Publication No. U-1376

RESEARCH LABORATORIES

TECHNICAL REPORT

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

FIRST QUARTERLY TECHNICAL SUMMARY REPORT

Prepared for:	Bureau of Naval Weapons (ARPA) Department of the Navy Washington 25, D. C.
Under Contract:	NOw 61-0905-c Task 1 (C) ARPA Order No. 22-61
Prepared by:	D. L. Hildenbrand L. P. Theard

15 September 1961

AERONUTRONIC
A DIVISION OF Ford Motor Company
FORD ROAD / NEWPORT BEACH, CALIFORNIA

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SUMMARY

From a mass spectrometric study of the temperature dependence of the major OBF monomer and trimer peaks produced by electron bombardment of vapors over a MgF_2-B_2O_3 mixture, the heat of the reaction $(OBF)_3(g) \rightarrow 3\ OBF(g)$ at 1200°K has been derived at 140.2 ± 15 kcal. This result, when combined with the heat of formation of $(OBF)_3$ and estimated heat content data, yields the value -141 ± 5 kcal/mole for the heat of formation of the gaseous OBF monomer at 298°K.

Torsion-effusion measurements of the dissociation pressure of aluminum nitride over the range 1700 to 1900°K yield a condensation coefficient of < 0.002. From derived equilibrium pressures, the heat of formation of crystalline AlN at 298°K is calculated as -70.7 ± 2.5 kcal/mole. This value is 5 kcal/mole less negative than results obtained recently by reaction calorimetry.

The vaporization of boric oxide has been studied over the range 1420 to 1560°K, from which a second law heat of vaporization at 298°K has been computed as 93.5 ± 1 kcal/mole. From this result, $\Delta H^\circ_{f\,298}$ for $B_2O_3(g)$ is derived as -207.5 ± 1 kcal/mole. An entropy for $B_2O_3(g)$ derived from the second law ΔH_{vap} is more compatible with a frequency assignment deduced from matrix isolation spectra than with a corresponding assignment based on vapor emission spectra.

Effusion weight loss measurements, when combined with torsion vapor pressure data, indicate that aluminum trifluoride and lithium aluminum floride mixtures vaporize to AlF_3 and $LiAlF_4$ gaseous molecules, respectively. Thermal properties have been derived on this basis.

Studies of the vaporization of Mg_3N_2 by mass spectrometry have shown that the material vaporizes to magnesium atoms and molecular nitrogen. No other molecular species were detected. A temperature study of the Mg + intensity yields an abnormally high second law heat for the dissociation reaction, giving additional evidence for the anomalous vaporization behavior observed earlier.

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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 measurement of vacuum cooling rates.

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

SECTION 2

EFFUSION STUDIES

2.1 EXPERIMENTAL

Because of the importance of accurate temperature measurement in studies of the thermodynamics of vaporization, care has been taken to establish the relation between brightness pyrometer temperature and effusion cell temperature for the inductively heated torsion-effusion apparatus[1]. Pyrometer temperatures were compared with the output of a standard platinum-rhodium thermocouple, the junction of which was located within the sample chamber of a sealed effusion cell. From comparison measurements over the range 1000 to 1600° C, it is believed that effusion cell temperatures are known to be within 10° C. An effective emissivity for the susceptor-cell arrangement can be deduced from the calibration data and can be used to establish effusion cell temperatures in the range above 1600° C. A series of check measurements of the vapor pressure of gold reported in the Appendix, indicates the temperature calibration to be reliable and the overall operation to be satisfactory.

2.2 THE VAPORIZATION OF ALUMINUM NITRIDE

As a continuation of studies of the thermodynamics and kinetics of vaporization of light metal nitrides[1,2], the dissociation pressure of crystalline aluminum nitride has been measured by the torsion-effusion method over the range 1700 to 1900° K. The experimental technique has been described previously[1,3]; establishment of the temperature scale is discussed in Section 2.1. A sample of crystalline AlN was generously supplied by Dr. G. Long, ALCOA Research Laboratories, and was reported to be of better than 99 percent purity. No impurities could be detected from the X-ray diffraction pattern of the sample, which showed only the peaks characteristic of highly crystalline AlN. Any volatile impurities which may have been present in small amounts were removed by out-gassing prior to the start of the measurements.

Torsion pressure data were obtained with three graphite effusion cells of different orifice size, and the results are presented in Table I. Pressures were computed from the relation

$$P_T = \frac{2k\theta}{\Sigma afq} \qquad (1)$$

where k is the torsion constant of the filament, θ is the observed angular deflection, and a, f and q are the area, force factor and moment arm of each of the effusion orifices. A plot of the observed pressure data, shown in Figure 1, indicates the results obtained with each cell to be reproducible, but shows the marked trend of pressure with orifice area which is characteristic of substances with a low condensation coefficient. It has been shown[1] that equilibrium and observed pressures are related to cell geometry through the expression

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

where P_e and P_T are equilibrium and observed pressures, respectively, C is the orifice Clausing factor, a is the orifice area, α is the condensation coefficient and A is the effective vaporizing surface area. Equation (2) indicates that a low value of α can cause observed pressures to be considerably below the equilibrium values. Since the cell geometrical factors are accurately known, α and P_e can be evaluated from the data in Table I by plotting the reciprocal of observed pressure versus the ratio Ca/A; the slope of such a plot will be $1/\alpha \, P_e$ and the intercept $1/P_e$. Equation (2) correlates the AlN data smoothly and leads to an α of 0.0022 if the effective vaporizing area is taken as the sample chamber cross-sectional area. The α value so derived is, of course, an upper limit; in deriving equilibrium pressures, only the product αA is needed. From α and the cell geometrical factors, ratios of equilibrium to observed pressure, P_e/P_T, were calculated as 10.45, 4.36 and 1.64 for cells 3, 4 and 5, respectively. These ratios were used to convert observed pressures to equilibrium values, as summarized in Table I. A plot of the derived equilibrium pressure data, shown in Figure 2, indicates that the orifice size correlation brings the data from all three effusion cells into good agreement.

TABLE I

ALUMINUM NITRIDE DISSOCIATION PRESSURES AND HEAT OF THE REACTION

$$2\ AlN(s) = 2\ Al(g) + N_2(g)$$

T^oK	$P_T x10^5$,atm	$P_e x10^5$,atm	ΔH_{298}, kcal
		Cell 3	
1738	0.70	7.3	299.2
1788	1.78	18.6	297.5
1834	3.78	39.5	296.6
1857	5.88	61.2	295.4
1848	5.28	55.1	295.3
1823	3.39	35.4	296.2
1801	2.56	26.7	295.7
1785	1.65	17.2	297.8
1742	.81	8.5	298.2
1699	.41	4.3	298.0
		Cell 4	
1758	3.40	14.8	295.1
1817	7.28	31.8	296.5
1839	12.6	55.0	293.9
1827	9.80	42.7	294.8
1780	4.66	20.3	295.2
1722	1.87	8.1	295.4
1735	1.87	8.2	297.5
1786	4.63	20.2	296.4
1827	8.70	38.0	296.1
1851	13.0	56.6	295.5
		Cell 5	
1786	12.7	20.8	296.0
1839	26.0	42.6	296.6
1859	34.6	56.7	296.2
1820	20.6	32.8	296.5
1785	11.6	19.0	296.8
1743	6.1	10.0	296.7
1716	4.0	6.6	296.5
1912	68.3	112.0	297.1
1874	40.3	66.0	297.2
		Av	296.4 ± 0.9

TABLE I (Continued)

	$\bar{a}$, cm^2	$\bar{C}$	Σafq, cm^3	k,dyne cm/rad
Cell 3	0.0105	0.75	0.01872	3.18
Cell 4	0.0046	0.61	0.00681	3.02
Cell 5	0.0010	0.54	0.000977	3.17

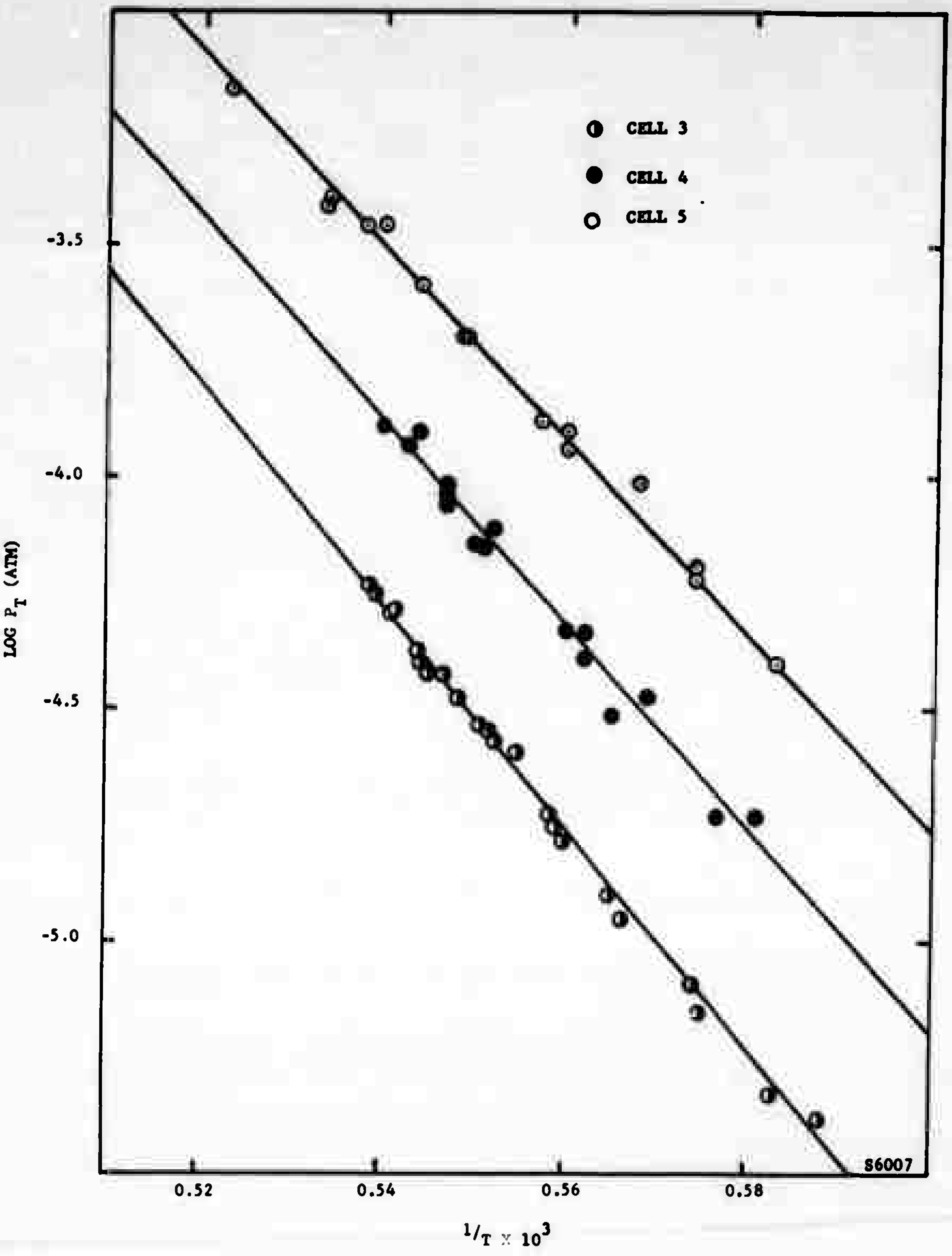

FIGURE 1. OBSERVED ALUMINUM NITRIDE DISSOCIATION PRESSURES

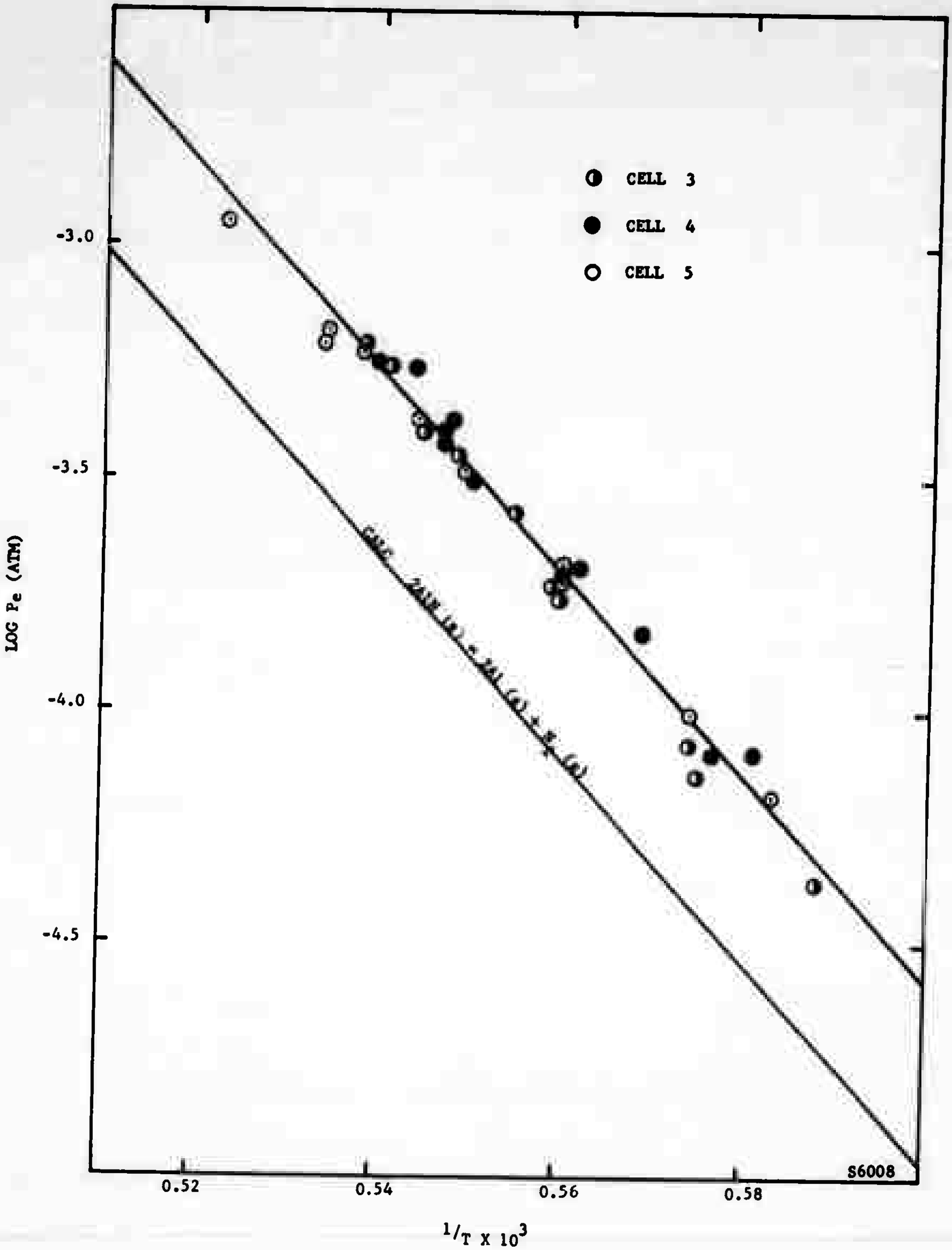

FIGURE 2. DERIVED ALUMINUM NITRIDE EQUILIBRIUM PRESSURES

Scheisel and Williams[5] have studied the mass spectrum of vapors effusing from a Knudsen cell containing AlN and detected no mixed gaseous species. It is assumed, therefore, that vaporization proceeds according to the reaction.

$$2\ \mathrm{AlN}\ (s) = 2\ \mathrm{Al}(g) + \mathrm{N_2}(g) \qquad (3)$$

and that the equilibrium constant for reaction (3) can be expressed as

$$K = 0.148\ P_e^3 \qquad (4)$$

where P_e is the total equilibrium pressure. Third law heats have been calculated from the pressure data using $-\Delta\ (F-H_{298}/T)$ values for reaction (3) of 111.64, 111.37 and 111.10 cal/mole degrees at 1700, 1800 and 1900° K, respectively, and are given in Table I. The average third law value of ΔH_{298}, 296.4 ± 0.9 kcal, can be combined with the heat of sublimation of aluminum, $\Delta H_{298} = 77.5$ kcal/mole, to derive the heat of formation of crystalline AlN. From an estimated error of ± 3.6 kcal in the ΔH_{298} for reaction (3) and an uncertainty of ± 1.5 kcal/mole in the heat of sublimation of aluminum, one derives ΔHf^o_{298} for crystalline AlN as -70.7 ± 2.5 kcal/mole. In a recent review[6], a ΔHf^o_{298} of -76.0 (no uncertainty given) kcal/mole has been selected for AlN(s), based on the reaction calorimetric results of Neugebauer and Margrave[7] and Kelley[8]. Other reported values range from -57 to -72 kcal/mole. The discrepancy between measured and calculated (assuming $\Delta Hf^o_{298} = -76$ kcal/mole) pressures is shown in Figure 2. No reason for the difference is immediately apparent, since the torsion technique has been shown to be reliable (see Appendix) and there are no reactions with the graphite cell which would produce a higher pressure than that of reaction (3).

2.3 THE VAPORIZATION OF BORIC OXIDE

The vapor pressure of boric oxide has been measured over the range 1420 to 1560° K by the torsion method using platinum effusion cells. The data are needed in analyzing the vaporization behavior of $\mathrm{LiBO_2}$ and other metal borates and, in addition, should be helpful in deciding on a firm vibrational assignment for gaseous $\mathrm{B_2O_3}$. Vapor pressure data previously reported are not in good agreement and lead to moderate uncertainties in the thermal properties of $\mathrm{B_2O_3}$ vapor. Measurements were made on an Amend Drug Co. sample of CP $\mathrm{B_2O_3}$ which was vacuum dried for several hours at 1000° C.

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The vapor pressure data obtained with two platinum torsion cells of different orifice area are given in Table II; the results are plotted in Figure 3. Slightly higher pressures are obtained in the cell with the smaller effusion orifices, indicating a condensation coefficient of about 0.01. On this basis, the pressures obtained with Cell 2 are about 20 percent below the equilibrium values. Possible departures from equilibrium have not been considered in previous effusion studies, which are summarized in Reference (9). Correction for an α value of 0.01 brings the earlier effusion results into closer agreement with the present results.

From the slope of the Cell 2 data, the heat of vaporization of B_2O_3 at 1500° K is calculated as 83.9 ± 0.8 kcal/mole; the Cell 1 data lead to the same second law heat, but with somewhat larger uncertainty. The entropy of B_2O_3 gas can be calculated from the sum of (1) the entropy of the liquid at 1500°K, 61.7 eu/mole[9], (2) the entropy of vaporization at 1500° K, 83900/1500 = 55.9 eu/mole, and (3) the entropy of compression to 1 atm, Rln $(4.47 \times 10^{-5}) = -19.9$ eu/mole. The entropy of ideal gaseous B_2O_3 at 1 atm is thus calculated as 97.7 eu/mole with a probable uncertainty of ± 2 eu/mole. Reasonably well established structural data together with the vibrational assignment of White et al[10] based on vapor emission studies, lead to a calculated entropy of 94.7 eu/mole at 1500° K. A frequency assignment for B_2O_3 based on matrix isolation studies at Union Carbide Research Corporation[11] results in a somewhat higher entropy of 99.2 eu/mole at 1500° K, although recent changes may raise this value somewhat. It appears that the results of this research favor the Union Carbide assignment or, more probably, an intermediate assignment. The difference between the two spectroscopic studies lies principally in assignment of the bending frequencies.

No attempt has been made to do a complete third law analysis of the vapor pressure data because of the previously mentioned uncertainties in the calculated thermodynamic functions of $B_2O_3(g)$. The saturated vapor, incidentally, is known to be monomeric. For the reaction

$$B_2O_3\ (\ell) = B_2O_3\ (g) \qquad (5)$$

one calculates second and third law ΔH_{298} values of 94.1 and 89.5 kcal/mole, respectively, using the vibrational assignment of White et al[10], while the assignment of reference (11) leads to second and third law ΔH_{298} values of 93.1 and 95.2 kcal/mole, respectively. An average of the two second law values yields $\Delta H_{298} = 93.5 \pm 1$ kcal/mole for reaction (5), from which ΔHf^{o}_{298} for $B_2O_3(g)$ is derived as -207.5 ± 1 kcal/mole. The frequency assignment of reference (11) leads to better agreement between second and third law heats.

TABLE II

THE VAPOR PRESSURE OF BORIC OXIDE

Cell 1		Cell 2	
$T^{o}K$	$P_{T}x10^{5}$,atm	$T^{o}K$	$P_{T}x10^{5}$,atm
Series I		**Series I**	
1521	5.02	1525	7.72
1503	4.00	1555	11.9
1489	2.95	1535	8.80
1466	1.91	1485	3.36
1518	4.90	1501	4.32
1502	3.87	1513	5.51
1494	3.25	1455	1.85
1492	3.08	1438	1.34
1448	1.40	1380	0.96
1470	2.00	1488	3.56
Series II		**Series II**	
1467	1.70	1527	7.30
1502	3.40	1536	8.90
1519	4.78	1557	12.8
1480	2.25	1550	11.2
1476	2.02	1512	5.20
1437	1.05	1526	7.17
1524	5.50	1463	2.05
1481	2.40	1426	1.08
1476	2.15		
1446	1.23		
1423	.78		

Cell 1:

$\bar{a} = 0.0112$ cm^{2}
Ca/A = 0.0059
Σ afq = 0.0213 cm^{3}
k = 3.03 dyne cm/rad

Cell 2:

$\bar{a} = 0.00506$ cm^{2}
Ca/A = 0.0025
Σ afq = 0.00868 cm^{3}
k = 2.98 dyne cm/rad

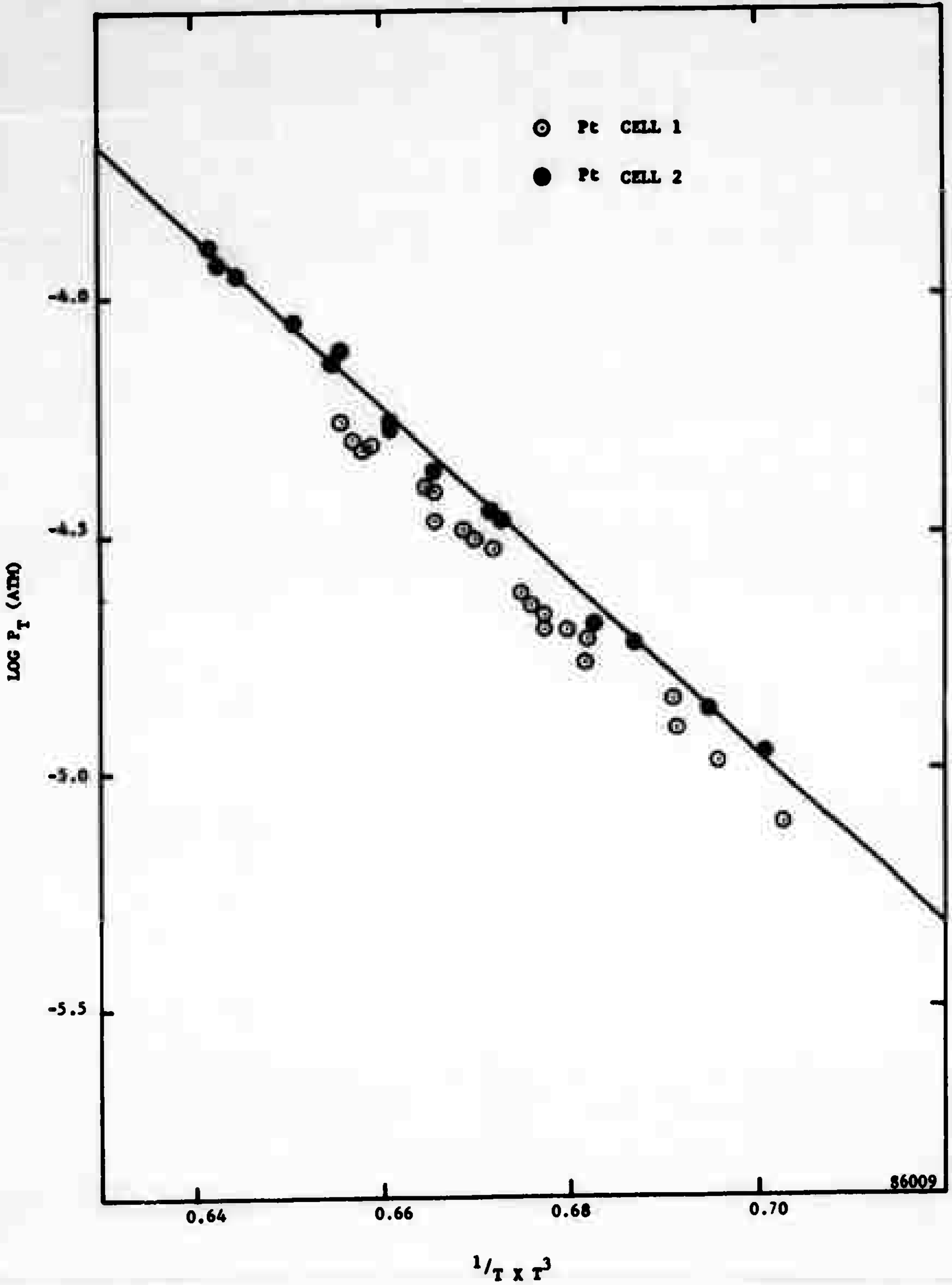

FIGURE 3. OBSERVED VAPOR PRESSURE OF BORIC OXIDE

In a recent review of boron compounds[9], the heat of sublimation of B_2O_3 at 0° K has been selected as 94.6 ± 0.5 kcal/mole, based principally on a third law treatment using the frequencies of White et al[10]. Various reported vapor pressure data lead to ΔH_o values ranging from 93.8 to 96.9 kcal/mole. For comparison, the Cell 2 data reported here yield $\Delta H_o = 93.3$ kcal/mole. Consideration of a condensation coefficient of 0.01 will lower the other ΔH_o values based on effusion measurements and bring them into better agreement with the result obtained here.

2.4 THE VAPORIZATION OF ALUMINUM TRIFLUORIDE AND LITHIUM ALUMINUM FLUORIDE MIXTURES

a. Aluminum Trifluoride

The molecular weight of saturated AlF_3 vapor has been determined by combining effusion weight loss measurements with previously reported[2] torsion pressure data. Three weight loss determination made over the range 1036 to 1050° K gave average molecular weights of 96.9, 88.9 and 105.0, with an average of 96.9 ± 5 (AlF_3 monomer = 84.0). It is evident that the saturated vapor is essentially monomeric in this range, especially since the experimentally determined molecular weights are weight average values. The heat of sublimation of AlF_3 at 298° K, 71.0 ± 0.5 kcal/mole, derived earlier from vapor pressure data assuming monomeric vapor, is therefore valid.

b. Lithium Aluminum Fluoride Mixtures

Effusion weight loss measurements have also been used to determine the composition of the vapor over a 1:1 mole ratio mixture of lithium fluoride and aluminum trifluoride. The results of four weight loss determinations made over the range 916 to 945° K, when combined with vapor pressure data[2] reported earlier, yield average molecular weights of 105.4, 121.6, 79.7 and 105.6, with an average value of 103.1 ± 12 ($LiAlF_4$ monomer = 109.9). This would indicate rather conclusively that a gaseous molecule of composition $LiAlF_4$ is the major gaseous species in the mixed fluoride system. The heat of formation of $LiAlF_4(g)$ at 298°K has been estimated[2] as -447 ± 7 kcal/mole from vapor pressure data.

The vapor pressures of the 1:2 and 2:1 $LiF:AlF_3$ mixtures were found to be essentially the same as that of the 1:1 mixture, indicating that mixed gaseous species other than $LiAlF_4$ are not important. The 3:1 $LiF:AlF_3$ mixture has a vapor pressure which is more than an order of magnitude lower than that of the 1:1 mixture; this is consistent with vaporization principally to AlF_3.

SECTION 3

TRANSPIRATION STUDIES

A quartz flow system has been constructed for use in transpiration studies of the reactions of metal oxides with HCl and other chlorine-containing gases. The system is essentially identical in design to the metal flow system previously used[3]. Some preliminary transpiration measurements of the vapor pressure of zinc chloride, using argon as flow gas, indicate satisfactory operation. The reaction of gaseous HCl with zirconia is presently being studied.

SECTION 4

MASS SPECTROMETRY

4.1 VAPOR SPECIES IN THE BORON-OXYGEN-FLUORINE SYSTEM

Mass spectrometric studies of vapor species over B_2O_3 - MgF_2 mixtures, begun last quarter[2], have continued. The spectrometer is a 60-degree sector, 12-inch radius of curvature direction focusing instrument that has been described previously[2,16].

a. Identification of Effusing Species

The mass spectrum of vapor from a 3:1 mole ratio B_2O_3 - MgF_2 mixture at 928° C is given in Table III along with appearance potentials of important ionic species. Total gas pressure was significantly less than that previously encountered with a 1:1 mixture. Appearnace potentials were determined by the vanishing current method[17], using the ionization efficiency curve of $^{202}Hg^+$ for calibration of the electron energy scale.

As before, relative heights of the BF_3^+, BF_2^+, BF^+ and B^+ peaks resemble those observed in the mass spectrum of boron trifluoride[12]. In addition, measured appearance potentials of BF_2^+ and B^+ agree with the values reported by Osberghaus[13] for production of the ions from BF_3, thus providing conclusive evidence for the presence of BF_3 in the effusing vapor.

Simple ionization of molecular $(OBF)_3$ appears to be the only significant mode of $(OBF)_3^+$ ion formation in view of the absence of detectable amounts of boron-containing ions at masses beyond m/e 138. OBF^+ ions, on the other hand, might be formed by ionization of molecular OBF

TABLE III

MASS SPECTRUM (IONIZING VOLTAGE = 60V) OF VAPOR FROM 3:1 MIXTURE OF B_2O_3 AND MgF_2 AT 928°C AND APPEARANCE POTENTIALS OF IMPORTANT IONIC SPECIES

m/e	Ion	Relative Intensity	Appearance Potential, ev
10,11	B^+	.56	31.3 ± 0.4
29,30	BF^+	1.41	
45,46	OBF^+	3.85	13.9 + 0.4
46,47	$BFOH^+$	.52	
48,49	BF_2^+	100	16.7 ± 0.4
65,66	BF_2OH^+	.39	
67,68	BF_3^+	5.24	16.4 ± 0.4
71,72,73	$B_2FO_2^+$	.51	
90,91,92	$(OBF)_2^+$	1.23	17.2 ± 0.5
93,94,95	$B_2OF_3^+$	2.59	16.6 ± 0.5
116,117,118,119	$B_3O_3F_2^+$	.43	13.4 ± 0.5
135,136,137,138	$(OBF)_3^+$	4.36	14.5 ± 0.4

TABLE IV

TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM $(OBF)_3(g) = 3\ OBF\ (g)$

Run 1		Run 2	
T°K	$\log[(I^+_{46})^3T^2/I^+_{138}]$	T°K	$\log[(I^+_{46})^3T^2/I^+_{138}]$
1259	10.26	1315	11.93
1206	9.17	1251	10.83
1171	8.46	1201	9.54
1125	7.67	1161	8.84
1085	6.36		

I^+ values in arbitrary units

and/or by fragmentation of a larger molecule such as $(OBF)_3$. If ionization of OBF is responsible for a significant fraction of the OBF^+ ion current one would expect to observe some change in the $OBF^+/(OBF)_3^+$ intensity ratio with changes in temperature. Such an effect has indeed been observed and will be discussed later. The ionization efficiency curve of OBF^+ contains no sharp breaks which might suggest more than one important process of formation. The value obtained for the appearance potential of OBF^+, 13.9 ± 0.4 ev, is low enough to preclude complex fragmentation processes. Based on the foregoing, it is concluded that most, if not all, of the OBF^+ ion current results from simple ionization of molecular OBF.

Intensities of the $(OBF)_2^+$, $B_2OF_3^+$, and $B_3O_3F_2^+$ ions relative to that of $(OBF)_3^+$ remain essentially constant over temperature changes in excess of 100°, indicating that these ions are produced by fragmentation of $(OBF)_3$. Thus, $B_3O_3F_2^+$ is probably formed by the process

$$(OBF)_3 + e \qquad B_3O_3F_2^+ + F^- + e$$

Simultaneous production of F^- would explain the fact that the appearance potential of $B_3O_3F_2^+$ is some 0.9 ev less than that of $(OBF)_3^+$. Formation of BF_2^+ from BF_3 also appears to be accompanied by F^- formation.

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

Intensities of the OBF^+ and $(OBF)_3^+$ ions were studied over the temperature ranges 1085 to 1259° K in one experiment and 1161 to 1315° K in another. For these studies the ionizing electron energy was made only a few volts greater than the appearance potentials of the ions of interest, thereby minimizing contributions due to fragmentation.

Assuming that under these conditions OBF^+ and $(OBF)_3^+$ are produced solely by simple ionization of the corresponding molecules, the following relationships hold:

$$(I^+_{OBF}\ T)\ k_1 = P_{OBF}$$

$$(I^+_{(OBF)_3}\ T) k_2 = P_{(OBF)_3}$$

where the I^+'s are ion currents, T the absolute temperature, P's the appropriate equilibrium partial pressures within the crucible, and the k's are temperature independent sensitivity factors which include ionization cross sections, ion collection efficiency, electron multiplier gain, etc. The equilibrium constant K of the reaction

$$(OBF)_3\ (g) = 3\ OBF\ (g) \qquad (6)$$

can be expressed as

$$K = \frac{P^3_{OBF}}{P_{(OBF)_3}} = \frac{(I^+_{OBF})^3\ T^2\ k_1}{I^+_{(OBF)_3}\ k_2} \qquad (7)$$

The intensity of the m/e 46 peak was used for I^+_{OBF} and that of m/e 138 for $I^+_{(OBF)_3}$. A second law heat for reaction (6) can thus be obtained from the slope of a plot of log $[(I^+_{46})^3\ T^2/I^+_{138}]$ versus 1/T. The data are given in Table IV, and a temperature plot is shown in Figure 4. The derived heats, ΔH_{1200}, for reaction (6) are 138.2 and 144.2 kcal for runs 1 and 2, respectively. Changes in instrument sensitivity during the period of days between the runs are probably responsible for the displacement of the two curves. An average of the two runs gives $\Delta H_{1200} = 140.2$ kcal for reaction (6). Taking $\Delta(H_{1200} - H_{298}) = 3.6$ kcal from estimated thermal functions, one calculates $\Delta H_{298} = 144 \pm 15$ kcal. From this value and the ΔHf^o_{298} for $(OBF)_3(g)$, -566 kcal/mole[1], the heat of formation of OBF(g) at 298° K is derived as -141 ± 5 kcal/mole. Another determination is presently being made in an attempt to obtain a more accurate second law heat.

The ΔHf^o_{298} for OBF(g) reported here is in agreement with other unpublished values determined by mass spectrometry. It also agrees with the value -142 ± 3 kcal/mole obtained from low pressure flow studies of the B_2O_3 - BF_3 reaction carried out in a silica flow system[14]. However, the validity of the flow studies has not been clearly established in view of recent results[15] which indicate that at moderate temperatures boron trifluoride reacts much faster with silica than with boric oxide. It would seem that reaction of BF_3 with silica, as shown in Reference (15), would produce relatively large amounts of SiF_4 and significantly lower the partial pressure of BF_3 in the reaction zone, making it difficult to specify the principal reaction under study.

The infrared measurements of Fisher et al[15] appear to confirm the ring structure for $(OBF)_3$.

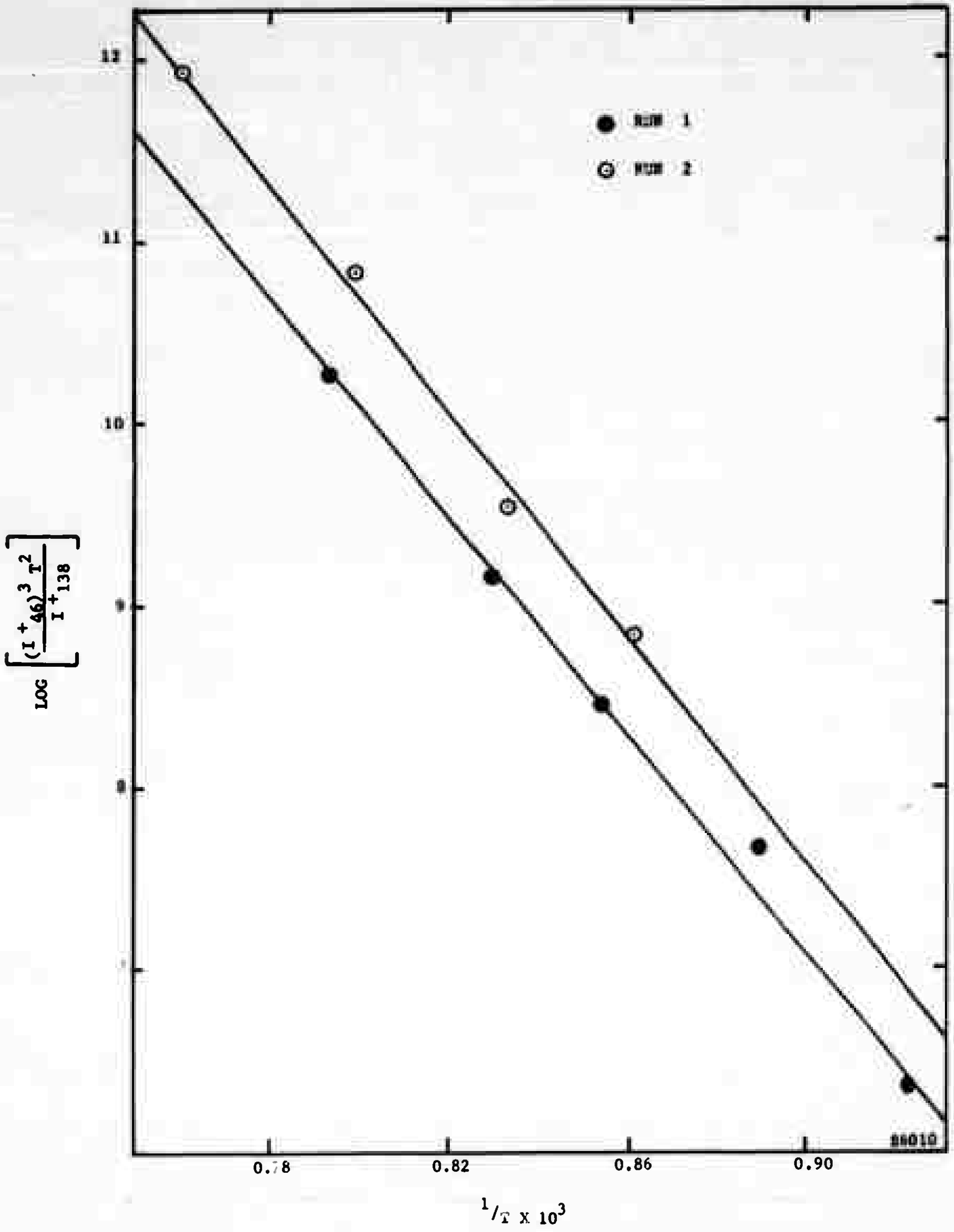

FIGURE 4. TEMPERATURE OF THE OBF MONOMER-TRIMER EQUILIBRIUM

4.2 THE VAPORIZATION OF MAGNESIUM NITRIDE

The vaporization of magnesium nitride has been studied mass spectrometrically in an attempt to shed light on the anomalous vaporization behavior[2] of this material. The sample was a portion of that used for the torsion-effusion studies[2], and was placed in a tungsten crucible.

The mass spectrum of vapor species at 834° C for 40-volt electrons contains N^+, Mg^+ and N_2^+ ions as shown in Table V. No measurable amounts of molecular and polymeric ions were present. The Mg^+ peaks could be completely extinguished by closing the shutter which separates the Knudsen and ion source compartments. For N_2^+ the effect of closing the shutter, as previously observed for ions from permanent gases[2], is a partial reduction of ion intensity.

Appearance potential measurements for each of the ions listed in Table V were made in an effort to determine the neutral species from which the ions are formed, and also to evaluate the suitability of the newly installed instrument for such measurements.

Ionization efficiency curves for the ions $^{24}Mg^+$, N_2^+ and N^+ are shown in Figure 5. Also shown is the curve for $^{202}Hg^+$, from background mercury which was used for calibration of the electron energy scale. Slopes of the straight line portions of all four curves have been made approximately equal by applying appropriate scaling factors to the ordinates. Appearance potentials were determined by the vanishing current method[17] and are given in Table VI.

The experimentally determined appearance potential of Mg^+, 7.4 ± 0.2 ev, agrees with the spectroscopic ionization potential of magnesium atoms, 7.6 ev[18], thereby indicating that magnesium atoms are produced in the vaporization of Mg_3N_2. Similarly, agreement between the measured appearance potential of N_2^+, 15.6 ± 0.2 ev, and the spectroscopic ionization potential of the nitrogen molecule, 15.55 ev[19], is evidence for the existence of molecular nitrogen in the effusing vapor. Further indication of the latter is given by the fact that the value obtained for the appearance potential of N^+, 24.3 ± 0.2 ev, has also been obtained for production of N^+ from molecular nitrogen by electron impact[20].

From a temperature study of the $^{24}Mg^+$ intensity over the range 956 to 1204° K, the heat of the reaction

$$Mg_3N_2(s) = 3\,Mg(g) + N_2(g) \qquad (8)$$

TABLE V

MASS SPECTRUM OF VAPOR SPECIES FROM Mg_3N_2 AT 834°C

IONIZING VOLTAGE = 40 VOLTS

m/e	Ion	Relative Intensity
14	N^+	2.4
24,25,26	Mg^+	1.8
28	N_2^+	100

TABLE VI

APPEARANCE POTENTIALS OF IONS FROM VAPOR PRODUCED BY Mg_3N_2 AT 834°C

Ion	$(I.V.)_o$,v	$\Delta(I.V.)_o$,v	A.P.,ev
$^{202}Hg^+$	8.2	--	10.4*
$^{24}Mg^+$	5.2	-3.0	7.4 ± 0.2
N_2^+	13.4	5.2	15.6 ± 0.2
N^+	22.1	13.9	24.3 ± 0.2

*Spectroscopic ionization potential of Hg.

$(I.V.)_o$ = Value of ionizing voltage corresponding to zero ion current; obtained by extrapolating foot of ionization efficiency curve to abscissa.

$$\Delta(I.V.)_o = (I.V.)_o\, x+ - (I.V.)_o\, Hg+$$

$$A.P. = \text{appearance potential} = 10.4 + \Delta(IV)_o$$

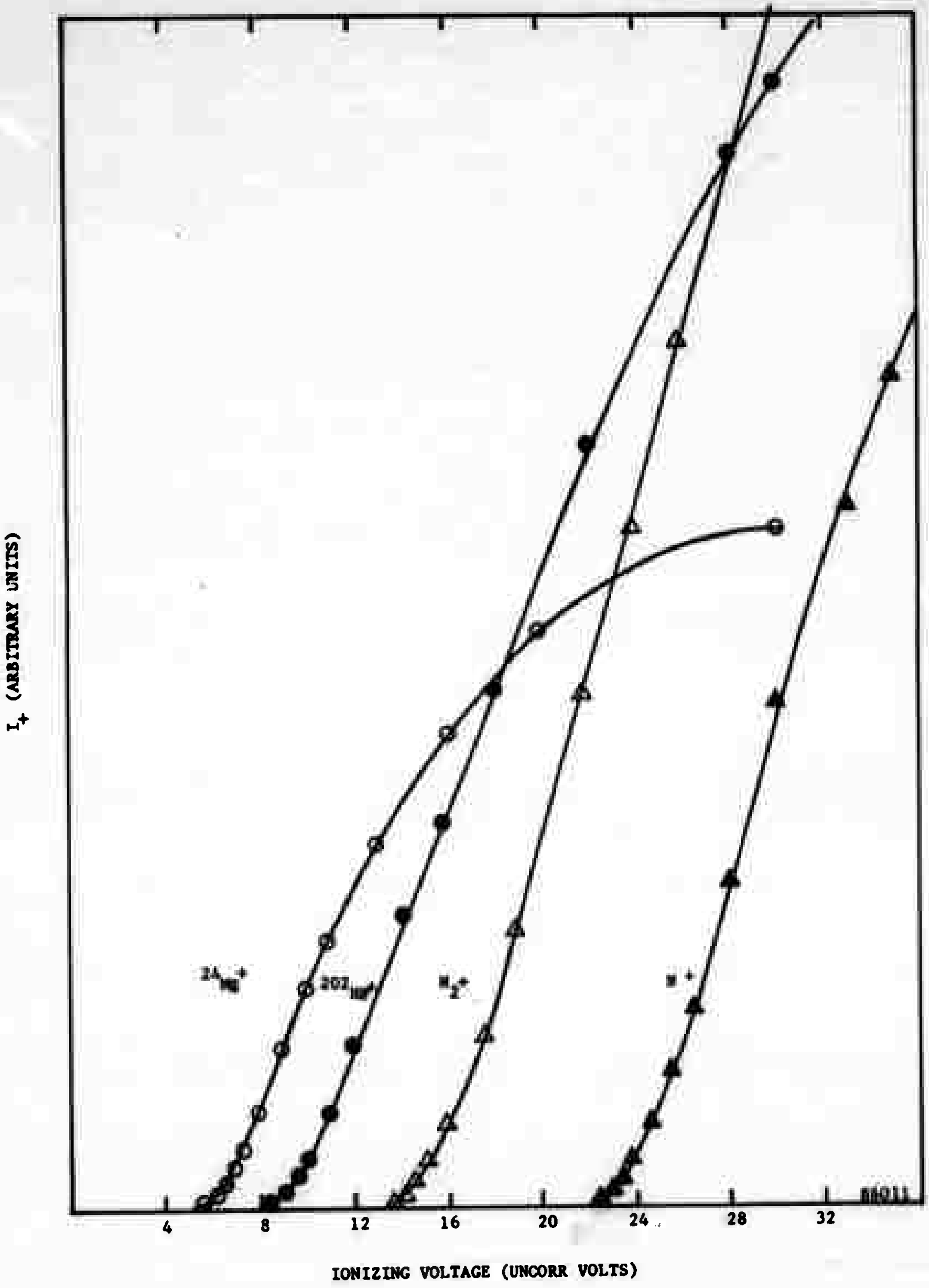

FIGURE 5. IONIZATION EFFICIENCIES OF IONS IN THE MAGNESIUM NITRIDE SYSTEM

has been obtained as 286 ± 5 kcal at 298° K, using second law methods. This value is somewhat lower than the second law ΔH_{298} of 309 kcal obtained from torsion-effusion studies[2], but is considerably higher than the third law result of 243.5 ± 0.5 kcal[2] and is in even poorer agreement with a ΔH_{298} of 217.0 calculated from thermochemical data. The mass spectrometric studies thus confirm the anomalous vaporization behavior, but give no indication as to its cause.

SECTION 5

SPECIFIC HEAT MEASUREMENT

Little progress has been made in the specific heat area in this period because of difficulties in making reliable temperature measurement. The principal problem centers on instability of the vacuum phototube used as sensor in the recording pyrometer. Although the phototube stability initially appeared to be acceptable, subsequent use of the instrument showed very erratic behavior. Some consideration is being given to other types of sensors in an effort to improve stability. Several recording pyrometers which have recently become commercially available are also being evaluated.

SECTION 6

FUTURE PROGRAM

Vaporization studies on Li_2O and $LiBO_2$, now in progress, will be completed. Results to date indicate a relatively stable gaseous $LiBO_2$ molecule is formed.

The reaction of elemental boron with gaseous BF_3 will be studied in the mass spectrometer in order to obtain thermal data on BF_2. A gas inlet system has been built and tested for this purpose.

The reaction of alumina with AlF_3 and other fluorides will be studied in the mass spectrometer so as to obtain information on gaseous aluminum oxyfluoride species.

Transpiration measurements on the ZrO_2-HCl system will be continued. The reaction of zirconia with HF or gaseous fluorides will also be studied, if a mass spectrometer survey indicates Zr-O-F species to be important.

The vaporization of lithium aluminate, $LiAlO_2$, will be studied by both effusion and mass spectrometric techniques. It is also planned to study the reactions of $LiAlO_2$ and other mixed oxides with H_2O and halogens.

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[1]

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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.

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[1] This work supported in part by the Advanced Research Projects Agency under Contract NOrd 17980.

Data reported here have been obtained by the torsion-effusion method, which has been described previously[2,3]. 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

$$P = \frac{2k\theta}{\Sigma\, afq} \qquad (1)$$

where k is the torsion constant of the filament, θ 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[4].

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.

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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[5] and Witt and Barrow[6], 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[7] 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.

---

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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[2] between the cell and the high frequency field was avoided, leading to entirely satisfactory operation. A 0.2 cm diameter hole drilled in the bottom of the tantalum susceptor served as a pyrometer sight hole. Additional holes of the same size were drilled in the susceptor side and these, in addition to 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, was evacuated to a pressure of 5×10^{-5}mm or lower. The bottom of the tube contained a planar optical window protected by a movable shutter as part of the optical sight path. Temperatures were measured with a calibrated disappearing-filament optical pyrometer signting on the hole in the susceptor bottom; the relation between pyrometer reading and effusion cell temperature had been established through a set of calibration experiments in which pyrometer temperatures were compared with the output of a standard platinum thermocouple, the junction of which was placed within the sealed sample chamber of an effusion cell. After correction for reflection losses at window and prism surfaces, the results indicated the susceptor arrangement to have an effective emissivity of 0.9 at 0.65μ, due, no doubt, to non-uniform heating of the susceptor by the induction field.

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[2,3]. 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. Data were obtained with two different orifice sizes; the two sets of results are in good agreement, indicating the observed pressures 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[8]. 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[9]. The assumption of monomeric vapor implicit in the calculations appears to be valid since

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mass spectra of the vapor obtained under both free evaporation[10] and Knudsen[11] 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, 86.5 kcal/mole, is assigned an overall accuracy uncertainty of ±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 (9).

TABLE II

COMPARISON OF RESULTS

Investigator	Reference	ΔH_{298}, kcal/mole
P. Harteck	12	90.7
L. D. Hall	13	84.7 ± 0.7
R. K. Edwards	14	87.0
E. G. Rauh	14	87.2 ± 0.8
A. N. Nesmeyanov et al.	15	87.3
This Research		86.5 ± 0.9

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All results are presumably based on effusion measurements although no details concerning the work of Edwards[14] or Rauh[14] are as yet available. Values of ΔH_{298} calculated from [illegible] data of Nesmeyanov et al.[15] showed a trend of 0.7 kcal/mole over the 200° range of the measurements; an average has been selected. The ΔH_{298} obtained from this research is in good agreement with the most recent values, and it would seem that 87.0 ±0.5 kcal/mole is the present best value for the heat of sublimation of gold at 298°K.

TABLE I

The Vapor Pressure and Heat of Sublimation of Gold

T°K	$\theta \times 10^3$, rad	$P \times 10^5$, atm	ΔH_{298}, kcal/mole
	Cell #4, Series I		
1796	115.8	10.7	86.2
1775	86.6	8.0	86.2
1747	55.7	5.2	86.6
1671	22.7	2.1	86.0
1819	140.2	13.0	86.5
1790	98.7	9.2	86.5
1752	60.7	5.6	86.5
1711	31.0	2.9	86.9
	Cell #4, Series II		
1828	148.7	13.8	86.7
1807	129.0	12.0	86.3
1787	89.0	8.3	86.7
1747	56.7	5.3	86.5
1690	25.9	2.4	86.5
	Cell #5, Series I		
1828	23.7	15.3	86.3
1881	43.9	28.2	86.4
1780	12.8	8.2	86.4
1730	5.7	3.7	86.9
	Cell #5, Series II		
1777	9.5	6.1	87.2
1841	27.5	17.7	86.3
1904	66.3	42.6	85.8
			Av. 86.5 ± 0.2

	Cell #4	Cell #5
a, cm^2	0.0046	0.0010
Σ afq, cm^3	0.00681	0.000977
k, dyne cm/rad	3.20	3.18

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