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OF GALLIUM NITRIDE

Zuhair A. Munir

(Thesis)

March 14, 1963

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OF GALLIUM NITRIDE

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ABSTRACT

Mass-spectroscopic measurements were used to demonstrate that gallium vaporizes almost exclusively as gallium atoms, and that gallium nitride vaporizes as gallium atoms and nitrogen molecules.

The vapor pressure of gallium was measured by the torsion-effusion method between 1174 and 1603°K. The pressure, in atmospheres, is given by the expression: $\log P = 5.458 - (13,743/T)$ in that temperature range. The heat of sublimation of gallium is calculated by the second-law method to be 63.5 kcal/mole when extrapolated to 298°K, while the value calculated by the third-law method is 65.44±0.23 kcal/mole. These values are in excellent agreement with the selected value of ΔH^o_{298} = 65.3±1.0 by Hultgren.

Gallium nitride was found to sublime congruently in a Knudsen cell when the ratio of orifice area to sample area was 1:25 or larger, and incongruently to leave liquid gallium in the cell when the ratio was 1:50 or less.

Equilibrium vapor pressures for gallium nitride cannot be obtained by the effusion method because of a very high activation energy for the sublimation process. The rate of the reaction $GaN(s) = Ga(g) + 1/2\ N_2(g)$ was measured by a torsion-Langmuir method. Heats of activation were calculated to be $\Delta H^{\ddagger}_{298}$ = 125.4 kcal/mole and $\Delta H^{\ddagger}_{298}$ = 127.50 kcal/mole by the second-law and third-law methods, respectively. Entropies of the slow step were found to be $\Delta S^{\ddagger}_{298}$ = 54.85 eu by the second-law method and $\Delta S^{\ddagger}_{298}$ = 52.92 eu by the third

law method. The close agreement in these values implies that the rate-determining step is the final step of escape of gallium or nitrogen molecules from the surface, rather than an earlier surface diffusion step. It is proposed that the slow step is the formation and immediate desorption of N_2 molecules from the surface.

I. INTRODUCTION

In recent years much attention has been given to compounds of elements formed between subgroup metals of group III and elements of group V because of their potentially useful semiconducting properties. Of these III - V compounds, the nitrides seem to have received relatively little attention. This may be due to the fact that nitrides are somewhat more difficult to prepare and fabricate as semiconducting devices because one of the constituents is, of course, a permanent gas.

It would seem, therefore, that additional information regarding the nature of vaporization and condensation mechanisms of these nitrides would be helpful and would perhaps suggest solutions to the problems encountered in industry.

A review of the literature for gallium nitride revealed some interesting results with regard to the nature of its vaporization.

Early mention of the thermal stability of gallium nitride was made by Johnson et al.[1] They reported that gallium nitride "sublimes" without decomposition at temperatures in excess of $800^{\circ}C$. They also reported that gallium nitride reacts slowly with oxygen at $900^{\circ}C$ to form gallic oxide.

More recently, Sime and Margrave[2] measured the vapor pressure of gallium nitride by a transpiration method and reported the rate to be too high, when compared with values calculated from estimated free-energy functions and the heat of formation,[3,4] to be explained by the expected reaction: $GaN(s) = Ga(g) + 1/2 \ N_2(g)$. From thermodynamic arguments, they postulated that GaN(g) is not the principal gaseous species above the solid and that a possible explanation for their observed vapor pressures was the formation of a polymer $(GaN)_x(g)$. This vaporization process would be analogous to those found in studies of various gaseous halides.[5,6]

No gaseous nitrides of elements as metallic as gallium have ever been unambiguously identified, so more detailed study of gallium nitride vaporization appeared to be of great scientific interest. This work was

initiated in order to determine the vapor pressure of solid gallium nitride by means of the torsion-effusion method, and especially to examine the nature of the gas molecules that are important in the vaporization process.

During the course of this investigation the fact emerged that the sublimation reaction has an activation energy that is much higher than the heat of sublimation; the major objective of the research became the determination of this activation energy. The vapor pressure of gallium was redetermined, because a precise vapor pressure value proved to be necessary for the interpretation of the nitride sublimation data.

II. VAPOR PRESSURE OF GALLIUM (ℓ)

A. Introduction

Harteck[7] in 1928 and Speiser and Johnston[8] in 1952 measured the vapor pressure of gallium by the Knudsen-effusion method with quartz effusion cells. However, more recently a mass-spectrometric study[9] showed that gallium reacted with quartz, giving a considerable concentration of $Ga_2O(g)$ above $865^{\circ}C$. This suggested that the reported gallium vapor pressures are too high. To clarify the situation, Cochran and Foster[10] investigated the apparent vapor pressures of gallium in both quartz and alumina Knudsen cells. Data from quartz cells agreed well with the data of Speiser and Johnston, but pressures measured in alumina cells were four- to fivefold lower. Cochran and Foster concluded that the alumina cell data were correct.

Based on the assumption that gallium vapor is monatomic, as substantiated by mass-spectrometric studies,[9,11] Cochran and Foster calculated the heat of sublimation $\Delta H_{s,298} = 68.96\pm0.19$ kcal/mole, compared with 65.00 and 65.3$\pm$1 selected by Stull and Sinke[12] and by Hultgren and associates,[13] respectively, from evaluation of the earlier two experimental studies.

Simple thermodynamic calculations showed that $Ga_2O(g)$ would be unstable in the presence of carbon. Therefore, a graphite cell was used in the present investigation of gallium.

B. Experimental

The torsion-effusion method has been described in several publications.[14-17] Recently Schulz[18] used an apparatus similar to the one used in this work to make a critical study of this method. No extensive details will be given here.

Figure 1 shows a schematic diagram, while Fig. 2 shows a photograph of the torsion apparatus. The main vacuum chamber is a cylinder about 14 in. in diameter and about 18 in. long. Situated in the center of this chamber is a cylindrical heating element made of 20-mil tantalum
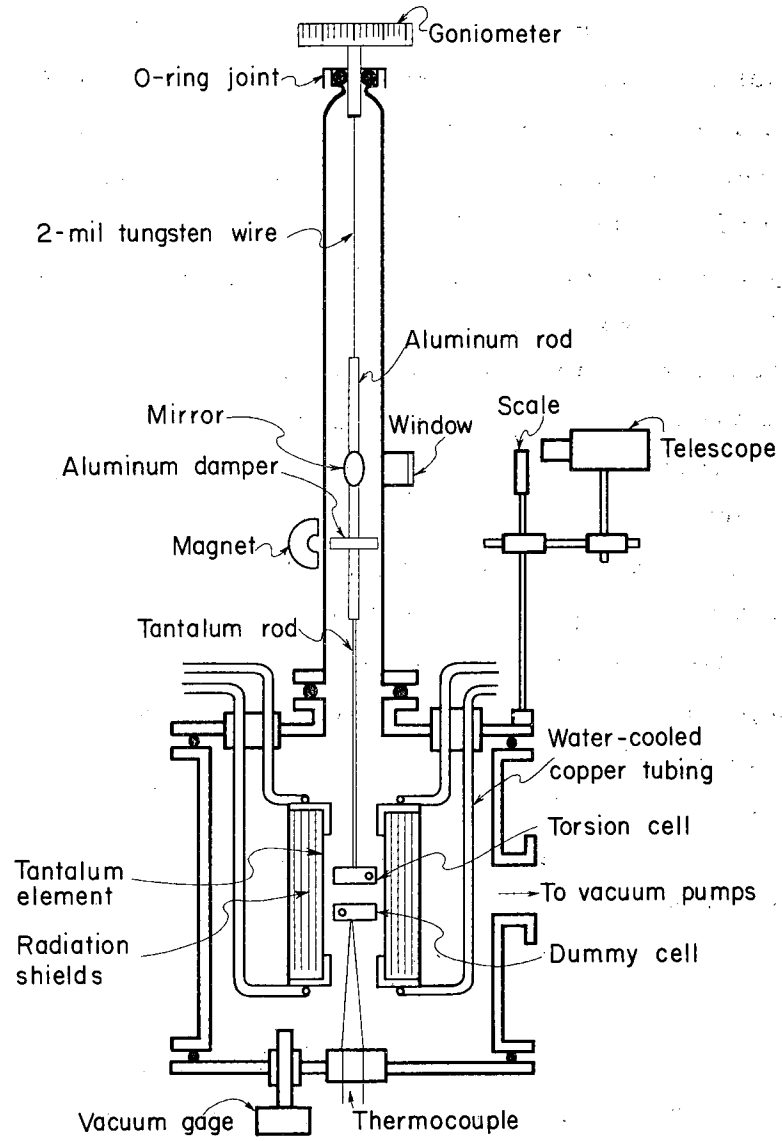
Fig. 1. Schematic diagram of torsion apparatus.
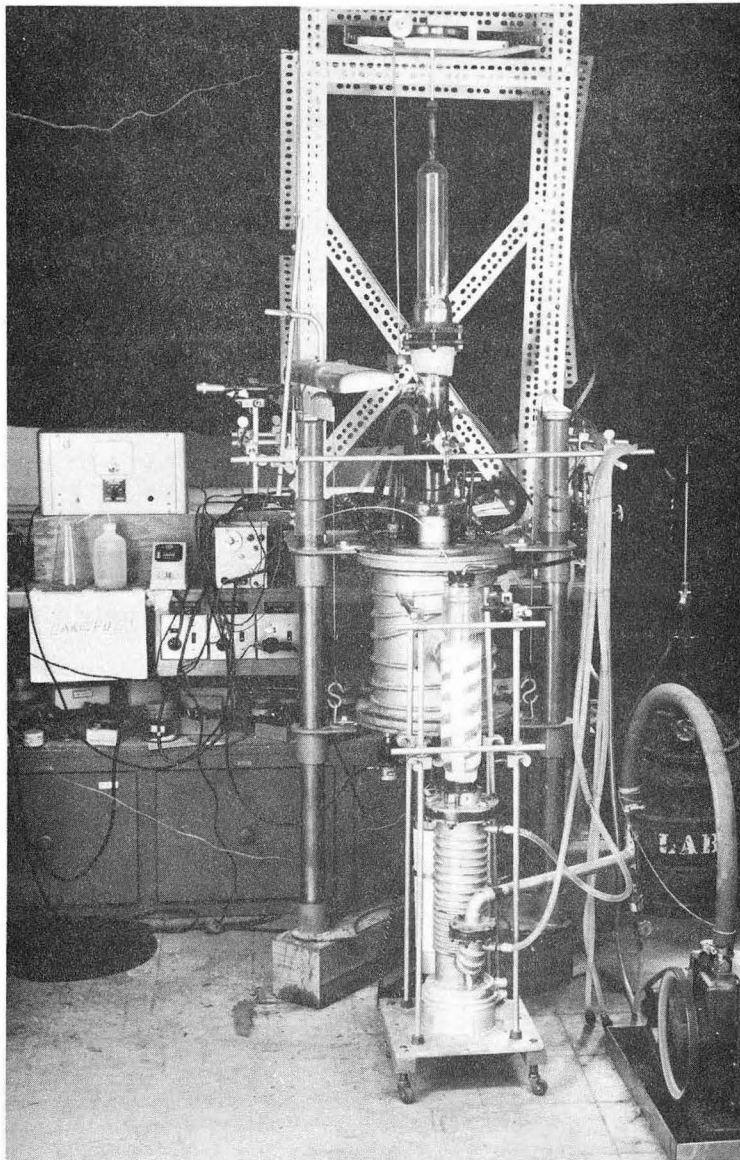
ZN-3632

Fig. 2. Photograph of torsion apparatus.

sheet, to give an approximate diameter of 3 in. Wrapped around the heating element are several layers of tantalum radiation shields. A glass tube of approximately 4-in. diameter and 3-ft length is joined to the top of the vacuum chamber and thus forms the upper part of the apparatus. Directly above this tube is a specially designed goniometer which acts as the anchor point for the entire suspension system by means of a 1/4-in. aluminum rod which enters the top of the glass tube through an O-ring joint. A 2-mil annealed tungsten wire 11 in. long is fastened to the lower end of the aluminum rod. To the lower end of the tungsten wire, a second 1/4-in. aluminum rod is attached. Glued to this rod is a 1/2-in.-diam circular mirror which hangs directly in front of a window with an optically flat surface. A circular aluminum disk attached to the rod a few inches below the mirror serves as a damper when a permanent magnet is placed near it.

The lower part of the suspension system is a 100-mil tantalum rod which is joined to the aluminum rod below the damper. The torsion cell is fastened to the free end of this rod. During a run the cell hangs free in the center of the heating element.

Two different designs of graphite cells were used in this work. The old type, which has been described by Searcy and Freeman,[19] was used in some early runs. A new design, shown in Fig. 3, was later employed. This design, similar in principle to a match box, has some advantages. Besides the obvious ease with which it can be charged with sample, the design also eliminated the possibility of having two different pressure conditions in the same cell. The cell was 1-1/2 in. long, 1/2 in. wide, and 1/2 in. deep. Several sizes of orifices were used. Detailed information is given in Appendix A.

Angular deflections resulting from the force of the effusing vapors were determined by returning the suspension system to its original (null) position. This was done by sighting through a telescope on the mirror that reflects a scale placed outside the vacuum system just below the telescope. After returning the suspension assembly to its original
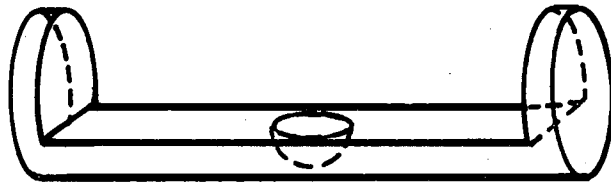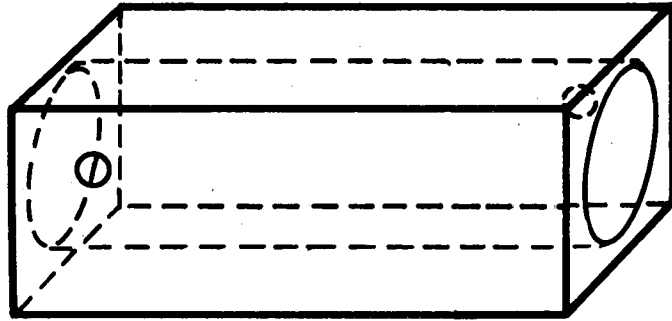
MU-29968

Fig. 3. Torsion cell.

position, as indicated by the scale, deflection angles were read from the goniometer. With this arrangement it was possible to measure angles to the nearest 0.01 deg.

Vacuum was maintained by a duoseal forepump and an MCF-300 oil diffusion pump with 300-liter/sec capacity. Use of liquid nitrogen in a trap above the diffusion pump made it possible to obtain a vacuum of better than 10^{-5} mm Hg.

A 10-V secondary of a 30-kVA transformer supplied power for the tantalum heating element. Water-cooled heavy-wall 1/4-in. copper tubing carried the power to the heating element through CGB connectors.

Temperature measurements were made by means of a calibrated 20-mil Pt-Pt + 10% Rh thermocouple. The calibration procedure is given in a following section. The thermocouple lead was inserted in a small hole in the bottom of a "dummy" cell located 1/2 in. below the effusion cell. The thermocouple wires were led through a Stupakoff connection to the outside of the vacuum chamber. Alumina protection tubes were used to insulate the bare portions of the wires. A mixture of ice and distilled water formed the cold junction and the resulting emf was measured by a Leeds and Northrup potentiometer.

The output of the thermocouple was fed to a Leeds and Northrup strip chart recorder. Measurements were made only after the temperature had reached a constant value for at least 5 min as indicated by the emf output on the recorder chart.

The gallium used was 99.99% pure material obtained from the Lawrence Radiation Laboratory in Livermore, California.

C. Thermocouple Calibration

The freezing points of gold, silver, copper, and aluminum were used as standard points in the calibration of the Pt-Pt + 10% Rh Thermocouple.

Samples of the standards were placed inside the dummy cell and were heated 50 to 100°C above their respective melting points. When

the power was turned off, the thermocouple output was monitored on a calibrated strip chart recorder. A cooling curve obtained in this manner contained an arrest which corresponded to the freezing point of the metal used as a standard. The results of several runs are given in Table I and are plotted in Fig. 4.

In order to verify the assumption that the temperature of the dummy cell is the same as that of the effusion cell for a given power setting, the dummy cell was moved up and down in the middle portion of the heating element. No difference in temperature was observed. This experiment was repeated at different power inputs and the results were all identical.

D. Results

Vapor pressures calculated from the torsion-effusion data for gallium are given in Table II and are plotted in Fig. 5. Pressures were calculated from the equation

$$P = \frac{2D\phi}{(q_1 a_1 f_1 + q_2 a_2 f_2)} ,$$

where

P = vapor pressure, atmosphere

D = torsion constant of the wire, dyne-cm

ϕ = angle of deflection, radians

q_1, q_2 = perpendicular distances from the center of the effusion hole to the axis of rotation, cm

a_1, a_2 = areas of effusion holes, cm^2

f_1, f_2 = force correction factor (Searcy's correction factor).

The heat of sublimation ΔH_s was determined by using both the second- and third-law methods.[20] Apparent pressures less than 10^{-6} atm were not used in making these calculations because background torsional effects obscured the lower pressure readings. Second-law calculation by the least-square method gave $\Delta H^o_{s,298}$ = 63.5 kcal/mole. Third-

Table I. Thermocouple calibration data.

| Material	Freezing point (^{o}C)	
	Apparent	True
Al	660	660
Ag	944	960
Au	1042	1063
Cu	1062	1083
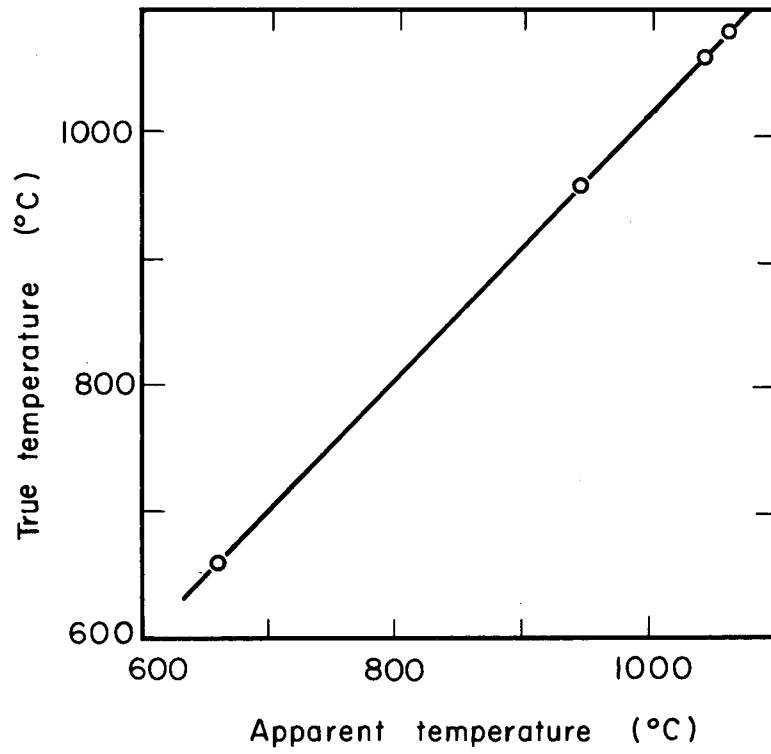
Fig. 4. Thermocouple calibration curve.

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Table II. Vapor pressure of gallium (ℓ).

T (°K)	P (atm)	T (°K)	P (atm)	T (°K)	P (atm)	T (°K)	P (atm)
1465	1.037×10^{-4}	1262	3.936×10^{-6}	1238	2.463×10^{-6}	1426	6.556×10^{-5}
1459	9.480×10^{-5}	1249	2.970×10^{-6}	1250	3.085×10^{-6}	1440	8.115×10^{-5}
1446	8.059×10^{-5}	1241	2.601×10^{-6}	1257	3.511×10^{-6}	1455	1.036×10^{-4}
1435	6.882×10^{-5}	1234	2.221×10^{-6}	1266	4.293×10^{-6}	1466	1.233×10^{-4}
1305	9.058×10^{-6}	1221	1.560×10^{-6}	1270	4.662×10^{-6}	1448	9.464×10^{-5}
1316	1.058×10^{-5}	1261	3.936×10^{-6}	1289	6.446×10^{-6}	1429	7.248×10^{-5}
1326	1.257×10^{-5}	1250	3.085×10^{-6}	1227	1.853×10^{-6}	1419	6.358×10^{-5}
1333	1.434×10^{-5}	1234	2.463×10^{-6}	1243	2.601×10^{-6}	1410	5.582×10^{-5}
1352	1.924×10^{-5}	1213	1.335×10^{-6}	1270	4.420×10^{-6}	1398	4.576×10^{-5}
1366	2.389×10^{-5}	1204	1.082×10^{-6}	1281	5.502×10^{-6}	1382	3.499×10^{-5}
1384	3.178×10^{-5}	1211	1.105×10^{-6}	1295	7.044×10^{-6}	1367	2.816×10^{-5}
1374	2.970×10^{-5}	1174	3.913×10^{-7}	1303	8.230×10^{-6}	1355	2.374×10^{-5}
1390	3.827×10^{-5}	1161	1.381×10^{-7}	1314	1.017×10^{-5}	1561	4.271×10^{-4}
1403	4.616×10^{-5}	1160	1.266×10^{-7}	1326	1.248×10^{-5}	1529	2.806×10^{-4}
1416	5.710×10^{-5}	1169	2.647×10^{-7}	1336	1.481×10^{-5}	1513	2.374×10^{-4}
1340	1.621×10^{-5}	1180	5.295×10^{-7}	1350	1.900×10^{-5}	1506	2.137×10^{-4}

Table II. (cont.)

T (°K)	P (atm)	T (°K)	P (atm)	T (°K)	P (atm)	T (°K)	P (atm)
1318	9.565×10^{-6}	1191	7.366×10^{-7}	1360	2.238×10^{-5}	1495	1.880×10^{-4}
1304	8.897×10^{-6}	1192	7.942×10^{-7}	1370	2.609×10^{-5}	1485	1.633×10^{-4}
1294	7.274×10^{-6}	1204	1.070×10^{-6}	1386	3.455×10^{-5}	1473	1.411×10^{-4}
1290	6.572×10^{-6}	1213	1.393×10^{-6}	1405	4.603×10^{-5}	1466	1.268×10^{-4}
1275	5.018×10^{-6}	1229	1.978×10^{-6}	1416	5.527×10^{-5}	1453	1.054×10^{-4}
1437	8.472×10^{-5}	1567	4.404×10^{-4}	1530	3.101×10^{-4}	1477	1.342×10^{-4}
1432	6.977×10^{-5}	1603	7.435×10^{-4}	1519	2.732×10^{-4}	1491	1.600×10^{-4}
1416	6.300×10^{-5}	1588	5.899×10^{-4}	1427	6.691×10^{-5}	1498	1.690×10^{-4}
1394	4.553×10^{-5}	1575	5.164×10^{-4}	1448	1.039×10^{-4}	1508	1.877×10^{-4}
1380	3.719×10^{-5}	1566	4.602×10^{-4}	1411	5.326×10^{-5}	1469	1.044×10^{-4}
1421	6.760×10^{-5}	1556	4.225×10^{-4}	1391	3.849×10^{-5}	1482	1.215×10^{-4}
1585	5.741×10^{-4}	1544	3.637×10^{-4}	1471	1.244×10^{-4}		
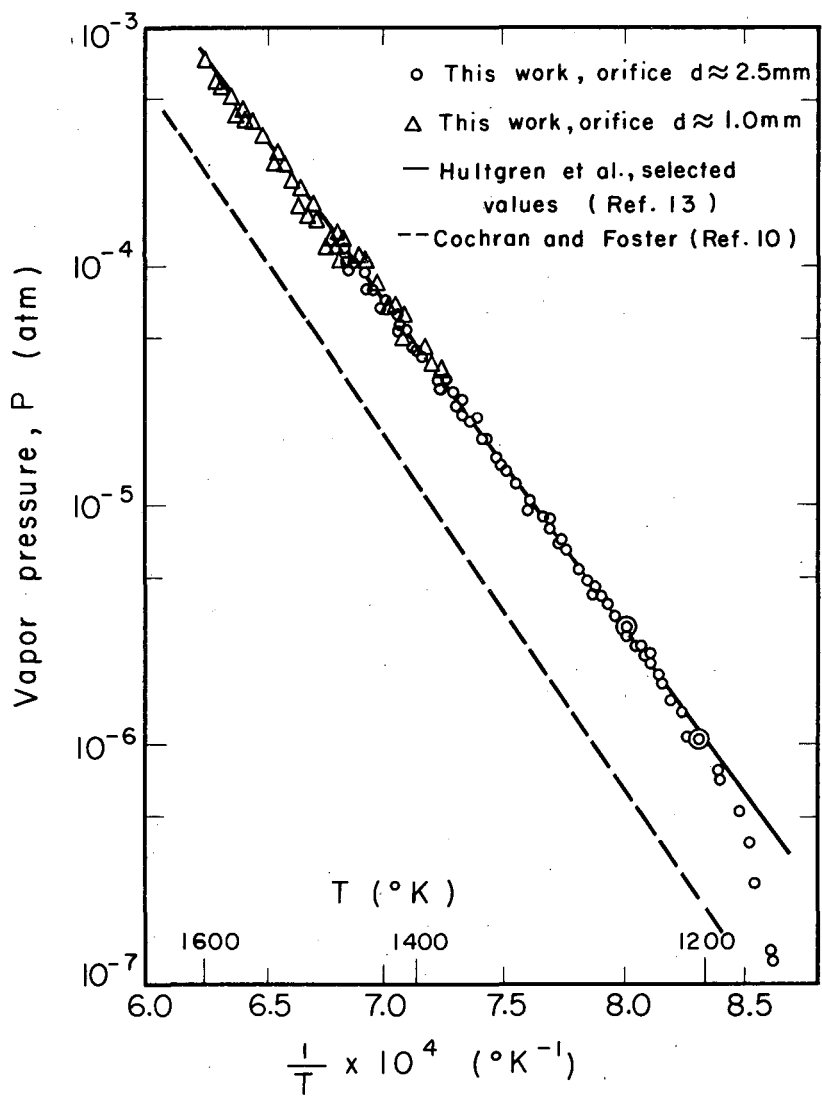
Fig. 5. Vapor pressure of gallium (ℓ).

law-method calculations based on free-energy functions selected by Hultgren[13] are given in Table III. The average value is $\Delta H^{o}_{s,298}$ = 65.44±0.23 kcal/mole as the heat of vaporization of gallium.

Least-square solution for the experimental data gave the following expression for the vapor pressure of gallium, in atmospheres, between 1174 and 1603°K:

$$\log P = 5.458 - \frac{13,743}{T} \ .$$

E. Discussion of Results

The mean value for the heat of sublimation of gallium, calculated by the third-law method, is $\Delta H^{o}_{s,298}$ = 65.44 kcal/mole. This value is somewhat lower than the value of 68.96 kcal/mole reported recently by Cochran and Foster.[10] However, the new value is in excellent agreement with the values selected by Stull and Sinke[12] and by Hultgren[13] from evaluation only of the earlier work of Harteck[7] and of Speiser and Johnston.[8]

The vapor pressures measured in this work are higher than those reported by Cochran and Foster by a factor of about 4. It is not possible to explain this difference as resulting from the presence of volatile impurities in the present investigation. Mass-spectrometer studies reported in a subsequent section of this thesis were conducted in graphite cells under conditions very similar to the conditions during these vapor pressure studies. Atomic gallium was present at concentration more than 50 times that of Ga_2O or any other oxide species.

In order to check for the possibility of a systematic error which might increase our apparent pressures, the vapor pressure of tin was measured. Three series of runs were made with tin in the temperature range of the gallium vapor pressure measurements. The results are plotted in Fig. 6. It is seen that these data are in excellent agreement with the evaluation of literature values[13] and with pressures measured recently by Schultz.[18]

Table III. Third-law heats of sublimation of gallium (ℓ).

T ($^\circ$K)	$-R\ell nP$ (cal/deg)	ΔH°_{298} (cal)	T ($^\circ$K)	$-R\ell nP$ (cal/deg)	ΔH°_{298} (cal)
1465	18.223	65,887	1262	24.721	65,252
1459	18.416	65,900	1249	25.280	65,232
1446	18.724	65,770	1241	25.544	65,217
1435	19.037	65,740	1234	25.859	65,243
1305	23.065	65,242	1221	26.559	65,438
1316	22.755	65,368	1261	24.721	65,195
1326	22.414	65,392	1250	25.205	65,245
1333	22.281	65,552	1234	25.652	64,987
1352	21.569	65,488	1213	26.869	65,399
1366	21.139	65,563	1204	27.286	65,425
1384	20.572	65,602	1211	27.244	65,749
1374	20.707	65,335	1174	29.306	66,218
1390	20.203	65,374	1180	28.706	65,840
1403	19.831	65,442	1191	28.050	65,653
1416	19.408	65,422	1192	27.900	65,522
1340	21.909	65,388	1204	27.308	65,452
1318	22.957	65,729	1213	26.784	65,296
1304	23.101	65,234	1229	26.088	65,275
1294	23.501	65,271	1238	25.652	65,192
1290	23.703	65,337	1250	25.205	65,245
1275	24.239	65,280	1257	24.948	65,281
1266	24.548	65,233	1448	18.404	65,393

Table III. (cont.)

T (°K)	$-R\ell nP$ (cal/deg)	ΔH°_{298} (cal)	T (°K)	$-R\ell nP$ (cal/deg)	ΔH°_{298} (cal)
1270	24.385	65,225	1429	18.934	65,334
1289	23.741	65,330	1419	19.195	65,258
1227	26.217	65,330	1410	19.453	65,224
1243	25.544	65,318	1398	19.848	65,236
1270	24.491	65,359	1382	20.381	65,248
1281	24.056	65,330	1367	20.812	65,154
1295	23.565	65,396	1355	21.152	65,070
1303	23.256	65,395	1561	15.411	65,654
1314	22.836	65,379	1529	16.246	65,620
1326	22.429	65,412	1513	16.579	65,471
1336	22.089	65,429	1506	16.787	65,493
1350	21.594	65,430	1495	17.041	65,403
1360	21.269	65,451	1485	17.321	65,393
1370	20.964	65,507	1473	17.611	65,325
1386	20.406	65,462	1466	17.823	65,335
1405	19.836	65,536	1453	18.192	65,305
1416	19.473	65,514	1437	18.624	65,233
1426	19.134	65,482	1432	19.010	65,564
1440	18.710	65,493	1416	19.213	65,146
1455	18.225	65,437	1394	19.858	65,073
1466	17.879	65,417	1380	20.260	64,991
1421	19.073	65,143	1427	19.093	65,459
1585	14.824	65,690	1448	18.219	65,125

Table III. (cont.)

T (°K)	$-R\ell n P$ (cal/deg)	ΔH°_{298} (cal)	T (°K)	$-R\ell n P$ (cal/deg)	ΔH°_{298} (cal)
1567	15.350	65,794	1411	19.546	65,391
1603	14.310	65,588	1391	20.192	65,396
1588	14.770	65,729	1471	17.861	65,593
1575	15.034	65,622	1477	17.711	65,638
1566	15.263	65,626	1491	17.361	65,716
1556	15.433	65,486	1498	17.253	65,852
1544	15.730	65,446	1508	17.044	65,961
1530	16.047	65,363	1469	18.210	66,023
1519	16.299	65,287	1482	17.908	66,146
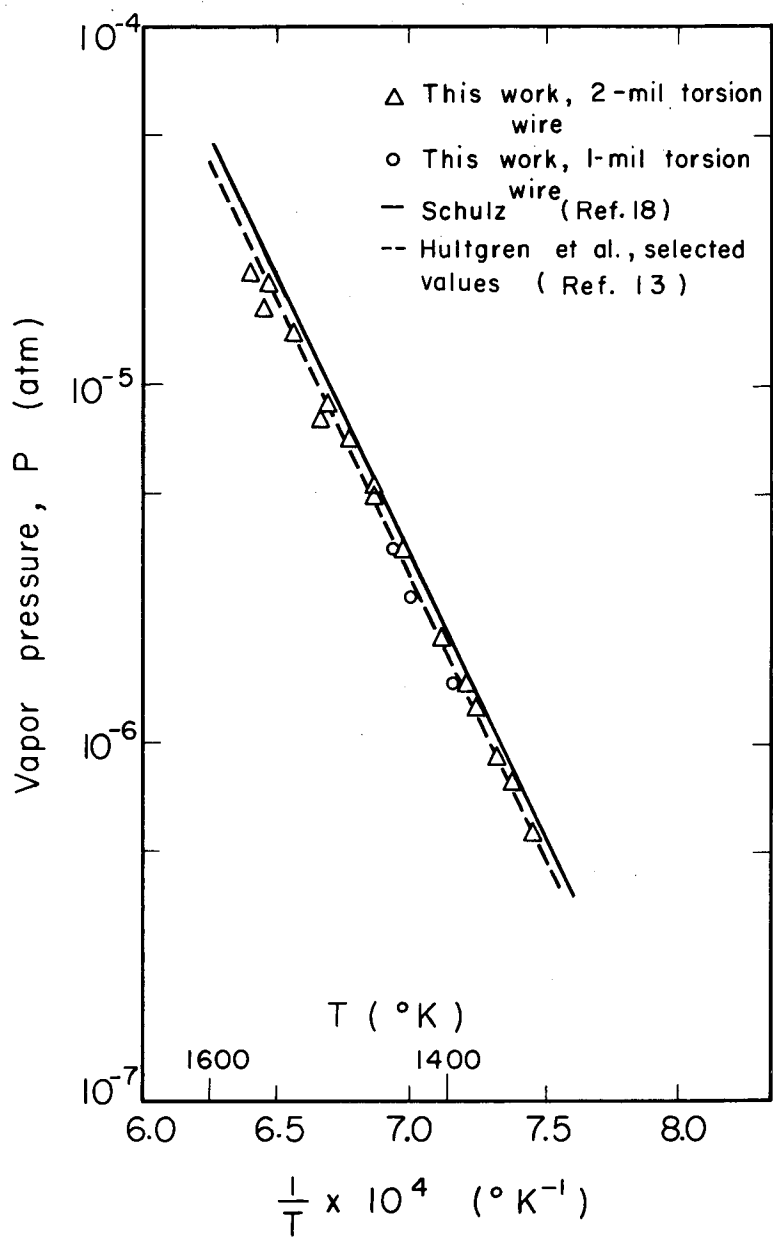
Fig. 6. Vapor pressure of tin (ℓ).

III. PREPARATION OF GALLIUM NITRIDE

Because gallium nitride is not available commercially, samples were prepared in the laboratory.

Several reports of preparation are available.[1,21-23] The most widely used method is by means of the reaction

$$2Ga(\ell) + 2NH_3(g) \rightarrow 2GaN(s) + 3H_2(g) .$$
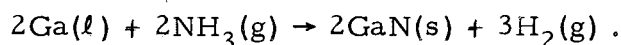
This method was adopted for our use.

A porcelain boat containing the metal was inserted into a McDonnel high-temperature mullite tube which was heated by an electric furnace. Ammonia which was dried by passing over magnesium perchlorate and phosphorus pentoxide was passed over the metal. The rate of ammonia flow was measured by a glass flowmeter of type 1/16-in. - 12 S.S. The rate of flow of ammonia gas was 10 to 15 cc/min.

Temperatures between 900 and 1000°C were required to complete the reaction within several hours. These relatively high temperatures of reaction are disadvantageous for two reasons: (1) considerable quantities of gallium metal vaporize and deposit in the cooler portions of the furnace, and (2) at these temperatures gallium nitride itself is appreciably volatile.

The gallium nitride prepared by the above method varied in color from light brown to dark gray. Our x-ray data showed no measurable difference in structure or lattice constants between samples of different colors. The nitride did not react with water, with acid, or with sodium hydroxide. Earlier workers[1,22] reported that gallium nitride is only attacked by hot concentrated alkali solutions.

A. X-Ray Analysis

The gallium nitride prepared by the action of ammonia gas on 99.99% pure gallium was analyzed by the powder method by using CuKα radiation. The best exposure time was about 15 h. The measured lines agreed exactly with data reported by Juza and Hahn.[24] Appendix B shows a comparison of our values with those of the reference cited above.

To ensure the absence of possible impurities—e. g. , Ga_2O_3—x-ray data were compared with data of $Ga_2O_3(\alpha, \beta, \gamma, \delta,$ and Σ modifications).[25,26] There was no evidence of any lines other than those of GaN.

It is noteworthy, however, that the presence of unreacted gallium metal in gallium nitride cannot be detected by room temperature x-ray diffraction. Gallium melts at $29.6^{\circ}C$. In an x-ray beam gallium crystals will melt. When room temperature diffraction studies of elemental gallium were attempted, we could obtain only a very few broad lines, indicating an amorphous phase.

To overcome the problem of melting, a small fiber was dipped in liquid gallium and immediately mounted in a Debye-Scherrer camera which had been cooled to below $0^{\circ}C$ by liquid nitrogen. After inserting the film, the camera was attached to the x-ray machine. A small non-metallic container was then placed around the camera and liquid nitrogen was allowed to flow into the container at a very slow rate. This maintained the temperature of the camera at well below $0^{\circ}C$.

A 14-h exposure yielded a sharp pattern which agreed with that reported for gallium.[27] When the same procedure was repeated with gallium nitride, the resulting pattern gave no evidence of gallium metal, thus indicating that the product of the reaction of gallium and ammonia as obtained in our laboratory was pure gallium nitride within the limits of accuracy of x-ray analysis, about 5%.

B. Chemical Analysis

A sample of our gallium nitride, kindly analyzed by the Pacific Coast Experiment Station of the U. S. Bureau of Mines, was found to be

Ga 82.98%
N 16.14%
  99.12% .

The probable source of the discrepancy in analysis is oxygen present either in nitrogen positions in the GaN lattice or in a separate Ga_2O_3 phase. Mass-spectrometer studies of the gallium nitride material reveal Ga_2O in the vapor. The concentration is, however, too low to affect the torsion-effusion studies significantly—about 1.7%.

IV. VAPORIZATION OF GALLIUM NITRIDE
FROM EFFUSION CELLS

When vapor pressure measurements were attempted by the tor-
sion-effusion method, two important observations were made: (1) The
ambient pressure of the system increased abnormally when gallium ni-
tride samples were heated to 800°C and above. This high background
pressure did not fall appreciably with time, nor did trapping with liquid
nitrogen have any noticeable effect on it. (2) Metallic droplets were
found on the radiation shield and on the tantalum support rod after a
run. These two observations led to the obvious conclusion that gallium
nitride was dissociating into nitrogen and gallium. However, it was not
possible to conclude whether this dissociation occurred inside the ef-
fusion cell or only upon impingement of vapor molecules against the
hotter surface of the heating element.

To determine whether dissociation of vapor molecules on the
tantalum surface was important, a gallium nitride sample was heated
by induction in a graphite cell without metal radiation shields. Here
again, the ambient pressure rose unexpectedly and did not decrease ap-
preciably even after a long waiting period at a steady temperature. Dur-
ing a two-hour heating period, a black deposit collected on the glass
wall of the system. An x-ray diffraction picture made of the deposit
showed no pattern. There was not enough deposit to be annealed and
thus its nature was left undetermined.

Low temperature x-ray patterns of the effusion samples were
obtained before and after several of these preliminary runs. In all
cases only the pattern of gallium nitride was obtained. This meant that
under the conditions of these experiments, gallium nitride vaporized to
a gas mixture of the same overall composition as the solid; i. e. , gal=
lium nitride sublimed congruently.

The total pressures obtained in these preliminary runs with
2.5-mm-diam effusion holes are shown as circles in Fig. 7.
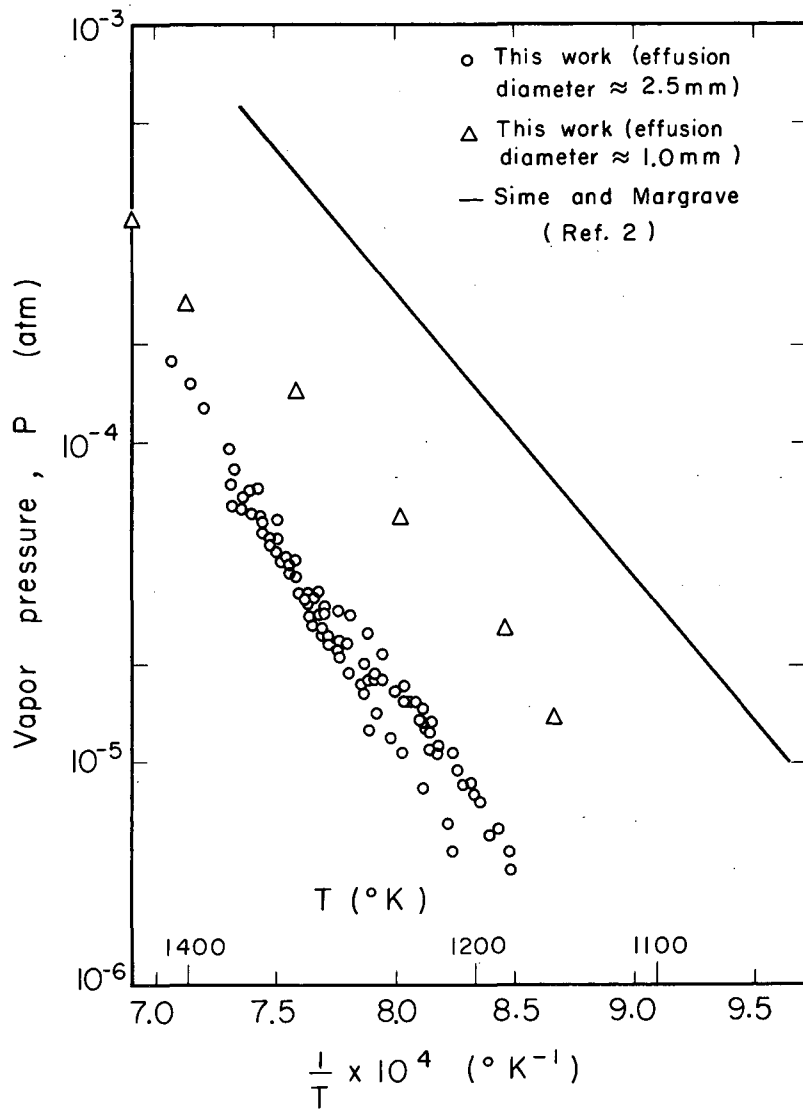
Fig. 7. Apparent vapor pressures of solid gallium nitride: torsion-effusion method.

V. INDICATIONS OF NONEQUILIBRIUM
CONDITIONS OF VAPORIZATION

While this work was in progress, Lorenz and Binkowski[28] published their results on the stability of gallium nitride. They heated samples in a container of constant volume and monitored the increase in pressure with time by means of a McLeod gage and a mercury manometer. At 800°C the dissociation rate remained constant for 85 h while the pressure rose from 10^{-6} to 10^{-2} atm. Additions of nitrogen to the system at higher pressures (1/2 atm) caused the dissociation to proceed at a slightly lower, but still constant, rate.

These results indicated that gallium nitride must vaporize by dissociation, that the rate is little influenced by nitrogen pressure over a wide pressure range, and that the equilibrium pressure must be far higher than the apparent pressures measured either by us or by Sime and Margrave.[2] There must be a slow step in the sublimation reaction.

The equilibrium pressures of nitrogen that could be roughly estimated from the kinetic studies of Lorenz and Binkowski were in reasonable agreement with pressures calculated from the -25-kcal/mole heat of formation for solid gallium nitride that was reported by Hahn and Juza,[22] whose value had seemingly been discredited by the work of Sime and Margrave. At 1400°K the equilibrium vapor pressure of nitrogen was calculated from the heat of formation to be of the order of one atm.

The measured vapor pressure of elemental gallium was only slightly higher than the apparent pressures measured for gallium nitride with the 2.5-mm-diam orifices. The interesting possibility existed, therefore, that in cells with only slightly smaller orifices equilibrium might be approached closely enough so that the vapor pressure of gallium would be exceeded and liquid gallium would be formed in the cell.

A torsion run with orifices of 1-mm diam was used to investigate this possibility. The resulting total pressure measured was from two- to fourfold higher than the previous runs with 2.5-mm orifices and were higher than the vapor pressure of gallium. In agreement with expectation under this circumstance, gallium liquid was found to be present in the cell after the run.

VI. MASS-SPECTROMETRIC INVESTIGATIONS

During the course of this work, a high temperature mass spectrometer of the type described by Chupka and Inghram[29] became available. Our observation of a metal and a permanent gas as products in the preliminary effusion studies strongly suggested that vaporization occurred chiefly by dissociation to the elements. But a mass-spectrometric investigation was undertaken to establish the gaseous species unambiguously.

A. Experimental

Gallium nitride samples which had been previously heated in vacuo for at least one hour were placed in a cylindrical graphite cell equipped with a tight-fitting graphite lid which had a small orifice in its center. The graphite cell was inserted inside a larger tantalum cell with a lid that had an orifice 3 mm in diameter. The entire cell assembly was placed in the furnace chamber of the mass spectrometer.

Six different runs were made, with two orifice diameters and three temperatures. Three runs were made with a lid that had an orifice diameter of 1 mm, and three runs were made with a lid that had an orifice diameter of 3 mm. The choice of orifice diameters was made from the knowledge that gallium nitride should sublime congruently in a cell with a 3-mm orifice, and incongruently in a cell with a 1-mm orifice.

Gallium nitride samples were investigated at 850, 950, and 1050°C. The lowest temperature was achieved by radiation from two 1/16-in. tungsten strips surrounding the cell assembly. Higher temperatures were obtained by electron bombardment. It was not possible to investigate gallium nitride at temperatures higher than about 1100°C, because of the sharp increase in the residual pressure in the mass sectrometer.

Temperatures were measured with the aid of a Pt-Pt + 10% Rh thermocouple embedded in the bottom of the tantalum cell. Observed variations in temperature for any given power setting were less than 4°C.

The accelerating electron voltage used was 70 V.

The N_2 peak at mass 28 was observed during heating. As the temperature approached $800^\circ C$, a rapid increase in the intensity of N_2 was noticed. The intensity reached a constant value after a few minutes, indicating that a constant temperature had been established. At each temperature, the effusing vapors were scanned from mass 14 to at least mass 300.

B. Results

Vapors emanating from the cell were essentially $N_2(g)$ and $Ga(g)$. Minor amounts of Ga_2 and Ga_2O were detected but usually constituted less than 2% of the total $Ga(g)$ intensity, with a maximum value of 2.5% and a typical value of 1.7%. No peaks that could be attributed to gallium metal nitride molecules were observed. Shutter effects for the nitrogen peak (mass 28) could not be reproduced and, because of the high intensity of residual nitrogen gas, the relative amounts of $Ga(g)$ and $N_2(g)$ could not be determined.

The material in the cell after heating showed the same results as observed previously. Gallium metal as well as gallium nitride remained in the cell with the 1-mm orifice, while only gallium nitride remained in the cell whose orifice diameter was 3 mm. The runs in which gallium metal remained after heating thus are made with gallium at the saturated vapor pressure for the element. The low intensities of all ion species other than gallium and nitrogen demonstrate, therefore, that in our torsion-effusion experiments made with elemental gallium in graphite cells under similar conditions, the observed torques were produced by gallium vaporization and not by vaporization of gallium oxide or other impurities.

VII. FREE-SURFACE SUBLIMATION OF
SOLID GALLIUM NITRIDE

A. Introduction

It can be concluded from the preceding observations that apparent dissociation pressures measured for gallium nitride in an effusion cell of practical orifice diameters are so far below the equilibrium pressures that there is no hope of obtaining equilibrium pressures or the heat of sublimation by an effusion method. However, from a free-surface sublimation study the activation energy of the slow step can be calculated. This quantity is of more general interest than thermodynamic data because very few reliable measurements of activation energies of sublimation are available for substances with slow steps in the sublimation process.

The first step in making free-surface sublimation runs[17] was the preparation of high-relative-density bodies of gallium nitride.

B. Preparations

1. Hot Pressing of Gallium Nitride

To obtain solid gallium nitride with a nonporous surface, some technique had to be adopted to compact the fine gallium nitride power. Hot pressing was the first method tried.

For this purpose a special graphite die was made to give samples 1/4 in. in diameter. Previously outgassed samples of gallium nitride powder were hot-pressed in vacuum at a maximum hydraulic pressure of 2000 psi. No evidence of sintering was noticed up to a temperature of $1000^{\circ}C$. At a higher temperature, $1060^{\circ}C$, the nitride began to yield. However, there was no point at which it was possible to establish the end of the sintering process; i. e., the sample continued to yield as long as pressing was continued.

Examination of the pressed sample revealed that dissociation had taken place. Significant quantities of gallium metal had deposited

on the inside walls of the hot-press chamber. Moreover, gallium metal was observed on the surfaces of the resulting pellet of gallium nitride. An x-ray pattern of one of the flat surfaces of the pellet proved the presence of gallium metal as well as the nitride. A second attempt to form pellets by hot pressing also resulted in partial dissociation. It became obvious, therefore, that the pressing operation had to be performed at lower temperatures.

2. Low-Temperature Pressing of Gallium Nitride

Through the courtesy of Professor George Jura of the Chemistry Department, it was possible to press samples of gallium nitride at room temperature. To obtain solid pieces, pressures of the order of 1.5×10^6 psi proved necessary.

About 0.25 g of the sample powder was placed between two anvils separated by an O-ring washer made from an oxide of iron. An initial pressing with a hand-operated hydraulic press was necessary. After this pressing, the "wafer" was examined under a microscope to ascertain whether or not a uniform distribution of the sample had been established inside the O-ring. Satisfactory samples were then placed in a specially designed press for high-pressure work. Each sample was held at 1.5×10^6 psi for a soaking period of 10 to 15 min.

Samples which microscopic examination revealed to have cracks or obvious defects were rejected. Through this technique several wafers were made with diameters ranging from about 1/8 in. to 1/2 in. and thicknesses of about 5 to 10 mil. All pressed samples were dark gray in color. It was impossible to remove the O-ring without breaking off some of the sample, and so the separated wafers had irregular peripheries, a circumstance that was not detrimental to the experiments described later.

Some of the wafers were crushed and examined by x-ray diffraction. The pattern obtained was that of gallium nitride only. Another x-ray examination was made of the same samples after exposure to the atmosphere for several weeks. No change was found.

No attempt was made to determine the density of the gallium nitride wafers; however, microscopic examination under 200X magnification showed no pores. A microphotograph of the "just pressed" wafer appears in Fig. 8(a).

A micrograph of a sample heated at $1200^{\circ}C$ for one hour is shown in Fig. 8(b). This photograph showed that there was no discernible change in the contour of the surface under a 200X magnification. The only noticeable change was that of the color of the sample from dark gray to light gray or white. This change was due to small variations in the concentration of gallium atoms. Changes in composition of much less than 1% may give rise to changes in color in many ceramic materials.

It is interesting to note that areas surrounding cracks in a sample remained dark in color after heating. The explanation for this observation was that a crack acted somewhat like a Knudsen effusion cell in that reflection of vapor molecules at the walls of a crack raise the pressure above the level characteristic of a free surface. Such conditions, as demonstrated in the torsion-effusion studies, tend to leave gallium metal behind and hence produce the dark color. Figure 8(c) shows this phenomenon. Only crack-free wafers were used in the torsion-Langmuir studies described in the next section, and no darkening of color was observed around the holes whose formation required termination of the torsion-Langmuir runs. The sublimation process studied, therefore, was that for a free surface.
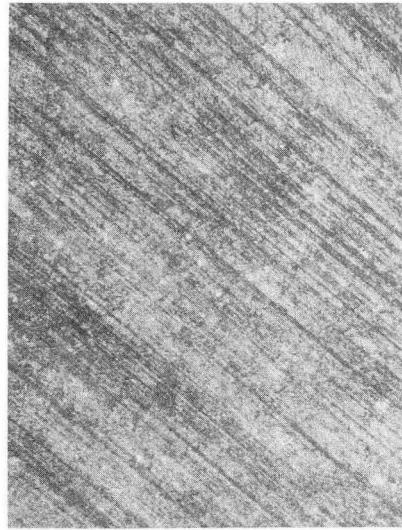
(a)
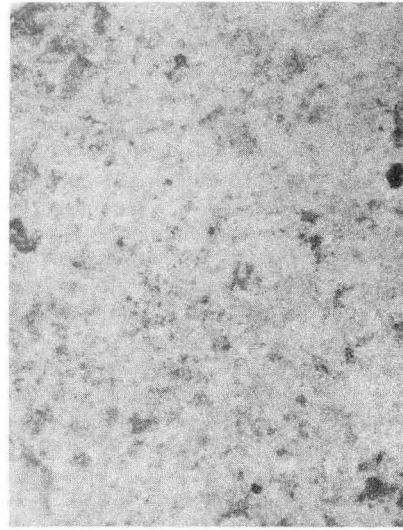
(b)

(c)

ZN-3631

Fig. 8. Microphotographs of gallium nitride solid
bodies: (a) before heating, (b) after heating,
and (c) a crack after heating.

VIII. TORSION-LANGMUIR MEASUREMENTS

A. Introduction

The torsion-effusion method of vapor pressure measurements was adopted to measure sublimation from a free surface. This was accomplished by arranging two gallium nitride wafers so that sublimation from their surfaces supplied additive torques to a graphite block in two faces in which they were mounted.

B. Experimental

The apparatus was that described for the torsion-effusion vapor pressure studies. The cell for this work was made from a graphite orthorhomboid 1-1/2×3/4×1 in. Two wells of 3/8-in. diam were drilled into opposite sides of the block. Each well had a shoulder of 5/8 in. diam drilled near the surface of the cell. Gallium nitride wafers were placed inside these shoulders and were secured there by specially de-signed graphite washers. Each washer had a flat surface that fit snugly against the gallium nitride wafer, and had a concave surface on the other side. When the washer was in place, the effective sublimation area of the sample was defined by 0.3- to 0.5-in.-diam openings through each washer. The thickness of the graphite at the periphery of the opening was negligible, so no correction was necessary for reflection of vaporizing molecules at the walls of the washers.

To prevent vapor that sublimed from the rear faces of the wafers from escaping in a manner that might contribute to the torque, an addi-tional feature was incorporated in the design. This feature was a pair of holes which were drilled from the top of the cell into cavities behind the two samples. The holes were relatively large (3 mm in diameter) and hence any vapors that sublimed from the rear face of a sample would escape through the hole in the top of the cell and give rise to no angular deflection.

Deflection measurements were made at progressively higher temperatures. At each new temperature, a waiting period was

necessary to establish uniform temperature distribution, and hence steady-state pressures. Deflections were recorded only after the temperature had remained constant for at least 5 min.

Readings were taken in this manner until deflections began to decrease with further increase in temperature or with increased time at constant temperature. A typical curve illustrating variations in apparent pressures with temperature is shown in Fig. 9.

Examination of the wafers after apparent pressures departed from the straight-line portion of a plot of log P vs 1/T always revealed that holes had developed completely through one or both wafers in at least one region. Only those points falling on the straight-line portion of a log P-vs-1/T plot were used in calculations of apparent pressures, since the rest represented deflections due to sublimation from a surface with an unknown area.

C. Results

Figure 10 shows a plot of the logarithm of the free-surface vapor pressure of solid gallium nitride vs 1/T. These results are given in Table IV. Pressures were calculated in exactly the same manner as were pressures of elemental gallium. Experimental total pressures were expressed in the form $\log P = a + (b/T)$ with the aid of the least-square method. Least-square solutions gave the following expression:

$$\log P = 7.862^6 - \frac{18{,}62^0}{T} ,$$

for solid gallium nitride in the temperature range 1166 to 1428°K. By defining $K = P_{Ga} \cdot P_{N_2}^{1/2}$, the above expression becomes
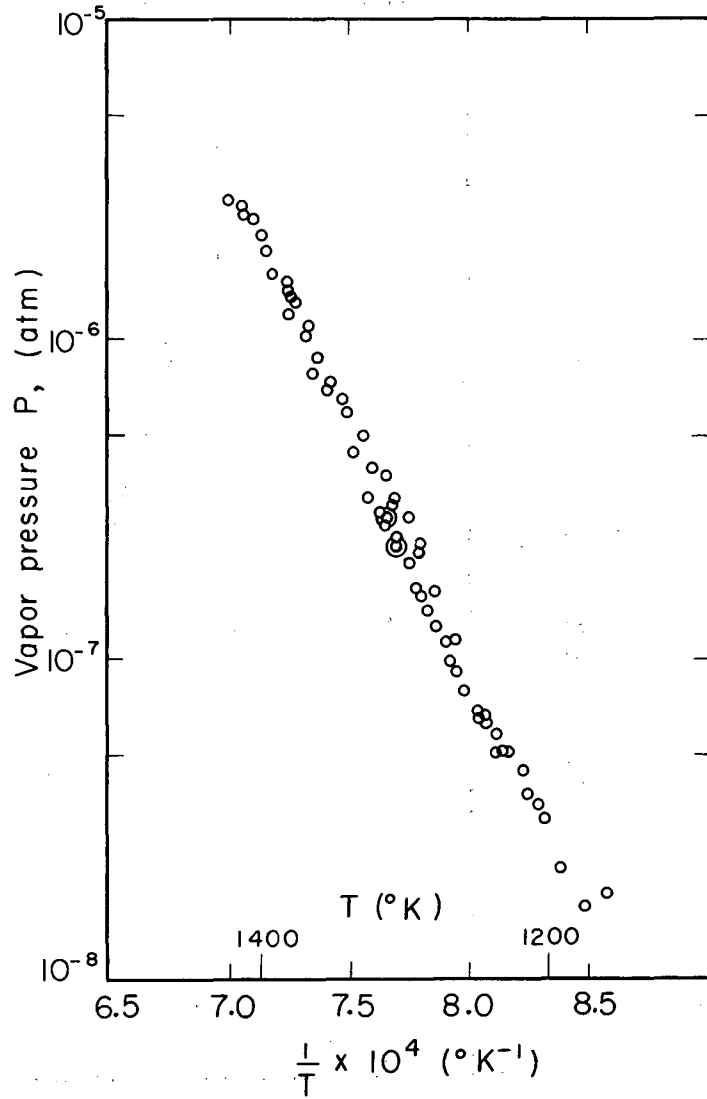
$$\log K = 11.36^6 - \frac{27{,}93^0}{T} .$$

The activation energy for the sublimation of gallium nitride was calculated by using both the second-law and third-law methods. From the above expression of K, the second-law heat of activation was calculated to be $\Delta H_{298}^{\ddagger} = 125.4$ kcal/mole. Third-law calculations were
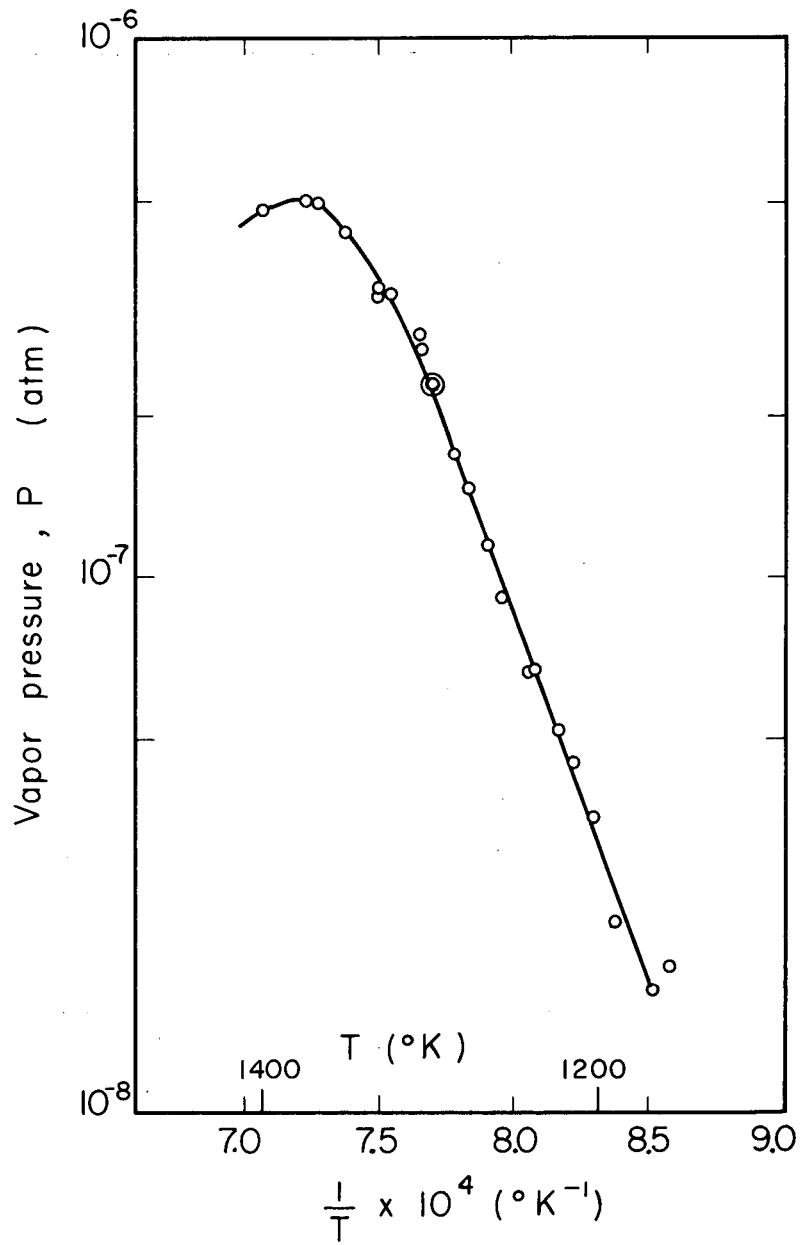
Fig. 9. Typical torsion-Langmuir run.

Fig. 10. Vapor pressure of gallium nitride:
torsion-Langmuir method.

MU-29974

Table IV. Langmuir vapor pressure of GaN(s).

T (°K)	P (atm)	T (°K)	P (atm)	T (°K)	P (atm)
1204	3.185×10^{-8}	1232	5.808×10^{-8}	1380	1.202×10^{-5}
1260	1.162×10^{-7}	1233	5.058×10^{-8}	1382	1.499×10^{-5}
1274	1.649×10^{-7}	1243	6.820×10^{-8}	1398	1.901×10^{-5}
1300	3.192×10^{-7}	1253	8.019×10^{-8}	1417	2.484×10^{-5}
1290	2.792×10^{-7}	1263	9.930×10^{-8}	1166	1.874×10^{-8}
1308	3.822×10^{-7}	1273	1.278×10^{-7}	1180	1.686×10^{-8}
1283	2.307×10^{-7}	1282	1.607×10^{-7}	1193	2.248×10^{-8}
1339	6.472×10^{-7}	1291	2.005×10^{-7}	1207	3.560×10^{-8}
1348	7.369×10^{-7}	1299	2.406×10^{-7}	1217	4.496×10^{-8}
1356	8.811×10^{-7}	1310	2.878×10^{-7}	1225	5.171×10^{-8}
1366	1.035×10^{-6}	1319	3.204×10^{-7}	1240	6.707×10^{-8}
1376	1.314×10^{-6}	1308	2.810×10^{-7}	1240	6.520×10^{-8}
1380	1.432×10^{-6}	1284	2.203×10^{-7}	1242	6.632×10^{-8}
1378	1.368×10^{-6}	1302	3.114×10^{-7}	1258	9.255×10^{-8}
1392	1.624×10^{-6}	1316	3.991×10^{-7}	1266	1.139×10^{-7}
1400	2.143×10^{-6}	1330	4.421×10^{-7}	1278	1.461×10^{-7}
1408	2.387×10^{-6}	1360	7.872×10^{-7}	1285	1.686×10^{-7}
1418	2.630×10^{-6}	1336	6.119×10^{-7}	1298	2.278×10^{-7}
1428	2.749×10^{-6}	1323	5.005×10^{-6}	1298	2.278×10^{-7}
1212	3.859×10^{-8}	1350	7.017×10^{-6}	1308	2.807×10^{-7}
1227	5.171×10^{-8}	1367	1.101×10^{-5}	1307	2.582×10^{-7}

employed in which we assumed the free-energy function for GaN(s) to be that of ZnO(s), a compound of similar formula and of approximately the same formula weight. These calculations gave $\Delta H_{298}^{\ddagger} = 127.50$ kcal/mole as the heat of activation for the sublimation of gallium nitride.

Similar calculations were made to determine the entropy of activation for this process. The second-law entropy was found to be $\Delta S_{298}^{\ddagger} = 54.85$ eu, and the corresponding third-law value extrapolated to 298°K was $\Delta S_{298}^{\ddagger} = 52.92$ eu.

D. Discussion of Results

From the heat of formation of gallium nitride measured by Hahn and Juza[22] from the known entropies of gallium and nitrogen vapors, and from estimated entropy for gallium nitride, the equilibrium constant for the reaction $GaN(s) = Ga(g) + 1/2 N_2(g)$ is calculated to be about 5×10^{-5} at 1400°K. The apparent equilibrium constant calculated from our Langmuir data is only 3×10^{-9}.

The marked difference between the apparent equilibrium constants for sublimation measured under Langmuir conditions and those measured in Knudsen cells demonstrates the existence of a free-energy barrier to the sublimation process. We will now turn our attention to the problem of identifying the step of the sublimation process that gives rise to this barrier.

The existence of a slow step in the sublimation of nitrogen from iron nitrides has been reported by Goodeve and Jack.[30] They proposed that either of two steps might be regarded as giving rise to the activation energy. The first step is the diffusion of the nitrogen atoms to the surface, and the second is the diffusion of N atoms on the surface of the solid toward each other to form N_2 molecules.

In free-surface sublimation of gallium nitride the composition of the solid is not changed and solid-state diffusion is not a necessary step in the process. Accordingly, the free-energy barrier must be imposed either by a step involved in transfer of gallium and nitrogen atoms from lattice positions in the surface layers to adsorption sites on

the surface,[31-36] by the desorption of gallium atoms, or by the step of formation and desorption of nitrogen molecules from two adsorbed nitrogen atoms.

The entropy of activation for the sublimation reaction as determined experimentally by the second-law treatment of our data is in excellent agreement with the entropy calculated for the overall reaction $GaN(s) = Ga(g) + 1/2\ N_2(g)$ by the third-law method. This fact strongly suggests that the rate-determining step is a final step in the sublimation process: either slow desorption of gallium atoms or slow formation and desorption of nitrogen molecules. Any step prior to the final vaporization step would only by coincidence have an entropy comparable to the entropy of activation that is much lower than the entropy of sublimation.

Gallium nitride forms readily from reaction of ammonia with gallium at temperatures for which N_2 gas rather than gallium nitride is the stable nitrogen-containing reaction product. This fact implies that formation of the N_2 molecules from nitrogen atoms adsorbed on a gallium nitride surface is hindered by a kinetic barrier. This same barrier to formation of N_2 molecules almost certainly is responsible for the low rate of sublimation of gallium nitride.

De Poorter[37] has demonstrated that energy interactions of nitrogen molecules with a tungsten surface are as weak as the interactions of rare-gas atoms. Nitrogen molecules are almost certainly bound by similarly weak forces to a gallium nitride surface and, once formed, desorb immediately. The formation of the molecule and its desorption can be viewed as a single step for which the heat of activation is the heat of formation of free N_2 molecules from bound nitrogen atoms.

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ACKNOWLEDGMENTS

APPENDICES

A. Cell Measurements and Related Information

Method used	Cell	a_1 (in.^{2})	a_2 (in.^{2})	q_1 (in.)	q_2 (in.)	$(L/r)_1$	$(L/r)_2$	f_1	f_2	Runs used
Torsion-effusion	OT-1	0.00801	0.00719	0.4971	0.4416	0.539	0.589	0.840	0.827	Ga, GaN, Sn
Torsion-effusion	OT-2	0.00241	0.00236	0.4558	0.4449	1.2166	0.9672	0.6906	0.7406	GaN
Torsion-effusion	OT-3	0.00126	0.00122	0.4426	0.4418	1.05	0.985	0.7726	0.7359	Ga
Torsion-Langmuir	LT-1	0.2505	0.2877	0.3348	0.3745	0.0	0.0	1.0	1.0	GaN

B. X-Ray Data for Gallium Nitride

d-values		d-values	
measured	reported[a]	measured	reported[a]
2.76	2.76	0.966	--
2.58^5	2.59	0.964	--
2.43	2.43	0.943	0.945
1.88^4	1.884	0.919	0.920
1.59	1.591	0.917	--
1.462	1.461	0.894	--
1.380	1.382	0.890	--
1.357	1.357	0.867	--
1.332	1.333	0.864	--
1.295	1.295	0.828	--
1.217	1.219	0.826	--
1.172	1.172	0.824	--
1.077	1.078	0.822	--
1.075	--	0.812	--
1.042	1.044	0.810	--
1.040	--	0.796	--
1.023	1.022	0.794	--
1.020	--		
1.004	1.004		
1.002	--		
0.970	0.969		

[a]R. Juza and H. Hahn, Z. Anorg. u. Allgem. Chem. 239, 285 (1938).

C. Calibration of Torsion Wire

Annealed wires of tungsten with 1- and 2-mil diameters were calibrated to obtain a torsion constant. The torsion constant, D, is calibrated from the period of oscillation, t, of the suspension system alone; and the period, t_w, with a weight of known moment of inertia, I_w, added to the system with the aid of the following equation:

$$D = \frac{4\pi^2 I_w}{(t_w^2 - t^2)} .$$

Typical values of D are:

Wire diameter	D
2 mil	3.561
1 mil	0.2176

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