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268 955

Publication No. U-1497

RESEARCH LABORATORIES

# TECHNICAL REPORT

AN EXPERIMENTAL PROGRAM FOR OBTAINING  
THE THERMODYNAMIC PROPERTIES OF PROPELLANT  
COMBUSTION PRODUCTS

SECOND QUARTERLY TECHNICAL SUMMARY REPORT

Prepared for: Bureau of Naval Weapons (ARPA)  
Department of the Navy  
Washington 25, D. C.

Under Contract: NOW61-0905-c Task 1C  
ARPA Order No. 22-61

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15 December 1961

**AERONUTRONIC**

A DIVISION OF *Ford Motor Company*

FORD ROAD / NEWPORT BEACH, CALIFORNIA



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## SUMMARY

Additional mass spectrometric studies of the boron oxyfluoride monomer-trimer equilibrium yield the value  $\Delta H_{298}^{\circ} = -146$  kcal/mole for the gaseous BOF monomer. From a consideration of all studies to date, the present best value for the heat of formation of gaseous BOF monomer at  $298^{\circ}\text{K}$  is considered to be  $-143 \pm 3$  kcal/mole.

The torsion-effusion system used for equilibrium pressure measurement at temperatures above  $1000^{\circ}\text{C}$  has been modified so that all temperature measurements are now made by observing the radiation emitted from a black body cavity in the bottom of the effusion cell. The only results significantly affected by this change are those for aluminum nitride. A re-determination of the dissociation pressure using the new arrangement yields the value  $-76.1 \pm 2.1$  kcal/mole for the heat of formation of crystalline AlN at  $298^{\circ}\text{K}$ , in good agreement with recent calorimetric values.

Torsion-effusion studies of the vaporization of lithium oxide indicate that the gaseous  $\text{Li}_2\text{O}$  molecule is more stable than previously believed. Measured pressures are an order of magnitude higher than pressures calculated for decomposition to the elements, and, in addition, indicate that the condensation coefficient may be as low as 0.003. The heat of sublimation of  $\text{Li}_2\text{O}$  at  $298^{\circ}\text{K}$  is derived as  $95.0 \pm 3$  kcal/mole, which leads to  $\Delta H_{298}^{\circ} = 47.6 \pm 3$  kcal/mole for  $\text{Li}_2\text{O}$  (g).

The vapor pressure and vapor molecular weight of crystalline magnesium chloride have been determined from torsion-Knudsen measurements. Results indicate a high degree of polymerization in the saturated vapor, and are compatible with 100 percent dimeric composition. The heat of



sublimation and heat of formation of  $Mg_2Cl_4$  (g) at  $298^\circ K$  have been derived as  $63.3 \pm 2$  kcal/mole and  $-243.5 \pm 2$  kcal/mole, respectively.

Transpiration studies of the reaction of zirconia with gaseous HCl are being made in the  $900 - 1400^\circ K$  range. Conditions for achieving saturation of the flow gas have been determined, and a temperature study of the reaction has been made. Possible stoichiometries and thermal properties are discussed.

A summary of present "best values" of thermodynamic properties obtained from this experimental program has been prepared and is included in this report.



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## SECTION 1

### INTRODUCTION

The studies reported here are part of an experimental program which is designed to provide thermodynamic data required in the analysis of propulsion systems. Specific areas of study are the thermodynamics of vaporization of light metal compounds and the specific heats of condensed phases. Vaporization data, from which heats and free energies of formation of important species can be derived, are being obtained by effusion, transpiration and mass spectrometric techniques. A method is under development for determination of specific heats from measurements of vacuum cooling rates.

The results of some of these studies are described in the following sections.

## SECTION 2

## EFFUSION STUDIES

## 2.1 EXPERIMENTAL

Attempts to improve the reliability and overall accuracy of temperature measurements associated with the inductively heated torsion-effusion apparatus (i.e., for effusion studies above 1200°K) were discussed in the previous report<sup>1</sup>. It appeared then that a reliable temperature scale could be established by comparing optical pyrometer readings, obtained by sighting through a small hole in the susceptor onto the bottom of the effusion cell, with the output of a standard platinum, platinum-rhodium thermocouple whose junction was located in the sealed sample chamber of the cell. Subsequent experiments, however, indicated that resultant temperatures were influenced by changes in the surface emissivity of the effusion cell bottom, in spite of the small sight hole and fairly uniform heating of the susceptor. Because of continued exposure of the cell to high temperature vapors of various kinds and consequent deposition, it is not possible to maintain a constant surface emissivity.

In order to avoid these difficulties, the experimental arrangement was modified so that the pyrometer could sight into a black body cavity in the cell bottom. For the graphite cells, a cylindrical cavity

0.25 cm in diameter and 1 cm deep was drilled in the solid center section. The tantalum centering stud attached to the susceptor bottom was moved off-center in order to accommodate the new sight path. This method of temperature measurement is believed to be one of the most reliable that can be devised, provided the pyrometer calibration and the prism and window transmissivities are known.

A check was made on possible temperature measurement errors in previously reported vaporization studies and the effects which these errors might have on derived thermal properties. Only the aluminum nitride results<sup>1</sup> require significant revision, and these are discussed in the next section. The comparison measurements of the vapor pressure of gold were repeated with the new experimental arrangement and the results are presented in the Appendix. The new data for gold, which differ somewhat from those previously reported,<sup>1</sup> are the more reliable and indicate highly satisfactory operation of the apparatus.

## 2.2 VAPORIZATION OF ALUMINUM NITRIDE

The torsion-effusion measurements of the dissociation pressure of crystalline aluminum nitride were repeated using graphite effusion cells equipped with black body cavities, making temperature measurement as described above. The purity of the sample and other details of the measurements have been described previously<sup>1</sup>. The new data confirm the low condensation coefficient observed earlier ( $\leq 0.0022$ ), but show that previously reported temperatures were low by  $60 \pm 5^\circ$ . A summary of the corrected dissociation pressure ( $P_T$ ) data, together with derived equilibrium pressures ( $P_e$ ) and heats of dissociation, is given in Table I. Free energy functions for AlN(s) were calculated from the recent entropy and heat content data of Kelley<sup>2</sup> and functions for the elements were taken from standard sources. For the reaction

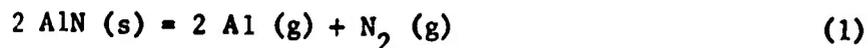


TABLE I

ALUMINUM NITRIDE DISSOCIATION PRESSURES AND HEAT OF THE REACTION



(Corrected)

T°K	P <sub>T</sub> × 10 <sup>5</sup> , atm	P <sub>e</sub> × 10 <sup>5</sup> , atm	ΔH <sub>298</sub> , kcal
Cell 3			
1894	3.78	39.5	307.8
1917	5.88	61.2	306.5
1908	5.28	55.1	306.4
1883	3.39	35.4	307.4
1861	2.56	26.7	307.0
1894	3.90	40.8	307.6
1908	5.13	53.6	306.7
1898	4.32	45.1	307.2
Cell 4			
1818	3.40	14.8	306.5
1877	7.28	31.8	307.8
1899	12.6	55.0	305.0
1887	9.80	42.7	306.0
1840	4.66	20.3	306.6
1782	1.87	8.1	306.6
1795	1.87	8.1	309.1
1846	4.63	20.2	307.8
1887	8.70	38.0	307.3
1887	9.34	40.6	306.5
1901	11.9	51.9	306.1
1911	13.0	56.6	306.6
Cell 5			
1846	12.7	20.8	307.4
1899	26.0	42.6	307.9
1919	34.6	56.7	307.3
1880	20.0	32.8	307.7
1845	11.6	19.0	308.2
1803	6.1	10.0	308.2
1776	4.0	6.6	308.1
1972	68.3	112.0	308.1
1934	40.3	66.0	308.4

Av. 307.3 ± 0.7

TABLE I (Continued)

	$\bar{a}, \text{cm}^2$	$\bar{c}$	$\Sigma \text{afq}, \text{cm}^3$	$P_e/P_T$
Cell 3	0.0105	0.75	0.01872	10.45
Cell 4	0.0046	0.61	0.00681	4.36
Cell 5	0.0010	0.54	0.000977	1.64

$$P_e = P_T \left( 1 + \frac{Ca}{2A} \right)$$

the values of  $-\Delta(F - H_{298}/T)$  used were 112.5, 112.3 and 112.1 cal/mole deg. at 1700, 1800 and 1900°K, respectively. The average third law heat of reaction (1),  $\Delta H_{298} = 307.3 \pm 0.7$  kcal, is assigned an accuracy uncertainty of  $\pm 2.8$  kcal, based on an analysis of experimental errors. Because of the correction for temperature error and the use of more reliable free energy functions for AlN (s), this new value for  $\Delta H_{298}$  is about 10 kcal higher than that reported earlier<sup>1</sup>. The heat of dissociation,  $307.3 \pm 2.8$  kcal, can be combined with the heat of sublimation of aluminum,  $\Delta H_{298} = 77.5 \pm 1.5$  kcal/mole, to derive the heat of formation of crystalline AlN at 298°K as  $-76.1 \pm 2.1$  kcal/mole. This result is in good agreement with the calorimetric determinations of Neugebauer and Margrave ( $-76.5$  kcal/mole)<sup>3</sup> and Kelley ( $-75.6$  kcal/mole)<sup>2</sup> which would indicate that the heat of formation of AlN is firmly established.

### 2.3 VAPORIZATION OF LITHIUM OXIDE

The vapor pressure of crystalline lithium oxide has been measured over the range 1510 to 1630°K by the torsion-effusion method. Measurements were made with two platinum effusion cells of different orifice size. The  $\text{Li}_2\text{O}$  sample was prepared by thermal decomposition of  $\text{Li}_2\text{CO}_3$ , as described by Brewer and Margrave<sup>4</sup>; after the initial preparation and loading of the effusion cell, all of the torsion measurements were completed without further exposure of the sample to the atmosphere. The resultant data are given in Table II and are shown graphically in Figure 1. Significantly higher pressures are obtained with the smaller orifices, indicating a condensation coefficient of about 0.003. It can also be seen from Figure 1 that the observed pressures are appreciably higher than pressures calculated assuming decomposition to the gaseous elements, which would indicate formation of a stable gaseous oxide molecule. Figure 1 shows that the results are in general agreement with the effusion data of Brewer and Margrave<sup>4</sup>,

**TABLE II**

**VAPOR PRESSURE OF LITHIUM OXIDE**

T°K	Pt Cell 1		T°K	Pt Cell 2	
	P <sub>T</sub> x 10 <sup>5</sup> , atm			P <sub>T</sub> x 10 <sup>5</sup> , atm	
	Series I		Series I		
1579	4.4		1566	6.0	
1568	3.3		1591	9.0	
1539	2.2		1606	10.3	
1522	1.6		1618	13.0	
1575	4.2		1616	11.8	
1559	3.3		1588	7.7	
1550	2.8		1573	7.4	
1532	2.2				
1513	1.6				
	Series II		Series II		
1573	3.8		1549	5.7	
1583	4.3		1598	9.0	
1594	5.1		1560	5.9	
1560	3.0		1626	15.4	
1540	2.4		1610	12.4	
			1601	11.5	

$\bar{a} = 0.0112 \text{ cm}^2$

$\text{Ca/A} = 0.0059$

$\Sigma \text{afq} = 0.0213 \text{ cm}^3$

$\bar{a} = 0.00442 \text{ cm}^2$

$\text{Ca/A} = 0.0021$

$\Sigma \text{afq} = 0.00770 \text{ cm}^3$

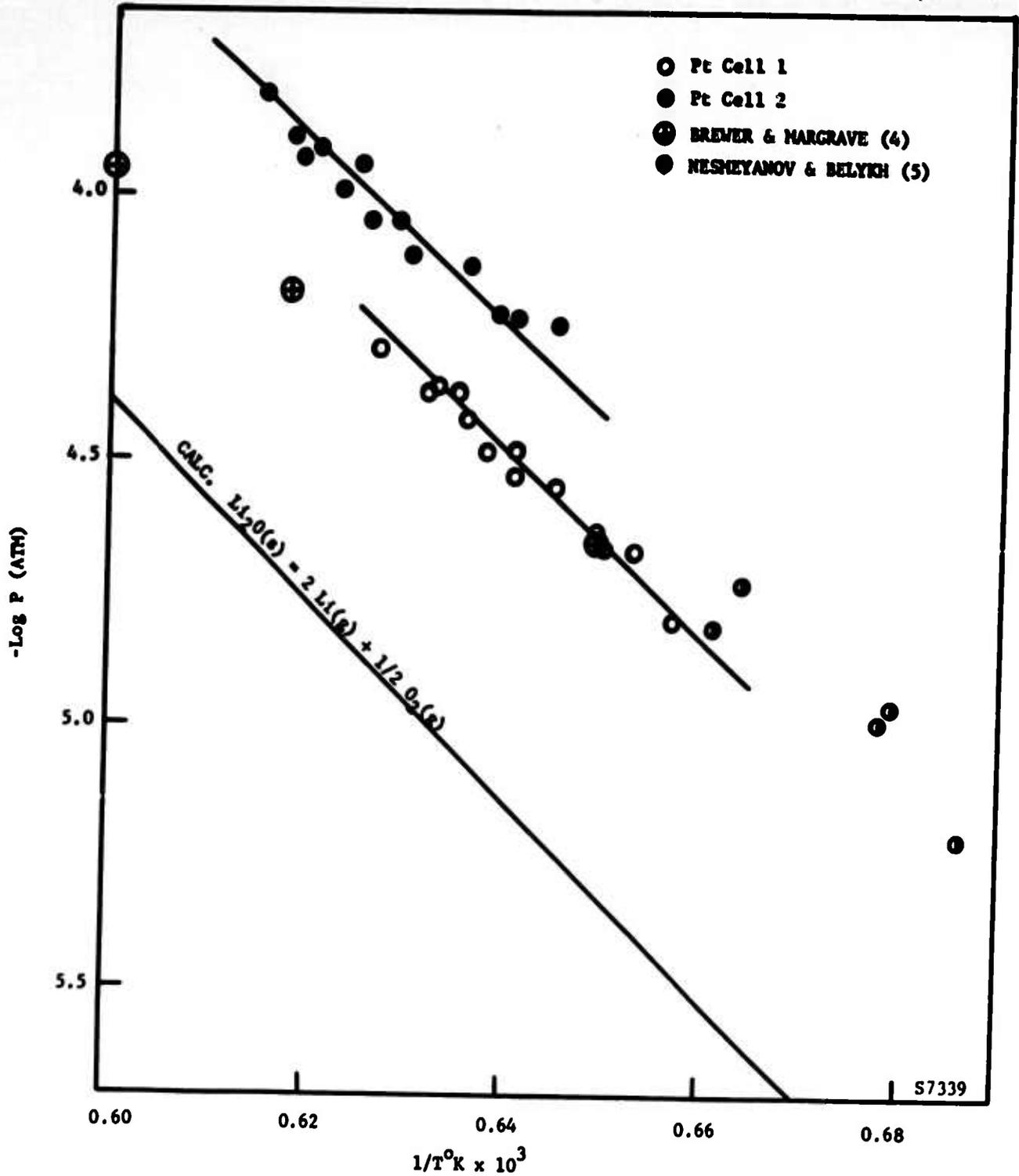


FIGURE 1. VAPOR PRESSURE OF LITHIUM OXIDE

whose data contain too much scatter for a hole size correlation, and Nesmeyanov and Belykh<sup>5</sup>, who used only one orifice size. These results, however, all differ considerably with the mass spectrometer-effusion studies reported by Berkowitz et al.<sup>6</sup>, which were interpreted in terms of sublimation by decomposition to the elements. The discrepancy may be due in part to the absolute pressure calibration, which involved directly the intensity of the  $m/e$  32 ( $O_2^+$ ) peak, a mass position with large background contribution. Because of the difficulty in distinguishing between effusing species and background for permanent gases, it would be hard to relate the  $I_{32}^+$  intensity to the oxygen pressure in the effusion cell.

The mass spectral data of Berkowitz et al.<sup>6</sup> do indicate that  $Li_2O$  is the most important gaseous oxide species in this system, with  $LiO$  being of very minor importance. On this basis, the data reported here are interpreted in terms of the sublimation process



as the principal reaction. From available thermal data for  $Li_2O (s)$  and estimated thermal functions for  $Li_2O (g)$ , values of  $-\Delta(F-H_{298}/T)$  for reaction (2) were calculated as 42.5 and 42.1 cal/mole deg at 1500 and 1600°K, respectively. A third law calculation using the pressure data of Cell 2 (smallest orifices) yields the value 96.6 kcal/mole for the heat of sublimation of  $Li_2O$  at 298°K, while a calculations made with equilibrium pressures derived from the hole size correlation yields

$\Delta H_{sub,298} = 95.0$  kcal/mole. Using the same free energy functions, one calculates  $\Delta H_{sub,298}$  values for  $Li_2O$  of 98.0 and 96.2 kcal/mole from the uncorrected Knudsen pressure data of Brewer and Margrave<sup>4</sup> and Nesmeyanov and Belykh<sup>5</sup>, respectively. The third law ( $\Delta H_{sub,298} = 108.2$  kcal/mole) and second law ( $\Delta H_{sub,298} = 115.9$  kcal/mole) heats of

sublimation of  $\text{Li}_2\text{O}$  derived from the mass spectrometric studies of Berkowitz et al.<sup>6</sup> seem much too high, and require further checking. For the present, the heat of sublimation of  $\text{Li}_2\text{O}$  at  $298^\circ\text{K}$  is taken as  $95.0 \pm 3$  kcal/mole, from which  $\Delta H_{298}^\circ$  for  $\text{Li}_2\text{O}$  (g) is derived as  $-47.6 \pm 3$  kcal/mole. The torsion measurements are being repeated with platinum effusion cells of somewhat different design in order to firmly establish the vaporization behavior and thermal properties in this system. Until these measurements are completed, the results reported here should be considered tentative.

#### 2.4 VAPORIZATION OF MAGNESIUM CHLORIDE

The torsion method has been used to measure the vapor pressure of crystalline magnesium chloride over the range  $870$  to  $985^\circ\text{K}$ . There are no previously reported vapor pressure data for the solid; in addition, the results will be useful in analyzing subsequent vaporization data on beryllium chloride, with particular reference to the extent of polymerization of the vapor. The resistance heated torsion apparatus has been described in a number of previous reports. Measurements were made with two different graphite effusion cells on a sample of  $\text{MgCl}_2$  prepared by dehydration of reagent grade  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in a stream of anhydrous  $\text{HCl}$ . Torsion pressures were calculated from the relation

$$P_T = \frac{2 k \theta}{\sum a f q} \quad (3)$$

where  $k$  is the torsion constant of the filament,  $\theta$  is the observed angular deflection and  $a$ ,  $f$ , and  $q$  are the area, force factor and moment arm of each of the effusion orifices. Results are presented in Table III and are plotted as  $\log P$  versus  $1/T$  in Figure 2. The measured pressures show no observable dependence on orifice size and are, therefore, assumed to be equilibrium values. Several other series of measurements with each cell completely reproduced the data of Table III.

**TABLE III**
**VAPOR PRESSURE OF MAGNESIUM CHLORIDE**

Cell 7		Cell 9	
$T^{\circ}\text{K}$	$P_T \times 10^5, \text{ atm}$	$T^{\circ}\text{K}$	$P_T \times 10^5, \text{ atm}$
952.6	6.09	931.7	2.90
985.7	14.50	904.9	1.15
973.9	10.96	958.8	6.77
967.8	9.22	942.0	3.99
959.6	7.30	921.2	2.07
949.0	5.02	912.2	1.55
938.1	3.45	898.0	0.942
		891.4	0.753
		887.7	0.588
		872.5	0.325
		867.6	0.266
$\bar{a} = 0.0053 \text{ cm}^2$		$\bar{a} = 0.0120 \text{ cm}^2$	
$\Sigma afq = 0.00928 \text{ cm}^3$		$\Sigma afq = 0.02255 \text{ cm}^3$	

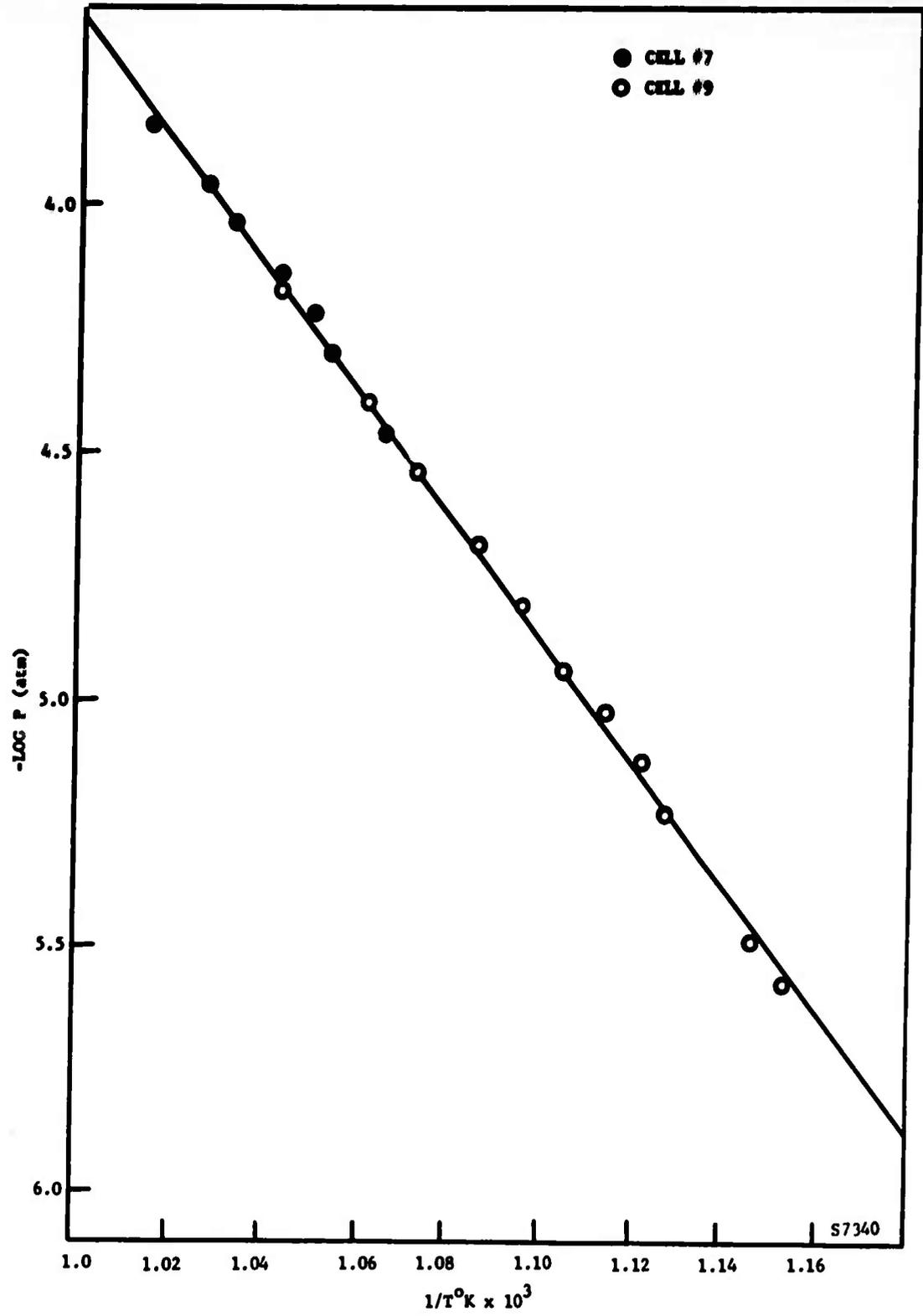


FIGURE 2. VAPOR PRESSURE OF MAGNESIUM CHLORIDE

Although Brewer<sup>7</sup> and others<sup>8</sup> have indicated that polymeric species will not be of importance in saturated  $\text{MgCl}_2$  vapor, the vapor molecular weight was determined by combining effusion weight loss measurements with the pressures measured by torsion-effusion. The quartz helix method of effusion weight loss measurement and the details of the vapor molecular weight determination have also been described in earlier reports on this program. From five weight loss measurements made with Cell 9 over the range 923 to 963<sup>o</sup>K, vapor molecular weights of 181.6, 208.9, 180.0, 195.1 and 196.4 were obtained ( $\text{MgCl}_2$  monomer = 95.23). Surprisingly, the average molecular weight of  $192.4 \pm 9$  indicates a high degree of polymerization in saturated  $\text{MgCl}_2$  vapor, and is, in fact, compatible with 100 percent dimeric composition ( $\text{MgCl}_2$  dimer = 190.46). An additional indication of vapor polymerization comes from calculated third law heats of sublimation which assume 100 percent monomeric vapor. These values of  $\Delta H_{298}$ , calculated with the aid of free energy functions which are quite reliable, show a consistent trend from 55.3 kcal/mole at 850<sup>o</sup>K to 54.4 kcal/mole at 985<sup>o</sup>K. Also, a second law calculation for monomeric vapor yields  $\Delta H_{298} = 60.6$ , some 6 kcal/mole higher than the third law value. These discrepancies are outside of experimental error and are indicative of sublimation to other than monomeric species.

Since it is expected that degree of polymerization will decrease with increasing atomic weight among the alkaline earths, saturated  $\text{BeCl}_2$  vapor must also be highly polymeric, although thermal properties now in use are consistent with only a small amount of polymerization. It is planned to investigate the vaporization of  $\text{BeCl}_2$  and  $\text{BeF}_2$  by the torsion method and also to check vapor species in both these and the  $\text{MgCl}_2$  system by mass spectrometry.

The presently accepted thermal properties for  $\text{MgCl}_2$  vapor, which are based on the liquid vapor pressure data of Maier<sup>9</sup>, must be in error. Considering sublimation to monomer, Maier's data yield

$\Delta H_{\text{sub},298} = 52.6$  kcal/mole, whereas the data reported here indicate

$\Delta H_{\text{sub},298} > 55$  kcal/mole for monomer. Based on the above results, it is assumed that the vapor is completely dimeric so that the pressure data can be interpreted in terms of the process



A second law calculation yields  $\Delta H_{900} = 57.5$  kcal/mole for reaction (4), and, if  $C_p \text{ dimer} (\text{g}) \approx 2 C_p \text{ monomer} (\text{g})$ ,  $\Delta H_{298} = 63.3 \pm 2$  kcal/mole. A third law calculation cannot be made until dimer thermal functions are available. These values lead to  $\Delta H_f^0_{298} = -243.5 \pm 2$  kcal/mole for  $\text{Mg}_2\text{Cl}_4 (\text{g})$ . The heat of dimerization of  $\text{Mg}_2\text{Cl}_4$  can be determined from torsion pressure measurements on the super-heated (and partially dissociated) vapor, and such measurements are planned.

## 2.5 VAPORIZATION OF LITHIUM FLUORIDE-ZIRCONIUM FLUORIDE MIXTURES

Because of interest in the properties of gaseous mixed halide species, the vaporization behavior of a lithium fluoride-zirconium fluoride mixture has been studied by the torsion method. The sample, a 1:1 mole ratio mixture, was prepared from pure fluorides used in other vaporization studies in this laboratory. The measurements indicated, however, that the vapor pressure of the mixture was lower than that of either of the constituent fluorides and, in addition, the pressure decreased steadily with time. Such behavior indicates preferential vaporization of the more volatile  $\text{ZrF}_4$ , and it is concluded that gaseous lithium zirconium fluoride species are not of major importance under these conditions.

SECTION 3

TRANSPIRATION STUDIES

3.1 THE ZIRCONIUM OXIDE-HYDROGEN CHLORIDE SYSTEM

The reaction of crystalline zirconium oxide with gaseous hydrogen chloride is being studied by the transpiration method in order to obtain information about the thermal properties of vapor species in the Zr - O - Cl system. The details of the transpiration apparatus and the methods of analyzing the data have been described previously<sup>10,11</sup>. For studies of the  $ZrO_2$  - HCl reaction, the transpiration tube and all interior fittings were constructed from fused silica. A sample of reagent grade  $ZrO_2$  powder, dehydrated under vacuum at  $1500^{\circ}C$ , was placed in a platinum boat and exposed to a stream of Matheson anhydrous HCl of about 99.5 percent purity. It was found that at temperatures of  $900^{\circ}K$  and above, significant and reproducible  $ZrO_2$  weight losses were obtained. It was necessary to keep the flow tube thoroughly flushed with HCl when inserting or removing the sample and to provide a long exit tube of reasonably small diameter in order to obtain reproducible results. The latter presumably prevented diffusion of air and/or reaction product back into the reaction zone. This would be necessary because of the relatively small extent of reaction observed.

In order to determine the conditions under which saturation of the HCl carrier gas could be achieved, the rate of  $ZrO_2$  weight loss was studied as a function of HCl flow rate at 1173 and 1380°K. It has been shown<sup>10</sup> that over the range of flow rates for which saturation is achieved without interference from diffusion, the rate of sample weight loss,  $k'$ , should vary linearly with carrier gas flow rate, and it should be possible to extrapolate a plot of  $k'$  versus  $v$  through the origin. The experimentally determined flow rate relations are shown graphically in Figure 3, from which it can be seen that the linear dependence, and thus equilibrium, is obtained up to at least 40  $cm^3/min$ . Furthermore, the plots can be extrapolated through the origin. It was found possible to extend the linear portion of the curve somewhat by increasing the sample surface area, but this had no effect on the slope. It is assumed, therefore, that under the conditions employed the flow gas is saturated with reaction product at flow rates in the range 10 to 40  $cm^3/min$ .

The extent of reaction has been studied at a number of temperatures over the range 900 to 1400°K, using HCl flow rates of about 30  $cm^3/min$ . Exposure times were approximately one hour. The experimental results are given in Table IV. Although the reaction stoichiometry has not been determined as yet, the results can be checked for consistency by plotting  $\log(k'/v)$  versus  $1/T$ . The partial pressure of gaseous reaction product "X" be expressed as

$$P_x = \frac{a k' RT}{v M} \quad (5)$$

where  $a$  is the number of moles of species "X" formed per mole of  $ZrO_2$  consumed,  $k'$  is the rate of  $ZrO_2$  weight loss,  $v$  is the HCl flow rate as measured at temperature  $T$ ,  $R$  is the gas constant and  $M$  is the molecular weight of  $ZrO_2$ . Since  $k'/v$  is directly proportional to  $P_x$ , and since

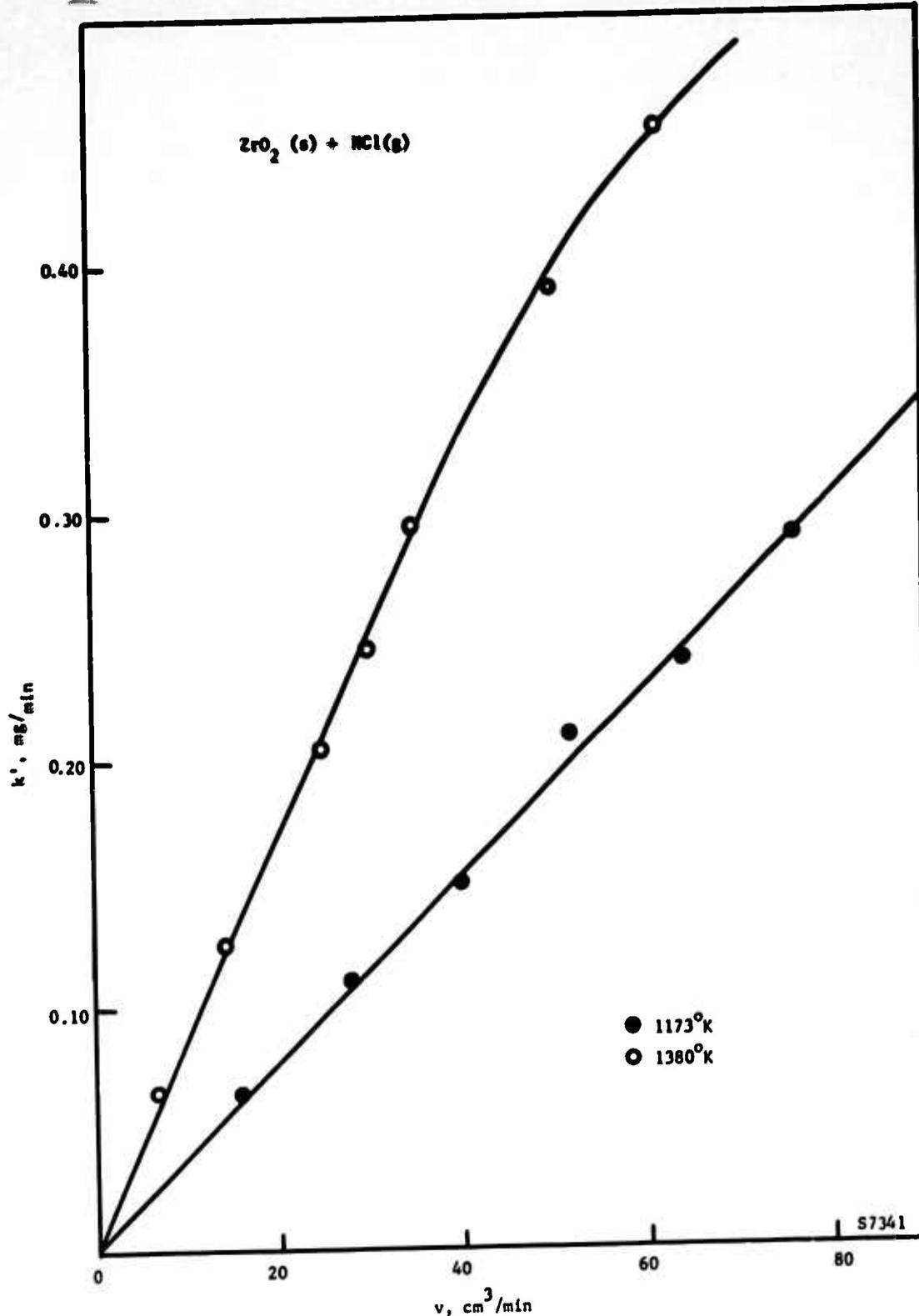


FIGURE 3. RATE OF  $ZrO_2$  WEIGHT LOSS AS A FUNCTION OF HCl FLOW RATE

TABLE IV

TEMPERATURE DEPENDENCE OF TRANSPIRATION  
WEIGHT LOSS FOR THE  $ZrO_2 + HCl$  REACTION

$T^{\circ}K$	$k'/v \times 10^6, g/cm^3$
915	1.32
962	1.72
1003	2.16
1061	3.11
1143	4.60
1184	5.28
1249	7.50
1368	8.23

the equilibrium constant for this reaction can be expressed as

$$K = A P_x^b \quad (6)$$

where A and b are constants determined by the stoichiometry, then  $\log (k'/v)$  is directly proportional to  $\log K$  and

$$\frac{d \log K}{d (1/T)} = b \frac{d \log (k'/v)}{d (1/T)} = \frac{-\Delta H}{R} \quad (7)$$

Therefore, a plot of  $\log (k'/v)$  versus  $1/T$  should be linear, and a second law heat can be evaluated from the slope when the constant b is known. Figure 4 shows such a plot of the data, which yields the second law heat

$$\Delta H_{1100} = (11.0) (b) \text{ kcal.}$$

The dependence of  $ZrO_2$  weight loss on HCl pressure is presently being studied so as to clarify the stoichiometry. HCl pressure is varied by dilution with purified argon; the total system pressure is held at one atmosphere.

A possible course of the reaction is



in which case  $b = 3$  and  $\Delta H_{1100} = \Delta H_{298} = 33 \text{ kcal}$  for reaction (8). A third law analysis indicates  $\Delta H_{298} = 29 \pm 1 \text{ kcal}$ . However, there are other possible reactions, particularly those leading to gaseous oxychloride formation. It seems better to postpone any further discussion of thermal properties until the stoichiometry is established.

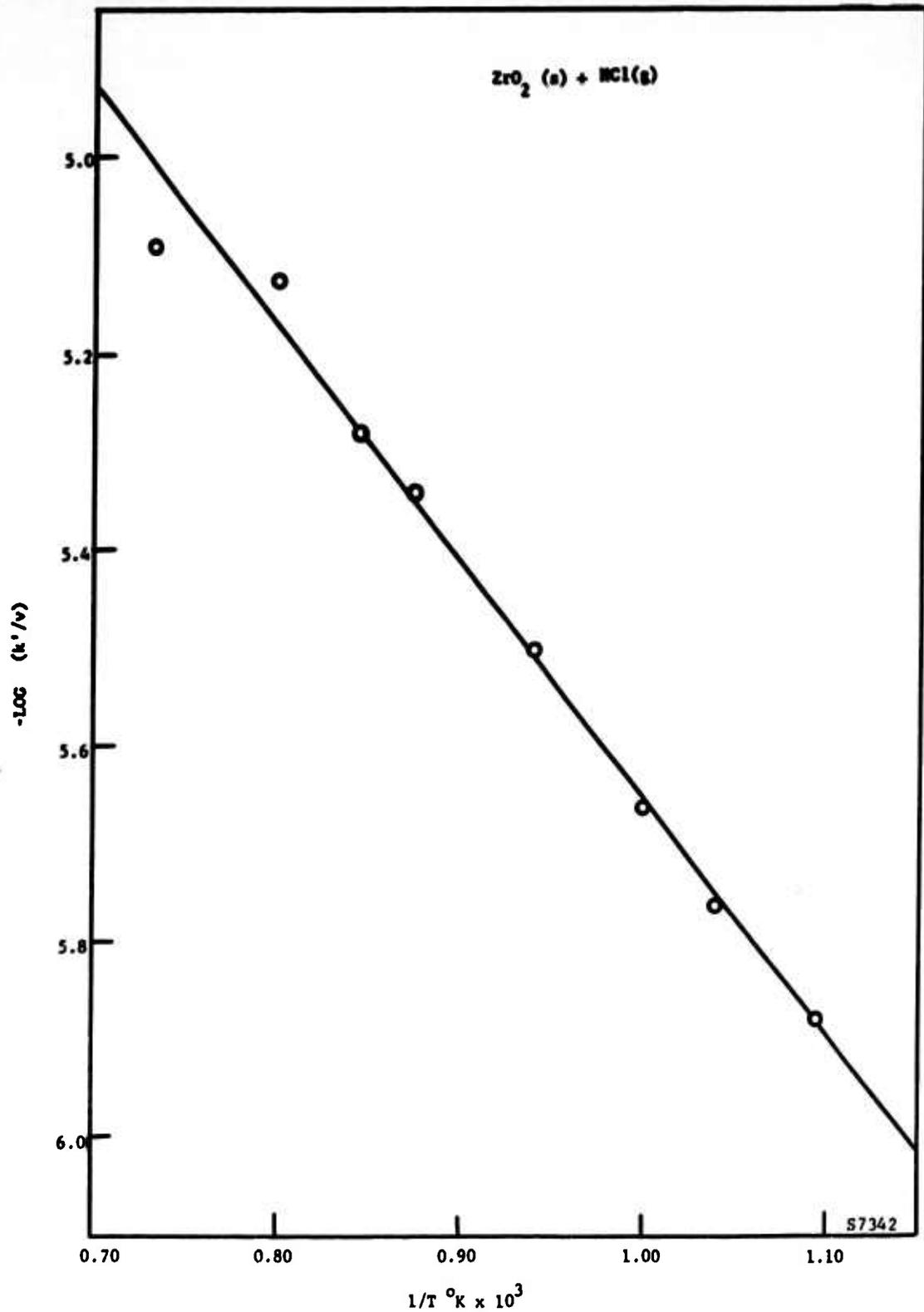


FIGURE 4. WEIGHT LOSS OF  $ZrO_2$  PER UNIT VOLUME HCl FLOW AS A FUNCTION OF TEMPERATURE

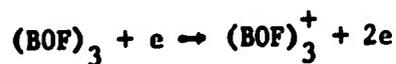
## SECTION 4

## MASS SPECTROMETRY

## 4.1 VAPOR SPECIES IN THE BORON-OXYGEN-FLUORINE SYSTEM

a. Mass Spectral Considerations

The problem of determining molecular progenitors of ion currents observed in the mass spectrometer was discussed briefly in the last quarterly report<sup>1</sup>. Appearance potential measurements and intensity ratio variations with temperature for ions from vapor species in equilibrium with condensed  $B_2O_3 - MgF_2$  mixtures indicate that  $(BOF)_3^+$  and  $BOF^+$  are formed predominantly by simple ionization of the corresponding molecular species, i.e.,



However, at higher ionizing electron energies it is possible that a part of the observed  $BOF^+$  ion current is due to a fragmentation process such as



In an effort to avoid contributions due to fragmentation, we have used 17-volt ionizing electrons for studying the  $(BOF)_3 - BOF$  equilibrium.

The mass spectrum of vapor in equilibrium with a 3:1 mole ratio mixture of  $B_2O_3$  and  $MgF_2$  at  $928^\circ C$  is given for both 17- and 60-volt electrons in Table V. Appearance potentials of important ions have already been reported<sup>1</sup>. Included in the Table is a spectrum obtained by Porter et al.<sup>12</sup> for products of the reaction between  $BF_3(g)$  and  $B_2O_3(l)$ . The instrument used was a 12-inch radius of curvature, direction focusing mass spectrometer, quite similar in design to the one in use at Aeronutronic. They employed  $BF_3$  pressures of one to  $10^{-3}$  mm of Hg inside an alumina crucible containing  $B_2O_3$  and temperatures between 100 and  $700^\circ C$ . Agreement between the spectrum obtained by Porter et al. and the corresponding portion of our spectrum for 60-volt electrons is very good, except for  $BOF^+$ . Porter et al. concluded, as did we, that  $B_3O_3F_2^+$ ,  $B_2OF_3^+$ ,  $B_2O_2F_2^+$  and  $B_2O_2F^+$  are all formed by fragmentation of  $(BOF)_3$ . They observed that the  $BOF^+/(BOF)_3^+$  ratio increased slightly as the pressure of  $BF_3$  was decreased, but considered the accuracy of the ratios not sufficient to allow a definite conclusion as to the number of molecular species giving rise to  $BOF^+$ . The disagreement in relative intensity of  $BOF^+$  between the two spectra strongly suggests that  $BOF^+$  is not formed solely by fragmentation. Furthermore, the direction of disagreement is in keeping with the assumption that much of the  $BOF^+$  ion current results from simple ionization of molecular  $BOF$ , whose pressure relative to that of  $(BOF)_3$  would be expected to decrease with decreasing temperature.

b. Equilibrium Between  $BOF$  and  $(BOF)_3$

Intensities of  $BOF^+$  and  $(BOF)_3^+$  for 17-volt electrons were studied in detail over the temperature range 1108 to  $1283^\circ K$ . Heights of the  $B^{11}OF^+$  peak, m/e 46, and the  $(B^{11}OF)_3^+$  peak, m/e 138, were assumed directly proportional to the equilibrium pressures of  $BOF$  and  $(BOF)_3$ , respectively. The equilibrium constant K of the reaction



TABLE V

MASS SPECTRAL DATA FOR VAPOR SPECIES  
IN THE BORON-OXYGEN-FLUORINE SYSTEM

m/e	Ion	This Work T = 928°C		Porter et al. T < 700°C
		17v* 100**	60v	75v
135,136,137,138	(BOF) <sub>3</sub> <sup>+</sup>	100**	100	100
116,117,118,119	B <sub>3</sub> O <sub>3</sub> F <sub>2</sub> <sup>+</sup>	6.9	9.8	9.6
93,94,95	B <sub>2</sub> OF <sub>3</sub> <sup>+</sup>		59.3	59.5
90,91,92	B <sub>2</sub> O <sub>2</sub> F <sub>2</sub> <sup>+</sup>		28.4	30.8
71,72,73	B <sub>2</sub> O <sub>2</sub> F <sup>+</sup>		11.7	11.3
67,68	BF <sub>3</sub> <sup>+</sup>	12.7	120	
65,66	BF <sub>2</sub> OH <sup>+</sup>	10.4	8.9	
48,49	BF <sub>2</sub> <sup>+</sup>	22.7	2294	
46,47	BFOH <sup>+</sup>	0.1	11.8	
45,46	BOF <sup>+</sup>	108	88.2	9.2
29,30	BF <sup>+</sup>		32.3	
10,11	B <sup>+</sup>		12.8	

\* Ionizing electron voltage.

\*\* Arbitrarily assigned intensity. All other ion intensities given relative to (BOF)<sub>3</sub><sup>+</sup>.

is then proportional to  $I_{46}^3 T^2 / I_{138}^+$ . A plot of the logarithm of this quantity versus  $1/T$  appears in Figure 5. From the slope of the straight line, the second law heat for reaction (9) is derived as  $\Delta H_{1200} = 124$  kcal. From estimated thermal functions,  $\Delta(H_{1200} - H_{298}) = 3.6$  kcal, and  $\Delta H_{298} = 128$  kcal. Combining the latter with  $\Delta H_{298}^{\circ} [(BOF)_3 (g)] = -566$  kcal/mole gives for  $\Delta H_{298}^{\circ} [BOF (g)]$ ,  $-146 \pm 5$  kcal/mole.

Because a greater number of points were taken, the present value for  $\Delta H_{298}^{\circ} [BOF (g)]$  is considered somewhat more accurate than the value previously reported,  $-141 \pm 5$  kcal/mole. The weighted average of all measurements to date is  $-143 \pm 3$  kcal/mole. However, the validity of the assumption of direct proportionality between ion intensities and equilibrium pressures is presently being reviewed. The effect of shutter position on ion currents due to permanent or semipermanent gases is somewhat different from that observed with condensible species and warrants special consideration.

#### 4.2 VAPORIZATION OF TIN

A study of the vaporization of tin was made with the mass spectrometer in order to evaluate certain operational characteristics of the instrument.

A mass spectrum of tin vapor effusing from a tungsten Knudsen cell at  $1469^{\circ}K$  is given in Table VI. Ion intensity for each isotopic species is given as percent of total  $Sn^+$  intensity. For comparison, percent natural abundances of the isotopes of tin are also given. The correlation is very good. The small differences observed can be almost completely accounted for on the basis of peak height reading error. Such agreement indicates the following:

- (1) Negligible mass discrimination from  $m/e$  112 to  $m/e$  124.
- (2) Linear detector response (electron multiplier, vibrating reed electrometer, recorder).

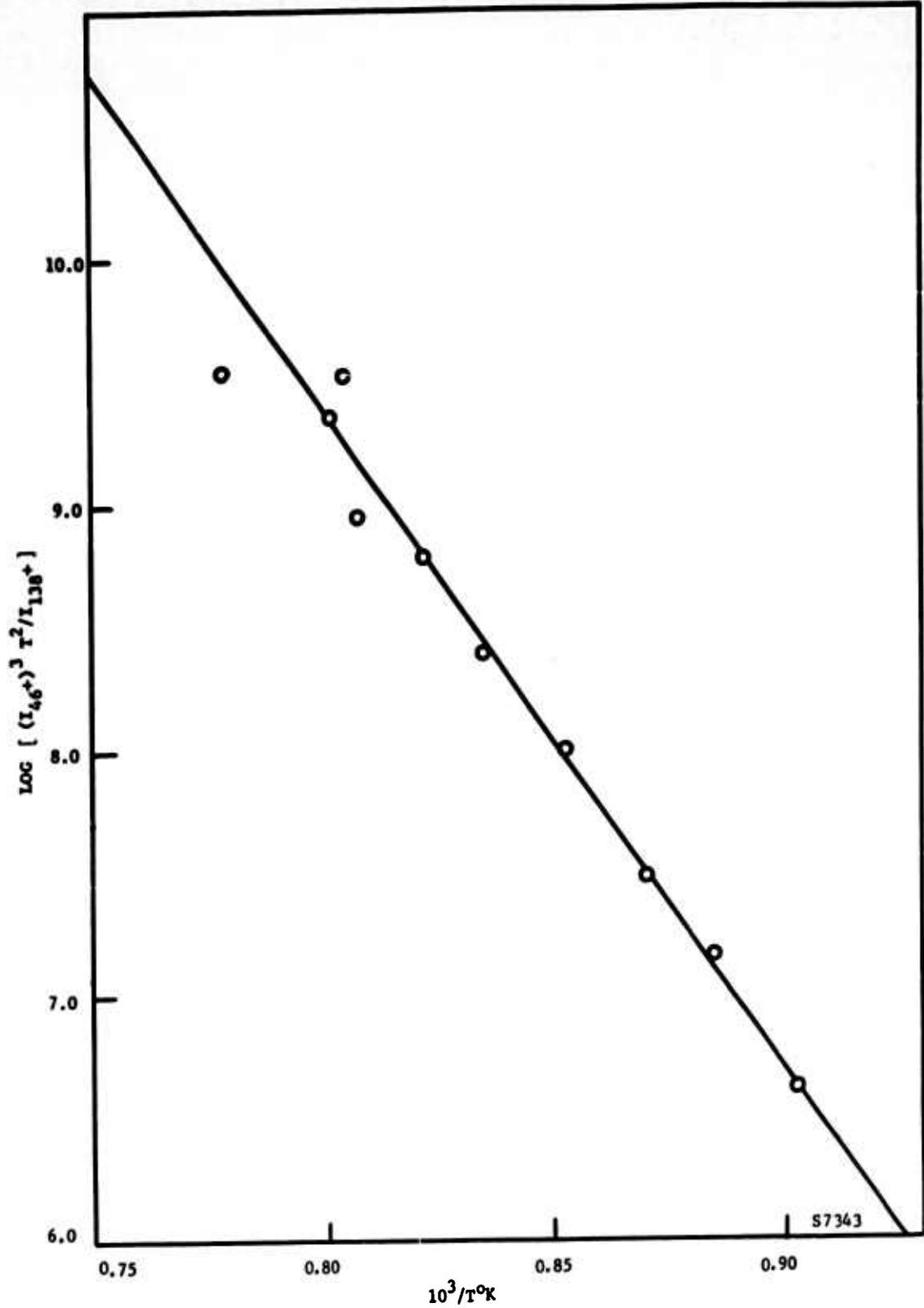


FIGURE 5. TEMPERATURE STUDY OF THE BOF MONOMER-TRIMER EQUILIBRIUM

TABLE VI  
MASS SPECTRUM OF TIN VAPOR  
IONIZING ELECTRON ENERGY = 70v

<u>Species</u>	<u>Ion Intensity % of Total</u>	<u>% Natural Abundance*</u>
$^{112}\text{Sn}^+$	0.8	1.0
$^{114}\text{Sn}^+$	0.5	0.7
$^{115}\text{Sn}^+$	0.3	0.3
$^{116}\text{Sn}^+$	14.8	14.3
$^{117}\text{Sn}^+$	7.8	7.7
$^{118}\text{Sn}^+$	24.7	23.8
$^{119}\text{Sn}^+$	8.5	8.7
$^{120}\text{Sn}^+$	32.4	32.7
$^{122}\text{Sn}^+$	4.6	4.7
$^{124}\text{Sn}^+$	5.6	6.0

\* "Chart of the Isotopes", Harshaw Chemical Co., 1953.

The appearance potential of  $^{120}\text{Sn}^+$  was measured by the vanishing current method<sup>13</sup> using background  $^{202}\text{Hg}^+$  for calibration of the electron energy scale. The value obtained was  $7.3 \pm 0.2$  ev, in excellent agreement with the ionization potential of tin,  $7.3$  ev<sup>14</sup>.

The temperature dependence of  $^{120}\text{Sn}^+$  over the range  $1367 - 1514^\circ\text{K}$  is given in Figure 6 as  $\log I_{\text{Sn}^+} T$  vs  $1/T$ . Points taken in order of increasing temperature form a straight having a slope somewhat different from that for decreasing temperature. This could be an indication of a lag in equilibration between the temperature of the base of the crucible (where the thermocouple is located) and the body of the cell. In view of this, it would seem advisable to randomize points in temperature studies, allowing sufficient time for equilibration at each temperature.

Though accurate thermal data were not being sought, it is interesting to note that the second law value for the heat of sublimation of tin at  $298^\circ\text{C}$  derived from the data for decreasing temperatures,  $71.7$  kcal/mole, agrees more closely with the third law value  $70.2$  kcal/mole\* than does the second law value for increasing temperatures,  $78.5$  kcal/mole.

A search for  $\text{Sn}_2^+$  in the spectrum of tin vapor was made with a crucible temperature of  $1469^\circ\text{K}$ . Several peaks exhibiting positive shutter checks were observed in the mass region corresponding to  $\text{Sn}_2^+$ . However, proper identification could not be made due to extremely low ion intensities. From relative intensities, an upper limit of 1% can be set for the concentration of  $\text{Sn}_2$  in the vapor. Drowart and Honig<sup>15</sup>, using a  $60^\circ$  mass spectrometer of 20 cm radius, observed that  $I_{\text{Sn}_2^+}/I_{\text{Sn}^+} = 2 \times 10^{-3}$  for free vaporization of tin at  $1200^\circ\text{K}$ .

\* Unpublished data obtained at Aeronutronic by torsion-effusion techniques.

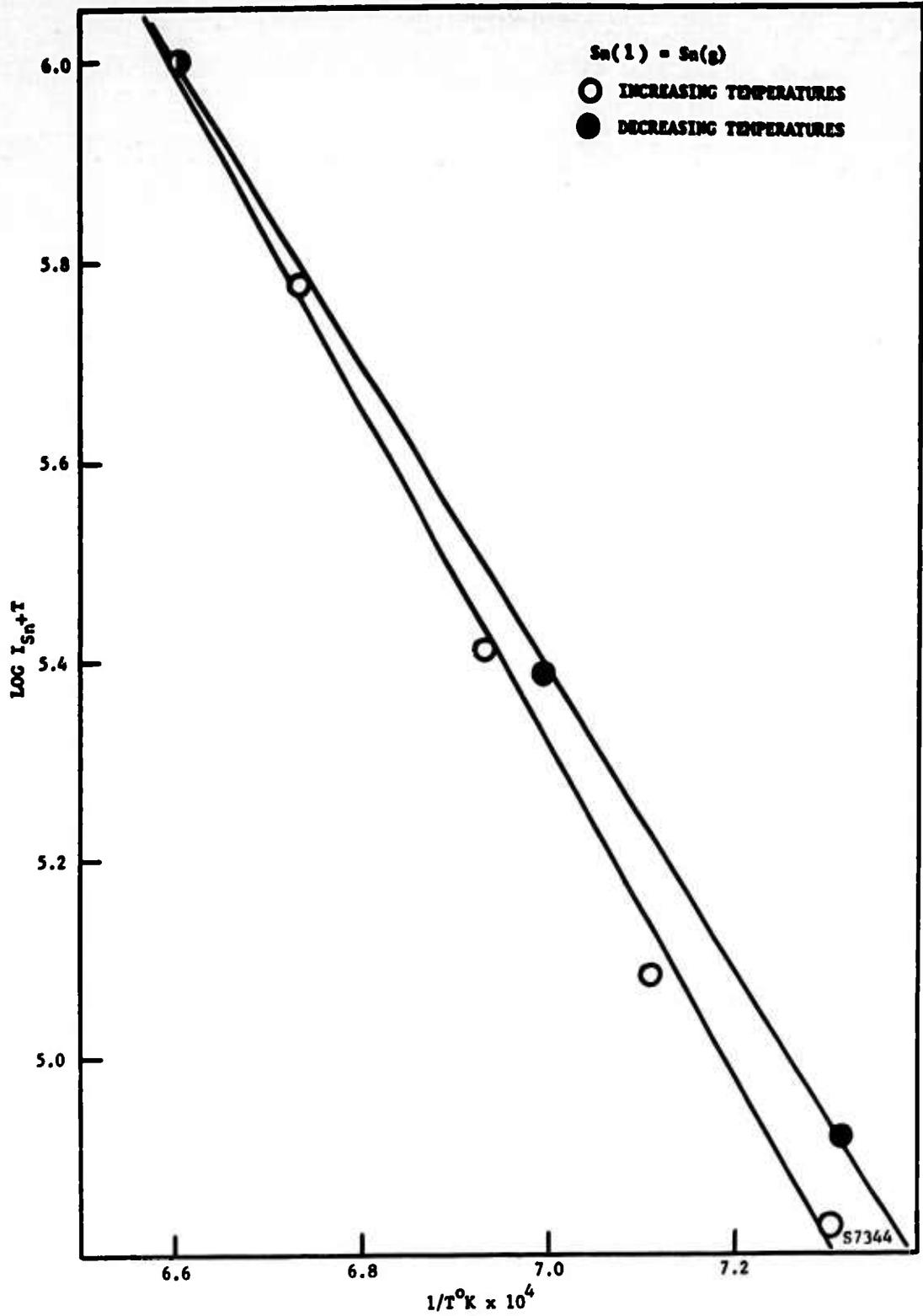


FIGURE 6. TEMPERATURE DEPENDENCE OF Sn<sup>+</sup> ION INTENSITY

#### 4.3 VAPOR SPECIES IN THE ALUMINUM-OXYGEN-FLUORINE SYSTEM

A preliminary mass spectrometric study has been made of vapor species in equilibrium with a mixture of crystalline aluminum oxide and aluminum fluoride in the range 1080° to 1170°K. The expected aluminum fluoride species were detected, indicating the presence of  $\text{AlF}_3$  and  $\text{Al}_2\text{F}_6$  in the vapor. In addition, the effusing vapor gave rise to a peak at  $m/e$  143 which could be due to the ion  $\text{Al}_2\text{O}_2\text{F}_3^+$ . The mono-isotopic composition, however, makes it difficult to confirm this. Studies are continuing.

## SECTION 5

## SUMMARY OF THERMODYNAMIC DATA

In order to maintain an up to date summary of thermodynamic data obtained as part of this experimental program, a listing of present "best values" is being included in this and subsequent reports. The data will be periodically revised as necessary when newer and more reliable auxiliary data used in their derivation appear. A summary of the data obtained to date is given in Table VII.  $\Delta H_{\text{sub},298}$  and  $\Delta H_f^{\circ}_{298}$  represent the derived heats of sublimation and heats of formation at 298°K. Changes in previously reported data are as follows:

## (1) LiF and LiCl Species

The previously reported<sup>16</sup> torsion vapor pressure data for these halides were combined with the heats of dimerization determined by Berkowitz et al.<sup>18</sup> and free energy functions for gaseous monomer and dimer in order to obtain the most consistent heats of sublimation for the LiF and LiCl monomer and dimer species. Considering only monomer and dimer, it was found that the best fit to the heat of dimerization data was obtained when the mole fractions of monomer were 0.6 and 0.5 for LiF and LiCl, respectively. These values are consistent with the most recent weight average vapor molecular weights determined here by combined torsion-Knudsen measurements, i.e.,  $34 \pm 3$  for LiF vapor (monomer = 25.9) and  $57 \pm 3$  for LiCl vapor (monomer = 42.4). The derived thermal data are given in Table VII.



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(2)  $\text{MgF}_2$

A small change in temperature calibration raises the heat of sublimation reported earlier<sup>11</sup> by about one kcal/mole.

TABLE VII  
SUMMARY OF EXPERIMENTALLY DETERMINED  
THERMAL DATA

Contracts NOrd 17980 and NOW 61-0905

<u>Species</u>	<u><math>\Delta H_{\text{sub}, 298}</math></u> <u>kcal/mole</u>	<u><math>\Delta H_f^{\circ}_{298}</math></u> <u>kcal/mole</u>	<u>References</u>
LiF(g)	$65.3 \pm 0.3$	$-79.8 \pm 1.3$	10, 16
Li <sub>2</sub> F <sub>2</sub> (g)	$69.3 \pm 1$	$-220.9 \pm 1.6$	10, 16
LiCl(g)	$49.9 \pm 0.3$	$-47.8 \pm 2$	10, 16
Li <sub>2</sub> Cl <sub>2</sub> (g)	$50.6 \pm 1$	$-144.8 \pm 2.3$	10, 16
BOF(g)		$-143 \pm 3$	1, 17
(BOF) <sub>3</sub> (g)		$-566.2 \pm 2.7$	11
MgF <sub>2</sub> (g)	$85.9 \pm 1$	$-178.1 \pm 4$	11
BN(s)		$-59.8 \pm 0.7$	11
ZrF <sub>4</sub> (g)	$55.8 \pm 2$	$-401.1 \pm 2$	11, 17
AlF <sub>3</sub> (g)	$71.0 \pm 0.5$	$-285.3 \pm 2$	1, 17
LiAlF <sub>4</sub> (g)	$65 \pm 3$	$-447 \pm 7$	1, 17
AlN(s)		$-76.1 \pm 2.1$	1
**B <sub>2</sub> O <sub>3</sub> (g)	$93.5 \pm 3^*$	$-207.5 \pm 3$	1
**Li <sub>2</sub> O(g)	$95.0 \pm 3$	$-47.6 \pm 3$	
Mg <sub>2</sub> Cl <sub>4</sub> (g)	$63.3 \pm 2$	$-243.5 \pm 2$	

\*  $\Delta H_{\text{vap}, 298}$

\*\* Tentative result; further work in progress.

## SECTION 6

## FUTURE PROGRAM

Vaporization studies on  $\text{Li}_2\text{O}$ ,  $\text{B}_2\text{O}_3$  and  $\text{LiBO}_2$  will be repeated with platinum effusion cells of somewhat different and more reliable design in order to firmly establish vapor thermal properties in these systems. Measurements will also be made on  $\text{LiAlO}_2$ .

A new torsion-effusion apparatus has been constructed for exclusive use in vaporization studies of beryllium compounds. Studies of the vaporization of beryllium fluoride under both neutral and reducing conditions are in progress. Other studies will include beryllium chloride, beryllium oxide and elemental beryllium, with emphasis on sub-halide, sub-oxide and gaseous Be species.

Studies of the  $\text{ZrO}_2\text{-HCl}$  reaction will be continued, with emphasis on determination of the reaction stoichiometry by pressure variation, or perhaps mass spectrometric studies.

The vaporization behavior of aluminum trichloride will be studied in order to obtain thermal data for vapor species in this system. A new type of torsion-effusion system is being designed with which the pressure and composition of the superheated vapor can be studied so as to obtain reliable heats of vapor polymerization. The apparatus will be used for studies on  $\text{AlCl}_3$ ,  $\text{MgCl}_2$  and the beryllium halides.

Mass spectrometric studies of vapor species in the Al-O-F system will continue. It is also planned to study the possible equilibrium formation of  $\text{BF}_2(\text{g})$  in the spectrometer by means of the reaction of  $\text{BF}_3(\text{g})$  with elemental boron. In addition, the mass spectrometer will be used as needed to check the vapor species in some of the metal halide systems studied by effusion methods.

Development of the vacuum cooling rate method for specific heat measurement will continue.

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## APPENDIX

## THE VAPOR PRESSURE AND HEAT OF SUBLIMATION OF GOLD\*

by D. L. Hildenbrand and W. F. Hall

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Although the available literature contains a number of references to experimental determinations of the vapor pressure of gold, the reported values are not in good agreement and the derived heat of sublimation is uncertain by at least several kcal/mole. Some additional vapor pressure data for gold has recently been obtained in this laboratory in the course of some studies of the reliability of the torsion-effusion method of vapor pressure measurement. It was felt worthwhile to report this information in view of the need for firmly establishing such basic data. When enough information of this type becomes available, it may be possible to establish a reliable set of high temperature vapor pressure standards such as those developed for the standardization of calorimetric measurements. Because of the fundamental importance of vapor pressure measurements in high temperature chemistry studies, the establishment of vapor pressure standards would appear to be desirable.

Data reported here have been obtained by the torsion-effusion method, which has been described previously<sup>1,2</sup>. With this method, one observes the angular deflection induced by effusion of vapor from a multi-hole effusion cell which is suspended from a filament of small restoring force. The pressure within the effusion cell can be evaluated from the relation

$$P = \frac{2k \theta}{\sum afq} \quad (1)$$

\* This work supported in part by the Advanced Research Projects Agency under Contract NOrd 17980.

where  $k$  is the torsion constant of the filament,  $\theta$  is the measured angular deflection, and  $a$ ,  $f$ , and  $q$  are the area, force factor and moment arm of each of the effusion orifices. The force factor corrects for the reduction in effusive force resulting from the finite thickness of the orifice and has been calculated for various tube geometries by Freeman and Searcy<sup>3</sup>. It should be noted that total pressure data so obtained are on an absolute basis and, in addition, are not dependent on the composition of the effusing vapor.

#### EXPERIMENTAL

Engelhard Industries mint grade gold of better than 99.99% purity was used for the vapor pressure measurements.

Since the torsion-effusion apparatus will be described in more detail in a forthcoming publication, only a brief description will be given here. All measurements were made using effusion cells machined from ATJ high density graphite. The cells were of square horizontal cross section and contained four effusion orifices, one each drilled in opposite sides of opposite vertical faces so that the moment arm of each of the orifices with respect to the center of suspension was about 0.55 cm. Orifice depths were of the order 0.04 to 0.05 cm. The effusion cell geometrical factors are given in Table I. Contrary to the experience of Pugh and Barrow<sup>4</sup> and Witt and Barrow<sup>5</sup>, the graphite cells used in this and other research in this laboratory have proven to be entirely satisfactory as far as reproducibility of results is concerned. In addition, there was no evidence for diffusion of the liquid metals or their vapors through graphite, as reported by Edwards and Downing<sup>6</sup> for mercury, silver and copper. However, it is highly unlikely that diffusion or permeation

effects could contribute a net torque and thus, even if present, they should have no effect on the torsion measurements.

A 30 cm length of tungsten wire, 0.005 cm. in diameter, served as the torsion filament. Oscillations were damped out magnetically. The effusion cell was heated by radiation from a surrounding hollow tantalum cylinder which was in turn heated by high frequency induction. By shielding the cell and heating indirectly, a coupling effect<sup>1</sup> between the cell and the high frequency field was avoided, leading to entirely satisfactory operation. A number of 0.2 cm diameter holes drilled in the susceptor side and a larger hole in the removable lid allowed for evacuation of the cell region and escape of vapor molecules. Thermal radiation shielding of the susceptor was provided by several layers of tantalum foil joined in such a way as to present a high resistance to eddy currents.

A fused silica tube enclosed the susceptor and cell arrangement and, while measurements were in progress, it was evacuated to a pressure of  $5 \times 10^{-5}$  mm or lower. The bottom of the tube contained a planar optical window protected by a movable shutter. Temperatures were measured with a calibrated disappearing-filament optical pyrometer sighting through the optical window and a hole in the susceptor bottom into a cylindrical black body cavity in the bottom of the effusion cell. The cavity was 1.0 cm deep and 0.25 cm in diameter. Temperatures were corrected for reflection losses at window and prism surfaces.

The remainder of the system, the method of determining the torsion constant and the measurement of angular deflection are essentially the same as described by others<sup>1,2</sup>. In this work, the torque angle could be observed directly to within 0.001 radian.

## RESULTS

The experimental vapor pressure data and derived heats of sublimation are given in Table I and are listed in the order of measurement. Data were obtained with three different effusion orifice sizes; the three sets of results are in good agreement, indicating the observed pressure to be equilibrium values. There is no reason to suspect a reaction of the metal with graphite, since it does not form a stable carbide<sup>7</sup>. The extent to which the results may be affected by solution of carbon in gold, with subsequent lowering of the activity, is not known with certainty, but the effect is believed to be inappreciable. The same gold sample was used throughout the measurements, with no observed change in pressure with time such as might be expected for a gradual solution of carbon in the metal in significant amount. Experimental pressures were within the molecular flow range, as required for application of equation (1).

Free energy functions used in the third law treatment of the vapor pressure data were taken from Stull and Sinke<sup>8</sup>. The assumption of monomeric vapor implicit in the calculations appears to be valid since mass spectra of the vapor obtained under both free evaporation<sup>9</sup> and Knudsen<sup>10</sup> conditions indicate less than one mole percent polymeric species to be present. The average third law value of the heat of sublimation at 298°K, 88.3 kcal/mole, is assigned an overall accuracy uncertainty of  $\pm 0.9$  kcal/mole, based on an analysis of experimental errors. An estimate of a possible error of 15° in temperature measurement contributes most of the uncertainty.

In Table II, the results of this research are compared with third law heats of sublimation derived from the work of other investigators, in all cases using free energy functions from Reference (8). Uncertainties are included where they have been estimated by the various investigators.

TABLE I

THE VAPOR PRESSURE AND HEAT OF SUBLIMATION OF GOLD

T°K	$\theta \times 10^3$ , rad	P x 10 <sup>5</sup> , atm	$\Delta H_{298}$ , kcal/mole
Cell #3			
1669	32.9	1.08	88.1
1691	43.4	1.42	88.3
1741	87.2	2.88	88.3
1722	68.2	2.25	88.3
1705	51.9	1.71	88.3
1655	24.2	0.80	88.3
1705	54.8	1.80	88.1
1744	90.0	2.95	88.3
1762	115.9	3.80	88.2
1733	77.7	2.55	88.3

Cell #4			
1796	60.2	5.88	88.3
1831	96.1	9.18	88.2
1814	73.9	7.14	88.5
1779	46.6	4.60	88.4
1785	48.4	4.78	88.6
1823	80.9	7.78	88.4
1841	107.0	10.22	88.3
1807	60.8	5.92	88.7
1767	36.4	3.66	88.5

Cell #5			
1966	77.7	48.5	88.0
1943	54.4	33.9	88.4
1923	44.3	27.6	88.3
1897	29.8	18.6	88.7
1960	71.6	44.6	87.9
1954	65.2	40.6	88.0
1943	56.7	35.4	88.2
1930	50.6	31.6	88.0
1830	13.8	8.6	88.4

Av. 88.3 ± 0.2

	Cell #3	Cell #4	Cell #5
$\bar{a}$ , cm <sup>2</sup>	0.0105	0.0046	0.0010
$\Sigma afq$ , cm <sup>3</sup>	0.01872	0.00681	0.000977
k, dyne cm/rad	3.12	3.20	3.09

TABLE II  
COMPARISON OF RESULTS FOR



Investigator	Reference	$\Delta H_{298}$ , kcal/mole
P. Harteck	11	90.7
L. D. Hall	12	$84.7 \pm 0.7$
R. K. Edwards	13	87.0
E. G. Rauh	13	$87.2 \pm 0.8$
A. N. Nesmeyanov et al.	14	87.3
R. D. Freeman	15	88.4
P. Grievesson et al.	16	$88.0 - 89.3$
This Research		$88.3 \pm 0.9$

All results except those of this research were obtained by the Knudsen effusion technique, although no details concerning the work of Edwards<sup>13</sup> or Rauh<sup>13</sup> are as yet available. Grievesson et al.<sup>16</sup> used both Knudsen and transpiration techniques; a trend of 1.3 kcal/mole in the derived third law heats over the range of their measurements, however, indicates a temperature dependent error. The ratio of orifice area to surface area employed in the effusion measurements of Harteck<sup>11</sup> appears too large to yield equilibrium pressures and the  $\Delta H_{298}$  value obtained from his data is high by about 0.6 kcal/mole. Except for the unaccountably high pressures obtained by Hall<sup>12</sup>, who used a radioactive tracer technique to monitor the effusion transport, the various sets of data are in reasonable agreement and indicate a best value of  $88.0 \pm 1$  kcal/mole for the heat of sublimation of gold at 298°K. The agreement between torsion and Knudsen pressures is further evidence that the vapor is highly monomeric under these conditions.

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