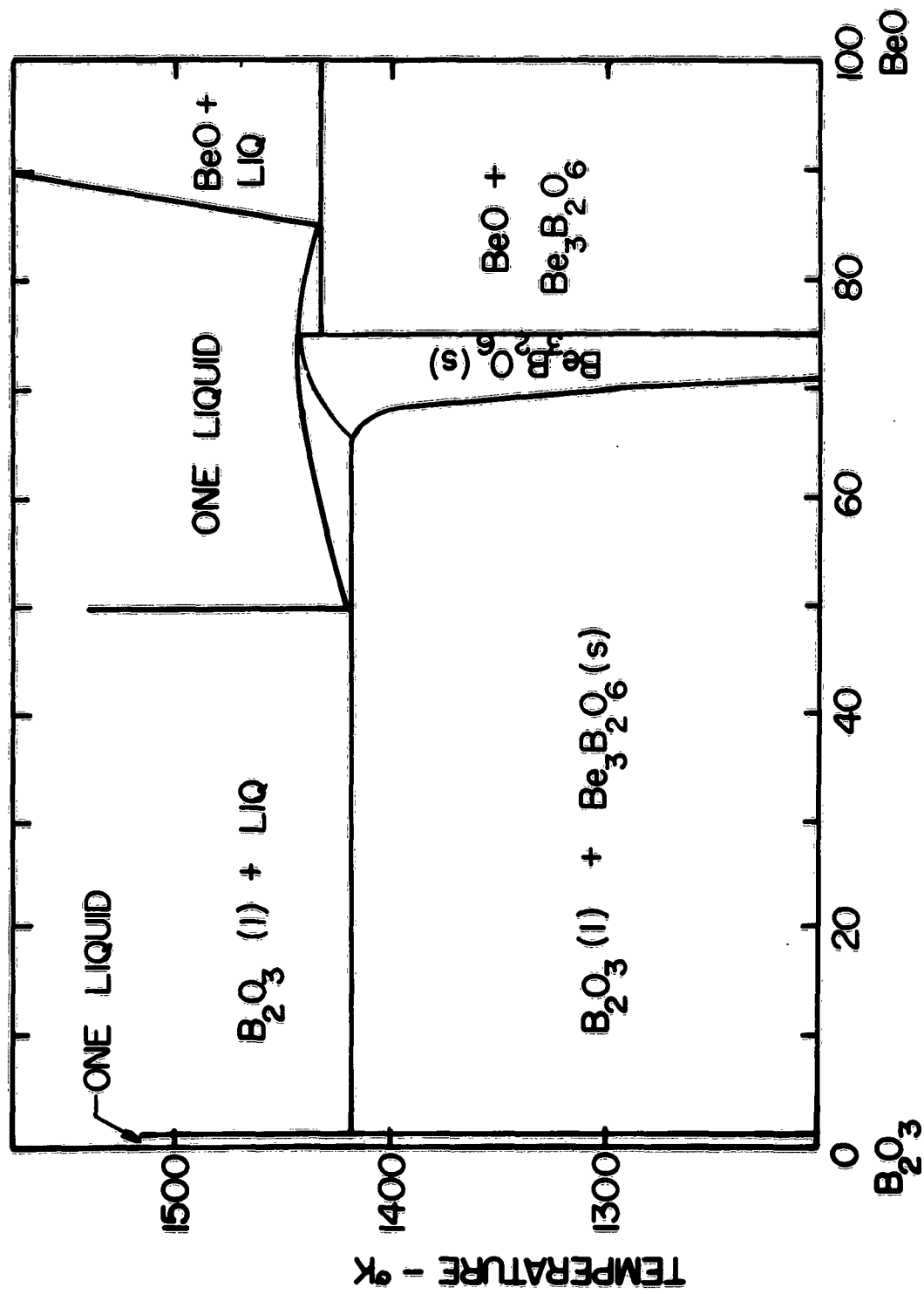


FIGURE 5 HYPOTHETICAL PHASE DIAGRAM FOR Be-B-O SYSTEM

A SURVEY OF CERTAIN THERMODYNAMIC DATA ON
SOME LIGHT-ELEMENT MIXED-METAL AND MIXED-NONMETAL COMPOUNDS

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This is an informal report devoted mainly to the present status of measurements at the National Bureau of Standards and elsewhere on (a) the condensed-phase heat capacities (and heats of fusion and transition) of light-element mixed-metal compounds and (b) solid-vapor equilibria of AlF_3 -containing systems and the thermodynamic properties of mixed halides of aluminum.

STATUS OF HEAT-CAPACITY MEASUREMENTS

Tables I-IV present a brief qualitative summary of the status of completion of condensed-phase heat-capacity data on most of the known fluorides, chlorides, oxides, nitrides, carbides, borides, and borates of beryllium, aluminum, lithium, and of combinations of two of these three metals. The tabulation is divided roughly into three temperature ranges — for 0° - $298^\circ K$ applying to adiabatic calorimetry, which, at NBS, is carried out by G. T. Furukawa and his coworkers, and usually from 14° to about $400^\circ K$. The NBS measurements at higher temperatures are by drop calorimetry, and so far have in general been limited to the temperature range from 273° to about $1200^\circ K$. For each temperature range the status of completion of measurements is given both at NBS and at other institutions, though in the latter category the information recorded may not be complete. A star (*) indicates the existence of completed data which are considered to be of satisfactory accuracy and temperature-range coverage for most purposes. A dash (-) indicates that no such measurements are planned, or that the compound is chemically unstable or possesses a very high vapor pressure in the given temperature range. (Question marks (?) follow two formulas representing samples procured by NBS but for which the existence of a compound between the stated components has not yet been proved or disproved.)

TABLE I. STATUS: HEAT-CAPACITY DATA ON Be COMPOUNDS

Compound	0° - $298^\circ K$		298° - $1200^\circ K$		$> 1200^\circ K$
	(NBS)	(Elsewhere)	(NBS)	(Elsewhere)	
$BeF_2(c)$	Planned	*?	Planned	*?	
$BeF_2(amorph)$	Planned?		Planned?		
$BeCl_2$	-	*?		*?	-
BeO	*?		*		Data exist.
Be_3N_2	*		*		
Be_2C	Planned?		Planned		
Be_2B	Planned?		Planned??		
$BeO \cdot B_2O_3(?)$	Planned?		Planned?		

TABLE II. STATUS: HEAT-CAPACITY DATA ON Al COMPOUNDS

Compound	0°-298°K		298°-1200°K		> 1200°K
	(NBS)	(Elsewhere)	(NBS)	(Elsewhere)	
AlF ₃		*		*	
AlCl ₃		*?		*?	-
Al ₂ O ₃	*		*		Data to M.P.
AlN		*		*	
Al ₄ C ₃	*		*		

TABLE III. STATUS: HEAT-CAPACITY DATA ON Li COMPOUNDS

Compound	0°-298°K		298°-1200°K		> 1200°K
	(NBS)	(Elsewhere)	(NBS)	(Elsewhere)	
LiF		*	*		Some data.
LiCl		*	*		
Li ₂ O		*		*	
LiOH		*		*	-
Li ₃ N	Planned?		Planned?		-
Li ₂ C ₂					-
LiH	*				-
LiBO ₂	Planned?		Planned?		

TABLE IV. STATUS: HEAT-CAPACITY DATA ON COMPOUNDS
CONTAINING TWO OF THE METALS Be, Al, AND Li

Compound	0°-298°K		298°-1200°K		> 1200°K
	(NBS)	(Elsewhere)	(NBS)	(Elsewhere)	
Li ₂ BeF ₄	Planned		*		
Li ₃ AlF ₆	Planned		(*)		
BeAl ₂ O ₄	*		*		
BeAl ₆ O ₁₀	Planned		Planned		
LiAlH ₄	*		-	-	-
Li ₂ O·BeO(?)	Planned?		Planned?		
LiAlO ₂		*		*	

As can be seen from Tables I-IV, the data are fairly complete (or measurements have been tentatively planned, with some reservations caused by relative priority) on nearly all the compounds listed, up to approximately 1000° to 1200 °K. In contrast, data above about 1200 °K are in general lacking, although the National Bureau of Standards (and probably other institutions too) have the apparatus and plans for filling some of these data gaps as time and priorities permit. In general, the best samples available of the nitrides, carbides, and borides of these metals leave much to be desired in terms of absence of impurities and conformity to stoichiometry — and even exact knowledge as to what phases are present since X-ray techniques of phase identification and estimation are unfortunately of low sensitivity. In many such cases, more phase-diagram studies, as well as the development of more accurate techniques of analysis, would clearly contribute to obtaining better defined samples or to correcting and interpreting such precise measurements as those of heat capacity.

In a complex system composed of several of these chemical elements, it is of course naive to suppose that every condensed phase is a pure two-element compound. This is particularly true at such high temperatures that the two-element (binary) components would melt and then in most cases would mix in wide or all proportions. However, in the absence of more specific data, the enthalpy or heat capacity of the complex system must often be assumed to be the sum of those of the two-element components, a simplification which is usually not far from correct so long as the correct physical state is assumed so that an error equivalent to a heat of fusion or transition is not made.

The measurement of the heat capacities of known three-element compounds such as those in Table IV affords a refinement over the above simple treatment, and at the same time gives definite information in specific cases as to how much error is made by ignoring the interaction of the two binary components. As an example, the heat capacities of BeO, Al₂O₃, and BeAl₂O₄ have all been measured accurately at NBS up to 1200 °K; at each temperature (at least above 298 °K) the heat capacity of BeAl₂O₄ was found to be additive within less than one percent. Similar measurements have been made on Li₂BeF₄, but in this case the heat capacity may prove to be not nearly so additive (i.e., when compared with the sum for 2LiF + BeF₂), owing to complex-ion formation which exists in neither binary fluoride. Another complication in the case of Li₂BeF₄ is, of course, the fact that between approximately 720 and 1120 °K Li₂BeF₄ is liquid but pure LiF is crystalline.

NBS TRANSPIRATION STUDIES ON AlF₃

A high-temperature transpiration apparatus was built, with a nickel core of about 1 cm wall thickness (to help minimize the temperature gradients). The apparent vapor pressures of AlF₃ were measured from 1233° to 1288 °K, and the results are plotted in Fig. 1. The line shown is the best "Third-Law" line, and is obviously also approximately the best "Second-Law" line, so that from these data the heats of vaporization as calculated by both methods are in excellent agreement. The saturated vapor is known from other work (see below) to contain an average of about 10 mole % of the dimer Al₂F₆ at these temperatures, but the 55-deg

temperature interval is too small for this fact to be reflected in Fig. 1.

Porter and Zeller [1] examined the vapor of aluminum fluoride mass-spectrometrically between 965° and 1065 °K, and they combined their ratios of monomer to dimer with the precise vapor pressures reported by Witt and Barrow [2] in the same temperature range to obtain the equilibrium constants K_p for the reaction



shown as points in Fig. 2. The "Least-Square" line through their points has too uncertain a slope to give a reliable Second-Law heat of the reaction, so they ignored it and instead estimated for the above reaction $\Delta S_{1000}^\circ = 32 \pm 3$ e.u., whence using their data they obtained $\Delta H_{1000}^\circ = 48 \pm 4$ kcal. In an attempt to set reasonable upper and lower limits to the abundance of dimer in the saturated vapor indicated by their results, we have drawn two additional lines in Fig. 2 as the highest and lowest which pass through any of their points and at the same time satisfy their assumption about ΔS_{1000}° .

We calculated the mean values of ΔH_0° for the reaction

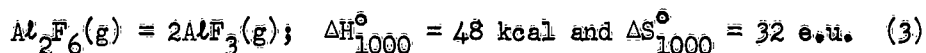


as given by the results of several different investigators, and these are plotted against mean observed temperature in Fig. 3. The value at each temperature (except 1000 °K) was calculated on three alternative assumptions: no dimer, and the limits of dimer corresponding to the two limiting lines in Fig. 2. The result for 1000 °K is from the effusion work of Witt and Barrow [2]. (The mean from Evseev et al [3] coincides exactly, but the precision was about ten times as poor.) The points at 1050 °K represent the mean of earlier torsion-effusion results of Hildenbrand and Theard [4]. The points at 1250 °K represent the NBS transpiration results referred to above. The points at 1425° and 1500 °K represent respectively the lower and upper temperature ranges of the direct pressure measurements of Ruff and LeBoucher [5].

The results on AlF_3 so far given here were described by Krause et al [6]. Figure 3 should include also a representation of 55 later measurements of Aeronutronic at a mean temperature of about 1050 °K [7] (which in Fig. 3 would give a mean point at $\Delta_s H_0^\circ(\text{m}) = 70.0$ kcal/mole on the assumption of no dimerization), and the 9 direct pressure measurements of Olbrich from 1371° to 1567 °K [8] (which would give "no dimer" values of $\Delta_s H_0^\circ(\text{m})$ 1-2 kcal/mole higher than those of Ruff and Le Boucher [5] in Fig. 3).

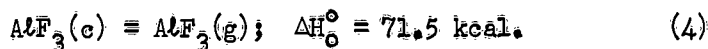
The inclusion and equal weighting of all the aforementioned sets of vapor-pressure data in a graph of the type of Fig. 3 would show such a scattering of points that no conclusion could be drawn as to the ΔH and ΔS of reaction (1) from the vapor-pressure data alone. However, results highly consistent with those derived by Porter and Zeller [1] were calculated [9] from the two most precise sets of vapor-pressure data, those of Witt and Barrow [2] and those of NBS. Using also a mean mass-spectrometric [1] value for ΔG° (the free-energy change) for reaction (1) at a

single temperature, 1000 °K, these calculations gave:



(Porter and Zeller [1] obtained the former value only after assuming the latter value.) These constants were then found to be in quite close agreement with the mean vapor-pressure results (at higher temperatures) of Ruff and Le Boucher [5], but not with those of Olbrich [8].

All the values of Fig. 3 were calculated using earlier NBS free-energy functions for $\text{AlF}_3(\text{c})$ and $\text{AlF}_3(\text{g})$ [10]. The revised JANAF tables for these species are based on more recent experimental data and hence are preferable. Making the corresponding changes raises each value of ΔH_0° for reaction (2) (in Fig. 3) by 0.5 kcal. The calculations described in the preceding paragraph gave, in addition to the results of (3), also the following value (based on the JANAF tables):



Büchler [11] recently obtained the following heats of reaction:



According to the JANAF tables, (5) corresponds to $\Delta H_0^\circ = 70.4 \text{ kcal.}$ Also, (5) and (6) give $\Delta H_{1000} = 48.8 \text{ kcal}$ for reaction (1), which is in very good agreement with the value 48 kcal cited above.

It is evident from (5) and (6) that the proportion of the dimer in saturated aluminum-fluoride vapor increases with temperature, and at rather high temperatures (say, above 1000 °K) the dimer is an important species. A table of thermodynamic functions of $\text{Al}_2\text{F}_6(\text{g})$ at high temperatures, to be considered provisional pending further experimental work, can be constructed whose use would lead to reproducing the mass spectrometric data (1) and several of the most precise sets of vapor-pressure data on aluminum fluoride. Such a table for $\text{Al}_2\text{F}_6(\text{g})$ would be completely determined by assuming the constants given in (3), the equipartitional C_p of $\text{Al}_2\text{F}_6(\text{g})$ ($43.7 \text{ cal mole}^{-1} \text{ deg K}^{-1}$), and the thermodynamic functions of $\text{AlF}_3(\text{g})$ [7].

NBS TRANSPIRATION STUDIES ON AlF_3 SYSTEMS

The NBS transpiration apparatus has recently been modified to permit the study of high-temperature reactions involving aluminum fluoride. The systems investigated or so far planned for study are:

- (a) $\text{AlF}_3\text{-Al}_2\text{O}_3$
- (b) $\text{AlF}_3\text{-HF}$
- (c) $\text{AlF}_3\text{-AlCl}_3$

In view of the recent work of Farber and Petersen [12] on AlOF(g) above 2200 °K, work on the system $\text{AlF}_3\text{-Al}_2\text{O}_3$ below 1700 °K did not promise to yield positive results. In fact, a single measurement on a mixture of AlF_3 and Al_2O_3 at 1250 °K was made, and showed no detectable interaction between the two components. Although the existence of equilibrium was not proved, the negative result is entirely consistent with the work cited above [12], which, however, would not preclude the possibility of the formation of associated forms of AlOF(g) in appreciable amounts at lower temperatures. NBS transpiration work in a search for possible species formed from AlF_3 and HF is planned for future investigation.

In the NBS work on the $\text{AlF}_3\text{-AlCl}_3$ gas system, AlCl_3 is evaporated at a constant low temperature (e.g., 373 °K) and passed over $\text{AlF}_3\text{(c)}$ at a constant high temperature (e.g., 1250 °K). In the two such experiments so far performed (using the above temperatures), the presence of the $\text{AlCl}_3\text{(g)}$ increased the amount of AlF_3 evaporating by a factor of almost 2, owing, it is believed, to the formation of considerable amounts of the species $\text{AlF}_2\text{Cl(g)}$ and/or $\text{AlFCl}_2\text{(g)}$. From such quantitative experiments at different temperatures and pressures it will be possible, at least in principle, to evaluate the heat and free energy of formation of each of these two mixed-halide species. In a more empirical sense, such data will indicate the amounts and total heats of the partial condensation occurring with given $\text{AlF}_3\text{-AlCl}_3$ gas mixtures at given temperatures.

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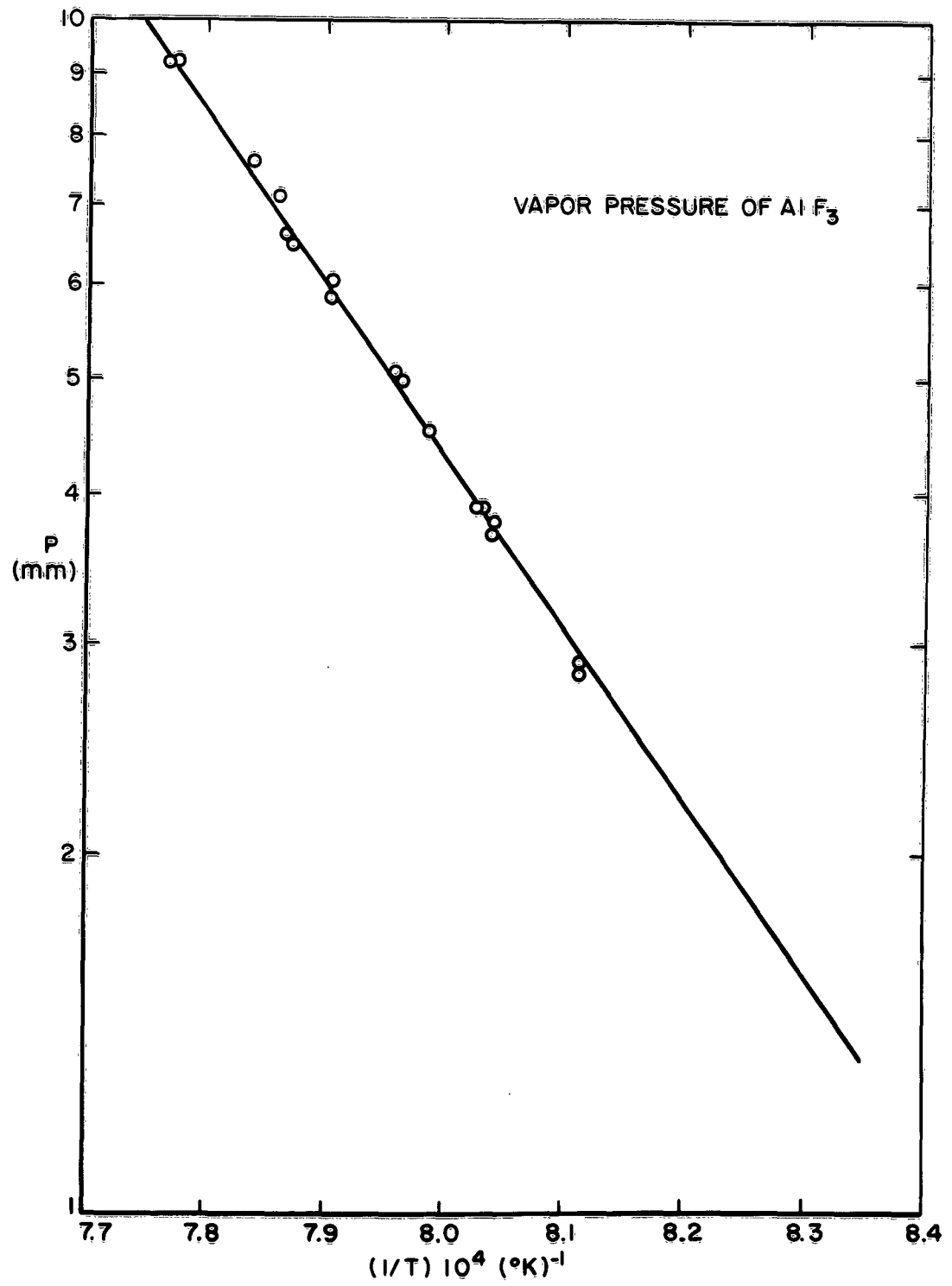


FIGURE 1. TRANSPIRATION DATA ON AlF_3 (NBS)

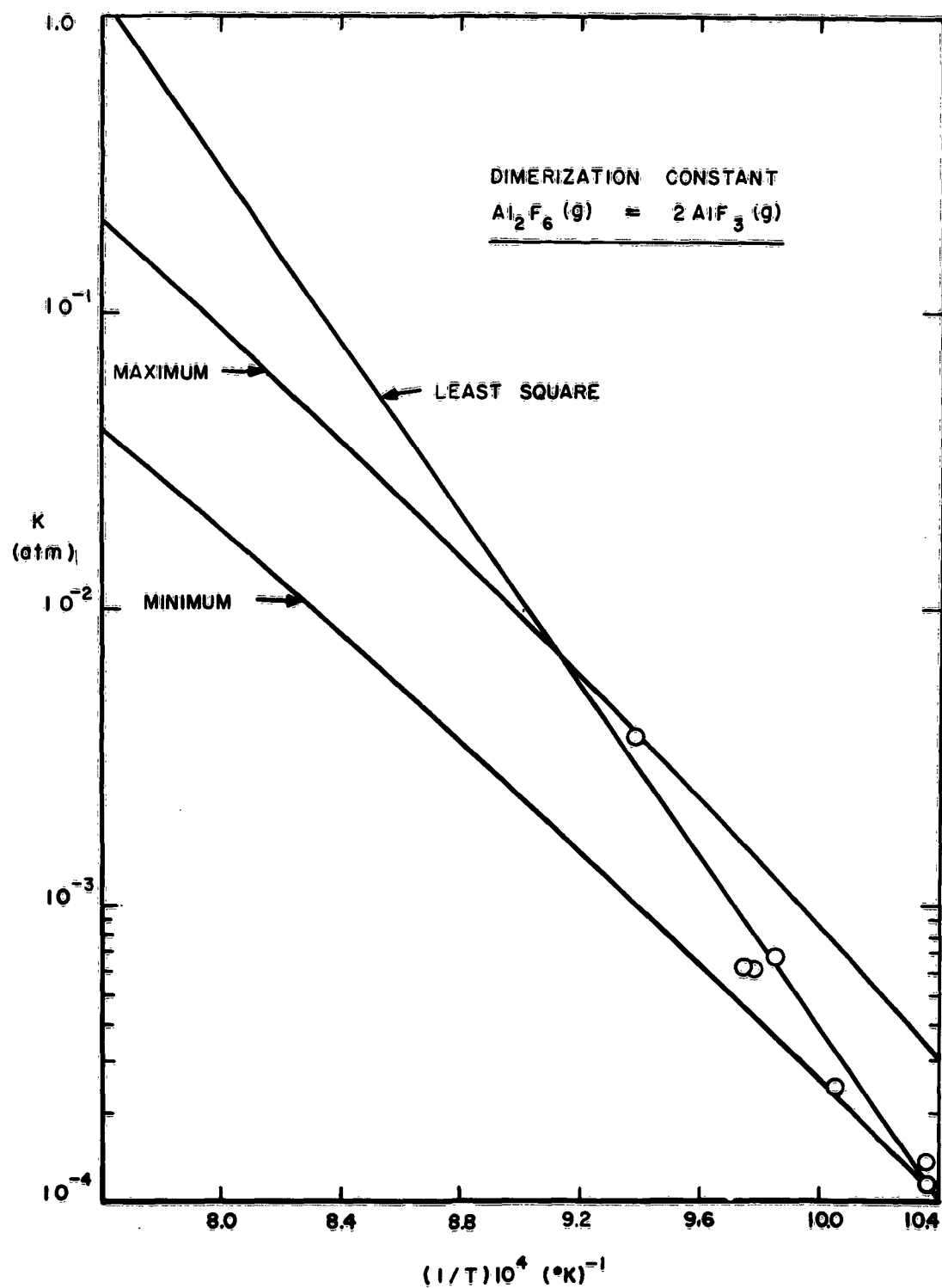


FIGURE 2. DIMERIZATION OF $\text{AlF}_3(\text{g})$ (PORTER & ZELLER)

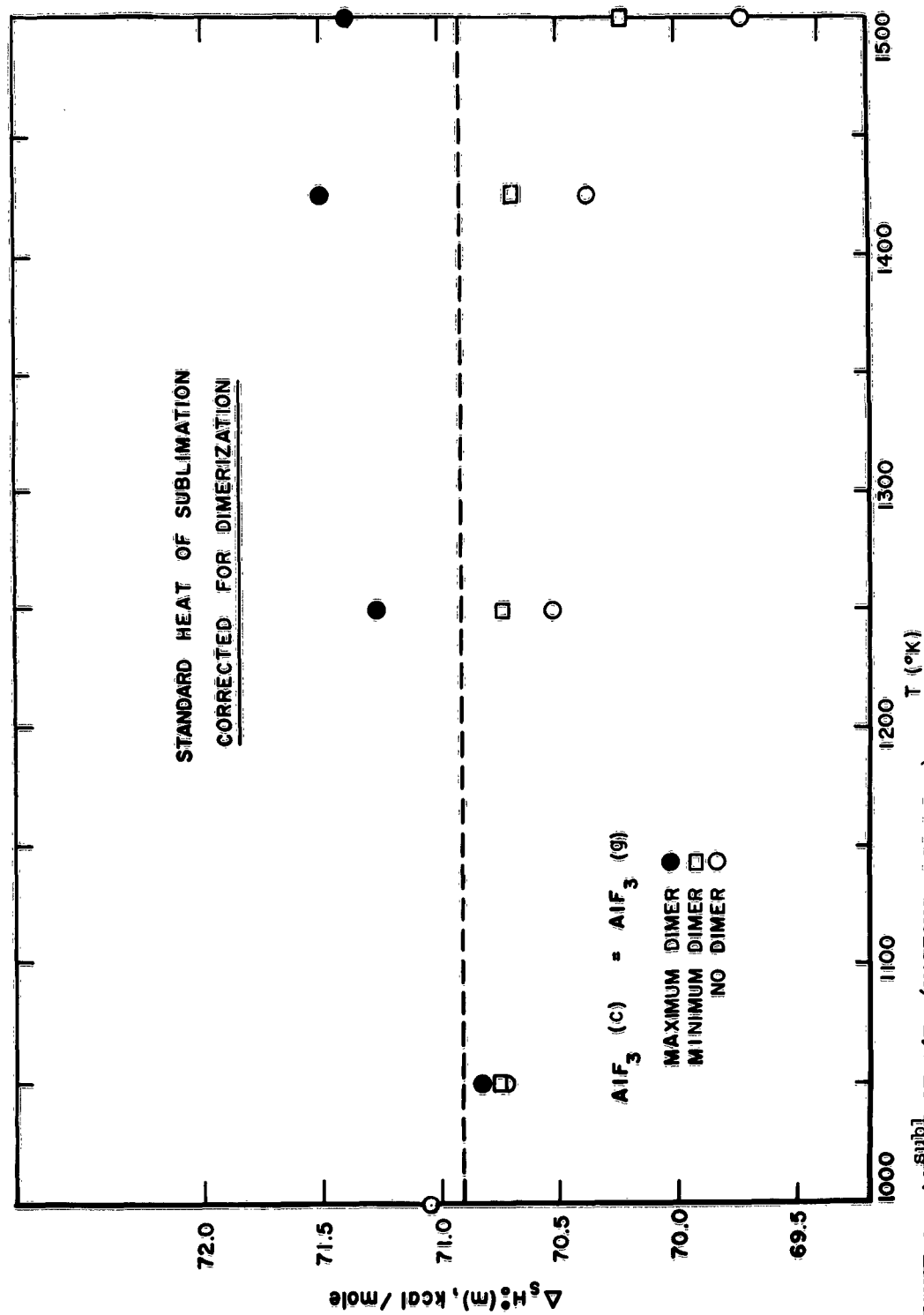


FIGURE 3. ΔH^{subl} OF AlF_3 (VARIOUS OBSERVERS)

THE THERMODYNAMIC PROPERTIES OF SOME OXYHALIDES OF THE LIGHT ELEMENTS

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Research and Development Laboratories · RPI

INTRODUCTION

Under a three year program with the Advanced Research Projects Agency, experimental investigations were carried out to determine the thermodynamic properties of the oxyfluorides and oxychlorides of boron and aluminum. As a result of this program a considerable amount of experimental data have been made available for aid in the computation of propellant performance. These data have been incorporated in the revised JANAF Tables.

Since the standard low pressure technique including mass-spectrometry were not directly applicable for the determination of the heat of formation of the monomer BOF a new experimental procedure, molecular flow effusion, was developed. This procedure allows transpiration type reactions to be carried out at very low pressures and very high temperatures. The determination of equilibrium constants was effected at temperatures in excess of 2400°K using specially designed furnaces and reaction cells. The study of a chemical reaction involving molten aluminum oxide in a non-reacting container was also accomplished. The use of rhenium as a totally unreactive container material for solid and liquid metal oxides at very high temperatures was extended to include its use in the presence of gaseous halides at temperatures above 1800°K with no trace of reaction. A new mathematical method for obtaining thermodynamic values on two species from two simultaneous reactions was developed.

At the completion of this contract the thermodynamic data for the compounds under investigation were completed and have been published or are in process of publication.

RESULTS

(BOF)₃ The reaction



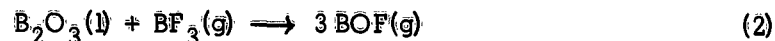
was studied between 330 and 1000°K using the transpiration technique. Effects of flow rate on the equilibrium constant were studied carefully. Analysis of the experimental data yielded values of 7.5 kcal/mole for the ΔH_{298}° and 15.1 cal/deg/mole for ΔS_{298}° . Combination of these values with the pertinent thermodynamic values resulted in the following values for the trimer of boron oxyfluoride gas.

$$\Delta H_f^{298} \text{ (2nd law)} = -567.8 \pm 0.5 \text{ kcal/mole}$$

$$S_{298}^{\circ} = 88.7 \pm 2.0 \text{ cal/deg/mole}$$

A third law analysis of the experimental data, coupled with the thermal data and theoretical entropy from the JANAF Tables, led to a value of -566.1 ± 2.0 kcal/mole for ΔH_f^{298} of $(\text{BOF})_3(\text{g})$. (J. Chem. Phys. 36, 661 [1962]).

BOF The requisite thermodynamic data for the gaseous monomer of boron oxyfluoride was obtained from a study of reaction (2) employing the newly devised molecular flow effusion technique.



This reaction was studied over the temperature range 1054-1253°K and at pressures in the vicinity of 10^{-3} to 10^{-4} mm hg. At 1160°K, the average temperature of reaction, the ΔH_r was found to be 135 ± 19 kcal/mole and the ΔS_r was 71 ± 16 cal/deg/mole. A second law analysis of the experimental data yielded a value of -144 ± 6 kcal/mole for the $\Delta H_f^{298^\circ\text{K}}$ of $\text{BOF}(\text{g})$. This compared very well with the third law value of -142 ± 3 kcal/mole. The $S_{298^\circ\text{K}}^\circ$ was found to be 53 ± 4 cal/deg/mole. (Trans. Faraday Soc. 58, 2090 [1962]).

(BOCl)₃ The reaction of liquid boric oxide with gaseous boron trichloride, equation (3), was studied by transpiration between 536 and 825°K to obtain thermodynamic data for the gaseous trimer of boron oxychloride.



The heat of this reaction at 675°K was found to be 5.0 ± 0.3 kcal/mole. The corresponding entropy of reaction was 3.1 ± 0.5 cal/deg/mole. Combination of these data with the thermodynamic values of B_2O_3 and BCl_3 and conversion to 298°K by means of the thermal functions in the JANAF Tables, leads to the following values for $(\text{BOCl})_3(\text{g})$:

$$\Delta H_f^{298^\circ\text{K}} \text{ (2nd law)} = -396.7 \pm 2.0 \text{ kcal/mole}$$

$$S_{298^\circ\text{K}}^\circ = 92.5 \pm 2.0 \text{ cal/deg/mole}$$

(J. Chem. Phys. 39, 158 [1963]).

BOCl The reaction



was studied between 1234 and 1389°K by means of the molecular flow effusion technique using a platinum effusion apparatus. The $\Delta H_r^{1307^\circ\text{K}}$ for reaction (4) was found to be 55.7 ± 7.0 kcal/mole. At the same temperature a value of 26.0 ± 5.0 cal/deg/mole was determined for ΔS_r . A second law treatment of the experimental data yielded the value of -74.8 ± 7.0 kcal/mole for the $\Delta H_f^{298^\circ\text{K}}$ of $\text{BOCl}(\text{g})$. The corresponding third law value was found to be -75.5 ± 2.0 kcal/mole. The $S_{298^\circ\text{K}}^\circ$ obtained from the experimental data was 57.8 ± 5.0 cal/deg/mole. (Trans. Faraday Soc. 60, in press.)

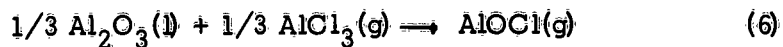
AlOF The reaction



was studied at 2200°K by means of the molecular flow effusion technique, employing a specially designed vacuum resistance furnace. The effusion cell was constructed of Al_2O_3 so no container problems were encountered. At 2200°K the ΔF_r was found to be 80.9 ± 1.9 kcal/mole, based on a large

number of individual measurements. Using the JANAF Tables the third law value of ΔH_{298}° for AlOF(g) was determined to be -139.2 ± 2.4 kcal/mole. (Trans. Faraday Soc. 59, 836 [1963]).

AlOCl An electron bombardment furnace and a specially designed rhenium cell were employed to study the reaction of molten aluminum oxide with gaseous aluminum chloride at 2400°K to yield a value for the heat of formation of gaseous monomeric aluminum oxychloride



The ΔF_{2400}° was found to be 29.9 ± 3.0 kcal/mole which leads to a value for ΔH_{298}° (3rd law) of -82.0 ± 3.0 kcal/mole for AlOCl(g) . (Trans. Faraday Soc. 60, in press.)

A REVIEW OF DATA ON HEAVY METAL REFRACTORY COMPOUNDS

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INTRODUCTION

I wish to thank the Chairman, Tom Dobbins, for the opportunity to speak to this group today. The JANAF work has set an excellent example after which much of our work at AVCO has been patterned. I would also like to acknowledge the assistance of many individuals, many of whom are here today. Before discussing the subject of this talk, it might be well to briefly describe the nature of the "Thermodynamics of Refractories Project" sponsored at Avco-RAD by ASD.* The first year's work covering the period May 1960-April 1961, was summarized in a 1962 ASD report.¹ A continuation of this project was initiated in June 1962 and will be ending shortly with a final report due January 31, 1964. The work accomplished thus far is summarized in five recent quarterly reports.²⁻⁶

SCOPE OF WORK

The thermodynamics work sponsored at AVCO has consisted of experimental and analytical work. The latter phase has been emphasized, however, with the ultimate objective being the production of quality thermodynamic tables for a selected list of refractory compounds for the range 0° to 6000°K.

All table preparation interest has been centered on the borides, carbides, nitrides, and oxides of several metallic elements. At the beginning of the first year's work nineteen metallic elements were included: Beryllium, calcium, chromium, hafnium, magnesium, manganese, molybdenum, niobium, osmium, rhenium, scandium, silicon, strontium, tantalum, technetium, titanium, tungsten, vanadium, and zirconium. Subsequently, iridium, platinum and rhodium were added giving a total of 22 metals and 4 non-metals. During the second year's work, additional metallic elements were added to this list giving 31 metals and 4 non-metals. The new additions were lanthanum, yttrium, and certain rare earths including cerium, dysprosium, gadolinium, neodymium, samarium, and thorium and uranium.

Figure 1 shows the elements currently being studied. Our effort has a small amount of overlap with the JANAF effort. In figure 2 are listed the elements being studied by the two groups. Ten of the elements being studied are common to both groups.

*All of the present work was sponsored by the Aeronautical Systems Division (Now RTD). Mr. P. Dimiduk is project engineer.

LITERATURE SEARCH

Because of the wide scope of elements and compounds being studied, it has been necessary to conduct a fairly comprehensive literature search.

Various abstracting journals are reviewed for thermodynamic and related data on the compounds and elements of interest. The bibliography of the previous contract as shown in Vol. II of the 1962 ASD report¹ and a similar bibliography for the present study are intended to cover the literature from 1949 to the present for all compounds of the 31 elements of interest.

It is felt that earlier compilations such as the NBS Circular 500 and other reviews etc., provide guides to older literature. It is recognized that the current bibliography has shortcomings and although attempts have been made to make it complete, there are obviously missing links. However, it is felt that use of the present bibliography will provide leads to most current work in the field.

In conducting the literature search, the procedure has been followed of using ASM punched cards to write out such information as authors, title of article, and reference. A sample card is shown in figure 3. A code number on this card is used for reference purposes. The information on the ASM cards is then key-punched onto IBM cards along with the reference numbers. These IBM cards are then stored alphabetically in a card file and on magnetic tapes so that copies of the existing bibliography can be run off when desired. An example of the form of the bibliography is shown in figure 4. A copy of the existing bibliography is available for inspection. It contains approximately 3000 references.

In conjunction with the bibliography, a property file has been issued. This property file is illustrated in figure 5. The second column gives the formula for the compound or element being studied. The third column gives the name of the author or authors followed by the year of the publication and a code number. This latter information makes it possible to locate a given reference in the bibliography which is arranged alphabetically. The left column of the property file contains a code to designate the type of information. Definitions of the various codes are shown in figure 6.

By using the property file in conjunction with the bibliography, access can be obtained to information on any of the borides, carbides, nitrides or oxides of the 31 elements of current interest to the project. At the present time, one makes the conversion from property file to bibliography file manually. However, some thought has been given to using a data retrieval system on magnetic tape to print out bibliographies pertinent to a particular compound or group of compounds if desired. An example of how a possible bibliography might look is shown in figure 7.

TABLE PREPARATION

Thermodynamic tables are prepared under the direction of a senior scientist. Usually one scientist is responsible for a particular group or groups of related compounds on the periodic chart. Throughout the project the level of effort has been about two senior men devoted to table preparation.

During the first year's work on this contract about 61 tables were prepared. During the present contract about 120 more tables have been completed. In general, these tables covered the temperature range from 0° to 6000°K, with a format similar to that of the JANAF tables. There are certain differences between the RAD tables and JANAF tables:

- a. RAD tables are prepared so that double entries are provided at any temperature for which a discontinuity exists in the thermal functions.
- b. In the cases of condensed phases, RAD prepares a single table of solid and melted phases corresponding to regions of thermal stability, whereas JANAF prepares two tables, both of which are extrapolated into regions of instability.
- c. For RAD tables uncertainty estimates are often prepared to give the table users an estimate of accuracy to be attached to the data.
- d. Comprehensive writeups are provided in RAD reports to illustrate data available and how choices were made.

A summary of the work which has been performed thus far is shown in figure 8. It is seen that considerable work remains to be done.

Several months ago, it was decided to concentrate the table effort on the compounds of beryllium, hafnium, niobium, molybdenum, silicon, tantalum, thorium, titanium, tungsten and zirconium. Hence, an effort has been made to complete tables on the borides, carbides, nitrides, and oxides of these ten elements before proceeding on the task of completing the rest of the table (figure 8).

POSSIBLE METHODS TO OBTAIN THERMODYNAMIC DATA

I will limit my comments primarily to the Groups IV and V transition metal compounds. In particular, the elements titanium, zirconium, hafnium, niobium, and tantalum will be considered. A small amount of data for vanadium is also included. These metals in the pure state are generally less refractory than the neighboring Group VI elements such as molybdenum and tungsten, but upon compound formation the most refractory properties occur in the Groups IV and V.

To obtain thermodynamic data there are two possible alternatives. One might use a purely theoretical approach to evaluate the cohesive or bonding energy and other desired properties of a compound. With this theoretical approach based on first-principles one conceivably would need only a limited amount of experimentally measured values for the basic physical constants. The rest of the work would be done on paper by the theoretician or by the electronic computer. As an alternative to this approach, one can use the wide variety of experimental observations reported in the literature as a basis for obtaining the proper thermodynamic values. First, it may be of interest to consider the theoretical approach.

At the present time there is no existing quantitative theory to describe the bonding in the elements and compounds of interest. This statement may need some qualification, since in principle quantum mechanics should be able to provide us the ground work to develop a quantitative understanding of the bonding. With this hope to lead us on, we can write down the Schrödinger equation

$$H\psi = E\psi$$

Here the Hamiltonian operator must be defined. If we consider the case of a condensed phase, in this case a pure metal*, we can follow the treatment used by Raimes.⁷ First, it is assumed that the temperature is zero so that nuclear vibrations (including zero-point vibrations) can be neglected. The metal is considered to consist of N atoms each with Z electrons. Hence, there are a total of ZN electrons, each having a charge -e. Also there are N nuclei, each having a charge Ze. Using as the zero of energy the system with widely separated electrons and nuclei at rest, one then obtains the Hamiltonian operator. This can be seen in figure 9.

In the expression for the Hamiltonian operator, r_i is the position vector of the i^{th} electron, R_a is the position vector of nucleus, a , and m is the electron mass.

Having the form of the Hamiltonian operator, one would next proceed to solve the Schrödinger equation. In principle one might first assume random positions of the nuclei and show that the minimum ground state energy, i. e., the lowest eigenvalue occurs when the stable lattice arrangement is achieved.

Before becoming too hopeful about this fundamental approach, the difficulties should be pointed out. The condensed phase may contain the order of 10^{23} atom/cm³, and thus $N \approx 10^{23}$. It becomes clear that we are dealing with a very large number of terms in the exact Hamiltonian. This complexity prevents the attainment of a precise solution.

*

A similar treatment is required for compounds.

At a Summer Session course sponsored by the Laboratory for Insulation Research, M. I. T., J. C. Slater⁸ has delineated the areas in which theory can give precise results and where it encounters difficulties. Slater states: "The problem which is hardest for the theorists is unfortunately the one of most direct interest for the experimenter; how are the atoms arranged in a given type of matter? We know in principle exactly how to solve this problem. We work out the energy of the system, as a function of the positions of the atoms (or free energy, if we are not working at the absolute zero of temperature). Of two structures, that of the lowest energy will exist. And as the pressure or temperature are changed, modifying the free energy of the various forms of the substances, the free energies of two phases may cross, leading to a polymorphic transition. All of this depends on a calculation of free energy, accurate enough to decide which of two free energies is lower. The differences we are concerned with are measured on a chemical scale-kilogram-calories per mole. But the total energies are the energies required to strip all the electrons off the atoms, which in moderately heavy atoms may come to many thousands of Rydberg units -- and a Rydberg unit is 13.6 e. v., and an electron volt is about 23 Kcal/mole. We are often dealing with energy differences of the order of magnitude of a millionth of the total energy."

To further illustrate the difficulties in theoretically predicting structures and the associated energies, one may note that Professor F. A. Cotton⁹ of M. I. T. has quoted Professor A. R. vonHippel who refers to the prediction of molecular structures as a branch of the "gambling profession." Cotton also notes that valence theory may need to be improved fifty-fold to afford reliable predictions. He also cites work by Sugano and Shulman¹⁰ which indicates "that the electrostatic crystal field theory is apparently not even a half-truth."

In a recent book Brewer¹¹ states: "Although in principle all the properties of metals should be deducible from the solution of the Schrödinger equation, in practice there is no hope in the foreseeable future that one will be able to deduce properties of a wide variety of metallic systems from first principles alone."

Nowotny¹² comments: "As we are far from the final goal in predicting the nature of a binary, ternary, or multicomponent system and hence in predicting crystal structure, free energy, and other essential properties of the occurring phases on the basis of mathematical methods, we still have to apply the fruitful language of chemistry or simplified quantum chemistry as well as a great many of well-established but empirical regularities."

Brooks¹³ has recently reviewed our knowledge of the binding in metals. After noting that much progress has been made in understanding the electronic properties he makes the following comments:

"However, relatively more attention has been devoted to the Fermi

surface than to the overall energy-level structure and the cohesive properties. There are several reasons for this. In the first place, the cohesive properties depend more fundamentally on electronic interactions, and hence on the many-particle aspects of electronic structure, which are much less well understood and more difficult to calculate than the one-electron aspects. In the second place, there are only a few specific properties to be computed theoretically and compared with experiment, and the discrepancies between theory and experiment are not of such a nature as to suggest ways of improving the theory."

Ackermann and Thorn¹⁴ recently reviewed bonding mechanisms in simple gases and in solids. In their discussion of the bonding in diatomic gases they state: "Although the various attempts to derive bond energies have not yielded sufficiently accurate results to be of thermochemical value, the experimental determinations on the other hand have not been sufficiently extensive to enable the theorist to simplify the wave mechanical formulation by suggesting all of the pertinent factors which are involved. And there have been few persons interested in and familiar with both aspects so as to effect a synthesis of the results of both. Recently, however, both the theoretical calculations and the experimental determinations have produced sufficient information that at least interpolation and extrapolations should be of use to thermochemistry and technology."

An example of the application of theory to diatomic molecules is provided by the work of Clementi¹⁵ who calculated the dissociation energy of LiF. Clementi believes that with experience it may be possible to compute bond energies with less than 1% error. It may also be noted that the problems become more difficult for the higher atomic weight species which are the ones of interest here, but at least for the diatomic gases it appears that progress is being achieved.

Although the theoretical methods starting from first principles are not directly applicable at the present time for our problems of determining such thermodynamic properties as the heats of sublimation, heats of formation, etc., it may be briefly mentioned that there are several semiempirical theories which explain some of the phenomena observed. For example, Dempsey¹⁶ suggests that upon formation of the refractory hard metals, the p electrons from non-metals such as B, C, N are taken into the transition metal d-band. That is, the non-metals act as electron donors. The maximum refractoriness occurs when the d-band population is increased to 5.5 to 6.5 electrons per metal-atom. The d-band is considered to have a substructure. Filling of one of these bands up to a maximum of about six electrons tends to increase stability, the filling of the other sub-band tends to reduce the stability.

Other theories and reviews of bonding in the refractory hard metals have been given by Schwarzkopf and Kieffer¹⁷, Robin¹⁸, Kiessling¹⁹, Johnson and Daane²⁰, Pauling²¹, Flodmark²², Mott²³, and Maradudin.²⁴

This review of the available theories of chemical bonding has not been intended to be comprehensive, but merely intends to show the state of the art. If further illustrates that in order to obtain the thermochemical data of interest, we must rely heavily on experimental work. Perhaps as time progresses, we shall achieve the capability of inserting a few values of physical constants on IBM cards and set an electronic computer to work to evaluate the thermodynamic data. But at the present time, it is necessary to depend on experimental observations, and our project has attempted to carefully evaluate such work.

Although the computer is not yet able to achieve all that we ask it, yet it has been of tremendous assistance in our current project. Various programs have been developed to compute different types of tables or to reduce raw experimental data to useable form. Some of these programs may be identified as (a) monatomic gas program, (b) diatomic gas program, (c) polyatomic gas program, (d) condensed phase program using an equation for heat capacity, (e) condensed phase program using tabular heat capacity data as input, (f) smoothing program, (g) least square fit program, (h) Shomate treatment of enthalpy data program, (i) equilibrium programs using magnetic tape to store data and which can evaluate equilibrium in systems containing up to 200 species, and (j) others for specialized uses.

Most of the computer programs mentioned which are used to calculate tables can evaluate a complete thermodynamic table in less than a minute. Someone might then ask why haven't literally millions of tables been generated? The answer is that the process of collecting, reading, analyzing and evaluating documents is time-consuming. Because of the wide variety of experimental data, the original documents must be read and analyzed carefully.

In the present project, considerable emphasis has been placed on maintaining consistency. It is felt that only in this way can the proper interrelationships be preserved. Thus, the old chemical scale of atomic weights in use prior to 1961 has been maintained throughout this compilation. This procedure was followed because the chemical atomic weight scale was being used when this work was initiated in 1960. Many other cases of the effort to preserve consistency could be cited but time limitations dictate otherwise.

THERMOCHEMICAL RESULTS

Turning now to some of the thermochemical data generated on this project, I would like to point out that properties of the elements were investigated first so as to provide a framework for later work.

In figure 10 are shown some values of the heats of sublimation (or dissociation) for some elements of most immediate interest. For the non-metals, I believe that the values listed are probably fairly accurate with the

possible exception of boron. In the case of boron there still exists a discrepancy between the data obtained by mass spectrometric work and that by other methods.

The mass spectrometric data tends to give heats of sublimation of about 129 Kcal/g atom whereas the conventional Knudsen effusion methods, Langmuir methods, and torsion effusion give higher values in the range 135 to 139 Kcal/g atom. The list of thermodynamicists who have worked on this problem is imposing. Those who have used non-mass spectrometric methods include: Searcy and Myers²⁵, Robson²⁶, Alcock and Grieve²⁷, Paule and Margrave²⁸, Hildenbrand et al²⁹, and Priselkov et al.³⁰ This group (excluding Priselkov et al who found an anomalously low value of ~ 101 Kcal/g atom) have used the conventional methods to get the higher values of 135 to 139 Kcal/g atom. On the other hand, the lower mass spectrometric values are represented by the works of Chupka³¹, Schissel and Williams³², Akishin et al³³, Verhaegen and Drowart³⁴, and Goldstein and Trulson.³⁵ In view of the discrepancies, we have adopted a middle-of-the-road approach, choosing a heat of sublimation of 133 Kcal/g atom. Ultimately, it may require a unified, one-laboratory, study using both methods to resolve the existing discrepancies in the boron vapor pressure data.

General agreement has been reached in recent years on the data for carbon, nitrogen, and oxygen. A possible shadow was cast on the N_2 data by Glockler³⁶ who advanced some reasons for a higher heat of dissociation than the presently accepted value of $D(N_2) = 9.765$ e. v. Glockler considered values of $D(N_2) = 11.8$ e. v., 12.14 e. v., and also 11.4 e. v. His observations were based primarily on plots of internuclear distances and force constants for a series of carbon, nitrogen, oxygen, and fluorine hydrides. As an alternative to changing the heat of dissociation value of N_2 , Glockler suggests that further theory may be required to explain his observations.

The vaporization data for all the six metals tabulated is believed to be accurate to ± 5 Kcal/g atom or less. Recent years have seen additional investigations for all these metals. The general agreement in these investigations gives a better basis for judging the uncertainties. There have been at least three investigations for titanium, three for zirconium, four for hafnium, two for vanadium, three for niobium, and five for tantalum. New work not already analyzed in our reports^{1, 4} includes work by Bedford³⁷, and Trulson and Goldstein³⁸ who found $\Delta H_{298.15} = 148.0$ and 149.5 Kcal/mole, respectively for hafnium. Blackburn³⁹ has reported a value of $\Delta H_0 = 174.8$ Kcal/mole for niobium. Work on the vaporization of vanadium has been performed by Saxer.⁴⁰

Next we consider the heats of formation of the oxides. Since this data is required to evaluate heats of formation of many of the other refractories, this logically should be considered before the others. In figure 11 are shown data for the condensed phase oxides. Values for V_2O_5 are not shown

on the figure, but Mah and Kelley⁴¹ have obtained a heat of formation of -370.640 Kcal/mole in 1961. The data for the oxides shown have been reported in our fourth and fifth quarterly reports with the exception of the lower titanium oxides. Most of the oxide heat of formation data has been confirmed by at least two investigations with the exception of the data for ZrO_2 and HfO_2 . As Huber and Holley⁴² have noted, these data may require further confirmation. The entropy value for NbO was estimated. That for TiO was based on experimental low temperature heat capacity data, but a contribution of 1.68 e. u. was added to account for the defect structure (random Ti and O vacancies) as reported by Hoch et al.⁴³ The effect of the increased entropy makes TiO have a more negative free energy. Thus, JANAF⁴⁴ lists $\Delta F_{2000} = -80.095$ Kcal/mole as compared with -83.568 in these tables. The free energy values for the other titanium oxides agree well with JANAF. Most of the other low temperature data has been summarized by Kelley and King⁴⁵ and in the quarterly reports of this project. Similarly, Kelley⁴⁶ has provided much of the required high temperature heat capacity data, but additional references to more recent work are discussed in our reports.

In figure 12 we consider some data for the gaseous monoxides. Available spectroscopic data were used to calculate the thermodynamic functions. Herzberg's⁴⁷ book and Rosen's⁴⁸ tabulation from the early 1950's have been very useful in this connection. Additional references to newer spectroscopic data are cited in the appropriate reports and such data was utilized whenever available. It should be noted here that the thermodynamic functions, heat capacity, entropy, free energy function, and heat content may be subject to appreciable error because of the fact that there may be low-lying electronic states for these transition metal oxides which have not yet been observed. Heats of formation for these monoxides have been derived from high temperature equilibrium vapor pressure data.

In figure 13 are shown some thermodynamic data for the gaseous dioxides. Thermodynamic functions for these polyatomic gases were computed using estimated spectroscopic constants. Details are in our reports, but in general the methods were similar to those of Brewer and Rosenblatt.⁴⁹ Vapor pressure data measured mass spectrometrically were then utilized with the present free energy functions to derive self-consistent heats of formation. It should be noted that the approximations used to estimate the spectroscopic constants, i. e. assumed linear structure, valence-bond approximations for vibrational frequencies, and ionic-model calculation of electronic energy levels could cause appreciable errors in the functions tabulated. However, even if such approximations are not the best, the use of the present free energy functions together with our calculated heats of formation should reproduce the original experimental vapor pressure data.

Having discussed the oxides, it is now appropriate to discuss the other

refractories of interest, that is the borides, carbides, and nitrides. It appears that in the Groups IV and V which we are presently discussing that there are no important gaseous metal carbides, borides, or nitrides. These materials vaporize to yield the elements. Hence, it is only necessary to tabulate data for the condensed phases.

In figure 14 are shown the data for the borides. The heat of formation value for ZrB_2 is considered to be the most accurate. It has been evaluated by oxygen-bomb calorimetry, fluorine bomb calorimetry, and vaporization experiments. Greenberg⁵⁰ has indicated that the latest fluorine combustion calorimetry work suggests a value of about -70 Kcal/mole for the heat of formation. It is believed that the TiB_2 heat of formation value is the next most accurate. For NbB_2 the heat of formation value is based on oxygen bomb calorimetry by Huber.⁵¹ Vaporization studies are being performed by Blackburn.⁵² The data for HfB_2 may need some revision. Trulson and Goldstein³⁸ have recently found a preliminary value $\Delta H_{298.15} = -61.3$ Kcal/mole from mass-spectrometric data. This value is still preliminary but it is likely that the value accepted in our tables may need to be revised. By analogy to the zirconium compounds, I might expect the correct value to be close to -75 Kcal/mole. The value for TaB_2 is merely a rough estimate.

The entropy data for ZrB_2 and NbB_2 shown in the figure is based on experimental results by Westrum and coworkers in conjunction with research programs at A. D. Little and Man Labs. The estimated data for TiB_2 , HfB_2 , and TaB_2 are in good agreement with recent low temperature experimental data. According to Kaufman⁵³, the recent data yields values of $S_{298.15} = 6.81$ e. u. for TiB_2 , 10.26 e. u. for HfB_2 , and 10.636 e. u. for TaB_2 .¹¹

A summary of thermochemical values for the carbides are shown in figure 15. The heats of formation for NbC and TaC are probably the most accurate, with expected uncertainties of perhaps 1 or 2 Kcal/mole. The others may have uncertainties of 3 to 5 Kcal/mole. It may be noted that for TiC which is probably the most studied carbide, that there have been widely varying results. On the one extreme, some vaporization experiments (1961) yielded $\Delta H_{298.15} = -31$ Kcal/gfw whereas some calorimetric data by Russian investigators in 1962 yielded a value of $\Delta H_{298.15} = -55.3$ Kcal/gfw. The heat of formation chosen for HfC was based on vaporization studies, calorimetry, and $Hf-C-O$ equilibria. The results varied from -49 to -62 Kcal/mole and the intermediate value of -55 Kcal/mole was chosen. More recently Trulson and Goldstein³⁸ have found a preliminary value of -50 Kcal/mole. Rudy and Nowotny⁵⁴ studied phase equilibria in the $Hf-Ta-C$ system. Using the present tables, a heat of formation for HfC of -48.5 Kcal/mole is calculated. On the other hand, Kaufman⁵³ prefers a more negative heat of formation value. It is clear that the data is still not precise. Experimental low temperature heat capacity data was available for TiC , ZrC , and TaC . Data for the other carbides was estimated.

In figure 16 are shown some data for the nitrides. At least one (usually only one) calorimetric heat of formation value has been obtained for each of these compounds. Experimental low temperature heat capacity data was available for TiN and ZrN. Estimates were required for the others. It is felt that there is need for considerable additional thermodynamic work for the nitrides.

Having now discussed the tabulated data, it may be appropriate to discuss very briefly the general behavior of the refractories. The highest melting binary compound appears to be TaC_{0.85} with a melting point of 4000°C (4273°K) taken from the phase diagram by Storms.⁵⁵ Hafnium carbide is believed to melt somewhat lower at about 3900°K. As mentioned in the quarterly reports, this value is based on the data of Avarde et al.⁵⁶ and observations by Bowman.⁵⁷ Additional phase data for the Hf-C and Ta-C systems are being obtained by Sara and Dolloff.⁵⁸

In terms of vaporization properties, tantalum carbide also has a larger heat of atomization of $\Delta H_{298.15} = 196.006$ Kcal/g atom, whereas HfC has a value of 185.407 Kcal/g atom. This may be compared with the heat of vaporization of metallic tungsten which is 202.809 Kcal/g atom. Other data is shown in figure 17.

In summary, it may be stated that this review of the properties of refractories, is necessarily limited in scope. Complete details will be found in the existing quarterly progress reports or in the final report to be issued. Also, it should be pointed out that most of the data obtained on this project has been obtained using as much care and as critical judgements as possible. In many cases, however, limitations of time have prevented even more thorough analyses. Throughout the project emphasis has been made to prevent this work from becoming a mere compilation, but rather a critical evaluation. With this viewpoint the work has indeed been challenging.

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IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	II B	IIIA	IVA	VA	VIA	VIIA		
													I		
4													H		
Be										6	7	8	9		
12										C	N	O	F		
Mg										14	15	16	17		
20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
		58	59	60	61	62	63	64	65	66	67	68	69	70	71
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		90	91	92	93	94	95	96	97	98	99	100	101	102	
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	

FIGURE 1. TABLE OF ELEMENTS CURRENTLY BEING STUDIED

<u>Elements for JANAF Only</u>	<u>Elements Common to Both Groups</u>	<u>Elements for RAD Only</u>
Al	B	Ca
Br	Be	Ce
Cl	C	Cr
F	Mg	Dy
H	N	Gd
Hg	O	Hf
I	Si	Ir
K	Ti	La
Li	W	Mn
Na	Zr	Mo
P		Nb
Pb		Nd
S		Os
		Pt
		Re
		Rh
		Sc
		Sm
		Sr
		Ta
		Tc
		U
		V
		Y

FIGURE 2. ELEMENTS COMMON TO RAD AND JANAF

E. Rudy and H. Nowotny

301165

Hafnium-Tantalum-Carbon Systems

Monatsh 94, 507-17 (1963)

CA 59, 7209

At $T = 1850^{\circ}\text{C}$

$$G_{\text{HfC}} - G_{\text{TaC}} = - 8.5 \text{ Kcal/mole}$$

$$G_{\text{Hf}_2\text{C}} - G_{\text{Ta}_2\text{C}} = - 5 \text{ Kcal/mole}$$

Hf_2C is ~ 10 Kcal/mole less stable than a mixture of $\text{HfC}_{1-x} + \text{Hf}$.

FIGURE 3. SAMPLE ASM CARD

ACKERMANN, R	601322
(ARGONNE NATL LAB LEMONT ILL)	601322
HIGH-TEMP-THERMODYNAMIC PROPERTIES OF UO ₂	601322
J CHEM PHYS 25, 1089 (1956)	601322
NSA 11, 2880 (1957)	601322
 ACKERMANN, R	601273
THE HIGH-TEMPERATURE, HIGH VACUUM VAPORIZATION	601273
AND THERMODYNAMIC PROPERTIES OF UO ₂	601273
ANL-5482	601273
NSA 9, 7981 (1955)	601273
 ACKERMANN, R GILLES, P THORN, R	601045
(UNIV KANSAS LAWRENCE KANSAS)	601045
HIGH-TEMPERATURE THERMODYNAMIC PROPERTIES OF	601045
URANIUM DIOXIDE	601045
J CHEM PHYS 25, 1089 (1956)	601045
CA 51, 5526 (1957)	601045

FIGURE 4. SAMPLE OF BIBLIOGRAPHY

MAIN PROPERTY FILE - SAMPLE - NOVEMBER 1963

BIB	B	SULLIVAN, R SEIBEL	60	701038
CEMP	B	NIEMYSKI, I OLEMP	62	300705
CEMP	B	SAMSONOV, G NESHPO	59	201052
CEMP	B	HOOD, C THURSTON,	62	300406
CPH	B	MCDONALD, R STULL,	62	300726
CPH	B	WILLIAMS, N N	61	700659
CPH	B	MAGNUS, A DANZ, H	26	700560
CRYS	B	HORN, F	61	700969
CRYS	B	HOARD, J	61	700998
CRYS	B	BECHER, H SCHAFER	60	400617
CRYS	B	HUGHES, R KENNARD	63	300901
CRYS	B	MALINCHKOV, O POVI	62	300948
THER	B	SCHICK, H ANTHROP	63	300994
CRYS	B	MALYUCHKOV, O POVI	62	300584
CRYS	B	CARPENTER, R KATO	60	600626

FIGURE 5. SAMPLE OF SUBJECT OR PROPERTY FILE

PROPERTY FILE CODE NOVEMBER 1963

BETA	COMPRESSIBILITY COEFF (BETA = $1/V * (DV/DP)_T$)
BIB	BIBLIOGRAPHY
CEMP	CONDENSED PHASE, ELEC OR MAGNETIC PROP
COPT	CONDENSED PHASE, OPTICAL PROP.
CPH	HIGH TEMPERATURE HEAT CAPACITY
CPL	LOW TEMPERATURE HEAT CAPACITY
CRYS	CRYSTAL STRUCTURE
CTEX	COEFF OF THERMAL EXPANSION
DF	FREE ENERGY OF FORMATION, REACTION, ETC.
DH	HEAT OF FORMATION, REACTION, ETC.
DHD	DISSOCIATION ENERGY
DHT	HEAT OF TRANSFORMATION
E	INTERNAL ENERGY
ELCH	ELECTROCHEMICAL
EMF	ELECTROMOTIVE FORCE
ERES	ELECTRICAL RESISTIVITY
F	FREE ENERGY FUNCTION
H	HEAT CONTENT
KIN	KINETICS
MISC	MISCELLANEOUS
MPP	MISCELLANEOUS PHYSICAL PROPERTIES
MSP	MASS SPECTROMETRIC DATA
PHAS	PHASE DATA, MELTING, TRANSITION, BOILING TEMPS
PMCH	MECHANICAL PROPERTIES
REAC	CHEMICAL REACTIONS
REV	REVIEW
RHO	DENSITY
S	ENTROPY
SPK	SPECTROSCOPIC DATA
SURF	SURFACE PROPERTIES
TCON	THERMAL CONDUCTIVITY
THEO	THEORY
THER	THERMODYNAMIC DATA
TRT	TRANSFORMATION TEMPERATURES
VAP	VAPORIZATION DATA
ZKP	EQ CONST

FIGURE 6. DEFINITIONS OF PROPERTY FILE

CRYS	ZR N	LOWRIE, R	60	701014
LOWRIE, R				701014
(UNION CAR NUC CO RES CENTER TUXEDO NY)				701014
RESEARCH IN PHYSICAL AND CHEMICAL PRINCIPLES				701014
AFFECTING HIGH TEMPERATURE MATERIALS FOR ROCKET				701014
NOZZLES				701014
NP-9843 (1960)				701014
NSA 15, 11592 (1961)				701014
DF	ZR N	SMAGINA, Y KUTSEV,	59	300345
SMAGINA, Y KUTSEV, V ORMONT, B				300345
INVESTIGATION OF THE EQUILIBRIUM IN THE SYSTEM				300345
ZIRCONIUM NITROGEN AT HIGH TEMPERATURES AND OF				300345
FREE ENERGY OF FORMATION OF ZRNX AS A FUNCTION				300345
OF ITS COMPOSITION AND STRUCTURE				300345
PROBLEMY FIZ KHIM 2, 118 (1959)				300345
COTS 46, 198 (1961)				300345
NSA 15, 32554 (1961)				300345

FIGURE 7. POSSIBLE FORM OF BIBLIOGRAPHY AFTER MECHANIZATION

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- e. Schick, H. L. et al, Thermodynamics of Certain Refractory Compounds, 4th Quart. Rept., Avco RAD-SR-63-105 (June 1963).
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LEGEND TO FIGURE 8

Name of Element	Ref.	Gas	Gaseous Monoxide	Gaseous Dioxide	Other Gas- eous Oxides	Cond. Phase Monoxide	Cond. Phase Dioxide	Cond. Phase Trioxide	Cond. Phase Tetraoxide	Cond. Phase Pentoxide	Cond. Phase Hexoxide	Cond. Phase Heptoxide	Cond. Phase Octoxide	Cond. Phase Nonoxide	Cond. Phase Decoxide	Cond. Phase Undecoxide	Cond. Phase Dodec oxide	Cond. Phase Misc.
	*C **P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C	C P/C
B	d	d																
Be	b	b			b(BeO)x=1-5	b												
C	b	b																
Ca	a	a																
Ga	c	c																
Gr	a	a			b(GrO ₂)													
Dy																		
Gd																		
Hf	d	d																
Ir	b	b																
La																		
Mg	b	b																
Mn	c	c																
Mo	a	a			a(MoO ₃)													
N	a	a																
Nb	d	d																
Nd																		
O	a	a																
Os	b	b			b(OsO ₄)													
Pt	c	c																
Rh	c	c																
Sc																		
Si	d	d																
Sm																		
Sr	a	a																
Ta	d	d																
Tc	c	c																
Th	c	c																
Ti	a	a																
U	e	e																
V	d	d																
W	a	a																
Y	d	d																
Zr	d	d																

*C = Completed
 ** P/C = Partly completed.

FIGURE 8. TABLE SHOWING STATUS OF WORK

$H = \text{K. E. of electrons} + \text{P. E. of electrons in field of nuclei} + \text{P. E. due to electron interaction (coulombic)} + \text{P. E. due to nuclei interaction (coulombic)}$

$$H = - \sum_{i=1}^{ZN} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^{ZN} \sum_{a=1}^N \frac{Ze^2}{|R_a - r_i|} + 1/2 \sum_{i \neq j}^{ZN} \sum_{j=1}^{ZN} \frac{e^2}{|r_i - r_j|} + 1/2 \sum_{a \neq b}^N \sum_{b=1}^N \frac{Z^2 e^2}{|R_a - R_b|}$$

FIGURE 9. HAMILTONIAN OPERATOR

Element	$\Delta_{H_{298.15}}$ Kcal/g atom
B	133.000
C	170.890
1/2 N ₂ *	112.980
1/2 O ₂ *	59.557
Ti	112.490
Zr	143.126
Hf	144.924
V	123.010
Nb	171.836
Ta	186.522

*
Dissociation

FIGURE 10. HEATS OF SUBLIMATION OF ELEMENTS

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw ⁻¹	$\Delta F_{298.15}$	ΔF_{1000}	ΔF_{2000}
			$\xleftarrow{\text{Kcal/gfw}^{-1}} \xrightarrow{\text{Kcal/gfw}^{-1}}$		
TiO ₂	-225.800	12.040	-212.593	-182.421	-140.356
Ti ₃ O ₅	-587.650	30.900	-553.778	-480.987	-382.016
Ti ₂ O ₃	-363.400	18.830	-342.726	-297.098	-236.958
TiO	-124.150	9.99	-117.637	-102.850	-83.568
ZrO ₂	-261.5	12.12	-247.732	-216.107	-172.518
HfO ₂	-266.06	14.188	-252.486	-221.648	-180.084
Nb ₂ O ₅	-454.600	32.8	-422.484	-349.583	-255.120
NbO ₂	-190.200	13.03	-176.790	-146.452	-107.890
NbO	-97.700	12.0	-91.289	-76.668	-57.156
Ta ₂ O ₅	-488.7	34.2	-456.453	-383.491	-287.064

FIGURE 11. DATA FOR CONDENSED PHASE OXIDES

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw ⁻¹	$\Delta F_{298.15}$ Kcal/gfw ⁻¹	ΔF_{1000} Kcal/gfw ⁻¹	ΔF_{2000} Kcal/gfw ⁻¹
TiO	13.000	55.989	5.798	-10.172	-29.838
ZrO	21.100	57.055	14.165	-1.368	-20.520
HfO	18.996	57.736	12.281	-2.260	-20.668
NbO	46.017	57.091	38.984	23.400	3.057
TaO	51.973	58.568	44.774	28.739	7.719

FIGURE 12. GASEOUS MONOXIDES

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw ⁻¹	$\Delta F_{298.15}$ Kcal/gfw ⁻¹	ΔF_{1000} Kcal/gfw ⁻¹	ΔF_{2000} Kcal/gfw ⁻¹
TiO ₂	-82.890	56.562	-82.957	-82.379	-79.348
ZrO ₂	-82.457	58.551	-82.533	-81.975	-78.979
HfO ₂	-70.000	60.475	-70.226	-69.956	-67.790
VO ₂	-55.876	59.912	-57.076	-59.814	-62.654
NbO ₂	-51.051	61.031	-51.953	-53.765	-56.477
TaO ₂	-46.708	62.527	-47.781	-49.646	-51.558

FIGURE 13. GASEOUS DIOXIDES

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw ⁻¹	$\Delta F_{298.15}$ Kcal/gfw ⁻¹	ΔF_{1000} Kcal/gfw ⁻¹	ΔF_{2000} Kcal/gfw ⁻¹
TiB ₂	-66.85	6.7	-65.832	-63.001	-57.048
ZrB ₂	-73.000	8.59	-71.961	-69.331	-64.248
HfB ₂	-80.000	11.068	-79.277	-77.637	-74.292
NbB ₂	-41.9	8.96	-41.058	-39.128	-37.024
TaB ₂	-50.	10.603	-49.374	-47.739	-45.064

FIGURE 14. BORIDES

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw ⁻¹	$\Delta F_{298.15}$ Kcal/gfw ⁻¹	ΔF_{1000} Kcal/gfw ⁻¹	ΔF_{2000} Kcal/gfw ⁻¹
TiC	-44.13	5.79	-43.266	-41.468	-37.940
ZrC	-48.0	7.964	-47.199	-45.810	-43.676
HfC	-55.0	9.852	-54.339	-52.786	-49.944
Nb ₂ C	-46.6	16.0	-45.599	-43.597	-41.110
NbC	-33.6	8.7	-33.105	-32.481	-32.174
Ta ₂ C	-47.2	19.5	-46.693	-45.730	-44.896
TaC	-34.6	10.11	-34.251	-33.898	-34.384

FIGURE 15. CARBIDES

Compound	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	$S_{298.15}$ cal degK ⁻¹ gfw	$\Delta F_{298.15}$ Kcal/gfw ⁻¹	ΔF_{1000} Kcal/gfw ⁻¹	ΔF_{2000} Kcal/gfw ⁻¹
TiN	-80.750	7.24	-73.900	-58.115	-35.801
ZrN	-87.3	9.29	-80.477	-64.762	-42.557
HfN	-88.24	10.7	-81.414	-65.645	-44.067
Nb ₂ N	-60.5	19.0	-53.975	-39.170	-19.455
NbN	-56.5	10.5	-50.124	-35.898	-17.755
Ta ₂ N	-64.6	22.0	-58.421	-44.770	-28.375
TaN	-59.95	12.0	-53.747	-39.973	-23.663

FIGURE 16. NITRIDES

Compound	M. P. (°K)	$\Delta H_{298.15}$ Kcal/gfw ⁻¹	ΔH (sublimation or atomization) 298.15, Kcal/gfw ⁻¹	ΔH (sublimation or atomization) 298.15, Kcal g-atom ⁻¹
TaC	4273	-34.6	392.012	196.006
HfC	3900	-55.0	370.814	185.407
Ta ₂ C	3773	-46.961	590.895	196.965
NbC	3753	-33.6	376.326	188.163
ZrC	3693	-48.0	362.016	181.008
HfB ₂	3523	-80.0	490.924	163.641
Nb ₂ C	3363	-46.6	561.162	187.054
ZrB ₂	3313	-73.0	482.126	160.708
NbB ₂	3273	-41.9	479.736	159.912
TiB ₂	3193	-66.85	445.340	148.446
HfO ₂	3173	-266.06	530.098	176.699
W ₂ C	3068	-11.0	588.090	196.030
WC	3058	-8.4	382.390	191.195
ZrO ₂	2973	-261.5	523.740	174.580
Mo ₃ C ₂	2923	-13.970	830.350	166.070
Mo ₂ C	2693	-11.535	498.825	166.275

FIGURE 17. SUMMARY OF DATA FOR SOME REFRACTORIES

THERMODYNAMIC STUDIES AT LOW AND HIGH TEMPERATURES

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The unclassified section of Dow's physical chemistry work for ARPA is divided into three areas; low temperature calorimetry, high temperature drop calorimetry, and high temperature heat capacities in the Arc-Image Furnace. Taking them in this order, the first figure shows a cross-section of the adiabatic liquid helium calorimeter. A is the sample container suspended by thread within the adiabatic shield B, which is in turn suspended from the floating ring C and the upper block D. The sleeve E connects the upper and lower blocks D and F, the whole system being enclosed by G, around the base of which liquid helium is condensed. By adding small measured amounts of heat to the system the temperature increase can be measured and the heat capacity calculated. Using the third law of thermodynamics we can then obtain the entropy of the system by evaluation

$$\int_0^T C_p d \ln T.$$

TABLE I. ENTROPY AT 298.15°K. IN CAL. DEG.⁻¹ MOLE⁻¹

AlCl ₃ (c)	=	26.45 ± 0.10
P ₄ O ₁₀ (c)	=	55.75 ± 0.10
LiCl(c)	=	14.185 ± 0.05
LiBO ₂ (c)	=	12.36 ± 0.05
BPO ₄ (c)	=	14.91 ± 0.05
BeCl ₂ (c) alpha	=	19.77 ± 0.05
BeCl ₂ (c) beta	=	18.12 ± 0.05

Table I shows the entropies of some of the materials measured by Dr. Franklin Oetting, he also has values for several other compounds which are still classified. We might note the differences between the measured values and those estimated earlier. AlCl₃ had been given as 40 e.u. in Circular 500, and in 1959 the Bureau estimated 22.4 e.u. - a difference of 4 e.u. P₄O₁₀ was estimated in 1959 by Dr. Sinke of the Dow Chemical Company to be 64.6 e.u. or 9 e.u. different, and LiCl was estimated as 12.3 e.u. by the Natl. Bur. Standards in 1959 a difference of 2 e.u. Thus while we might think we can estimate entropy to + 1 e.u. these comparisons hardly support the notion, and lend strong support for the necessity for further measurements. Figure 2 shows the smoothed heat capacities for LiCl(c), this curve is the normal sigmoid shape. The sample was 99.5% pure and was vacuum dried at 200°C. before use. Figure 3 shows a quite different curve, P₄O₁₀, this has a small hump in the

curve, which may be due to impurity even though the sample was 99.2% pure.

Figure 4 shows a schematic of the dropping calorimeter which has a maximum temperature of 1700°K. The furnace, B, is platinum-rhodium wound and the calorimeter, C, a copper block, while the sample container A can be platinum, platinum-rhodium, or stainless steel. This calorimeter measures heat contents, and heat capacities are obtained from the slope of the heat content-temperature curve. The next few figures show some of the results obtained by R. A. McDonald. Figure 5 is the heat capacity of elemental Boron (1) up to 1700°K., showing the agreement with the low temperature values, while figure 6 shows a similar plot of the data for boron nitride (2); again up to 1700°K. These measurements on B and BN have been valuable in fixing the thermodynamic properties of boron compounds at high temperatures. Figure 7 has the heat capacity of ZrF_4 (3) plotted from 300°K. to 1200°K., also measured were $\Delta H_m = 15.35 \pm 0.10 \text{ kcal. mole}^{-1}$, the m. pt. 1205°K., and the liquid heat capacity of roughly 29 cal. deg.⁻¹ mole⁻¹.

The next few figures are plots of both low and high temperature data determined at the Thermal Research Laboratory by F. L. Oetting and R. A. McDonald. Figure 8 has the results for solid and liquid AlCl_3 , here the drop measurements were also taken below 298°K., this can be done because the furnace is water cooled. Figure 9 shows the combined results for BPO_4 up to 1200°K. and Figure 10 for lithium metaborate. In addition to the data on the slide the heat capacity of the liquid up to 1700°K. was found to be 34.56 cal. deg.⁻¹ mole⁻¹, the melting point $1117 \pm 1^\circ\text{K.}$ and the heat of fusion 8.16 kcal. mole⁻¹. Figure 11 brings us up to date on BeCl_2 , these values being previously unreported. Dr. Oetting recently completed the low temperature measurements on a sample of Beta- BeCl_2 which fit well with the drop calorimeter values and give $S_{298.15} = 18.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. McDonald's measurements show that at 676°K. the beta form goes over to the alpha- BeCl_2 and at 688°K. this melts. The alpha- BeCl_2 was reported earlier to have an entropy of 19.77 cal. deg.⁻¹ mole⁻¹ at 298°, indicating that the two forms have measurably different heats of formation.

Moving on to the determination of high temperature heat capacities in an arc imaging furnace, which are of interest because we can go higher in temperature, 2100-2200°K., and obtain results with much less labor than in a drop calorimeter. Figure 12 shows a schematic view of the furnace, the radiation from the 1.3 cm.² anode crater at roughly 3800°K. is transferred by means of the elliptical mirror system to the sample. The basis of the method is the fact that at any instantaneous temperature T°K.

$\dot{q}_{\text{input}} = \dot{q}_{\text{gain}} + \dot{q}_{\text{loss}}$
 where $\dot{q}_{\text{gain}} = m \cdot C_p \cdot dT/d\theta$, the rate of gain of heat; m being the mass, C_p the heat capacity, and $dT/d\theta$ the rate of change of temperature with time.

Also $\dot{q}_{\text{loss}}$ can be split into three parts:

$$\dot{q}_{\text{radiative}} = K_1(T^4 - T_0^4) = K_1 T^4 \text{ (above } 1300^\circ\text{K.)}$$

$$\dot{q}_{\text{convective}} = K_2(T - T_0)$$

$$\dot{q}_{\text{conductive}} = K_3(T - T_0)$$

In the special case when $\dot{q}_{\text{input}} = 0$, that is heating to a high temperature and then removing the power input and allowing to cool, we obtain:

$$\begin{aligned}
 -m \cdot C_p \cdot dT/d\theta &= K_1 T^4 + K_2(T - T_0) + K_3(T - T_0) \\
 &= K_f(T) + K_0
 \end{aligned}$$

Thus if K and K_0 can be kept the same for materials of different heat capacity, then by measuring the cooling rates the heat capacity can be compared to a standard. Because of the high temperatures and small containers the cooling rates are extremely high and we found it impractical to measure the direct cooling rates. The system shown in Figure 13 is the one developed for actual use. This shows the sample container at the focal point of the mirror, with its supports, shields, and temperature measuring system. The shield and sample always have the same spatial relation to each other and so if the surface of the shield is reproducible, then, the environment is one which still has the heat loss rate by radiation a function of the temperature of the container. Similarly the conduction is defined by the temperature of the container and the brass support, if the graphite support is reproducible. The temperature of the brass support is unaffected by the limited amount of heat conducted down the graphite support during the two minute heating cooling cycle. Thus conduction is a variable only of the temperature of the container. Convection is also made a function of the vessel temperature by keeping a constant temperature flow of argon through the system.

Figure 14 shows a cross-section of our graphite container and support. Here we can see the temperature sensor - the re-entrant black-body well, down which a total radiation pyrometer is sighted. The system is automatically in alignment because the spatial position of the container is always the same. The sample is shown interleaved with graphite. This is done to approximate the situation within the container during calibration with graphite. The large surface area for radiant energy transfer helps to maintain uniformity of temperature, in practice we use disks roughly 0.009" thick. Because of the fact that our temperature

detector does not always follow temperature changes rapidly enough, it is necessary to calibrate with a known material and an empty vessel. However, as such a dual calibration can be made easily in an afternoon this is not a real hardship. Our procedure is then to heat our sample up to around 2300°K., extinguish the arc, drop the shield, and then follow the cooling curve down to 1300°K. This is repeated until identical cooling curves are obtained; the time temperature curve is then fitted by computer and the rate of cooling at specified temperatures calculated. These are combined with similar values from the calibration runs and the heat capacities are then calculated by computer.

The basis for all our work, the heat capacity of SPK graphite was determined by R. A. McDonald using drop calorimetry and extrapolated to 2300°K. using the Shomate function plot. Figure 15 shows a plot of the results for boron nitride, and Figure 16 the results for aluminum oxide. These are already published in the literature (4), but the remaining results have not been given before. The values for BeO are given in Figure 17, there is a long story behind this result - we have probably made as many measurements on the BeO system as all our other determinations. This arose because our first sample of cold pressed-fired beryllia exhibited a dual nature, occasionally we obtained the curve shown but more often we obtained results from 10-80% higher - which were quite reproducible. Apparently the form and thermal history of the sample were involved as we have no such troubles with the hot pressed sample shown here. Figure 18 shows the excellent agreement with earlier work for titanium nitride and Figure 19 similar good agreement with zirconium nitride. Figure 20 is titanium diboride - showing fair agreement, Figure 21 zirconium diboride showing the distinct difference caused by the sample form. Westrum and Feick (5), and Margrave, et al. (6), used the same zone refined single crystal, all the data on the upper curve was done using powdered or sintered material (8)(9). Figure 22 is for WB, this was most unusual in that an exotherm was detected on the cooling curves at 1278°K. This was thought to be due to a solid state transition and is supported by the large difference between the values measured above and below this temperature. W_2B_5 shown in Figure 23. The agreement is not too bad especially in view of the difficulty of characterizing these refractory borides.

Now we come to a series of carbides which were given to us by Dick Kebler and Ira Binder of Union Carbide Corporation. They were very pure, highly characterized hot pressed samples which were much thicker than our normal disks. To check that this would not affect the results the first two were repeated with normal samples from a commercial source. Figure 24 shows the two samples of tantalum carbide agreeing very well and recently Levinson of Los Alamos has published (7) high temperature drop calorimeter values which have been included. These results in excellent agreement with each other are 7-15% lower than one would expect from extrapolation from the lower temperature data

of Margrave, et al. (1) and S.W.R.I. (8). Figure 25 shows similar data for niobium carbide, again the two samples agree quite well with each other and with data from S.W.R.I. but are 2-7% higher than Levinson's data. Results for zirconium carbide are given in Figure 26, here again the material of Westrum and Feick and of Margrave is zone refined single crystal, whereas ours is hot pressed. Hafnium carbide shown in Figure 27 agrees well with S.W.R.I. and the data for tungsten carbide, Figure 28, are the only reported measurements.

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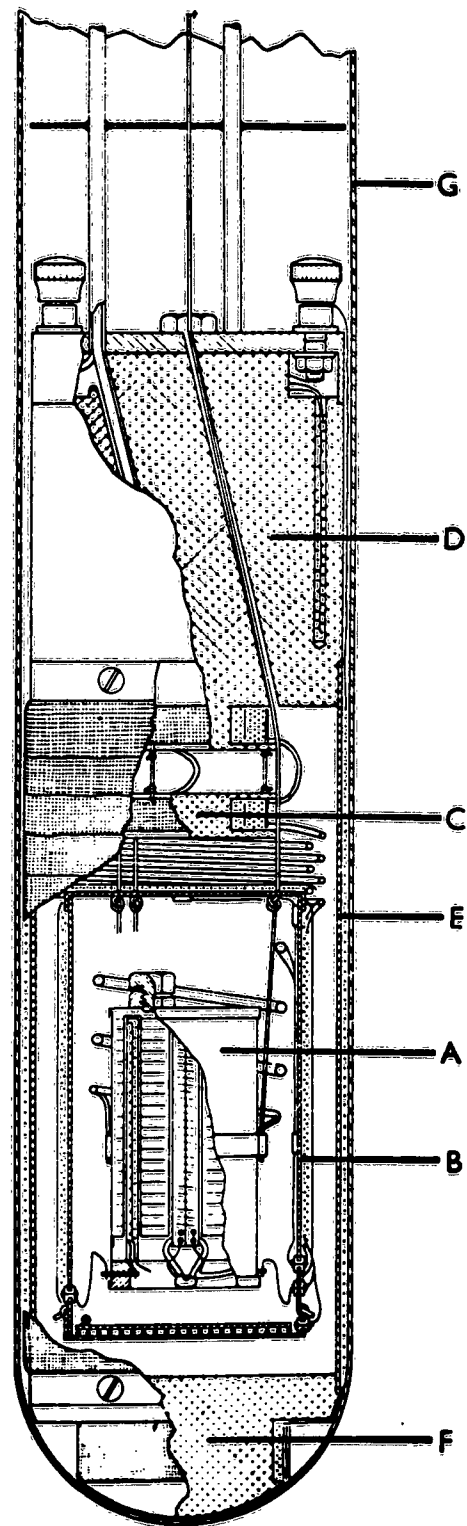


FIGURE 1

The calorimeter.

LITHIUM CHLORIDE LiCl

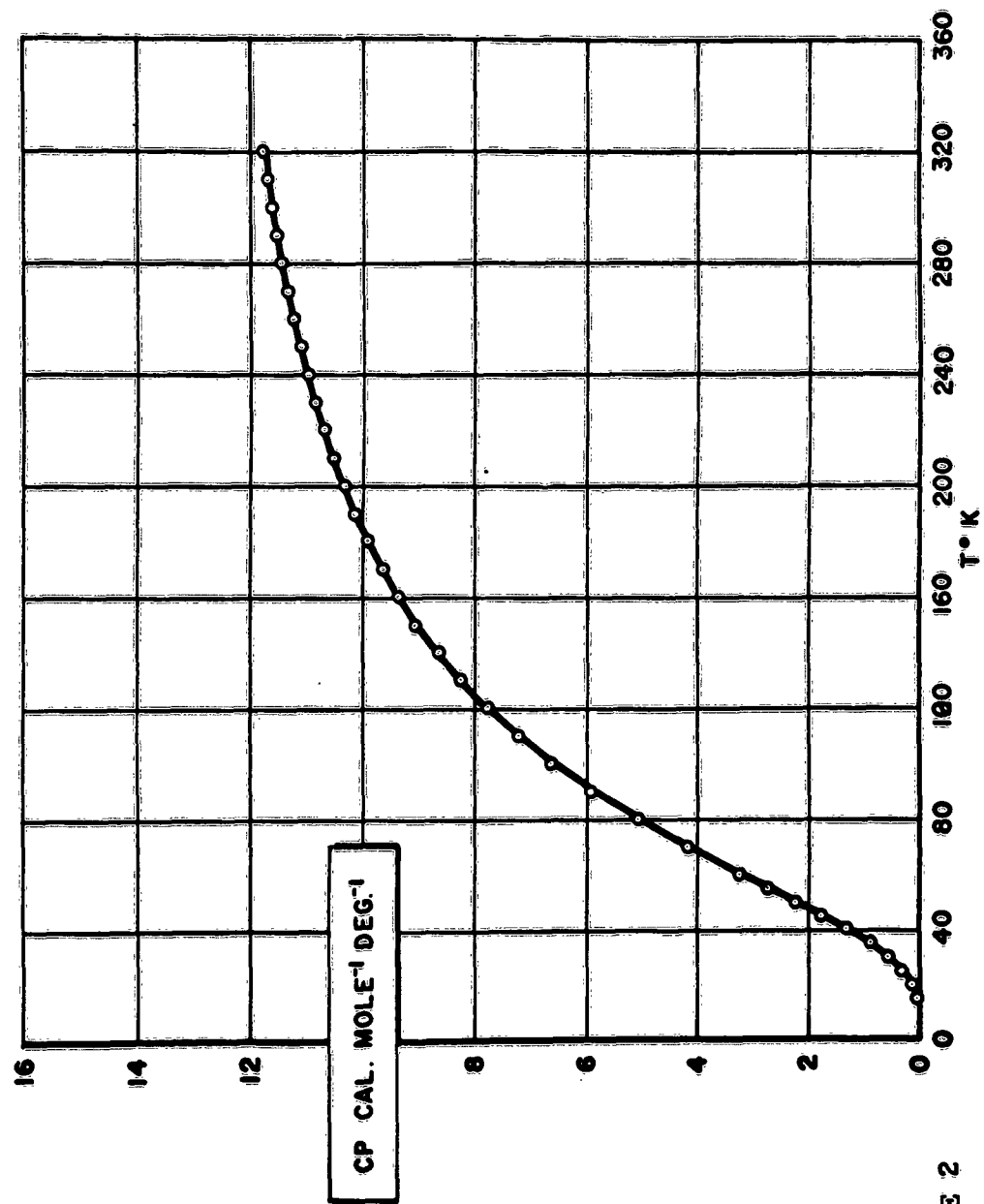


FIGURE 2

PHOSPHORUS PENTOXIDE P_4O_{10}

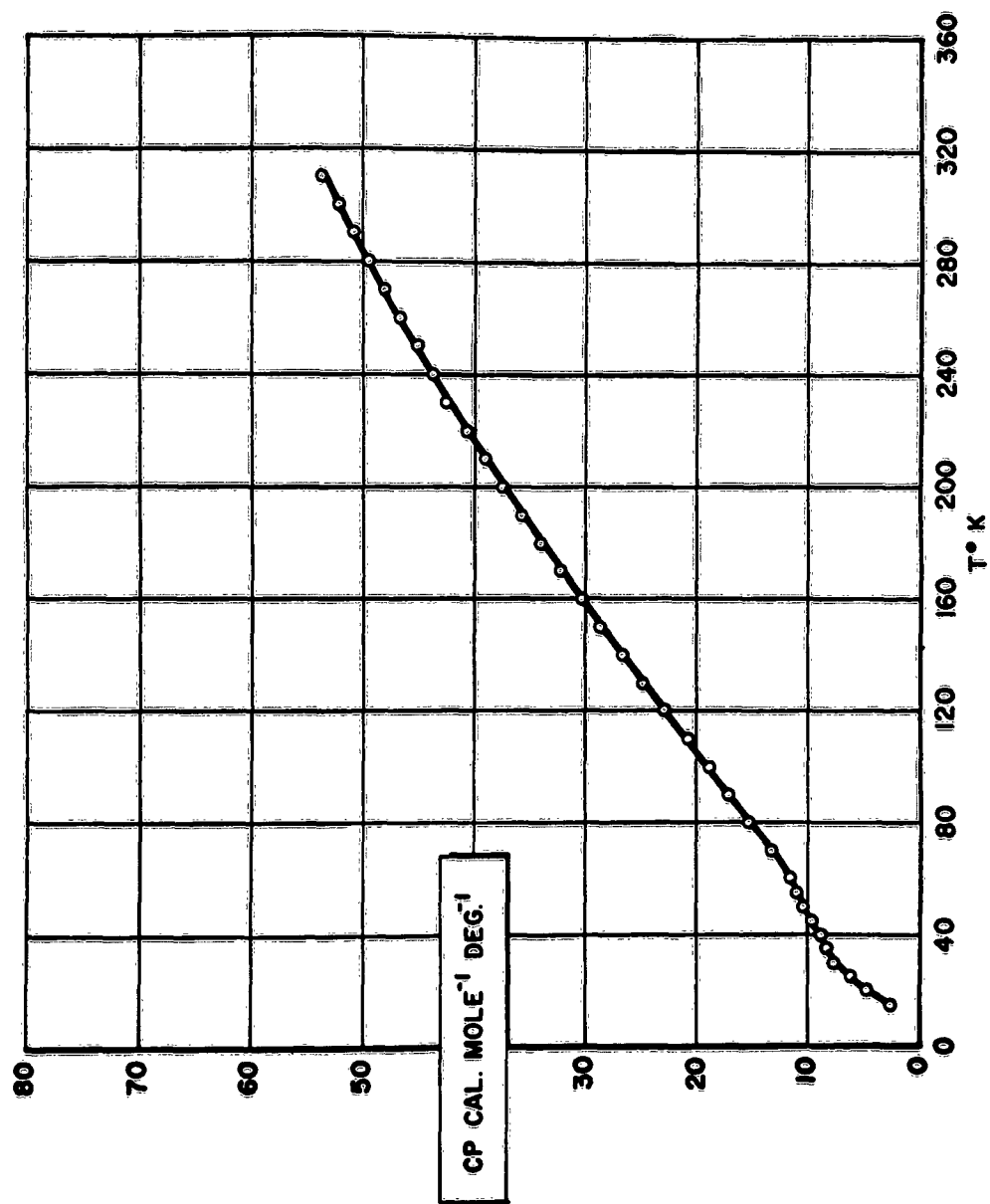


FIGURE 3

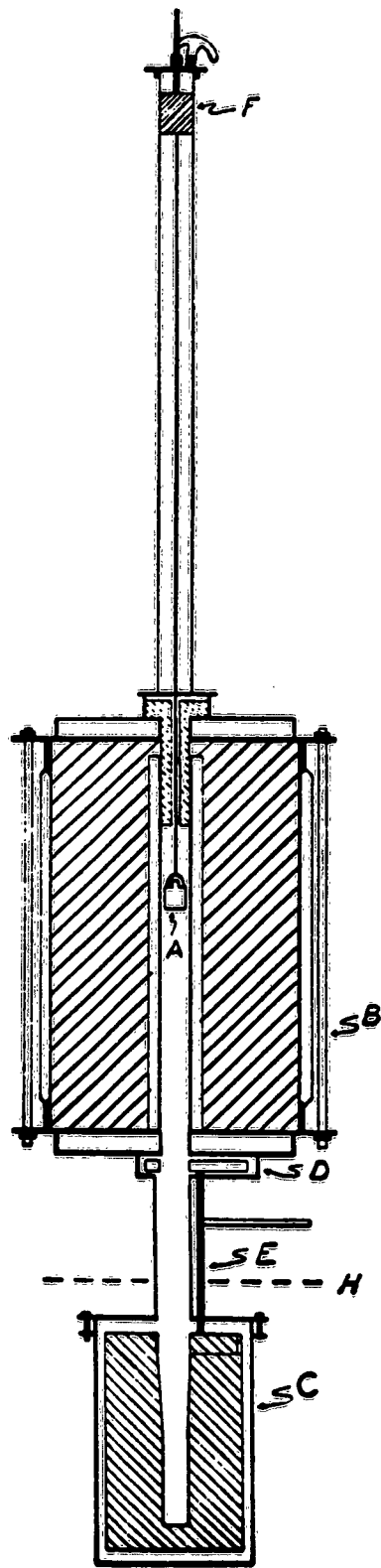


FIGURE 4

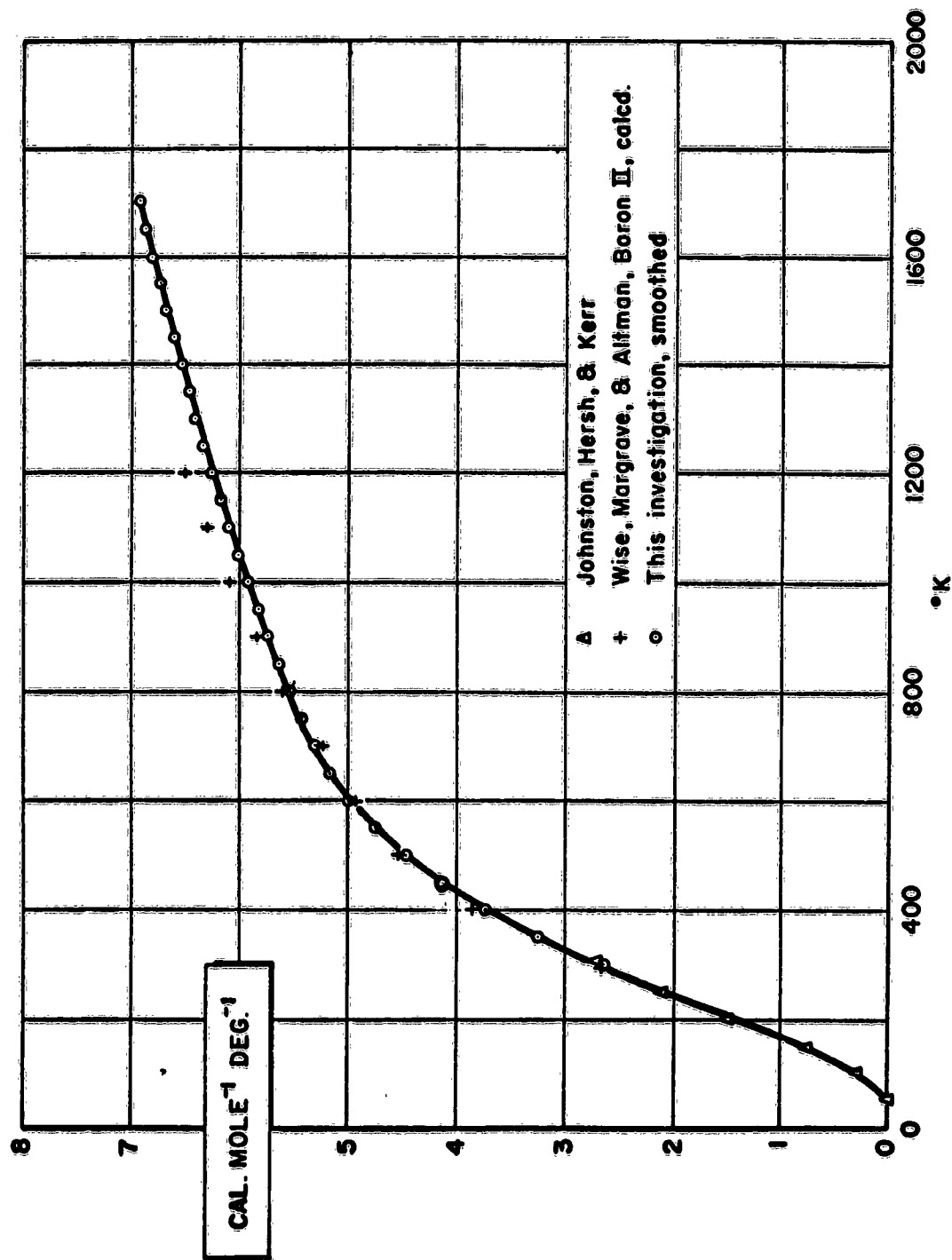


FIGURE 5. HEAT CAPACITY OF BORON UP TO 1700°K.

BORON NITRIDE BN

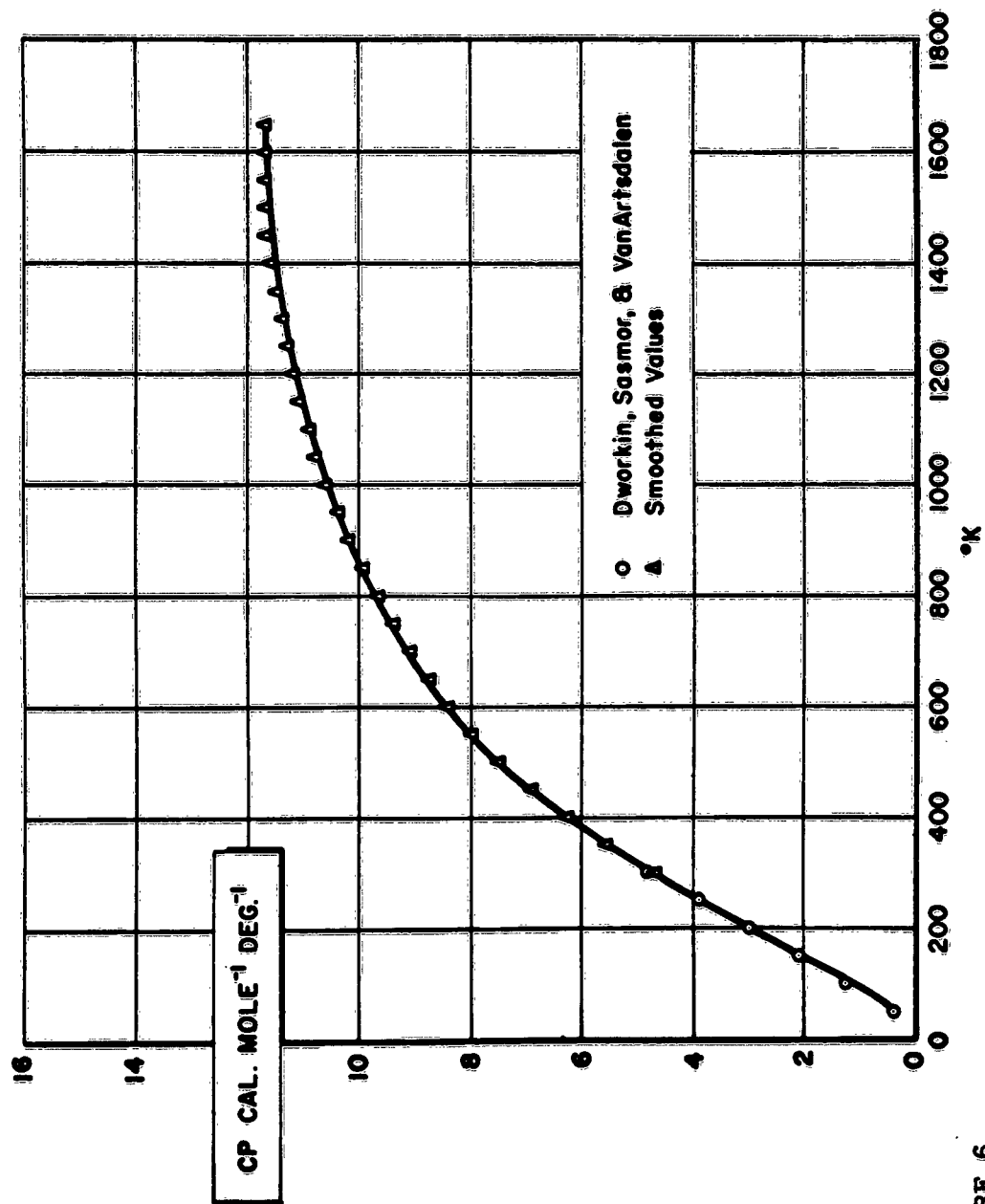


FIGURE 6

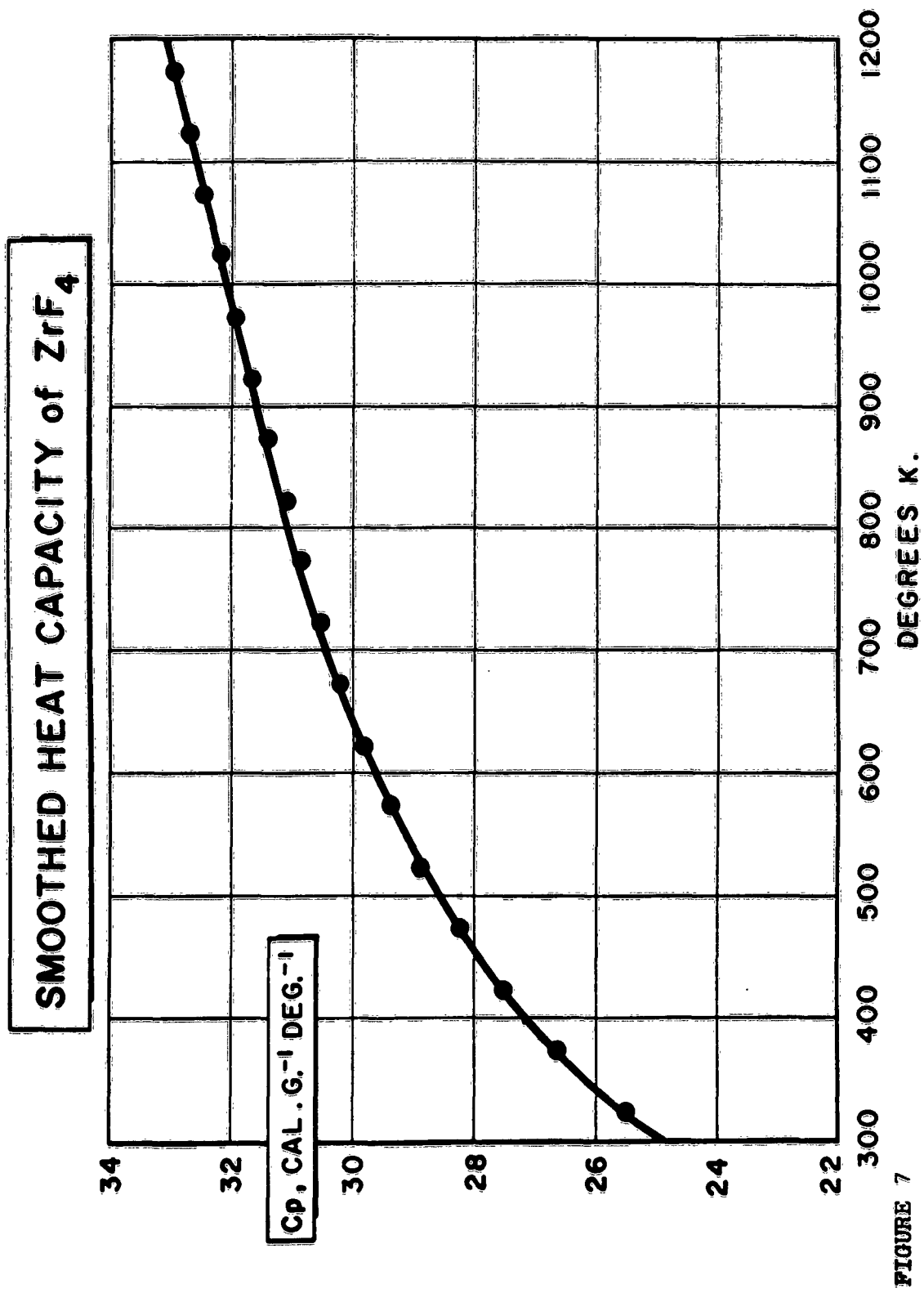


FIGURE 7

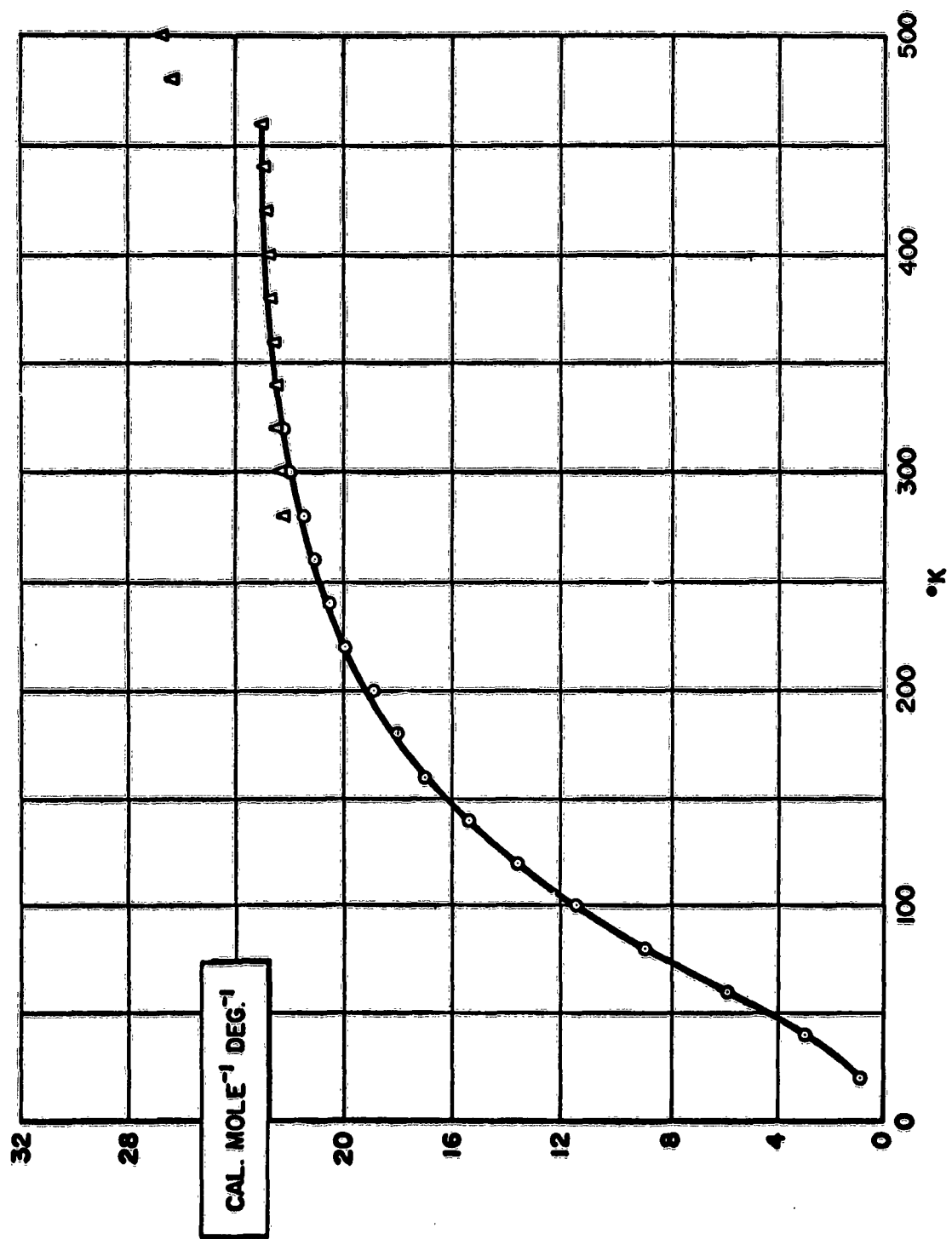


FIGURE 8. HEAT CAPACITY OF ALUMINUM CHLORIDE UP TO 500°K.

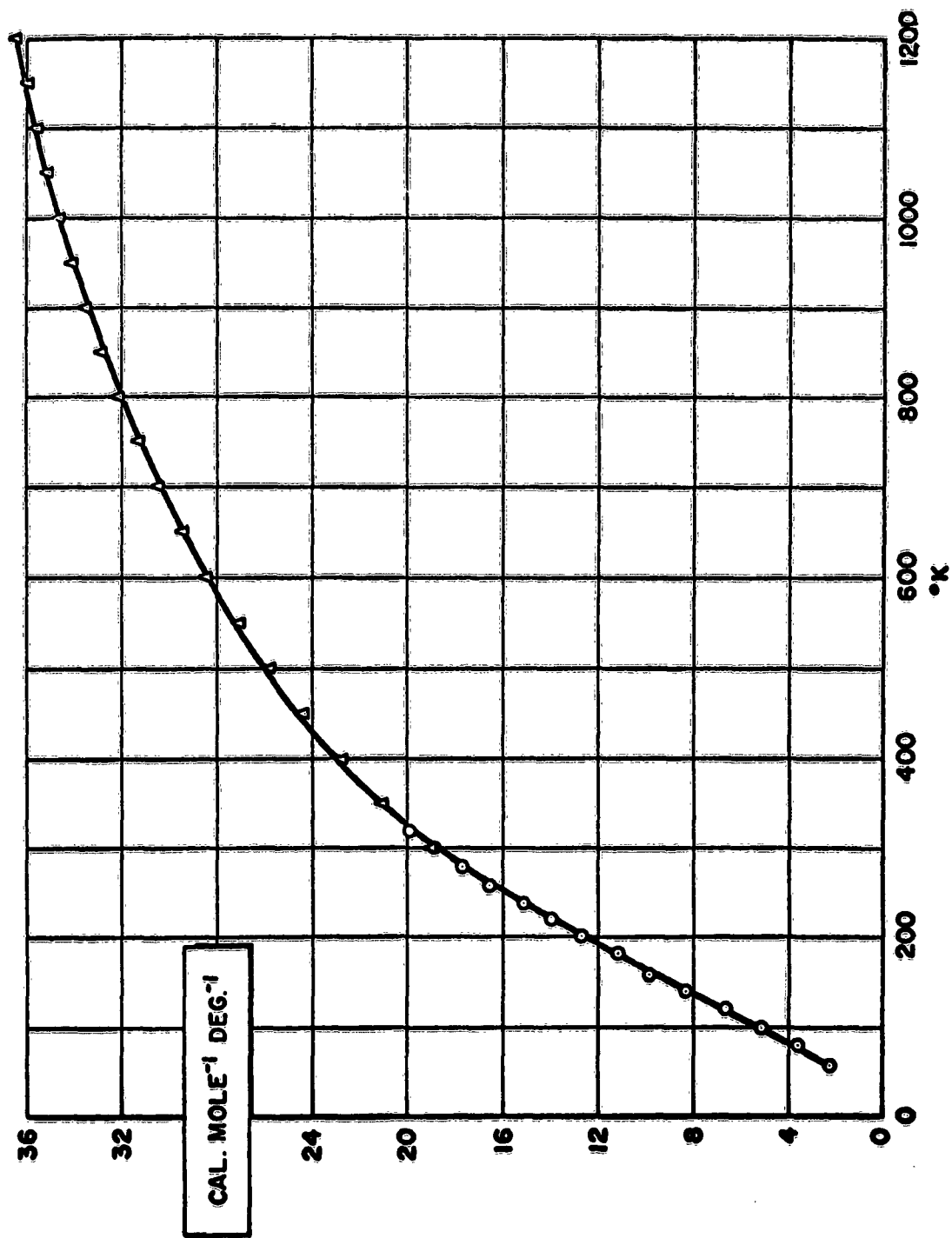


FIGURE 9. HEAT CAPACITY OF BORON PHOSPHATE UP TO 1200°K.

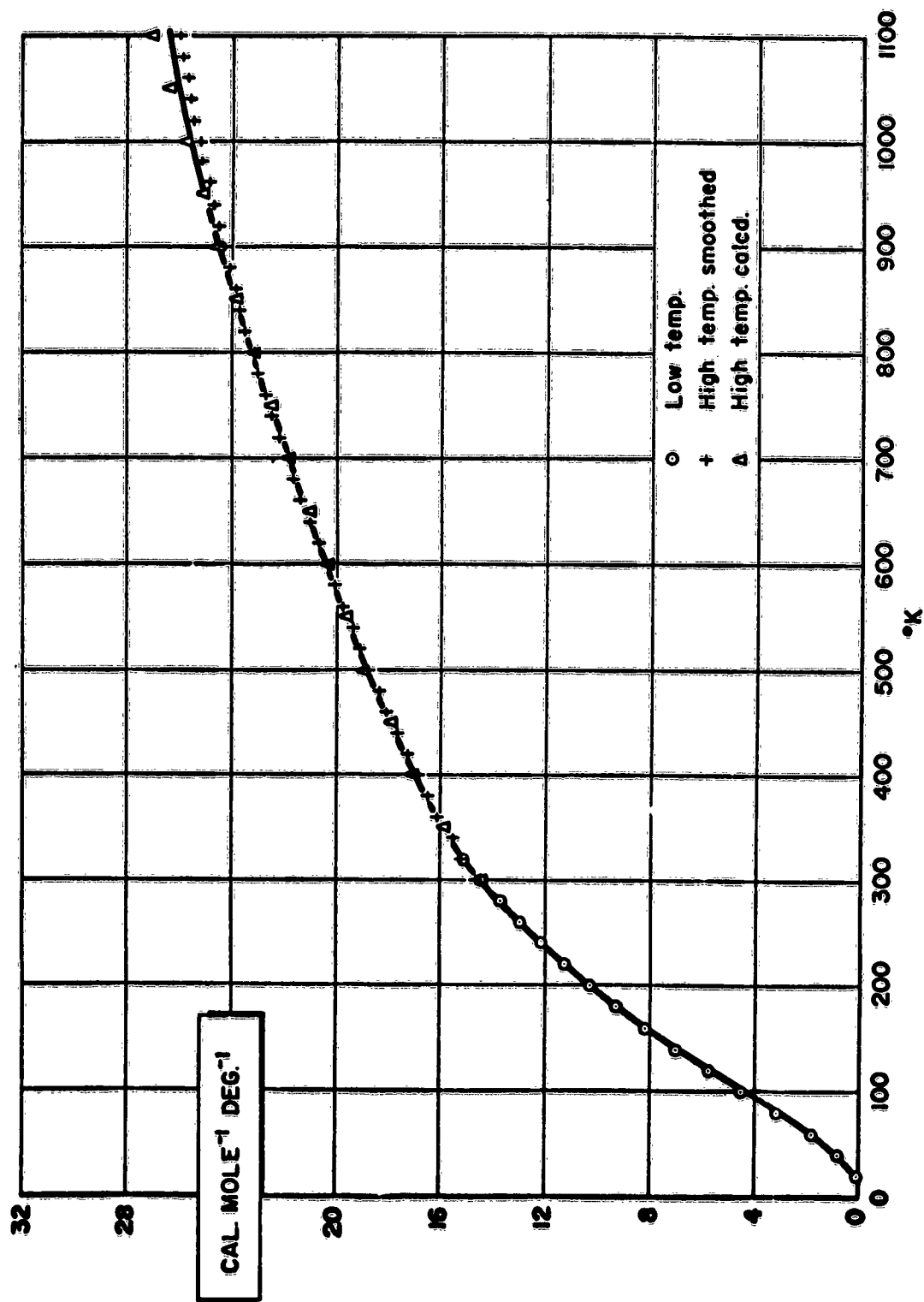


FIGURE 10. HEAT CAPACITY OF LITHIUM METABORATE UP TO 1100°K.

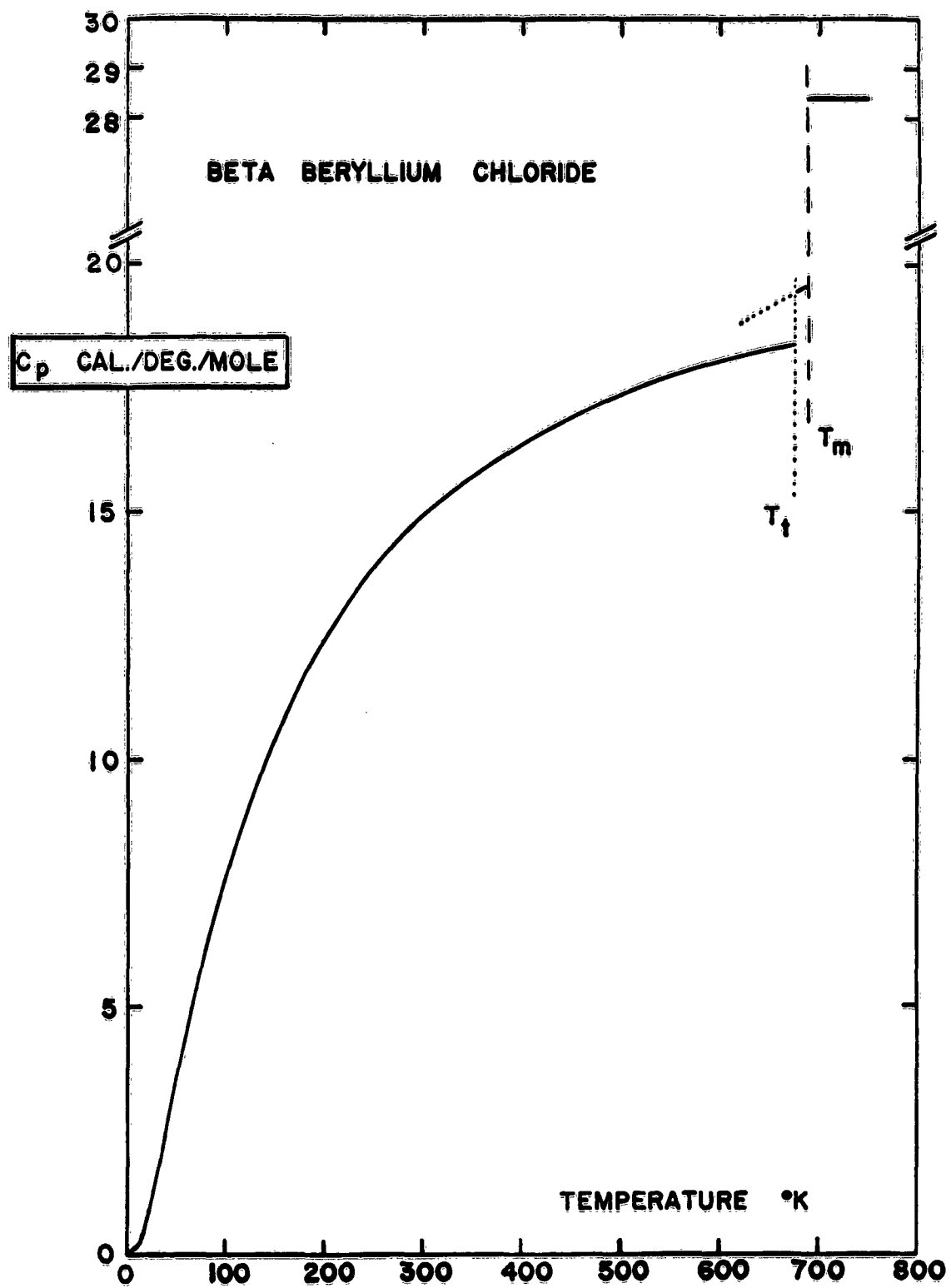


FIGURE 11

ARC IMAGING FURNACE

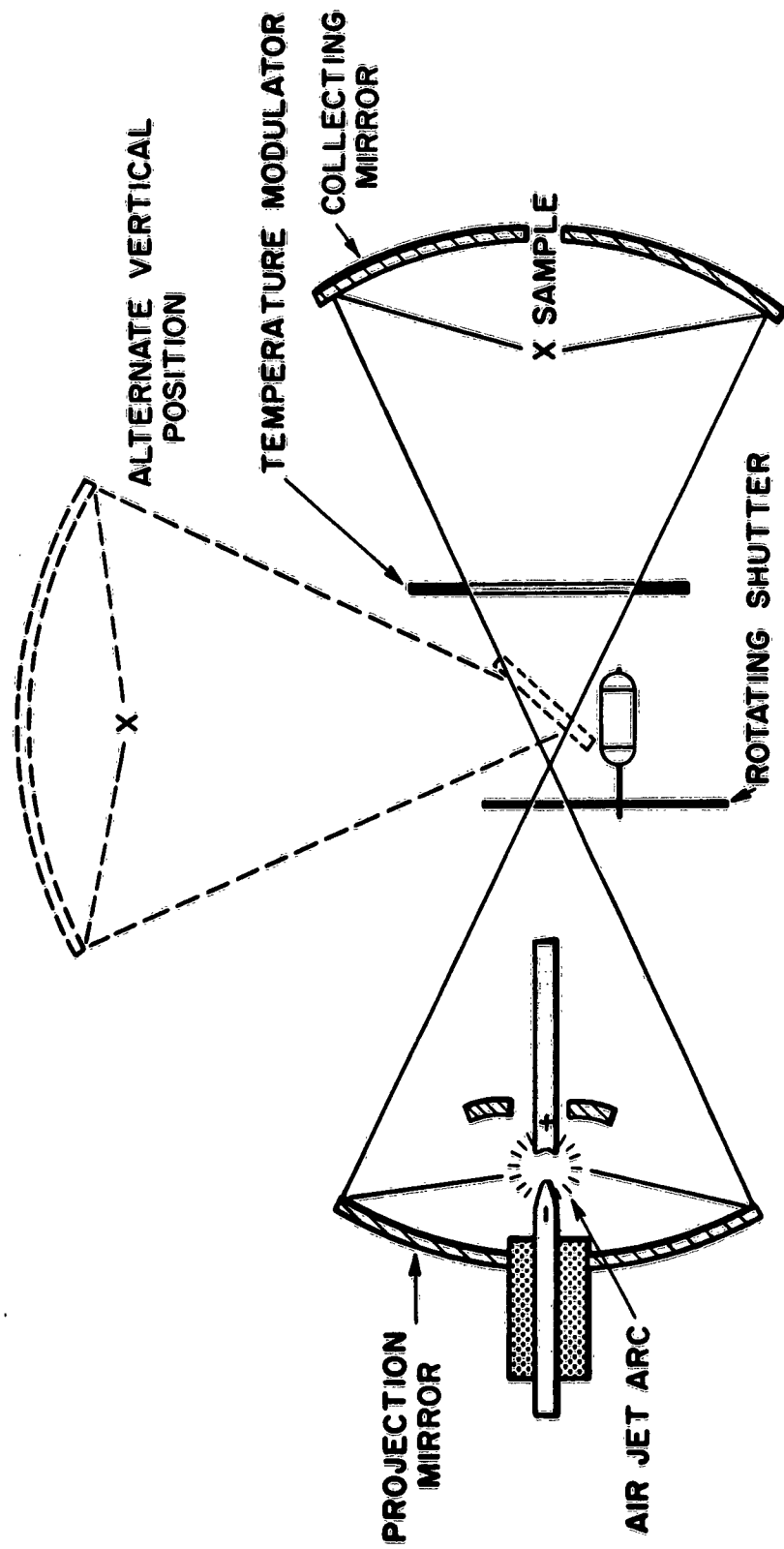
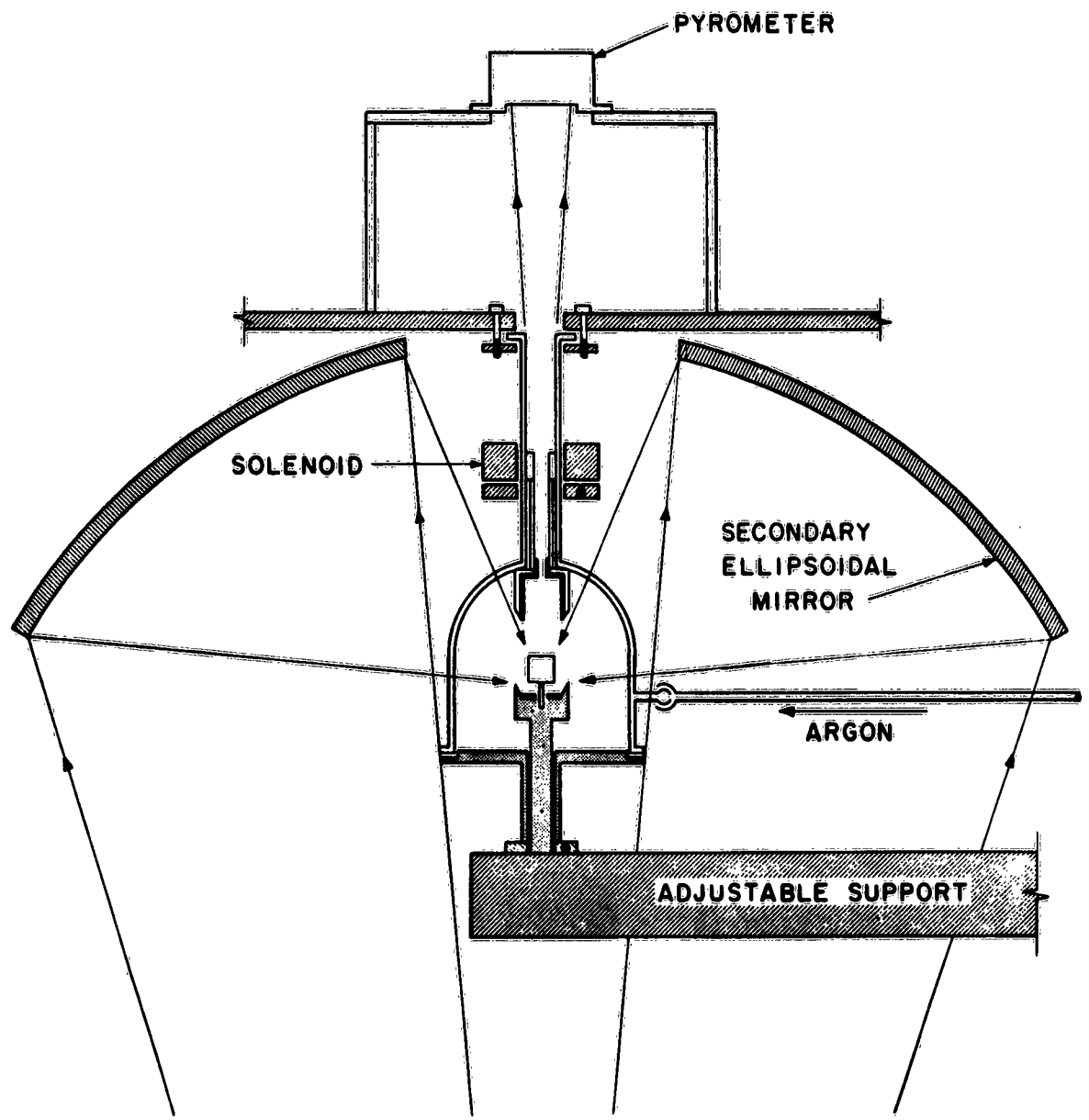
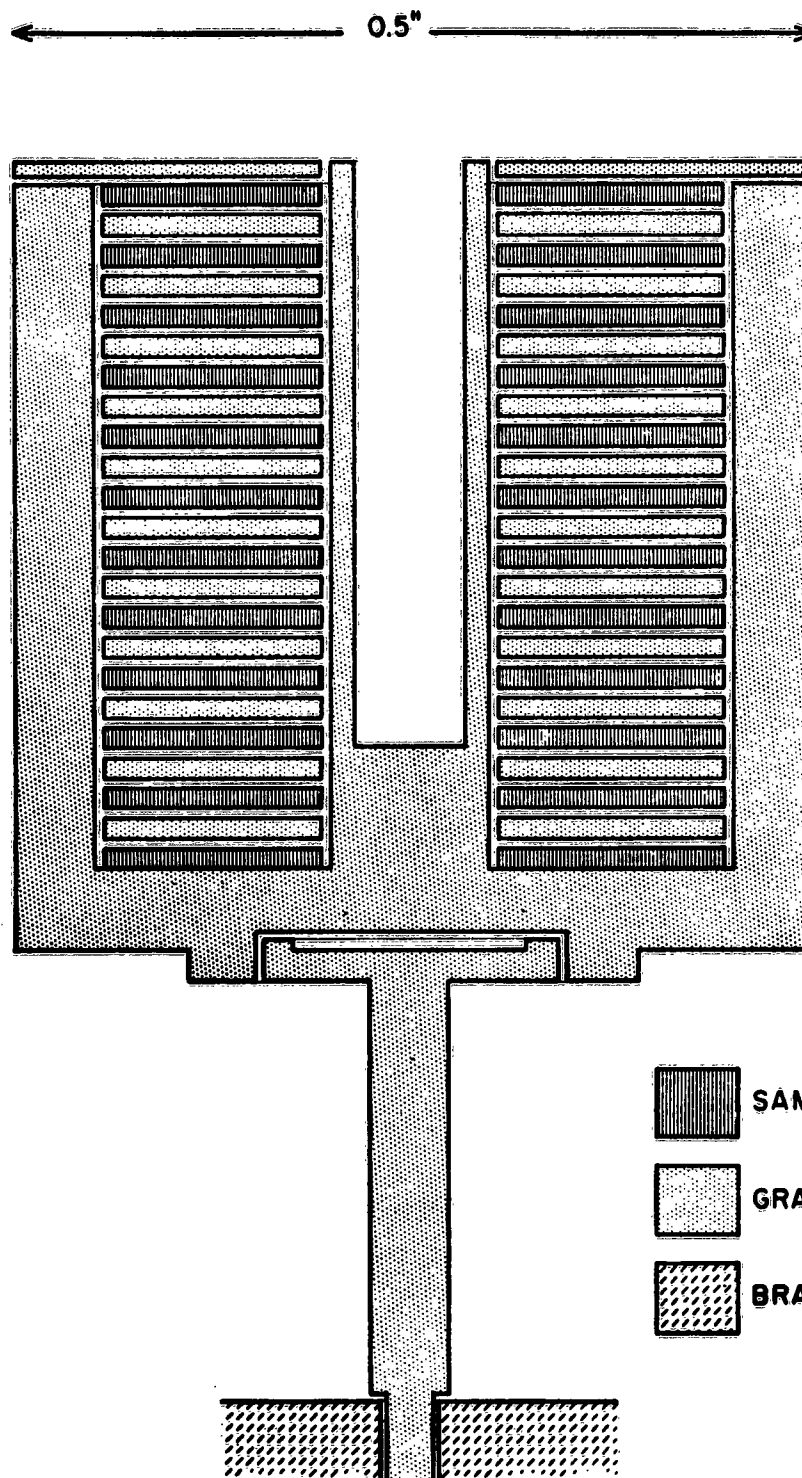


FIGURE 12.



ASSEMBLED SYSTEM

FIGURE 13



FILLED CONTAINER & SUPPORT

FIGURE 14

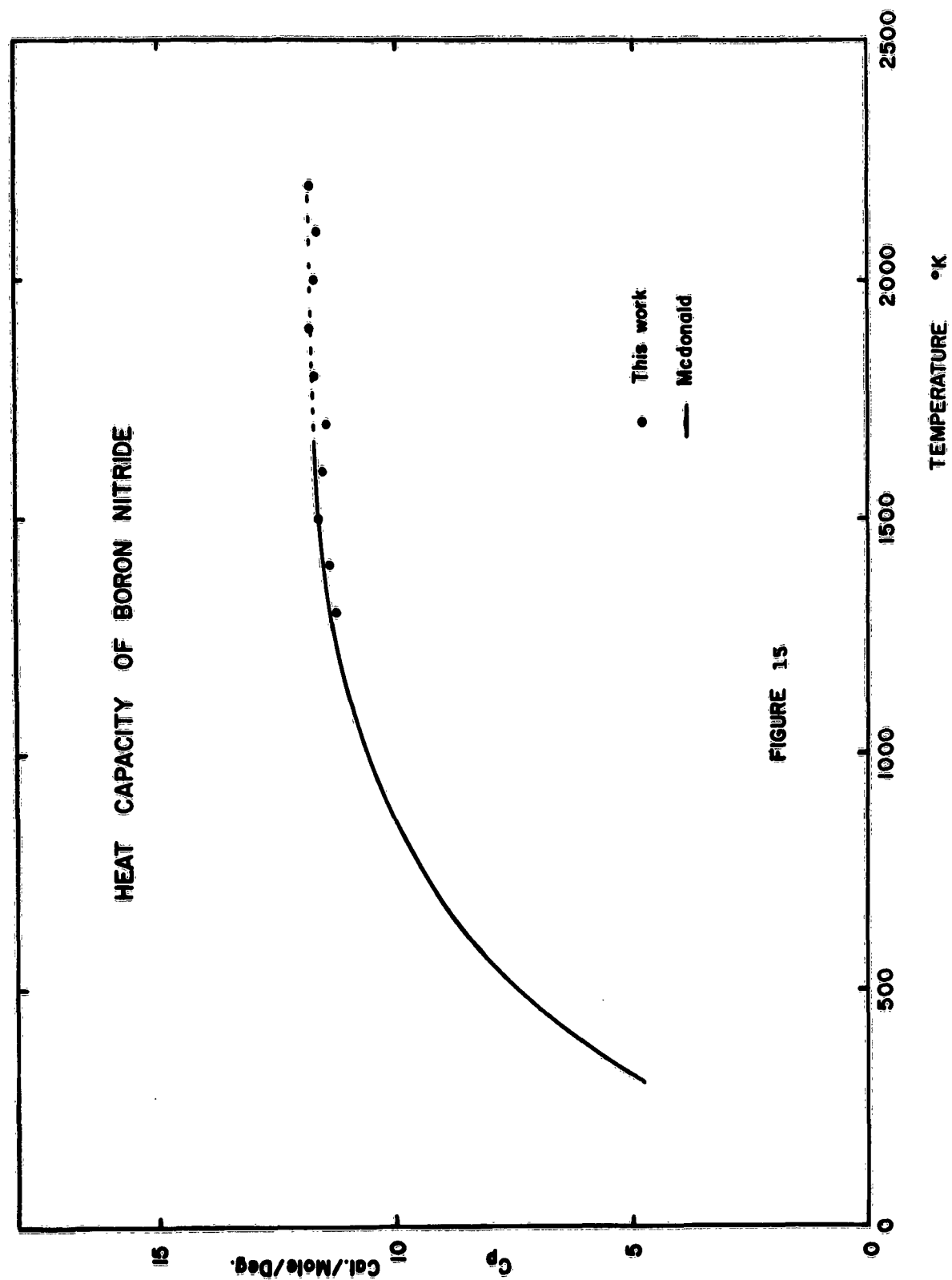


FIGURE 15

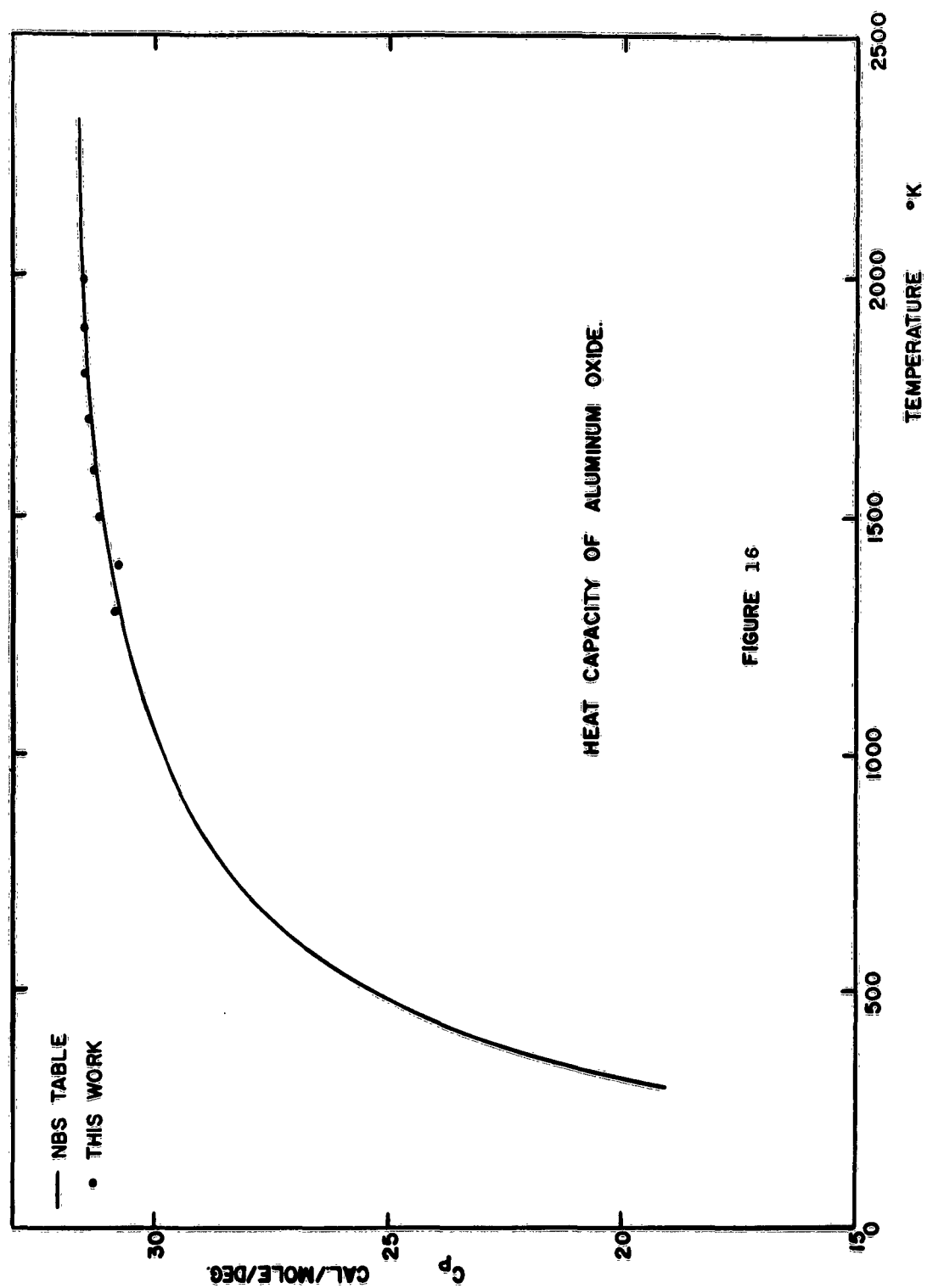
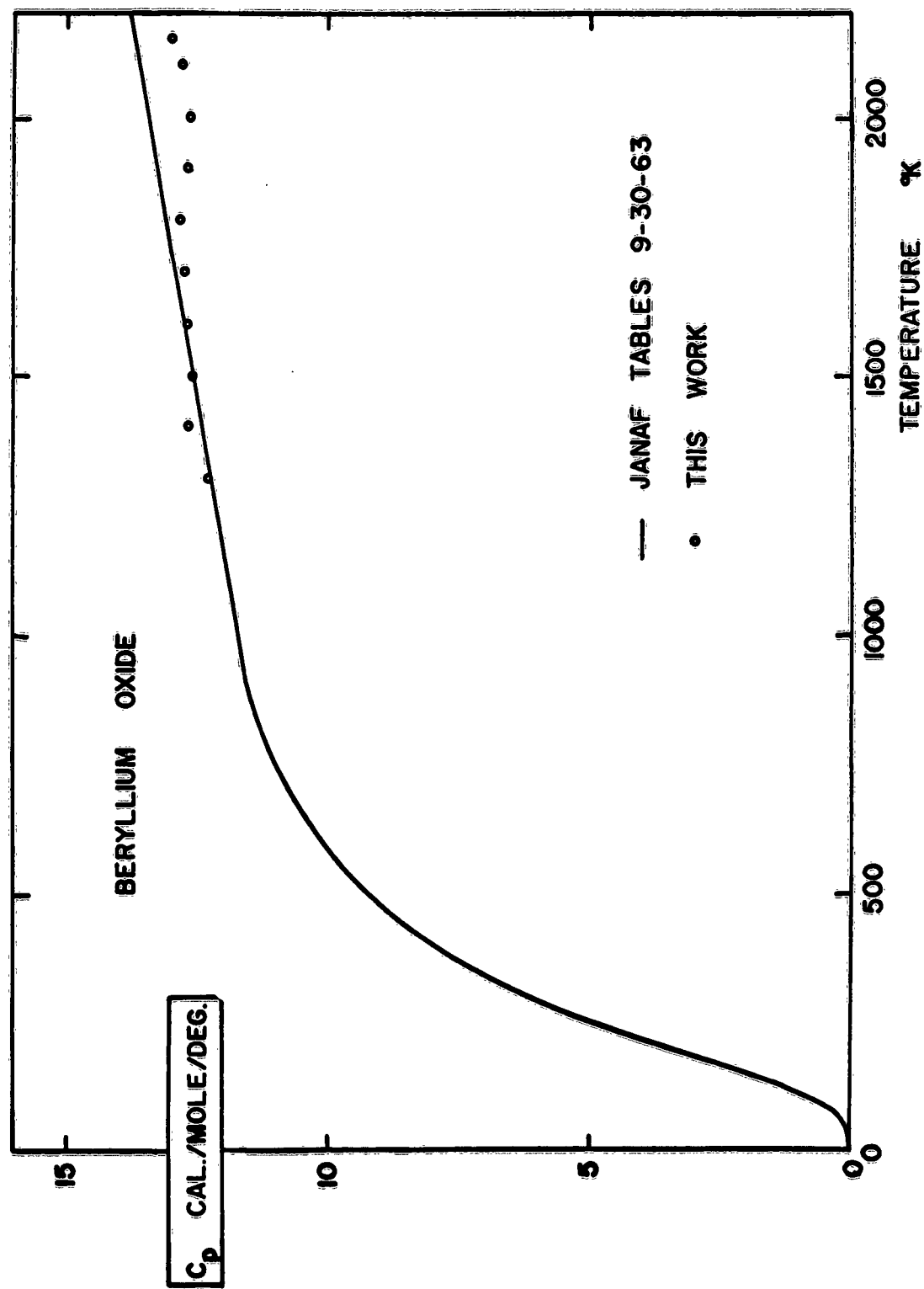


FIGURE 16

FIGURE 17



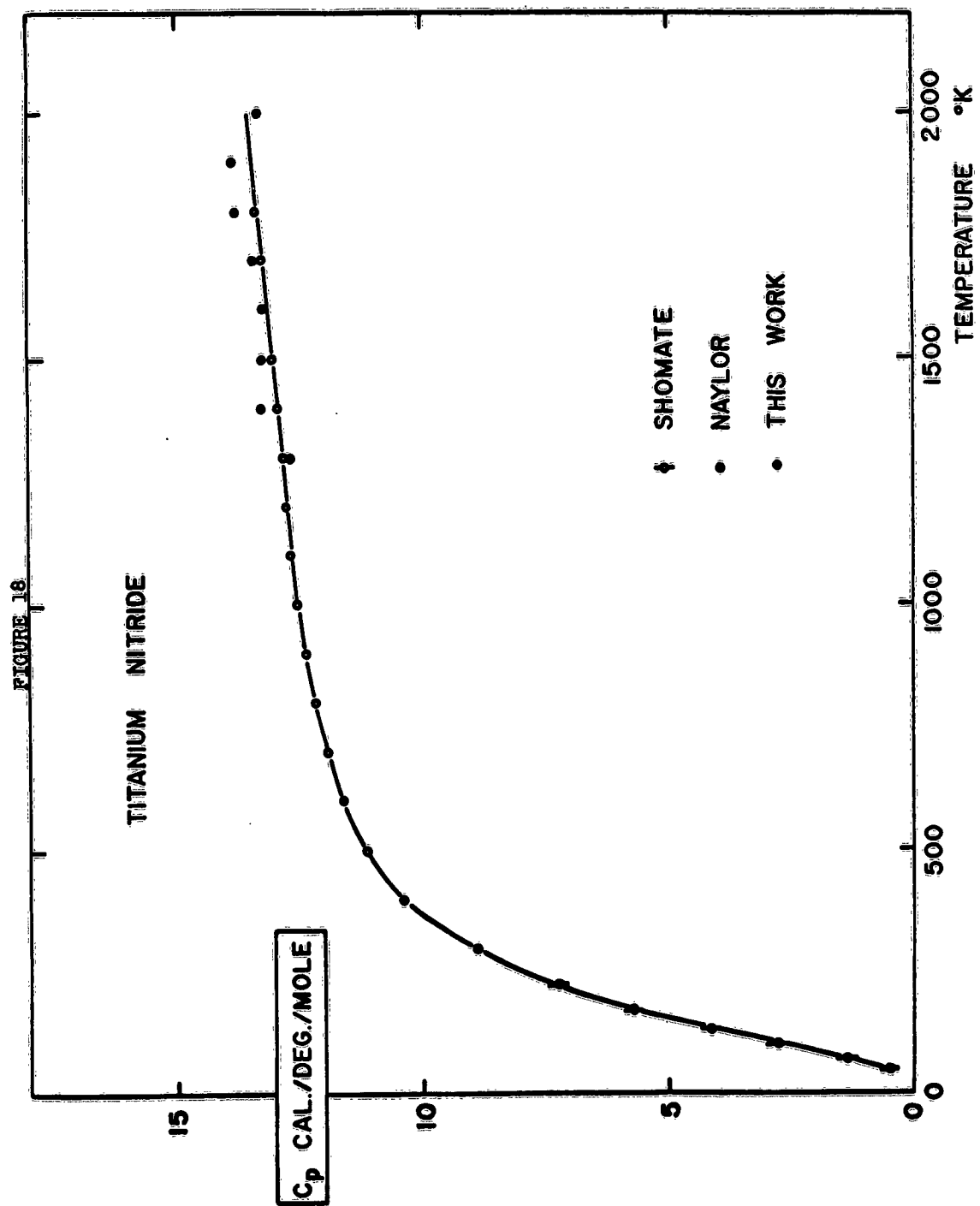


FIGURE 19

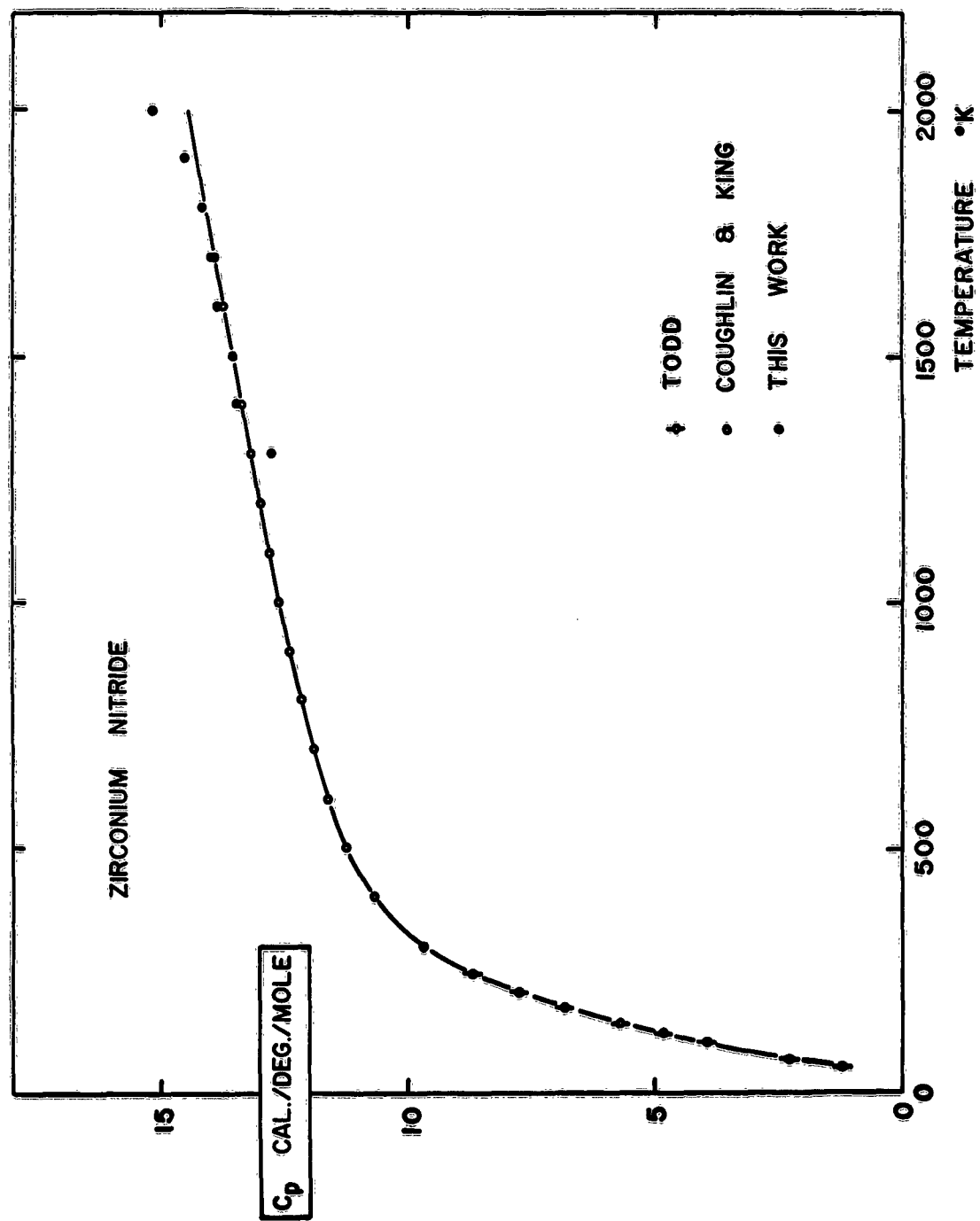
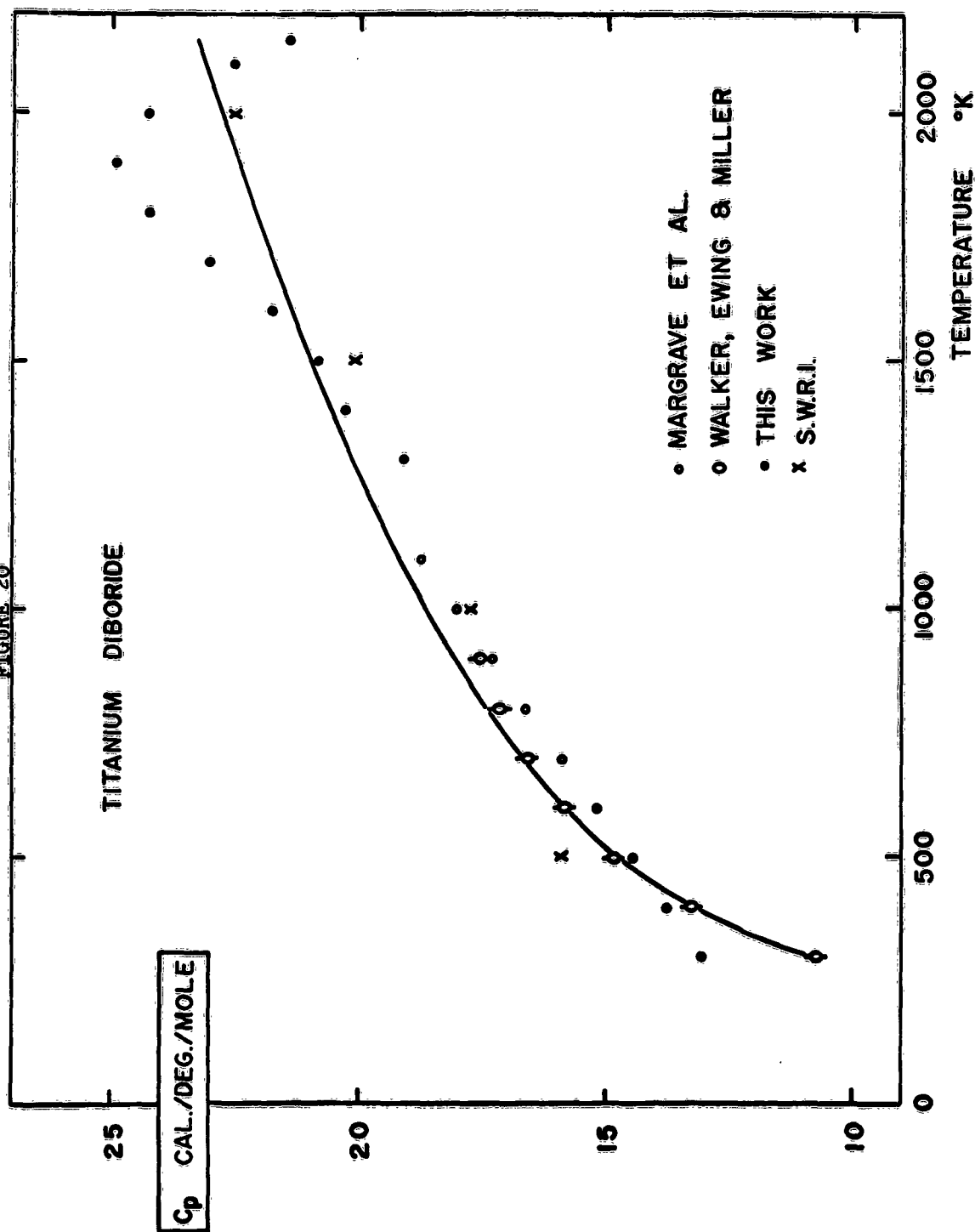


FIGURE 20



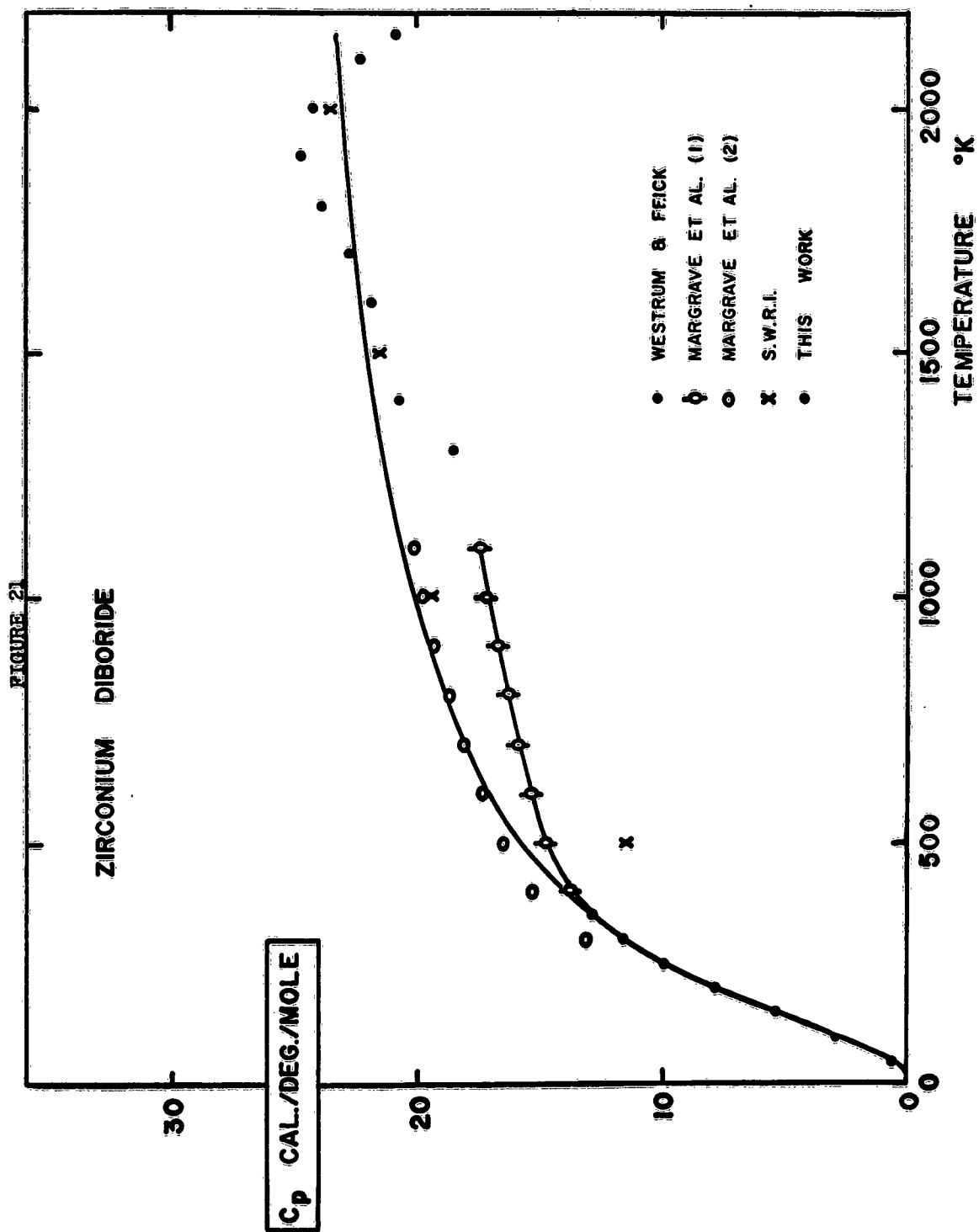


FIGURE 22

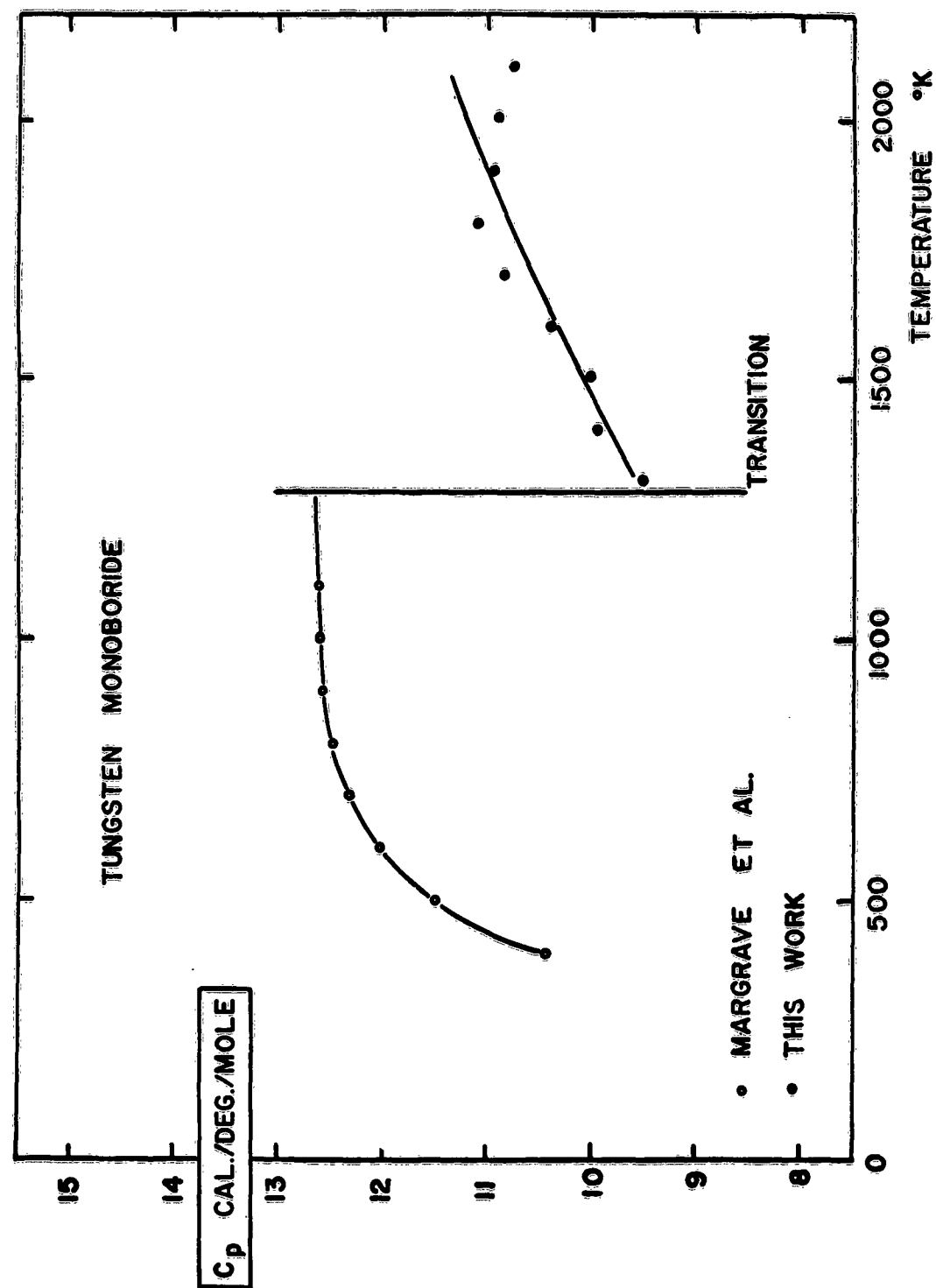


Figure 25 is a plot of specific heat (C_p) in cal./deg./mole versus temperature in degrees Kelvin for Ditungsten pentaboride. The y-axis ranges from 0 to 40+ cal./deg./mole, and the x-axis ranges from 0 to 2000 K. The plot shows two sets of data points: open circles representing Margrave et al.'s data and filled circles representing data from 'this work'. A smooth curve is drawn through the data points, showing a steady increase in specific heat with temperature. The data from 'this work' closely follows the curve established by Margrave et al.'s data.

Temperature (°K)	C_p (cal./deg./mole) - Margrave et al.	C_p (cal./deg./mole) - This Work
0	28	28
500	31	31
1000	35	35
1500	39	39
2000	42	42

FIGURE 24'

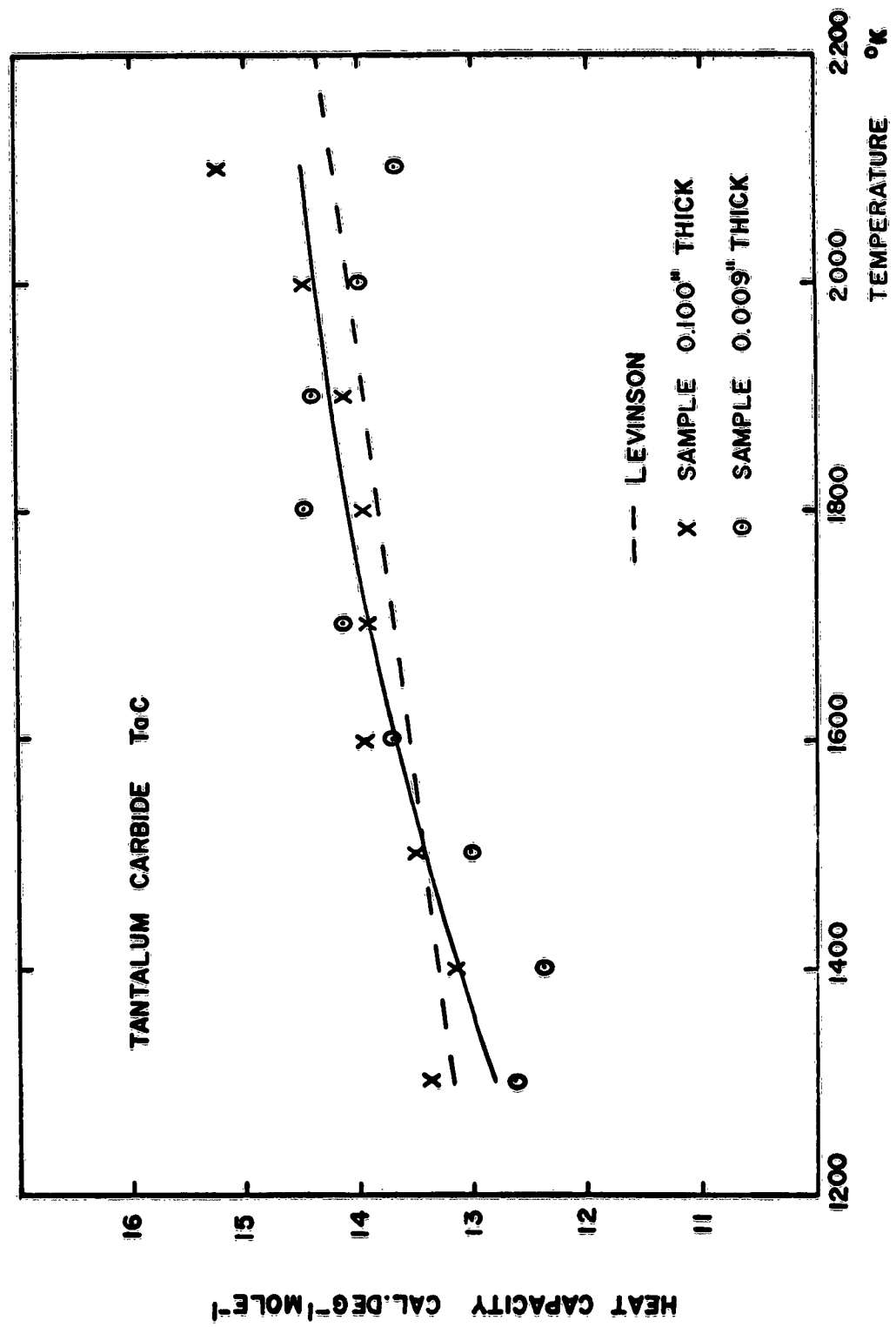


FIGURE 25

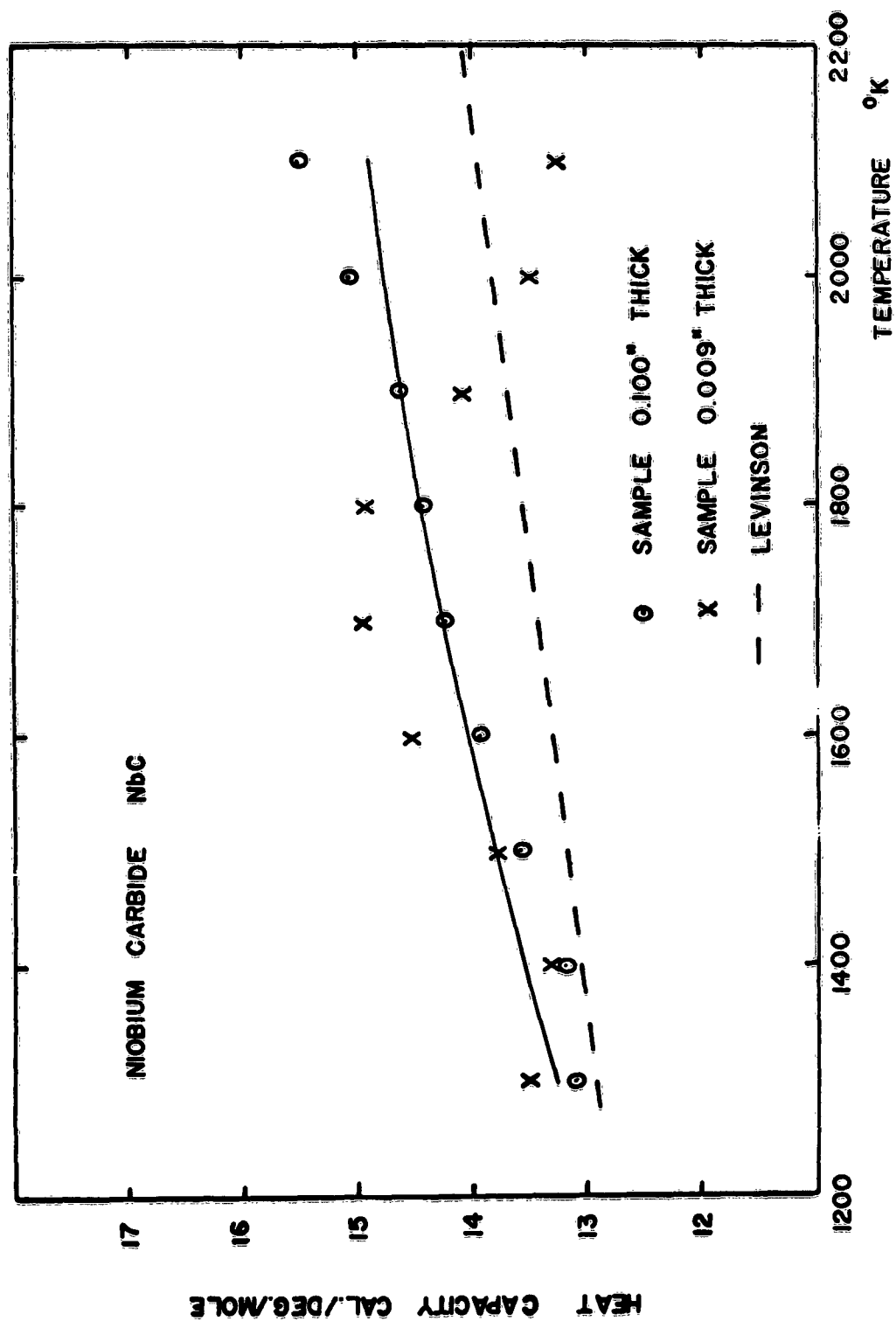


FIGURE 26

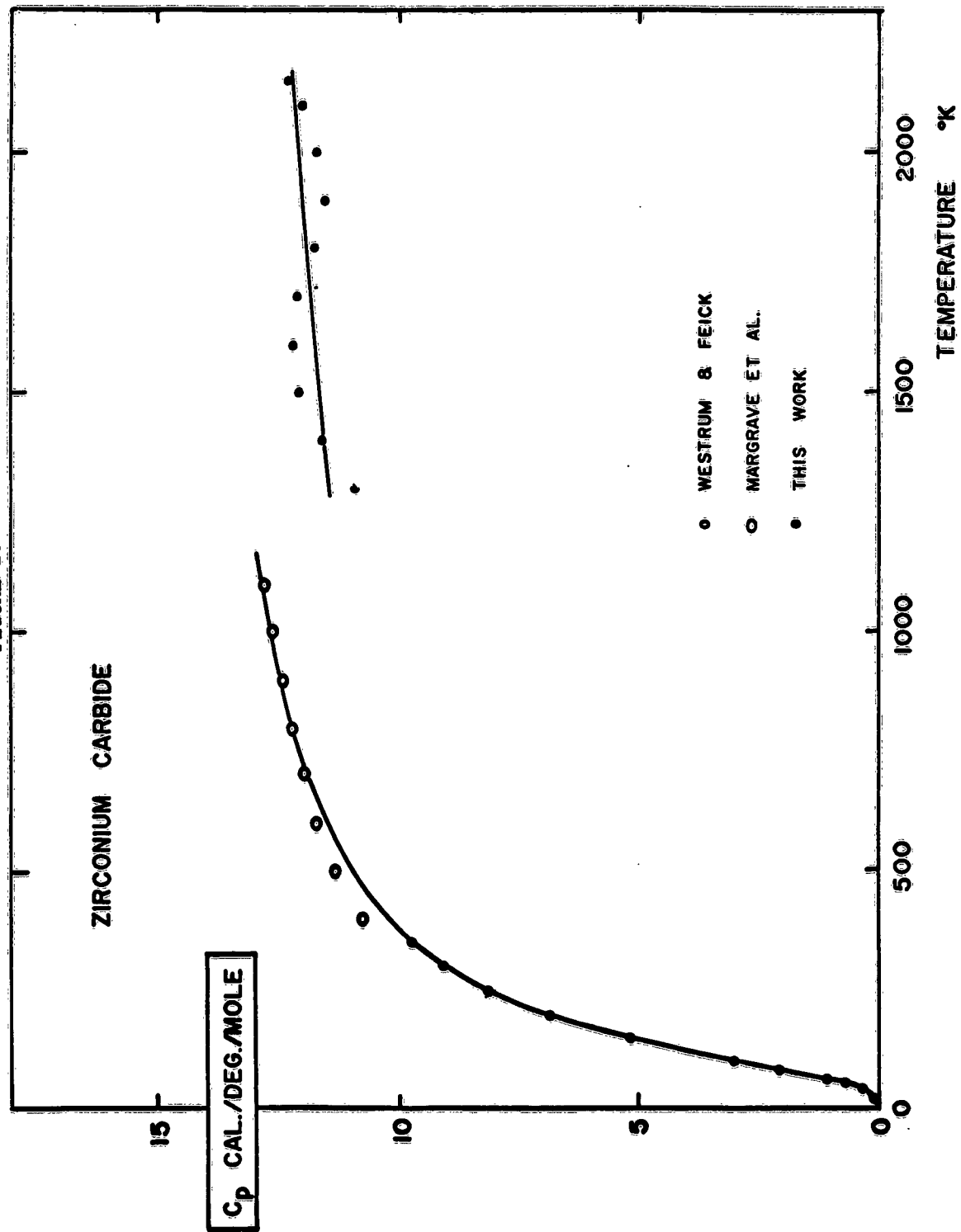


FIGURE 27

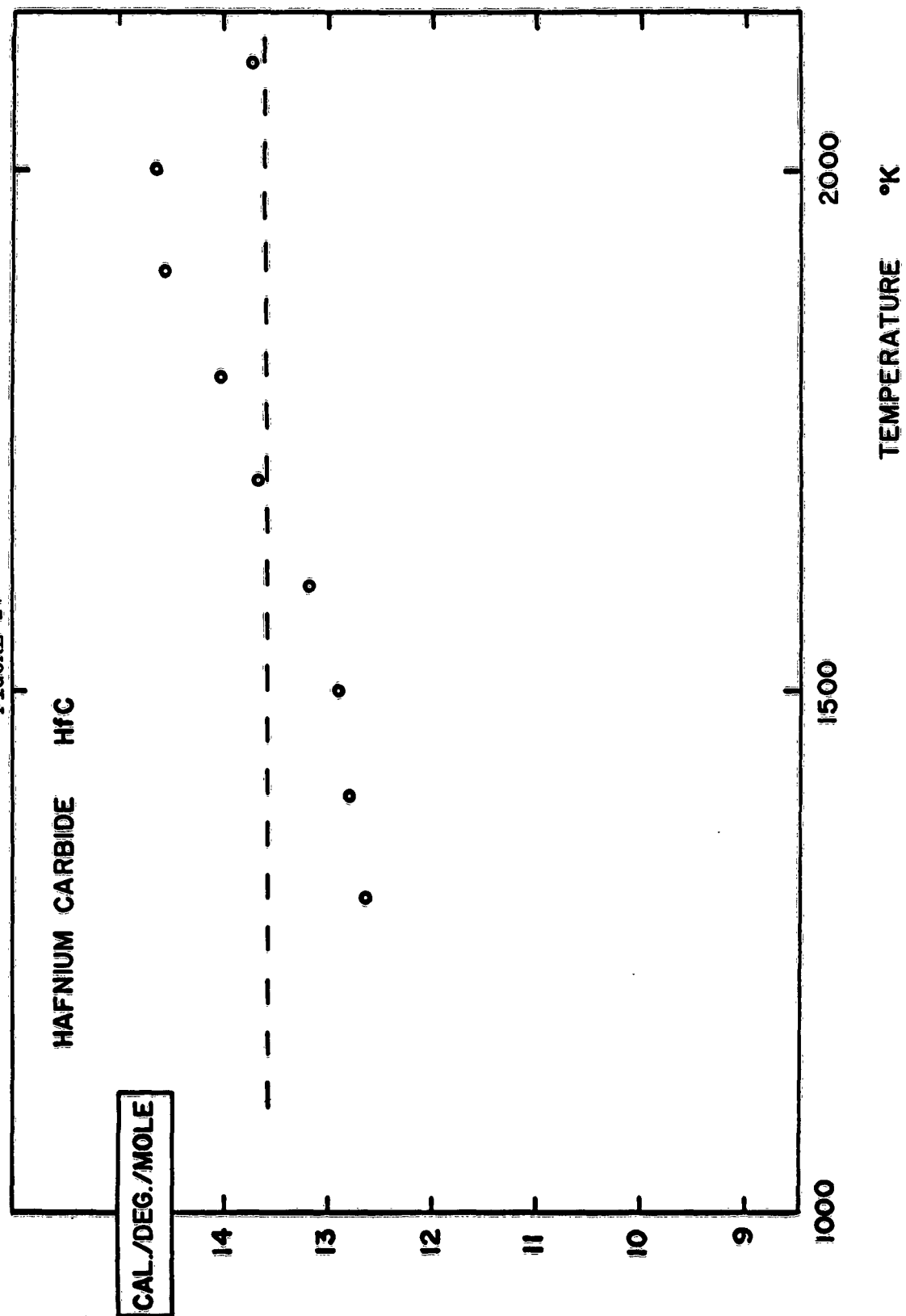
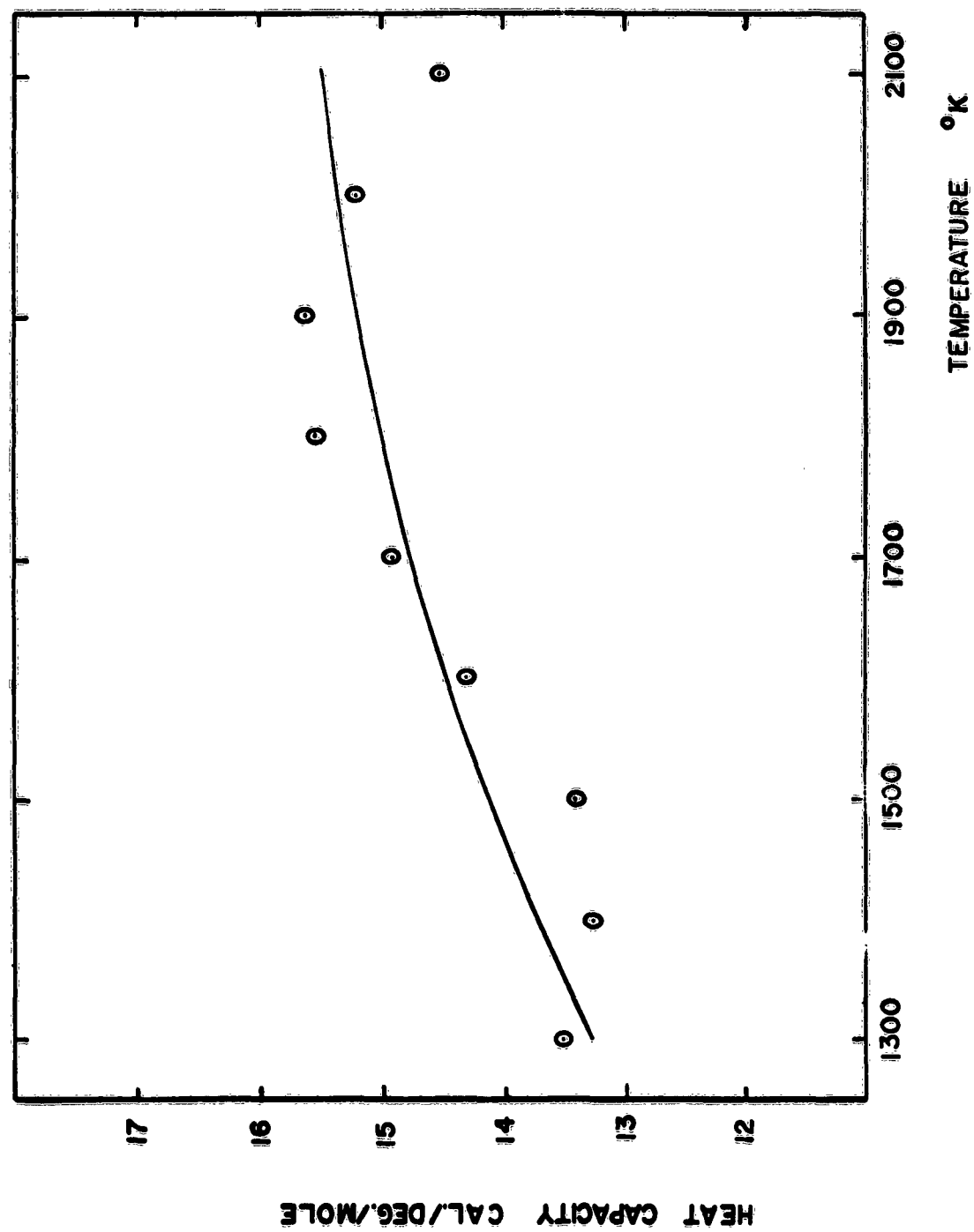


FIGURE 28



ATTENDANCE ROSTER

Armstrong, George T.
Beckett, Charles W., Jr.
Berkowitz, Joseph
Blackburn, Paul
Breazeale, Jack D.
Brown, Billins
Buchler, Alfred
Butts, Philip G.
Buell, Charles R.
Calsibet, Roger A.
Coates, Ralph L.
Cooper, William J.
Coughlin, James P.
Cubiciotti, Daniel D.
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