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December 31, 1964

THE ACTIVATION ENERGY FOR THE SUBLIMATION OF GALLIUM NITRIDE+

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ABSTRACT

Gallium nitride was found to sublime congruently from a torsion-effusion cell when the ratio of orifice area to sample area was about 1/30 and incongruently to yield nitrogen gas and liquid gallium when this ratio was about 1/100 or less. A mass spectrometer investigation revealed no measurable concentrations of gallium nitride vapor molecules. The heat of activation for the reaction $2GaN(s) = 2Ga(\ell) + N_2(g)$ was calculated to be 39 kcal at 1300°K from the temperature dependence of the effusion data.

The rate of the reaction $2GaN(s) = 2Ga(g) + N_2(g)$ was measured by a torsion-Langmuir method. From the temperature dependence of sublimation the heat of activation for this reaction was calculated to be $\Delta H^{\ddagger}_{1300} = 218.6$ kcal compared to 173 kcal for the equilibrium reaction, and the entropy of activation was calculated to be 74.3 cal/deg.

+ From the thesis submitted by Z. A. Munir in partial fulfillment of the requirements for the Ph. D. degree in Engineering Science, University of California, Berkeley, June 1963.

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I. INTRODUCTION

First mention of the thermal stability of gallium nitride was made by Johnson et al.[1] who reported that gallium nitride sublimes without decomposition at temperatures in excess of 800°C. 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 an estimated heat of formation for GaN(g) to be explained by GaN monomer vaporization. They postulated the existence of a polymer $(GaN)_x(g)$.

No gaseous nitrides of elements as metallic as gallium have ever been unambiguously identified, so the existence of a gaseous gallium nitride would be of considerable chemical interest. The present study was undertaken to obtain more information about gallium nitride vaporization.

No gaseous nitride has been found, but an important result of this study has been the demonstration that gallium nitride has a high enthalpy of activation for sublimation. Several previous investigations have demonstrated free energy barriers to sublimation reactions, but for all of those investigations of which we are cognizant, either no enthalpy or entropy of activation could be obtained from the data or enthalpies of activation no larger than the enthalpies of sublimation were found.[5]

II. EXPERIMENTAL

A. Preparation of Gallium Nitride

An ammonia stream was dried over magnesium perchlorate and phosphorus pentoxide before the stream was introduced into a mullite tube at a flow rate of 10 to 15 cc/min. Gallium nitride was produced by

the reaction of the ammonia with gallium metal which was held in a porcelain boat:

$$2Ga(\ell) + 2NH_3(g) \rightarrow 2GaN(s) + 3H_2(g).$$

At temperatures between 900 and 1000°C the reaction was completed within several hours. Considerable quantities of gallium distilled into the cooler portions of the furnace during the preparative period.

The gallium nitride prepared by this method varied in color from light brown to dark gray, but samples of different colors did not differ detectably in x-ray diffraction pattern line spacings. The x-ray pattern was compared with patterns for Ga_2O_3 (α, β, γ δ, and σ modifications).[6,7] There was no evidence of any lines other than those of gallium nitride.

The gallium nitride was found by Mr. K. C. Conway of the Berkeley Thermodynamics Laboratory of the U. S. Bureau of Mines to be Ga 82.98%, N 16.14%, compared to the theoretical values Ga 83.27%, N 16.73% by weight. The probable source of the small discrepancy in analysis was oxygen present either in solution in the GaN lattice or in a separate Ga_2O_3 phase. Mass-spectrometer studies of the gallium nitride revealed Ga_2O in the vapor. The concentration was only 1 to 2%, however, too low to affect the torsion-effusion studies significantly.

B. Torsion-Effusion Studies

The apparatus and techniques used in the torsion-effusion measurements were identical with those described in a recent paper.[8] Samples were heated in graphite cells that were suspended inside a tantalum tube resistance heating element. Temperatures were measured with Pt-Pt 10% Rh thermocouples which were inserted in a dummy cell that was placed just below the sample-containing cell in a region that had been

demonstrated to be uniform in temperature. The thermocouple was calibrated by measurement of the apparent melting temperatures of aluminum, copper, silver, and gold in the dummy cell. Experimental techniques were demonstrated to be reliable by determination of the vapor pressure of tin with the apparatus. From 19 measurements with two different torsion wires, the heat of sublimation of tin at 298°K was calculated to be 72.4 ± 0.5 Kcal, in good agreement with the value 72.2 reported by Hultgren et al.[9] from evaluation of previous studies.

The total pressures obtained in runs with 2.5-mm-diam effusion holes (ratio of orifice area to upper surface area of sample approximately 1/30) are shown as circles in Fig. 1. These pressures lay several orders of magnitude below the nitrogen pressures observed in gallium nitride decomposition studies which appeared while our studies were in progress.[10] Obviously, the pressures measured in the cell with 2.5-mm-diam holes must be nonequilibrium values.

A puzzling observation, to be analyzed in the discussion section, was that although the measured pressures were 1.5 to 2 times the vapor pressure we have found for elemental gallium, no gallium was found in the cells after the experiments. X-ray diffraction patterns of the samples were obtained before and after several runs in a cell with 2.5-mm-diam orifices. The diffraction camera was cooled during the passage of the x-ray beam in a manner that had been demonstrated to be adequate to prevent melting of any gallium present by the heat generated by the x-rays, yet 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., gallium nitride sublimed congruently.

Cells fitted with smaller orifices should yield higher pressures inside the cell. If the partial pressure of gallium should become as high as the vapor pressure of gallium, the sublimation process should become incongruent and elemental gallium should remain in the effusion cell after heating.

To test this hypothesis, a sample was heated in a cell fitted with 1.4-mm-diam orifices, which made the ratio of orifice area to upper surface area of sample about 1/100. The pressures indicated by triangles on Fig. 1. were then obtained and drops of elemental gallium were found in the cell after heating.

C. Mass Spectrometric Studies

The vapor species above gallium nitride were identified by means of an Inghram-type mass spectrometer. Samples were heated in the spectrometer in a graphite Knudsen effusion cell. The graphite cell was fitted inside a larger tantalum cell with a lid that had an orifice 3 mm in diameter.

Three runs were made with a graphite 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 could be expected to sublime congruently in the cell with a 3-mm orifice, and incongruently in the cell with a 1-mm orifice.

Gallium nitride samples were investigated at 850, 950, and 1050°C with each cell. The lowest temperature was achieved by radiation from two 0.16 cm tungsten strips surrounding the cell assembly. Higher temperatures were obtained by electron bombardment. It was not

possible to investigate gallium nitride at temperatures above about 1100°C because of the high residual nitrogen pressure produced by rapid decomposition of the nitride.

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. At each temperature the effusing vapor was scanned from mass 14 to mass 300 at 70V accelerating electron voltage.

The principal ions detected were N_2^+ and Ga^+. Minor amounts of Ga_2^+ and Ga_2O^+ were detected but usually constituted less than 2% of the total Ga^+ intensity, with a maximum value of 2.5% and a typical value of 1.7%. No peaks that could be attributed to gallium nitride molecules were observed. Intensity measurements for the nitrogen peak (mass 28) could not be reproduced and, because of the high background of residual nitrogen gas, the relative amounts of Ga(g) and N_2(g) could not be determined. Elemental gallium as well as gallium nitride remained in the cell after heating with the 1-mm orifice, while only gallium nitride remained in the cell with the 3-mm orifice.

D. Torsion-Langmuir Studies

In order to study free-surface sublimation, wafers of solid gallium nitride were substituted for orifices in the side walls of the torsion-effusion cells. This method for pressure determination may appropriately be called the torsion-Langmuir method.

Ordinary cold pressing failed to produce high-density gallium nitride wafers, and hot pressing at 1000 to 1100°C and 2000 psi resulted

in disproportionation of much of the sample with free gallium metal as a product. Fortunately, satisfactory wafers could be prepared at room temperature under loads of 1.5×10^6 psi in the ultra-high pressure apparatus of Professor George Jura.

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, and the sample was compacted with a hand-operated hydraulic press. After this pressing, each wafer was examined under a microscope to ascertain whether or not a uniform distribution of the sample had been established inside the O-ring. Uniform samples were then placed in the high-pressure press and were held at 1.5×10^6 psi for 10 to 15 min.

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. Wafers of 0.3 to 1.3 cm diam and .012 to .025 cm thickness were obtained. Any wafers which examination at 200 magnifications revealed to have cracks or obvious defects were rejected. X-ray examination of powdered wafers showed only the gallium nitride pattern, and no change was found in diffraction patterns or appearance of samples that had been exposed to the atmosphere for several weeks.

Microscopic examination at 200 magnifications showed no pores (Fig. 2a.). A micrograph of a sample heated at 1200° for one hour (Fig. 2b.) showed no discernible change in the contour of the surface. The only noticeable change was that the color of the sample was altered from dark gray to light gray or white. This change was probably due to small variations in the stoichiometry of the gallium nitride phase. 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 (Fig. 2c). Only crack-free wafers were used in the torsion-Langmuir studies, and no darkening of color was observed around the holes whose eventual formation required termination of the torsion-Langmuir runs.

The cell for the torsion-Langmuir study was made from a graphite orthorhomboid with the dimensions 3.7 cm long x 19 cm wide x 2.5 cm high. Two wells of 1 cm diam were drilled into opposite sides of the block at positions offset about 1 cm from the center of support of the side walls in direction to yield additional torques during vaporization. Each well had a shoulder of 1.7 cm diam drilled near the surface of the cell. Gallium nitride wafers were placed inside these shoulders and were secured there by graphite washers. Each washer had a flat surface that fit snugly against the wafer, and had a tapered, concave surface on the other side. When the washer was in place, the effective sublimation area of the sample was defined by 0.8 to 1.3 cm diam openings through each washer. The thickness of the graphite at the inside periphery of these washers was negligible, so no correction was necessary for reflection of vaporizing molecules at the walls of the washers. A pair of 3-mm holes which were drilled from the top of the cell into cavities behind the two samples permitted vapor that sublimed from the rear faces of the wafers to escape

upward in a manner that would not contribute to the torque.

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 after each temperature had remained constant for at least 5 min.

Eventually, for any given run, the deflections began to decrease with further increase in temperature or with increased time at constant temperature. 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 obtained before the deflections began to decrease systematically with time were used in calculations of apparent pressures, since the other deflections resulted from sublimation from surfaces with decreasing and unknown areas.

Figure 3 shows the free-surface vapor pressure as a function of 1/T. Total pressures were calculated in the same manner used for equilibrium torsion effusion studies.[8, 11] Least-square solutions gave the following expression:

$$\log P_{atm} = 5,699 \pm 15,923/T ,$$

for solid gallium nitride in the temperature range 1166 to 1428°K. Since $P_{Ga} = 2P_{N_2}(M_{Ga}/M_{N_2})^{\frac{1}{2}}$, where the M's are molecular weights, the apparent equilibrium constant K^* for the reaction:

$$2GaN(s) = 2Ga(g) + N_2(g) \qquad (1)$$

is given by:

$$\log K^{*} = 16.239 - 47,769/T.$$

The activation energy for the sublimation of gallium nitride was calculated exactly as is done for equilibrium vaporization processes by the second-law method.[12] From the above expression for K^{*}, the enthalpy of activation for (1) was calculated to be $\Delta H^{\ddagger}_{1300} = 218.6$ kcal and the entropy was calculated to be 74.3 cal deg^{-1}. It should be noted that if the data were interpreted as normally done in kinetic studies, the enthalpy of activation would be taken as the value of $-R\, d \ln Z_{GaN}/d\, \frac{1}{T}$, where Z_{GaN} is the number of moles of GaN lost per unit time per unit area, while we report $R\, d \ln\left(P^{2}_{Ga} \cdot P_{N_2}\right)/d\, \frac{1}{T} = -3 \times R\, d(\ln Z_{GaN} - \frac{3}{2} \ln T)/d\, \frac{1}{T}$. We choose this approach because it facilitates comparison with the enthalpy of reaction (1), which is equal to $R\, d(\ln P^{2}_{Ga} \cdot P_{N_2})/d\, \frac{1}{T}$ where equilibrium pressures for reaction (1) are used.

III. DISCUSSION

The validity of almost all determinations of evaporation coefficients are to some extent in question because of uncertainty about the surface temperatures.[5, 13] But in the present research, the surface temperature can scarcely differ by more than 5° from the measured temperature because the sample cell and dummy cell with which the temperature measurements were made are in the uniform temperature zone of a hot walled furnace. The sample surfaces in the free surface evaporation studies were directly heated by radiation from the furnace walls; there appears to be no reason to expect the temperature measurements in a torsion-Langmuir study to be less reliable than those for a torsion-effusion

vapor pressure study. The apparatus was calibrated by measurement of melting points of four metals in place and has been shown to give pressures for tin that are in close agreement with accepted measurements.

A possible source of error might be evaporation of a significant fraction of the escaping vapor from pores or cracks in the sample. Experience with sublimation of stannic oxide, zinc oxide, and beryllium nitride indicates that if cracks or pores develop in a material of low evaporation coefficient, these cracks and pores enlarge and are readily seen under 100 magnifications or less.[14] Examination of our samples at 200 magnifications after vaporization runs showed no evidence of crack or pore development. We believe, therefore, that our results were not much influenced by sublimation from pores or cracks.

The possibility that the sublimation kinetics for gallium nitride were influenced by surface impurities cannot be excluded because neither the original sample purity nor the vacuum provided were good enough to prevent accumulation of impurities at the sample surface if such segregation were chemically favorable. The mass spectrometer experiments indicates, however, that the most obvious impurity, oxygen, was continuously evaporated as Ga_2O. Furthermore, from the measured pressure of gallium vapor during congruent sublimation of the nitride and the known stabilities of solid Ga_2O_3 and gaseous Ga_2O,[15, 16] the partial pressure of Ga_2O at equilibrium is calculated to be about two orders of magnitude higher than the pressures of gallium and nitrogen, which means that, unless gallium oxide is characterized by a high free energy barrier to sublimation, any oxygen present either as Ga_2O_3 or as a solute in the nitride phase should be vaporized as rapidly as

the oxygen reaches the surface and no separate surface layer of gallium oxide should form.

The enthalpy of reaction (1) can be calculated from the enthalpy of formation of gallium nitride measured by Hahn and Juza[17] and from the known enthalpy of sublimation of gallium.[8] The entropy of reaction can be calculated from known entropies of gallium vapor and nitrogen gas[18] and from an estimated entropy for gallium nitride. Solid gallium nitride is estimated to have the same entropy as ZnO,[19] an isoelectronic solid. The equilibrium constant for reaction (1) is calculated to be about 10^{-6} at 1400°K. The apparent equilibrium constant calculated from our Langmuir data is only 6×10^{-18}.

Of more theoretical interest than the low sublimation rate is the fact that the experimental enthalpy of activation exceeds the enthalpy of reaction (1) by about 46 kcal. In the recent comprehensive review of evaporation and condensation reactions by Hirth and Pound,[5] of the substances discussed which evaporate at rates lower than the theoretical maximum rate predictable by use of the Langmuir equation, none is reported to do so because of an activation energy barrier that exceeds the equilibrium energy of evaporation, and the chief theories of evaporation attribute low evaporation coefficients* to factors that adversily influence

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* The evaporation coefficient for any vapor species is the ratio of the actual rate of evaporation of that species to the rate of evaporation predicted from substitution of the equilibrium pressure into the Hertz-Langmuir equation: $Z = Peg/(2\pi MRT)^{\frac{1}{2}}$, where Z is the rate in moles per second per unit area, Peg is the equilibrium pressure, M is the molecular weight, R the gas constant, and T the absolute temperature. It should be noted that if the heat of activation for evaporation differs from the heat of the sublimation reaction, the evaporation coefficient will vary with temperature.

the number of molecules that are on sites suitable for evaporation[5, 20] or the number that have proper orientation for evaporation.[21] Such factors are in effect entropy barriers rather than energy barriers to evaporation.

Because of pores and fissures in the Langmuir sample, the true surface area for sublimation exceeds the apparent area used in the Langmuir calculations by some unknown amount. The effect of neglect of this additional area is to make the apparent pressures high by an amount that is essentially temperature independent as long as the evaporation coefficient remains so low that condensation of vapor molecules which have vaporated in sample pores remains negligible. The enthalpy of activation measured in the Langmuir experiments for this highly irreversible reaction should, therefore, be reliable even if the sample is porous. The apparent entropies on the other hand must be recognized as upper limits to the true entropy of activation.

The low apparent entropy of activation, 74.3 cal deg^{-1} at 1300°K found for reaction (1), compared to 101 cal deg^{-1} calculated for the equilibrium sublimation to the gaseous products at the observed pressures, indicates that the activated complex probably is not made up of the gaseous products of reaction (1) or of these species physically adsorbed on the gallium nitride surface. An intriguing possibility is that a significant fraction of evaporation from a Langmuir surface may be by a reaction such as $nGaN(s) = (GaN)_n(g)$. Our mass spectrometer experiments

demonstrated that gallium nitride vapor species are not important in the Knudsen cell experiments, but the possibility remains that such gaseous species may be observable at the lower pressures that characterize the Langmuir experiments. This possibility is to be investigated for gallium nitride single crystals.

As remarked in the experimental section, the pressures found in the Knudsen experiments with the larger diameter orifice were slightly higher then the vapor pressure of gallium so that liquid gallium would be expected to have condensed in the cell during sublimation, while gallium was actually found in the cell only when the orifice of smaller diameter was employed. Since the vapor pressure of gallium was determined in the same apparatus as that used in the gallium nitride studies, an experimental error in either study high enough to account for the discrepancy seems very unlikely. We consider the most probably explanation to be that liquid gallium effused or defused through the graphite cell walls in quantities approaching the quantity that escaped through the orifices. Weight loss experiments with cells that have no orifice would verify or disprove this hypothesis, but such experiments have not been made. Experiments were made, however, with elemental gallium which demonstrated that no significant torque is imparted to cells of the design used in this study by any leakage that may occur.[8]

The rate determining step must be very different for sublimation in the experiments in which liquid gallium is present from that in the free surface Langmuir experiments.

The temperature dependence of the pressures measured in the Knudsen experiment made with the orifice of smaller diameter can be

used to calculate the heat of activation, 39 kcal, for the reaction $2GaN(s) = 2Ga(\ell) + N_2(g)$ at 1400°K, which is smaller than the equilibrium heat of reaction, about 47 kcal at this temperature. Despite the low heat of activation, the N_2 pressures found in the Knudsen study are less than 1/10 the pressure calculated from the heat of formation.

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FIGURE CAPTIONS

Fig. 1. Apparent vapor pressures of solid gallium nitride: torsion-effusion method.

Fig. 2. Microphotographs of gallium nitride solid bodies: (a) before heating, (b) after heating, and (c) a crack after heating.

Fig. 3. Vapor pressure of gallium nitride: torsion-Langmuir method.

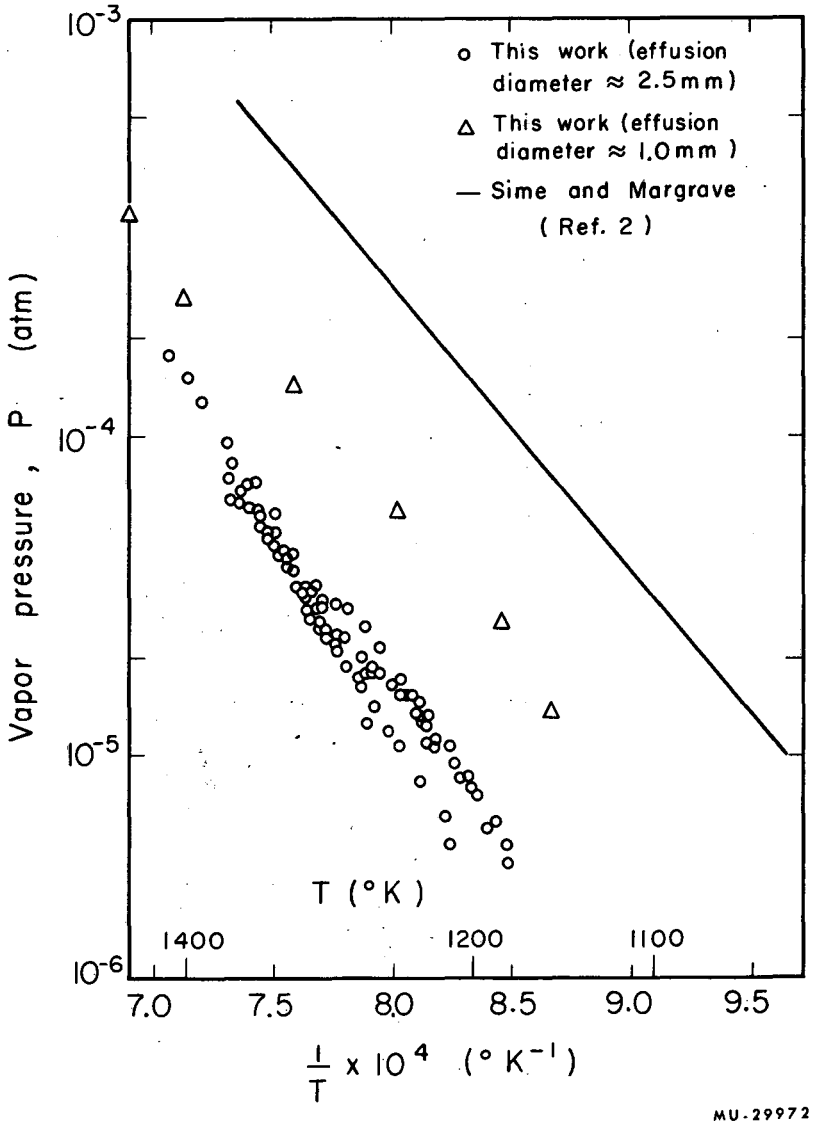
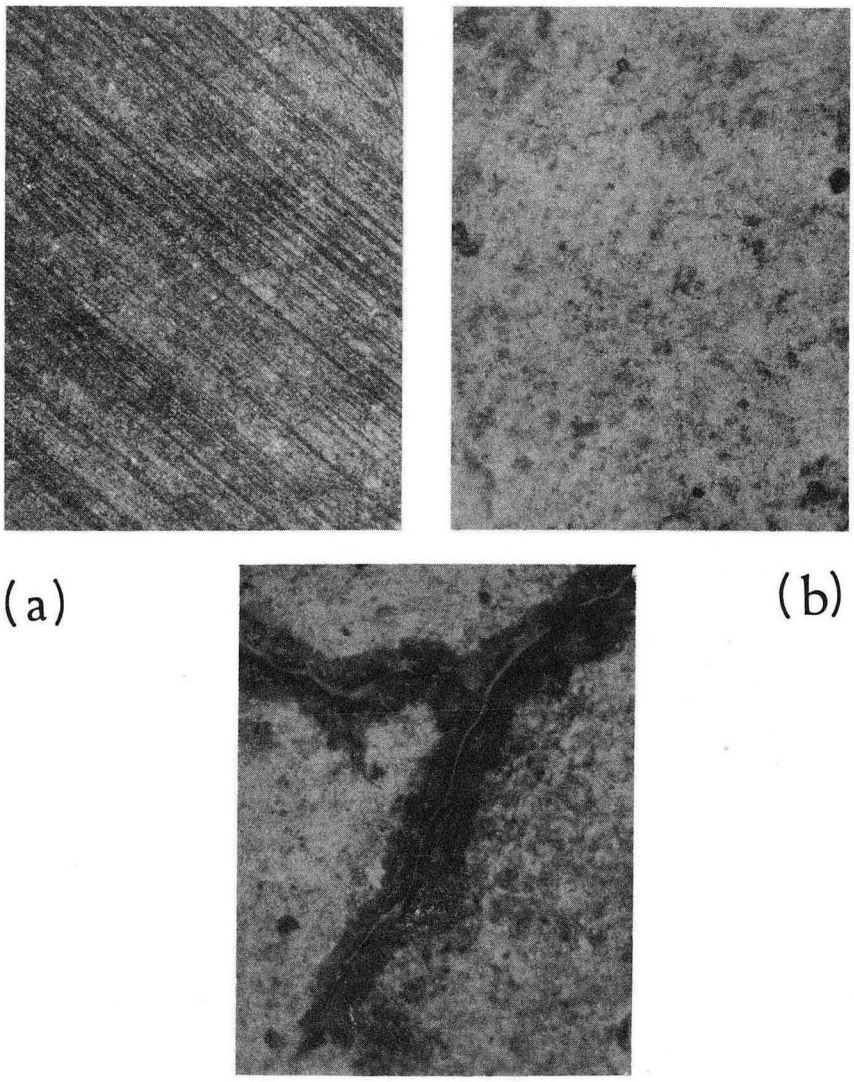

o This work (effusion diameter ≈ 2.5mm)
Δ This work (effusion diameter ≈ 1.0mm)
— Sime and Margrave (Ref. 2)
Vapor pressure, P (atm)
10^-3
10^-4
10^-5
10^-6
T (°K)
1400
1200
1100
7.0
7.5
8.0
8.5
9.0
9.5
1/T x 10^4 (°K^-1)
MU-29972

Fig. 1



ZN-3631

Fig. 2

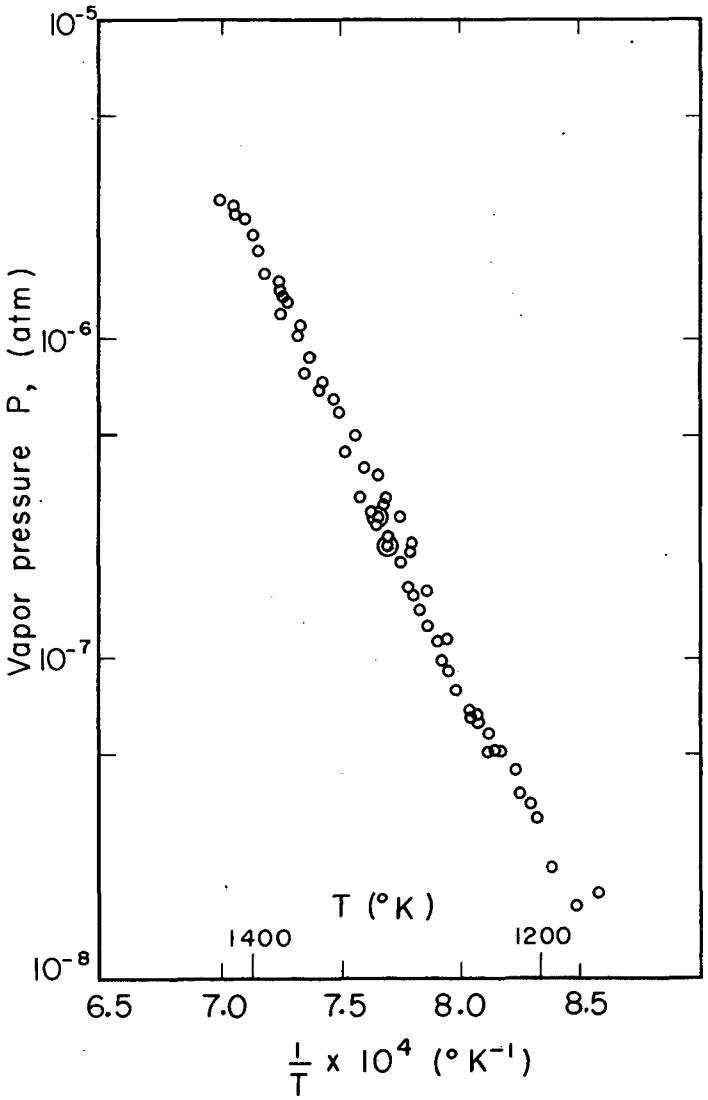

10^{-5}
10^{-6}
10^{-7}
10^{-8}
Vapor pressure P, (atm)
T (°K)
1400
1200
6.5
7.0
7.5
8.0
8.5
$\frac{1}{T} \times 10^4$ (°K^{-1})
MU-29974

Fig. 3.

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